

Smart Nanomaterials Technology

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Nanomaterials: The Building Blocks of Modern Technology

Synthesis, Properties and Applications

 Springer

Smart Nanomaterials Technology

Series Editors

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Nanotechnology is a rapidly growing scientific field and has attracted a great interest over the last few years because of its abundant applications in different fields like biology, physics and chemistry. This science deals with the production of minute particles called nanomaterials having dimensions between 1 and 100 nm which may serve as building blocks for various physical and biological systems. On the other hand, there is the class of smart materials where the material that can be stimulated by external factors and results in a new kind of functional properties. The combination of these two classes forms a new class of smart nanomaterials, which produces unique functional material properties and a great opportunity to a larger span of application. Smart nanomaterials have been employed by researchers to use it effectively in agricultural production, soil improvement, disease management, energy and environment, medical science, pharmaceuticals, engineering, food, animal husbandry and forestry sectors.

This book series in Smart Nanomaterials Technology aims to comprehensively cover topics in the fabrication, synthesis and application of these materials for applications in the following fields:

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- Agricultural—agricultural production, soil improvement, disease management, animal feed, egg, milk and meat production/processing,
- Forestry—wood preservation, protection, disease management
- Environment—wastewater treatment, separation of hazardous contaminants from wastewater, indoor air filters.

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Preface

Nanotechnology has revolutionized the field of materials science, with the ability to manipulate and control matter at the nanoscale level. Nanomaterials, materials with dimensions in the nanometer range, exhibit unique properties that differ from their bulk counterparts. These unique properties have led to the development of a wide range of applications in various fields, including electronics, medicine, energy, and environmental remediation. This book, *Nanomaterials: The Building Blocks of Modern Technology (Synthesis, Properties and Applications)*, provides a comprehensive overview of the current state of the art in the field of nanomaterials. It covers the synthesis and characterization of various nanomaterials, including metals, metal oxides, and carbon-based nanomaterials. The book also discusses the properties of nanomaterials and their applications in different fields. The book is organized into several chapters, with each chapter covering a specific aspect of nanomaterials. Chapter “[Introduction to Nanomaterials and Their Features](#)” introduces the basic concepts of nanomaterials, including their definition, properties, and classifications. Chapter “[Synthesis, Characteristics, and Applications of Nanomaterials](#)” covers the various synthesis methods for nanomaterials, including chemical, physical, and biological methods. Chapter “[Soft Nanomaterials and Their Applications](#)” discusses the characterization techniques for soft nanomaterials, including microscopy, spectroscopy, and thermal analysis. Chapters “[Biological Nanomaterials and Their Development](#)”–“[Antimicrobial Potential, Drug Delivery and Therapeutic Applications of Bio-nanoparticles in Medicine](#)” cover the properties and applications of biological nanomaterials in different fields, including electronics, medicine, and energy. Chapters “[Composite Nanomaterials and Their Development](#)”–“[Advances in Hybrid Energy and Power Density-based Supercapatteries](#)” focus on the composite-based nanomaterials and applications of nanomaterials, including supercapacitors. Chapters “[The World of Green Nanomaterials and Their Development](#)”–“[Green Nanotechnology: A Roadmap to Long-Term Applications in Biomedicine, Agriculture, Food, Green Buildings, Coatings, and Textile Sectors](#)” focus on the green nanomaterials and their applications. Chapters “[Carbon-Based Nanomaterials and Their Properties](#)” and “[Two-Dimensional Nanomaterials as Technology Marvels](#)” provide an insight on some carbon-based nanomaterials and 2D nanomaterials including organic

frameworks. Finally, chapter “[Future Enabled by Nanomaterials: Editor Summary](#)” discusses the future prospects of nanomaterials and their potential impact on various fields. The editors and authors of this book have worked hard to ensure the accuracy and quality of the information presented. However, given the rapid pace of research in the field of nanomaterials, some information may become outdated quickly. Therefore, we encourage readers to consult the latest research articles and reviews for updated information. Overall, this book is a valuable resource for researchers, scientists, and students interested in the field of nanomaterials. It provides a comprehensive overview of the current state of the art in the field and highlights the potential of nanomaterials for various applications. We hope that this book will serve as a valuable reference and guide for researchers, students, and professionals in the field of nanomaterials and will inspire new ideas and innovations in this exciting and rapidly evolving field. We will keep updating this book in the subsequent editions. We thank all the authors who contributed to this book and who made our proposal come true. We also thank the Springer Nature, Singapore, for their help and support.

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Serdang, Malaysia
Serdang, Malaysia
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We would like to express our deepest gratitude and appreciation to all the individuals who have contributed to the creation of this book, *Nanomaterials: The Building Blocks of Modern Technology: Synthesis, Properties and Applications*. First and foremost, we would like to thank the authors of this book for their tireless efforts and dedication in researching, writing, and editing this comprehensive guide on nanomaterials. Their expertise and insights have helped to make this book an invaluable resource for anyone seeking to learn more about this rapidly evolving field. We would also like to extend our thanks to the publishers and all the editorial members who have played a crucial role in bringing this book to fruition. Their guidance, support, and attention to detail have been instrumental in ensuring that the book meets the highest standards of quality and accuracy.

In addition, we are grateful to the reviewers who provided valuable feedback and constructive criticism, which helped to improve the content and readability of the book. Last but not least, we would like to acknowledge the contributions of all the researchers, scientists, and engineers who have dedicated their careers to advancing the field of nanomaterials. Their groundbreaking work has paved the way for many of the technological innovations we enjoy today.

Thank you to all who have contributed to the creation of this book, and we hope it serves as a valuable resource for students, researchers, and practitioners in the field of nanomaterials.

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Introduction to Nanomaterials and Their Features



M. Manikandan, Balbir Singh, and Tabrej Khan

Abstract This chapter presents a comprehensive taxonomy of nanomaterials, based on their dimensions, shape, and composition. Nanomaterials are classified into three types, namely nanoparticles, nanotubes, and nanofilms, depending on their dimensions. These materials may consist of a single element, such as metals or carbon, or a combination of components, such as metal oxides or composites. The chapter also highlights the commonly used nanomaterials, along with their morphologies. When a material is in nanoform, its physicochemical properties can differ significantly from those of its bulk counterpart, depending on the material type, size, shape, and functionalization. Therefore, the chapter examines the critical physicochemical characteristics of nanomaterials, such as shape, dispersibility, crystalline phase, melting temperature, and magnetic properties.

Keywords Nanomaterials classification · Nanoparticles · Nanomaterials physicochemical properties · Magnetic properties of nanoparticles · Toxicity of nanoparticles · Melting temperature of nanoparticles

1 Introduction

The origin of the term “nano” can be traced back to the Latin word “nanus” and the Greek word “v,” both of which refer to a person of short stature or a dwarf. However, in the context of modern science, the term “nano” is used as a prefix in the International

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System of Units (SI) to denote one billionth (10^{-9}) of a unit. For instance, nanometer represents one billionth of a meter, nanoliter represents one billionth of a liter, and nanogram represents one billionth of a gram. Contrary to its original meaning, the term “nano” does not typically refer to a person or object of exceptionally small size in scientific contexts. Instead, it is used to describe materials or structures that fall within the nanoscale range, which can vary depending on the field of study and the specific application [1]. It is important to note that the term “nano” does not exclusively refer to materials or structures in the field of science. For example, a “nanostar” may refer to a star that has a mass similar to, or smaller than, that of our sun. However, in the context of nanomaterials, a simple and practical criterion for their definition is to consider their size. Nanomaterials are typically characterized as materials with dimensions falling within the range of 1–100 nm. This size range is commonly used to distinguish nanomaterials from bulk materials, which have much larger dimensions [2]. Nanoparticles, as their name suggests, have all three dimensions within the nanometer range. On the other hand, nanoplates have only one dimension that falls below 100 nm, while the other two dimensions are larger than this size. Similarly, nanofibers have two dimensions in the nanoscale range but are considerably longer than nanoplates or nanoparticles [3]. However, it should be noted that the upper limit for a nanomaterial is not universally accepted to be 100 nm. Different organizations worldwide have set varying size limits for nanomaterials, although 100 nm remains the most commonly recognized limit. It is crucial to use appropriate methodologies for accurately determining the size of nano-objects. Table 3 summarizes the various methods currently available for measuring the size of objects within the nanometric range. To avoid incorrect results and classification, special attention should be given to (i) preparing a representative sample for analysis, (ii) following proper sample preparation procedures, (iii) utilizing the most appropriate mathematical analysis to obtain size distribution, and (iv) ensuring comparability among different laboratories [4]. In 2014, the Joint Research Center (JRC) published a technical study that provided comprehensive guidelines for the preparation of samples for GMO analysis. As for the topic of this book, nanosponges are materials that possess pores or cavities in the nanometer scale within their macroscopic or microscopic outer dimensions. Nanosponges may exist in various forms, including natural or artificial, organic or inorganic [5]. Figure 1 illustrates a simplified diagram of nanosponges based on cyclodextrin. This means that although the size of a given sample may exceed 100 nm in the x , y , and z dimensions, nanosponges are classified as nanomaterials because they contain a network of cavities in the nanometer scale within their bulk structure [2]. This interpretation suggests that nanosponges possess structural properties in the nanometer scale but are not necessarily considered nanoparticles. Due to their unique characteristics at the nanoscale, a hierarchical classification of nanomaterials has been proposed [6]. Figure 1 provides a visual representation and relevant specifications for nanosponges. Accurately determining the nanometer range of a material is crucial for ensuring safety and protecting health. According to the IUPAC Glossary of Toxicology Terms, a nanoparticle is a minute particle whose size is measured in nanometers, often limited to particles that are considered nanosized (NSPs) with an

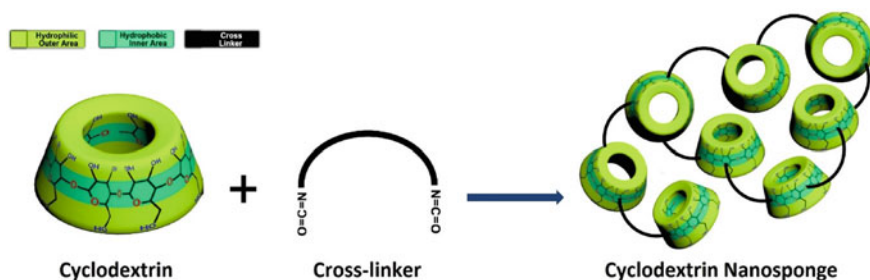


Fig. 1 Cyclodextrin nanosponge from cyclodextrin [35]

aerodynamic diameter of 100 nm or less. They are also known as ultrafine particles. However, no specific definition of nanomaterial has been listed yet [7].

Nanomaterials can also be blended with other bulk materials to produce nanocomposites with outer dimensions exceeding 100 nm, while containing nanoparticles within the bulk. Although there is ongoing debate, these materials should still be regarded as nanoparticles [8]. This is evident in antibacterial materials made of dispersed nanoparticles in various media, such as textiles, plastics, chitosans, and others. Likewise, nanoparticles of reducing agents distributed in a hydrogel showed superior performance compared to molecular systems in reducing organic pigments. Polymers serve as an ideal matrix for dispersing nanoparticles [9]. PVDF membranes have the ability to incorporate TiO_2 nanoparticles, leading to enhanced surface hydrophilicity and permeability, while reducing protein adsorption capacity. This highlights the antifouling properties of PVDF membranes that have been modified with TiO_2 nanoparticles [10].

2 Uniqueness of a Nanomaterial

Although the term “nanomaterials” has become increasingly popular in popular culture, it is important to recognize that many nanomaterials are naturally occurring and widely present in the environment. Examples include dust released into the atmosphere, ocean spray, soot generated from forest fires, and volcanic eruptions [11]. Although some nanomaterials occur naturally, the majority of them are intentionally manufactured for particular applications. Engineered nanomaterials are increasingly being used in a range of consumer products, including cosmetics, sporting equipment, electronics, tires, and medicine. Nanomaterials can aid in diagnostics and enhance the pharmacokinetics and bioavailability of medications in the field of medicine [12]. Despite the recent emergence of the term “nano,” several types of nanomaterials have been in use for many years. For instance, “carbon black” was first utilized to strengthen vehicle tires in 1915 and continues to be widely used today. It is estimated that the annual production of carbon black now exceeds 10

million tons, with approximately 85% being employed in rubber-based industries. Fumed silica, titanium dioxide, zinc oxide, and, more recently, silver nanoparticles are other commercially available nanomaterials that are widely recognized [13]. The reason for the considerable interest in nanomaterials is due to the discovery that the essential properties of matter alter at the nanoscale level. In fact, reducing the size of particles has far-reaching implications for their characteristics [14]. An incomplete list of these implications encompasses heightened strength, hardness, and fracture ductility, reduced melting point, elevated heat capacity, decreased Debye temperature, enhanced conductivity for nanometals, reduced Curie temperature, onset of nonlinear optical properties, heightened catalytic activity, altered solubility, and even variations in color as a function of particle size [15].

3 Nanomaterial Development

Although many nanomaterial categories have an arbitrary, size restriction of 100 nm, it is commonly asserted and widely acknowledged that the maximum size for detecting size-dependent property changes through experimentation is 30 nm. This is because the significant increase in surface area and the emergence of unique quantum effects are the two primary factors that govern the behavior of nanomaterials [16]. Nanomaterials can be formed using either a single element or a combination of many elements, and all nanomaterials can be modified or functionalized. The method of fabrication yields diverse results for nanomaterials with zero-dimensional, one-dimensional, two-dimensional, and three-dimensional structures [17]. It is widely recognized that nanomaterials can be produced through physical, chemical, or bio-based processes.

Figure 2 illustrates two primary manufacturing techniques. The first approach is known as the “top-down” method, and it typically involves milling the original large-sized material. This technique requires a significant amount of starting material, resulting in significant material loss and substantial waste output [18]. The “top-down” approach is effective in producing metallic and ceramic nanoparticles. However, it is important to note that extended milling can subject the material to high heat stress. To alleviate this issue, cryogenic liquids are often used to aid the milling process and increase brittleness. Additionally, the milling process can lead to container abrasion and subsequent contamination [19]. The nanoparticles produced using the “top-down” approach often have a significant degree of polydispersity and poor particle shape homogeneity. Other “top-down” methods include photolithography, anodization, and plasma etching. Alternatively, nanomaterials can be generated through the “bottom-up” approach, which involves assembling atoms or molecules to create the desired nanomaterial [20]. The “bottom-up” approach involves a reaction that can occur in both the gaseous and liquid phases, which can be time consuming, challenging, and costly. However, this method often results in more consistent particle size and shape. Examples of “bottom-up” techniques include sol-gel processing, gas-phase synthesis, flame-assisted ultrasonic spray pyrolysis, gas

condensation processing, chemical vapor condensation, sputtered plasma processing, microwave plasma processing, and laser ablation [21]. Among the various techniques, gas-phase synthesis appears to be the most promising for industrial-scale production of nanomaterials in both powder and film forms. Fullerene and carbon nanotubes are the most well-known nanomaterials produced using this method. On the other hand, the liquid-phase process can be carried out at a lower temperature than the gas-phase process. Although nearly monodisperse nanomaterials can be obtained, significant polydispersity is often observed. It is worth noting that size distribution plays a crucial role in the classification of nanomaterials [22]. The categorization of nanomaterials can differ significantly based on whether the size distribution is based on the number of particles or the mass concentration. When it comes to safety, it is more beneficial to use the number distribution as a more conservative option. Through adhesion processes, the main particles of a given substance may form larger unit structures, such as agglomerates or more stable aggregates. The main difference between agglomerates and aggregates is that the overall surface area of agglomerates does not change much compared to the area of single particles, while aggregates typically have a smaller total surface area than parent particles. Agglomerates can be easily separated into smaller agglomerates, for instance, by using ultrasound [23].

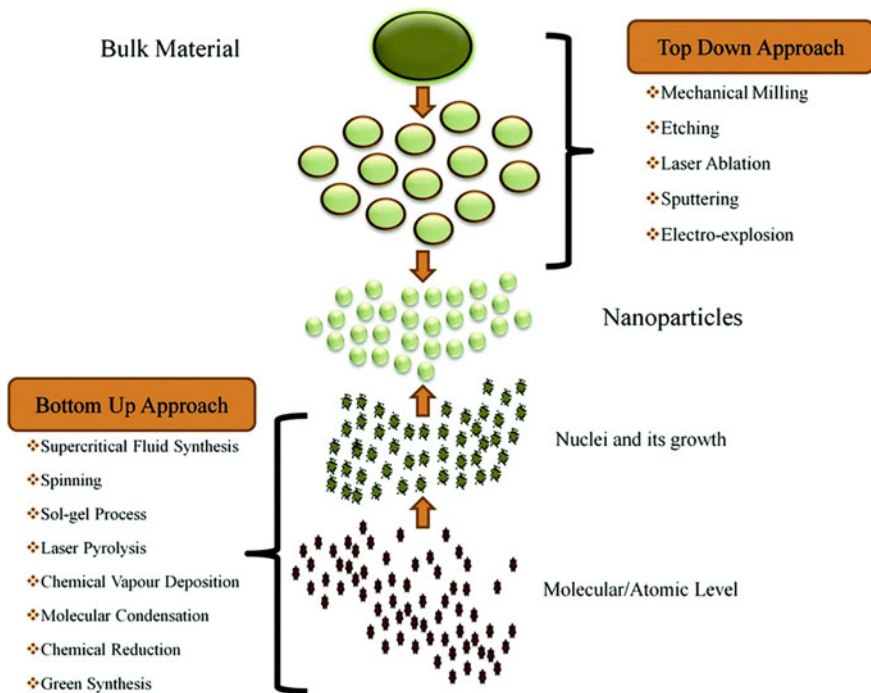


Fig. 2 Nanomaterial synthesis and development approaches [36]

4 Nanomaterials and Associated Risks

The popularity of nanomaterials is reflected in the vast number of publications covering the subject, which shows the number of papers published on selected keywords, including “nanomaterials” in the article title (source: www.scopus.com). The uses of nanomaterials continue to grow rapidly, with around one-third of all nanomaterials produced worldwide being utilized in cosmetic products, especially sunscreens [24]. Nanomaterials are utilized in a wide range of applications, including but not limited to: (1) cosmetic and personal care products, (2) paints and coatings, (3) household products, (4) catalysts and lubricants, (5) sports products, (6) textiles, (7) medical and healthcare products, (8) food and nutritional ingredients, (9) food packaging, (10) agrochemicals, (11) veterinary medicines, (12) construction materials, (13) weapons and explosives, and (14) consumer electronics [25].

The broad and growing use of nanomaterials has raised concerns regarding their safety and potential health impacts for several reasons. First, nanomaterials are more reactive in solvents or condensed phases than molecular analogs. Second, their small size allows for easier migration in biological systems. And third, they can pass through biological membranes in the lung, gut, and even the brain, potentially causing damage to intracellular structures and cellular functions. The respiratory system is particularly vulnerable as it provides an easy pathway for nanoparticles to enter the body [26]. The unique structure of the lung with its 100 million alveoli and large surface area makes it highly susceptible to interactions with nanomaterials. However, the good news is that the majority of inhaled nanoparticles are cleared from the body quickly through mucociliary transport or by macrophages, especially for smaller particles. Only long-term or excessive exposure, such as that caused by smoking, has been found to pose a significant health risk [27]. According to studies, less than 0.05% of the dose delivered via inhalation actually enters the circulation. Another possible pathway for nanoparticles to enter the body is through the olfactory nerve, which is more effective as it is directly connected to the brain. Despite the very low amount of nanoparticles that can reach the brain through this pathway, it can still allow the particles to enter the central nervous system. However, skin is an effective barrier against the entry of nanoparticles, especially non-lipophilic ones [28].

5 Policy/Legislations on Nanomaterials

The EU approved a definition of a nanomaterial in 2011 (2011/696/EU) but recognized the need for a revision “in light of experience and scientific and technological developments.” The review should focus on whether the 50% number size distribution criteria should be strengthened or weakened. The investigation was set to be completed by 2016 or shortly thereafter. According to the recommendation, “nanomaterial” refers to a natural, accidental, or produced substance consisting of particles

in an unbound state, as an aggregate, or as an agglomeration, where one or more exterior dimensions are in the size range of 1–100 nm for 50% or more of the particles in the number size distribution. In specific cases or for competitiveness, the number size distribution criteria of 50% may be replaced by a threshold between 1 and 50%. Fullerenes, graphene flakes, and single-wall carbon nanotubes having one or more exterior dimensions less than 1 nm should be considered nanomaterials [29].

The primary purpose of the definition of nanomaterial is to identify materials that may require specific regulations, such as risk assessment or ingredient labeling. The definition itself does not include these requirements, as they are established by the laws and regulations in which the term is used. It is important to note that nanomaterials are not necessarily hazardous, but they may require additional considerations in their risk assessment. Therefore, the definition aims to provide a clear and unambiguous criterion for identifying materials that require such evaluation. [29]. The purpose of the recommendation is to ensure consistency across legal domains regarding the use of nanomaterials, as the same materials may be used in different settings. Various pieces of EU law and technical guidelines exist that support legislative implementation and include specific references to nanoparticles. However, the ultimate determination of whether a nanomaterial is hazardous and requires additional action will depend on the findings of a risk assessment. Therefore, the recommendation aims to provide a comprehensive and consistent reference for identifying nanomaterials to which specific concerns apply, regardless of the sector in which they are used [30].

6 Nanoparticle Applications

Nanoparticles find applications in various fields. For instance, nanoparticles made of different compositions such as silver, zinc oxide, palladium, and carbon exhibit antibacterial properties against pathogens such as *Staphylococcus aureus* and *Escherichia coli*. Nanoparticles have a wide range of applications in industries such as cement, coatings, paints, and insulation materials. They are also used as electrocatalysts for advanced energy conversion and storage, functionalized textiles, food contact materials, and in cosmeceutical treatments for conditions like photoaging, hyperpigmentation, and wrinkles. Additionally, theranostic nanoparticles have diagnostic and therapeutic properties that can be used in personalized treatment for a range of diseases [31]. Nanoparticles find applications in various biological fields, such as targeted drug delivery, imaging, and photothermal ablation of cancer cells. Magnetic nanoparticles hold the potential to be used in the detection and treatment of Alzheimer's disease, while gold nanoparticles can be used as theranostics. However, as the use of nanoparticles continues to expand, it is important to develop nanoparticle-specific legislation that takes into account their potential toxicity. It is difficult to predict which nanoparticles may be harmful and at what concentration, as their toxicity is determined by their physicochemical properties. Therefore, before using nanoparticles in various sectors, it is crucial to undertake screening and toxicity

prediction of different nanoparticles. To address this issue, predictive toxicological techniques and screening technologies are currently being developed [32].

7 Nanomaterials and Their Production Approach

In early 2017, the United States Environmental Protection Agency (EPA) released the first regulation for collecting information about the risks associated with the production and processing of nanoparticles. This regulation marked the culmination of a lengthy process that began in 2005 with the intention of creating a voluntary reporting scheme. The EPA included nanoscale materials in the broader Toxic Substances Control Act (TSCA). According to the TSCA, nanomaterials are defined as “chemical substances” with dimensions ranging from 1 to 100 nm that are expected to have different properties than the same chemical substance in bulk. These unique properties raise concerns about potential unpredictable and unknown behavior under certain conditions. The primary aim of the EPA’s comprehensive regulatory strategy is to reduce unreasonable risks to human health and the environment associated with the production and use of nanomaterials [33]. The EPA’s regulatory strategy for minimizing hazards associated with the production and use of nanomaterials involves two steps: premanufacture notifications for new nanomaterials and an information collection rule for both new and old nanomaterials. To determine what constitutes a “new” substance or chemical under TSCA, the EPA maintains a TSCA Inventory of existing substances. Chemicals not listed in the inventory are considered “new.” The molecular identity is the fundamental criterion used to categorize chemicals as “new” or “existing,” as demonstrated in the study “TSCA Inventory Status of Nanoscale Substances: General Approach,” available for public download from the EPA website. Particle size is not a molecular identity parameter for the TSCA Inventory. The section of the cited text dealing with existing substances, either on a molecular or nanometric scale, is worth quoting [34].

8 Conclusions

In summary, many nanoparticles have been found to be harmful to living organisms, and their toxicity is determined by various physicochemical properties whose relative importance is unclear. Nanoparticles have been linked to various disorders that can appear shortly after exposure or years later. Since it is difficult to predict the toxicity of a nanomaterial based on its bulk material properties, a case-by-case approach is required to identify hazardous nanomaterials. Therefore, caution must be exercised when handling and using nanoparticles in applications.

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Synthesis, Characteristics, and Applications of Nanomaterials



Tabrej Khan, Balbir Singh, and M. Manikandan

Abstract The field of nanotechnology is expanding rapidly and holds enormous potential for developing new materials and technologies. Nanomaterials, defined as materials with at least one dimension less than 100 nm, exhibit distinct physical, chemical, and biological properties that make them attractive for various applications. These applications range from electronics and energy to medicine and environmental remediation. This chapter presents an overview of the synthesis methods of nanomaterials, including top-down and bottom-up approaches, and discusses the unique properties that arise from their small size and high surface area-to-volume ratio. Moreover, we describe some of the most promising applications of nanomaterials, such as drug delivery, catalysis, sensors, and energy storage, and emphasize some of the challenges that require attention to enable their widespread use. Finally, we conclude by discussing the ethical and safety concerns linked with the production and use of nanomaterials and suggest some possible directions for future research in this thrilling field.

Keywords Nanomaterials · Nanotechnology · Carbon nanotubes · Nanocomposites · Applications

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1 Introduction

Nanomaterials are a fascinating group of materials that have found numerous practical applications. They are defined as materials with at least one dimension in the range of 1–100 nm, with a nanometer being the length of ten hydrogen atoms or five silicon atoms lined up. Although it is difficult to pinpoint the exact history of human use of nanoscale materials, evidence suggests that they have been used for various applications for a long time. For instance, around four thousand years ago, asbestos nanofibers were utilized to reinforce ceramic blends, representing one of the earliest instances of unintentional nanomaterial use by humans [1]. Ag and Au nanoparticles were present in the ancient Lycurgus Cup, created by the Romans in the fourth century A.D. This unique cup exhibits dichroism, appearing green in direct light and red in transmitted light. The color change is attributed to the size and distribution of the nanoparticles, which interact with the incident light and cause the cup to display different colors [2].

In 1914, Zsigmondy coined the term “nanometer.” In 1959, Feynman gave a talk on nanotechnology, titled “There’s Plenty of Room at the Bottom,” where he proposed creating smaller machines at the molecular level. He asked, “Why can’t we write the entire Encyclopedia Britannica on the head of a pin?” This was the first scholarly discussion on nanotechnology [3]. Feynman argued in this address that the rules of nature do not limit our capacity to operate at the atomic and molecular levels, but rather a lack of proper equipment and approaches. The notion of contemporary technology was thus planted. As a result, he is frequently referred to as the “Father of Modern Nanotechnology [4].” Norio Taniguchi is attributed as potentially being the first person to use the term “nanotechnology” in 1974. According to Taniguchi, the field of nanotechnology primarily involves manipulating materials at the level of individual atoms or molecules through processes such as processing, separation, consolidation, and deformation. Although it was initially a topic of discussion prior to the 1980s, the concept of nanotechnology was gradually introduced to researchers as a promising area for future development [5]. The advancement of various spectroscopic techniques has hastened the progress and innovation in the domain of nanotechnology. In the year 1982, IBM scientists introduced the technique of scanning tunneling microscopy (STM) which enabled visualizing single atoms on “flat” surfaces without using any probe tips. Subsequently, atomic force microscopy (AFM) was developed in 1986 and has now emerged as the principal technology for scanning probe microscopy [6]. The need for high-density hard disks has driven the exploration of electrostatic and magnetic forces, leading to the development of Kelvin-probe, electrostatic, and magnetic force microscopy. The field of nanotechnology has rapidly expanded and now permeates almost every aspect of materials chemistry. With constant advancements, sophisticated techniques for characterizing and synthesizing nanomaterials are now readily available, enabling the creation of nanomaterials with increasingly precise dimensions [7].

Nanotechnology is an excellent illustration of a developing technology that offers customized nanomaterials capable of producing high-performing products. These

nanomaterials have already found commercial applications in a wide range of fields, including scratch-resistant paints, surface coatings, electronics, cosmetics, environmental remediation, sports equipment, sensors, and energy storage devices [8]. The purpose of the chapter is to offer a comprehensive overview of nanomaterials, covering their basic concepts, latest developments, and emerging trends in a single platform. The discussion will delve into the synthesis techniques, properties, and potential applications of these materials, highlighting the vast and exciting prospects in this field [9]. While it is not feasible to encompass the entire body of literature on nanomaterials, the chapter presents a comprehensive summary of significant research conducted in the past and present. By gathering information on various types of nanomaterials in a single location, this study serves as a fundamental resource for researchers, providing them with an overview of accomplishments and characteristics in the field.

Nanomaterials are complex to define as there is no agreed-upon, comprehensive definition. The absence of a clear definition allows for varying interpretations and classifications of nanoparticles. Some researchers define nanomaterials as particles with a size of a few nanometers or less, while others use the term to describe particles with a size less than a micrometer. The properties of nanomaterials are influenced by their composition, shape, and size [10]. The effects of nanomaterials on both health and the environment are influenced by various factors, including their size, shape, and other distinctive properties. Defining nanomaterials precisely has been a subject of intense debate within the scientific community, making it challenging to establish a universally accepted definition. Nevertheless, the terms used to describe nanomaterials are not fixed and instead reflect a general understanding drawn from available scientific literature [11].

2 Approaches for the Synthesis of Nanomaterials

In the synthesis of nanomaterials, two techniques are utilised: (Fig. 1), top-down approaches and bottom-up approaches.

3 Top-Down Approaches

Top-down techniques split bulk materials to make nanostructured materials. Mechanical milling, laser ablation, etching, sputtering, and electro-explosion are examples of top-down processes.

Mechanical milling. Mechanical milling is a cost-effective technique that can produce nanoscale products from bulk materials. It is particularly effective in creating phase blends and nanocomposites. The process typically involves ball milling, as depicted in Fig. 2. This method has been successfully employed to fabricate aluminum alloys reinforced with oxides and carbides, wear-resistant coatings, and

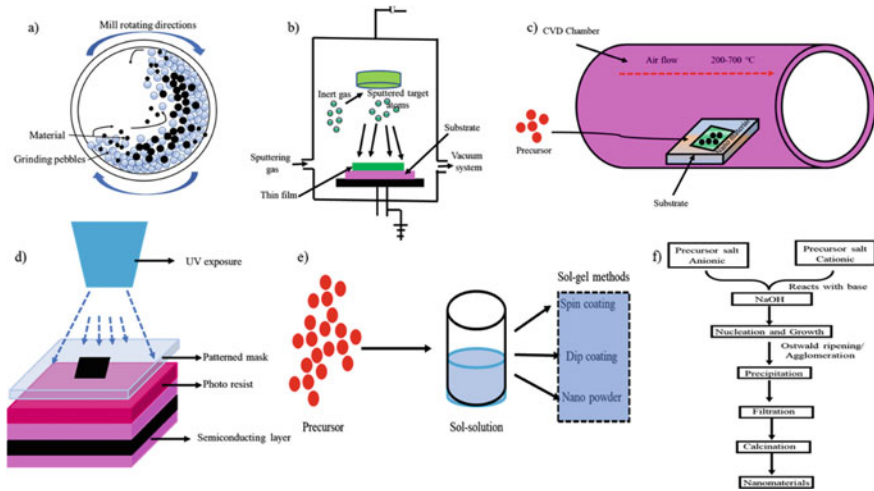


Fig. 1 Nanomaterials' synthesis approach: list of top-down and bottom-up approaches to synthesize nanomaterials. (a) Ball milling, (b) PVD, (c) CVD, (d) lithography, (e) sol-gel method, and (f) co-precipitation method [40]

nanoalloys of aluminum, nickel, magnesium, and copper. Furthermore, ball milling has been utilized to produce carbon-based nanomaterials, which have applications in environmental remediation, energy storage, and conversion. These nanomaterials are unique and versatile, making them an exciting area of research and development [12].

Electrospinning. Electrospinning is a fundamental top-down process that produces nanostructured materials, particularly nanofibers from polymers. One significant improvement in electrospinning is the development of coaxial electrospinning, which utilizes a spinneret composed of two coaxial capillaries. This method allows for the creation of core-shell nanoarchitectures using two viscous liquids or a non-viscous liquid as the core and a viscous liquid as the shell, under an electric field. Coaxial electrospinning is a straightforward and efficient technique for producing large-scale core-shell ultrathin fibers that can reach lengths of several centimeters. This method has been used for developing various types of materials, including inorganic, organic, and hybrid materials, as well as core-shell and hollow polymers. Figure 3 presents a schematic illustration of the typical electrospinning technique [13].

Lithography. Lithography is a useful technology for creating nanostructures by using a focused beam of light or electrons. There are two main types of lithography: masked and maskless. In masked lithography, a specific mask or template is used to transfer nanopatterns onto a large surface area. Photolithography, nanoimprint lithography, and soft lithography are examples of masked lithography. In contrast, maskless lithography, such as scanning probe lithography, focused ion beam lithography,

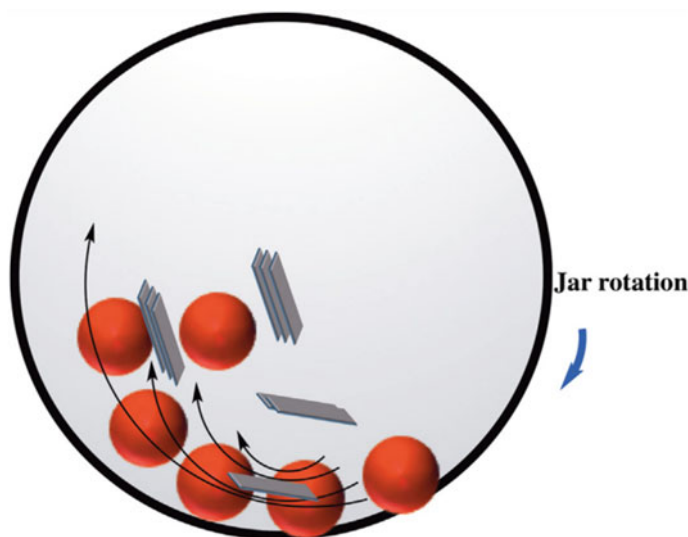


Fig. 2 Mechanical ball-milling process of graphite to graphene in a rotating jar. Reprinted with permission from ref. [39]. Copyright: © 2017, Elsevier B.V. All rights reserved

and electron-beam lithography, does not require a mask, enabling arbitrary nanopattern printing. One approach for achieving 3D micro-nanofabrication is by using ion implantation with a focused ion beam, combined with wet-chemical etching, as shown in Fig. 4 [14].

Sputtering. Sputtering is a method used to produce nanomaterials by bombarding solid surfaces with high-energy particles such as gas or plasma. It is an efficient process for creating thin films of nanomaterials. The technique involves bombarding the target surface with energetic gaseous ions, resulting in the physical ejection of tiny clusters of atoms, which depends on the incident gaseous-ion energy, as shown in Fig. 5. Sputtering can be achieved using various methods, including magnetrons, radio-frequency diodes, and DC diode sputtering, typically conducted in an evacuated chamber where sputtering gas is delivered. By applying a high voltage to the cathode target, free electrons collide with the gas, producing gas ions. The positively charged ions are accelerated toward the cathode target in the electric field, repeatedly striking it, and causing the ejection of atoms from the target's surface. To create WSe_2 -layered nanofilms on substrates like SiO_2 and carbon paper, magnetron sputtering is utilized. This approach is intriguing because the sputtered nanomaterial composition is the same as the target material but with fewer contaminants, making it a less expensive alternative to electron-beam lithography [15].

The arc discharge method. The process of arc discharge can be utilized to produce a wide range of nanostructured materials, including carbon-based ones such as fullerenes, carbon nanohorns (CNHs), carbon nanotubes, few-layer graphene (FLG), and amorphous spherical carbon nanoparticles. The synthesis of fullerene

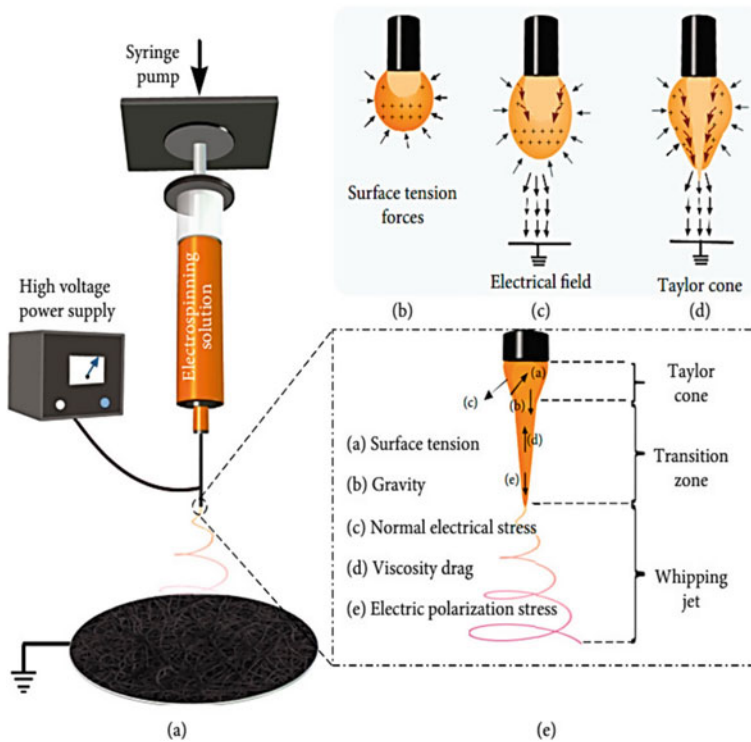


Fig. 3 Nanomaterials' electrospinning approach [32]

nanomaterials holds a particular significance in this method. To generate these materials, a chamber is prepared with two graphite rods, and helium gas is introduced and maintained at a specific pressure level. It is crucial to ensure that the chamber is filled with pure helium since the presence of moisture or oxygen can hinder the formation of fullerenes. By applying an arc discharge between the ends of the graphite rods, the carbon rods are vaporized, leading to the formation of the desired nanostructured materials [16] (Fig. 6).

Laser ablation. Laser ablation synthesis is a technique for producing nanoparticles by subjecting the target material to a high-intensity laser beam. This process causes the precursor material to vaporize and subsequently form nanoparticles. As no stabilizing agents or other chemicals are necessary, laser ablation can be considered an eco-friendly method for producing noble metal nanoparticles. This process can be used to synthesize a diverse range of nanomaterials, including metal nanoparticles, carbon nanomaterials, oxide composites, and ceramics. A novel method for producing monodisperse colloidal nanoparticle solutions without the use of surfactants or ligands is pulsed laser ablation in liquids. The nanoparticle parameters, such as average size and distribution, can be modified by adjusting the fluence, wavelength, and laser salt addition. Figure 7 illustrates the TEM image of Tb_2O_3 nanopowder

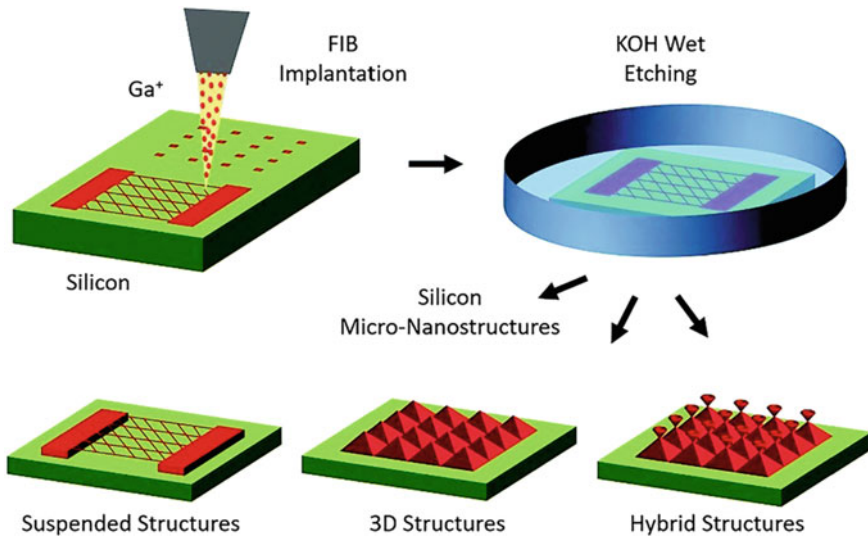


Fig. 4 Schematic diagram of the fabrication of 3D micro-nanostructures with an ion beam through bulk Si structuring. The implantation in Si is done through Ga FIB lithography. Reprinted with permission from ref. [33]. Copyright: ©2020, Elsevier B.V. All rights reserved

synthesized by the laser ablation method along with the histogram of particle size distribution [17].

4 Bottom-Up Approaches

Chemical vapor deposition (CVD). Chemical vapor deposition (CVD) is a crucial technology for producing carbon-based nanomaterials. It involves the chemical reaction of vapor-phase precursors, which results in a thin coating on the substrate surface. For a precursor to be ideal for CVD, it must meet several criteria such as high volatility, chemical purity, evaporation stability, low cost, non-hazardous nature, long shelf life and should not produce any leftover contaminants upon breakdown. For instance, the production of carbon nanotubes using CVD involves heating a substrate to high temperatures in an oven, followed by gradual injection of a carbon-containing gas (like hydrocarbons) as a precursor. At high temperatures, the gas breaks down, releasing carbon atoms that recombine to form carbon nanotubes on the substrate. However, the type of nanomaterial formed depends heavily on the catalyst used. For example, the use of Ni and Co catalysts results in the production of multilayer graphene in CVD-based graphene synthesis, while Cu catalysts produce monolayer graphene. CVD is a highly effective method for creating high-quality nanomaterials and is well-known for producing two-dimensional nanomaterials, as shown in Fig. 8 [18].

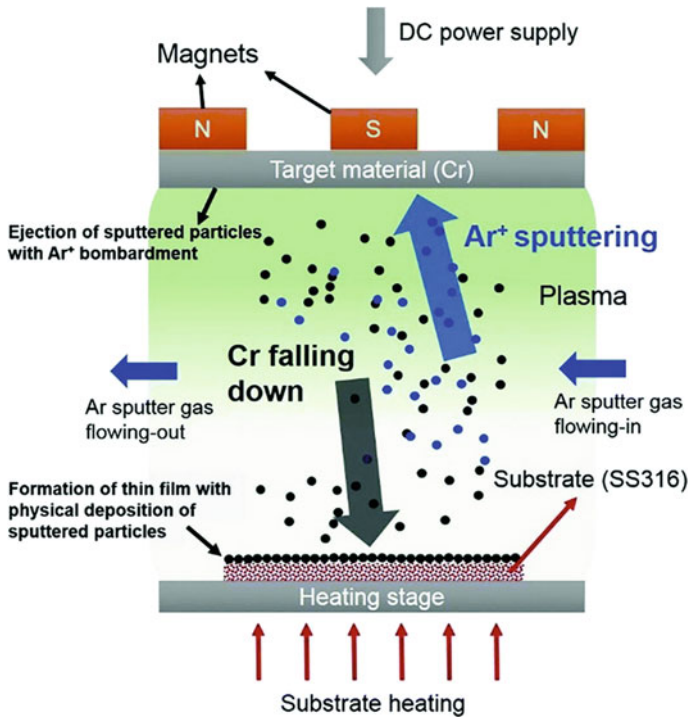


Fig. 5 DC magnetron sputtering process. Reprinted with permission from ref. [34]. Copyright: ©2017, Elsevier Ltd. All rights reserved

Solvothermal and hydrothermal methods. The hydrothermal process is a widely used method for producing nanostructured materials. This technique involves a heterogeneous reaction in an aqueous medium at high pressure and temperature near the critical point in a sealed vessel. Similarly, the solvothermal approach is used to produce nanostructured materials but is performed in a non-aqueous liquid. Both hydrothermal and solvothermal procedures are typically used in closed systems. The microwave-assisted hydrothermal approach, which combines the advantages of both hydrothermal and microwave processes, is gaining popularity for engineering nano-materials. These methods can create a variety of nanogeometries such as nanowires, nanorods, nanosheets, and nanospheres, making them fascinating and useful for producing diverse nanostructures [19].

The sol-gel method. The sol-gel method is a popular wet-chemical technique used for creating high-quality nanomaterials based on metal oxides. This method involves the conversion of liquid precursor into a sol during the production of metal-oxide nanoparticles. Eventually, the sol is transformed into a network structure called a gel. Metal alkoxides are commonly used as precursors for this process. The sol-gel technique can be executed in multiple phases. In the first phase, the metal oxide is hydrolyzed in water or alcohol to produce a sol. Subsequently, condensation occurs,

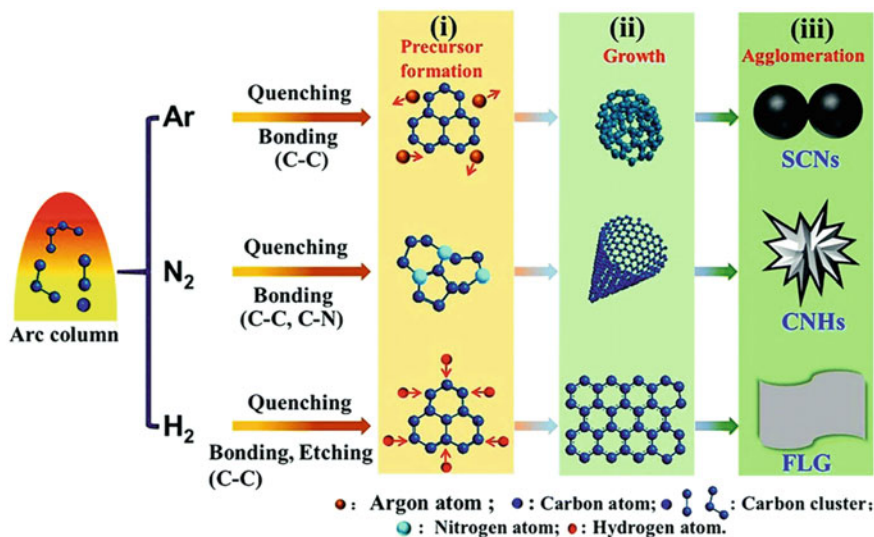
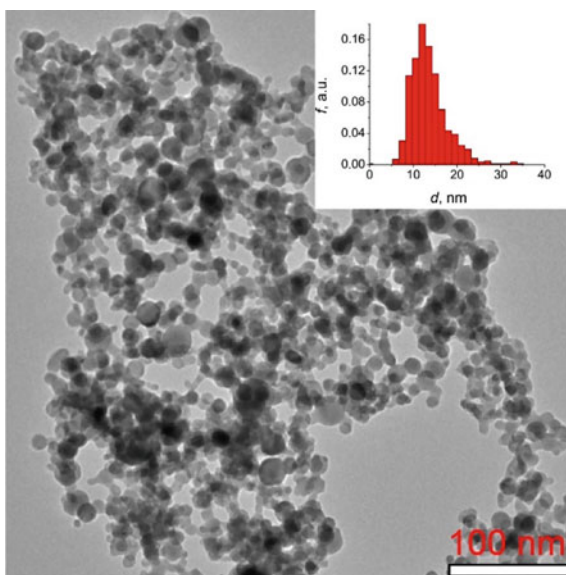


Fig. 6 DC arc discharge approach. Reprinted with permission from ref. [35]. Copyright: ©2019, Elsevier Ltd. All rights reserved

Fig. 7 TEM image of Tb₂O₃ nanopowder synthesized by the laser ablation method. The inset presents the histogram of particle size distribution [36]



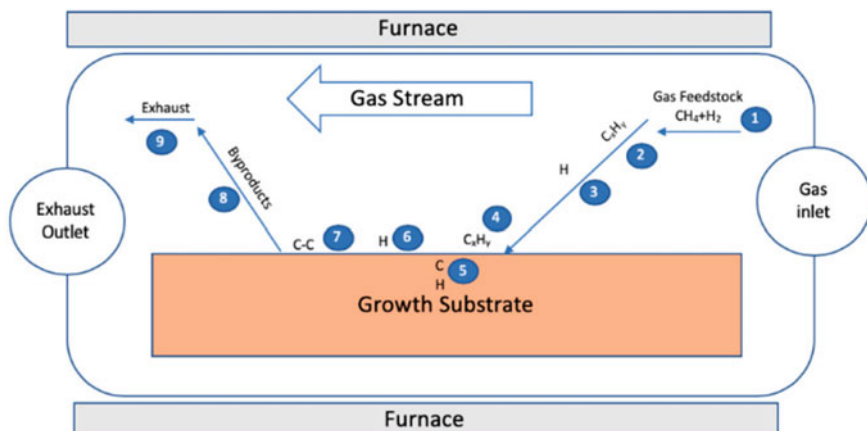


Fig. 8 Schematic diagram of thermal chemical vapor deposition (CVD) growth of graphene [37]

which increases the viscosity of the solvent and results in the formation of porous structures. These structures are then left to age [20]. During the process of condensation or polycondensation, hydroxo-(M-OH-M) or oxo-(M-O-M) bridges can be formed, leading to the formation of metal-hydroxo- or metal-oxo-polymer in solution. This process can continue during aging, which can cause structural changes, altered characteristics, and reduced porosity. As the aging progresses, the porosity decreases, and the space between colloidal particles increases. Once the aging process is complete, the gel is subjected to drying, which eliminates water and organic solvents. Finally, nanoparticles are produced through calcination.

The sol-gel process for creating films and powders, as shown in Fig. 9, is influenced by various factors such as the precursor type, hydrolysis rate, aging duration, pH, and molar ratio of H_2O to the precursor, which all play a role in determining the final product. One of the significant advantages of the sol-gel technique is its cost-effectiveness, as well as the homogeneity of the resulting material, low processing temperature, and its simplicity in producing composites and intricate nanostructures [21].

Soft and hard templating methods. Nanoporous materials can be created through two widely used techniques, namely soft and hard template approaches. Among these, the soft template approach is a traditional and straightforward method for producing nanostructured materials. This technique has gained popularity due to its simplicity, low experimental requirements, and the ability to produce materials with diverse morphologies. Soft templates, which include block copolymers, flexible organic molecules, and anionic, cationic, and non-ionic surfactants, are employed in the soft template approach to generate nanoporous materials [21]. Soft templates play a crucial role in the formation of ordered mesoporous materials by facilitating the most prevalent interactions such as hydrogen bonding, van der Waals forces, and electrostatic forces between the templates and precursors. The 3D-structured liquid

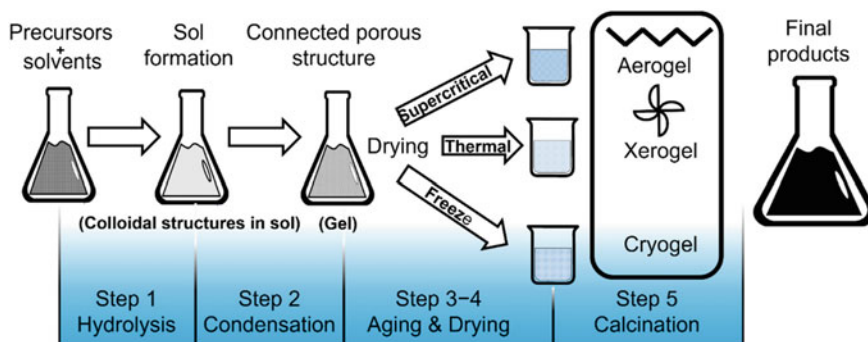


Fig. 9 Schematic of the sol–gel method of synthesis [38]

crystalline micelles are used as soft templates to create 3D-ordered mesoporous structures. Alkyltrimethylammonium surfactants are employed to generate different types of mesoporous solids, such as lamellar (MCM-50), cubic (MCM-48), and hexagonal (MCM-41) ordered mesoporous silicas. Two techniques, namely cooperative self-assembly and “true” self-assembly, are generally employed to synthesize ordered mesoporous materials using a soft templating method [22].

5 Liquid–Crystal Templating is Adopted

Reverse micelles can be used to produce nanoparticles of specific shapes and sizes. In a water-in-oil emulsion, the hydrophilic heads of the surfactant molecules are oriented toward a water-filled core, resulting in the formation of reverse micelles. This core acts as a nanoreactor for the creation of nanoparticles, serving as a reservoir for the development of nanomaterials. By adjusting the water-to-surfactant ratio, the size of these nanoreactors can be controlled, which in turn affects the size of the nanoparticles produced using this method. Decreasing the water concentration leads to the formation of smaller water droplets, resulting in the creation of smaller nanoparticles. Conversely, increasing the water concentration results in larger water droplets and larger nanoparticles [22].

6 Unique Nanomaterial Features

The properties of matter at the nanoscale exhibit notable differences from their bulk counterparts. Size-dependent effects become more pronounced at this scale, leading to changes in the characteristics of materials. For instance, while Au (gold) appears yellow in bulk, it appears purple or crimson at the nanoscale. By varying the size

of nanomaterials, their properties can be altered. Electrical characteristics, in particular, exhibit significant variations at the nanoscale, compared to bulk materials. For instance, boron, which is not considered a metal in its bulk form, can become an excellent 2D metal when arranged in a two-dimensional network of borophene. Additionally, nanomaterials possess enhanced mechanical properties as compared to their bulk equivalents due to improved crystal perfection or decreased crystallographic flaws [23]. Semiconductor electronic properties in the size range of 1–10 nm are governed by quantum mechanics, and this principle applies to nanospheres called quantum dots. The optical properties of nanomaterials, including quantum dots, are greatly influenced by their size and shape. The diameter of an exciton, which is an electron–hole pair generated by light, ranges from 1 to 10 nm. Therefore, by varying the size of nanoparticles within this range, absorption and emission of light by semiconductors can be controlled. In contrast, the electrical and optical effects in metals are expected to be observed in the 10–100 nm range due to the mean free path of electrons being in that range. The hue of metal nanoparticle aqueous solutions can be changed by altering their aspect ratio. For instance, aqueous solutions of Ag NPs exhibit different hues at varying aspect ratios, with an increase in aspect ratio leading to a red shift in the absorption band [24].

7 Carbon-Based Nanomaterials

Carbon-based nanomaterials have been extensively investigated due to their remarkable properties, making them a promising candidate for various applications. The exceptional properties of these nanomaterials, which can be tailored, have attracted the attention of many researchers, offering potential solutions to contemporary challenges in diverse fields. The carbon family encompasses a wide range of nanomaterials, including carbon nanotubes (CNTs), fullerenes, graphene, carbon nanohorns, carbon-based quantum dots, and many more. This section provides a concise overview of these nanomaterials, highlighting their primary characteristics and significance [25]. Here, we will discuss about fullerenes. The separate chapter is dedicated to carbon-based nanomaterials in this book.

Fullerenes, discovered in 1985, are a unique allotrope of carbon. These sp^2 -hybridized carbon atom cages are highly symmetrical and distinct from other carbon allotropes because they consist of a specific number of carbon atoms. Fullerenes are available in different sizes based on the number of carbon atoms they contain, such as C₆₀, C₇₀, C₇₂, C₇₆, C₈₄, and C₁₀₀. Among these, the most well-known and commonly studied fullerene is C₆₀. C₆₀ fullerene has a hollow structure with 60 carbon atoms arranged in 12 pentagons and 20 hexagons. The carbon atoms are bonded together through sp^2 -hybridized covalent bonds, and the structure has icosahedral symmetry. The five-membered rings of the fullerene are separated by six-membered rings. Due to its small size, spherical shape, and isotropic nature, C₆₀ fullerene is considered as a perfect zero-dimensional material. The spherical shape of

fullerene is known to be one of the most stable structures in nature, and C60 fullerene is no exception [26].

Fullerenes, which were the first symmetric material among carbon-based nanomaterials, revolutionized the field of nanotechnology, paving the way for the discovery of other nanostructured materials such as carbon nanotubes and graphene. Their unique properties have made them a promising material for diverse applications. In addition to being found in nature and interstellar space, fullerenes were recognized as the “chemical of the year” in 1991 due to the significant research efforts dedicated to them. Unlike other carbon allotropes, fullerenes exhibit some solubility in various solvents, which sets them apart and enhances their potential for use in various sectors [27].

The chemical alteration of fullerenes, which improves their application efficacy, is an intriguing topic. There are two methods for modifying fullerenes: inner-space modification and outer-surface modification.

The solitary pentagon rule is not always followed by endohedral fullerenes (IPR). Due to their valuable prospective uses, fullerene nanocages have garnered considerable attention in the field of materials chemistry to date. In open space, neutral and charged single atoms are highly reactive and unstable. These reactive species can be stabilized in the limited environment of fullerenes; for example, the LaC60^+ ion does not react with NH_3 , O_2 , H_2 , or NO [28]. Thus, reactive metals can be shielded from the environment by encasing them in fullerene cages. Endohedral fullerene containing lithium (Li@C60) is another new carbon nanomaterial. Because lithium metal is very reactive, it must be stored or used under strict environmental controls. In other words, lithium storage necessitates the use of secure buildings. Endohedral fullerene based on lithium exhibits novel solid-state characteristics [29, 30]. Lithium atoms are protected from external influences due to their encapsulation in fullerene. Endohedral fullerenes based on lithium have the potential to enable nanoscale lithium batteries. Larger fullerenes are often required for the production of endohedral metallofullerenes because they have big cages that can accept lanthanide and transition metal atoms more smoothly. Fullerene nanocages can be used to store gases. Fullerene is being considered as a hydrogen storage material [31]. Nanomaterials therefore are the building blocks of modern technology and are useful in many applications [41].

8 Conclusions

Nanomaterials are materials that have at least one dimension between 1 and 100 nm, making them extremely small in size. They can have unique optical, electrical, thermophysical, or mechanical properties. Nanomaterials come in various shapes and sizes, such as one-dimensional, two-dimensional, or three-dimensional, and can be spherical, tubular, irregular, solitary, fused, aggregated, or agglomerated. Some examples of nanomaterials include carbon nanotubes, fullerenes, metal oxides (such as zinc oxide, iron oxide, titanium dioxide, and cerium oxide), metals (such as gold, silver,

and iron), and quantum dots (cadmium sulfide and cadmium selenide). Nanomaterials can be produced using gas- and liquid-phase techniques as well as photolithography methods. Imaging of nanomaterials is possible using microscopy methods such as TEM, AFM, and STM. Carbon nanotubes are notable for their high tensile strength, low density, high thermal conductivity, and flexible electrical activity. They also have a large surface area and high electron conductivity due to their “perfect” configuration of carbon–carbon bonds. Nanocomposites are composite materials made up of at least one component on the nanoscale and can be used in various applications. For example, nanocomposite coatings can greatly decrease water vapor permeability, while inorganic–organic composites can be coated with strong and scratch-resistant coatings for glasses and lenses. Nanomaterials can also be found in nature, such as in lotus leaves and gecko feet, which inspire the development of clean and smooth fabrics, building exteriors, and the ability to move quickly on any surface. Nanomaterials have a wide range of applications in various industries, including the car industry, energy, the military, the environment, food and agriculture, cosmetics, and sports.

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Soft Nanomaterials and Their Applications



Sara Dua, Hilal Ahmed, and Najmul Arfin

Abstract Soft nanomaterials have garnered significant attention in recent years due to their unique mechanical and chemical properties. This chapter provides an overview of the synthesis, characterization, and applications of soft nanomaterials, including hydrogels, liposomes, and self-assembled macro-molecules. We begin by discussing the properties and synthesis methods of these materials, such as solution mixing, emulsification, and self-assembly. The chapter also explores the various applications of soft nanomaterials, including in drug delivery, tissue engineering, biosensors, and personal care products. Finally, the chapter concludes with a summary of the current state of research and suggests possible directions for future work in this exciting field.

Keywords Soft matter · Nanomaterials · Synthesis · Classification · Applications · Drug delivery · Tissue engineering

1 Introduction

A nanomaterial can be defined as any material having at least one dimension in the range of 1–100 nm (nm) [1, 2]. Nanomaterials with varied morphological features, viz. spherical, cubical, triangular, rod-shaped, star-shaped, flower-shaped, sheets, etc., and with different compositions have been synthesized by various research groups [3]. The science that deals with the design, development, modification, characterization, and application of such materials is known as nanotechnology.

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2 Types of Nanomaterials

Nanomaterials can be classified into different categories based on their size and dimensions:

2.1 Size and Dimension

On the basis of size and dimensions, nanomaterials can be categorized as zero dimensional (0D), one dimensional (1D), two dimensional (2D), and three dimensional (3D) [1, 4–6]. The above categorization is pictorially depicted in Fig. 1.

1. **Zero-dimensional nanomaterials:** Zero-dimensional nanomaterials are described as materials having all the three dimensions in the nano-range. This group of nanomaterials is represented by nanoparticles, fullerenes, quantum dots, etc.
2. **One-dimensional nanomaterials:** One-dimensional nanomaterials possess only one direction larger than 100 nm with the other two dimensions being in nano-range. The common examples of this class include nanotubes, nanorods, nanowires, nanofibers, nanofilaments, and nanoribbons. These materials have an inherently high aspect ratio (ratio of the length to diameter).
3. **Two-dimensional nanomaterials:** Two-dimensional nanomaterials have two dimensions beyond nano-range while the third dimension is confined within

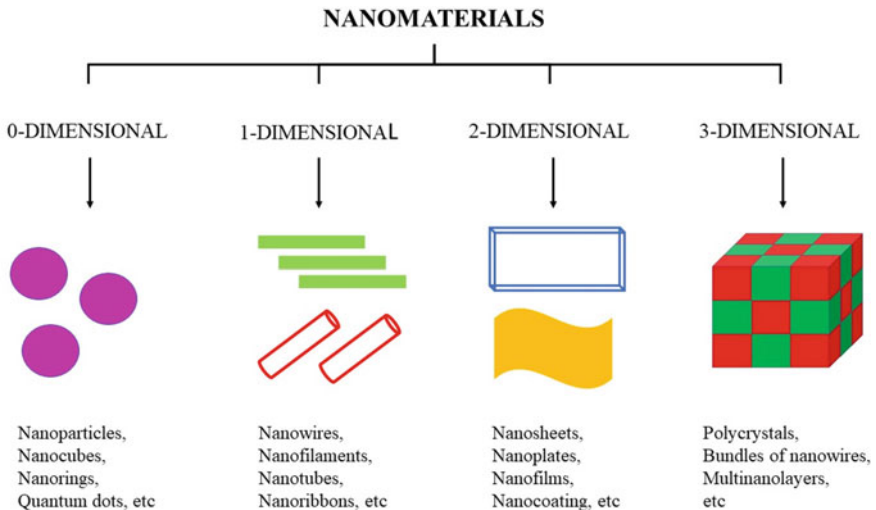


Fig. 1 Different types of nanomaterials based on their dimensions

the nano-range (1–100 nm). This category comprises of nanofilms, nanolayers, nanoplates, nanonetworks, nanosheets, and nano-coatings.

4. **Three-dimensional nanomaterials:** Three-dimensional nanomaterials are bulk materials that have no dimension in the nano-range, however, are composed of individual building blocks of zero, one-, or two-dimensional nanomaterials. They include multi-nanolayers, bundles of nanowires, polycrystals, etc.

2.2 *Origin*

Nanomaterials can also be classified into various categories—natural, incidental, engineered, and bioinspired, based on their origin.

1. **Natural nanomaterials:** Naturally occurring nanomaterials are formed in the nature through physical, chemical, mechanical, and/or biogeochemical processes without the involvement of any human activity, such as halloysite nanotubes (HNT clay), montmorillonite (MMT clay) nanocellulose fibres, nanocellulose crystals, metal oxides, viral capsid and protein structures, milk colloids, blood colloids, etc. [7–9].
2. **Incidental nanomaterials:** Any nanomaterial produced unintentionally due to direct or indirect anthropogenic activities (mining, smelting, welding, agricultural practices) is categorized as incidental nanomaterial, for example, welding fumes, soot, Magneli phases, nano plastics, fumed silica, pigments, etc. [7–9].
3. **Synthetic/Engineered nanomaterials:** Any nanomaterial produced intentionally by humans in the laboratory or industry is known as engineered nanomaterial, for example, carbon nanotubes, liposomes, laponite clay, quantum dots, metallic nanoparticles, etc. [7–9].
4. **Bioinspired nanomaterials:** Bioinspired nanomaterials are a type of engineered nanomaterials, nanoscale systems or device that are designed based on the principles of biology and mimic natural nanomaterials and living matter [7, 10]. Such bioinspired or biomimetic nanomaterials with biological functions include smart robotic devices, organs-on-chips, soft, polymeric nanomaterials used for tissue engineering and bone implants, nanoscale biosensors, etc. [7, 11].

The incidental and engineered nanomaterials are grouped together as anthropogenic nanomaterials [8].

2.3 *Nature of Their Structural Components*

The nature of the nanomaterial components that construct their structure also affects the type of nanomaterial.

1. **Soft nanomaterials:** Nanomaterials composed of organic materials, such as natural or synthetic polymers, proteins, DNA, lipid, and natural or synthetic clay,

are known as soft nanomaterials. These are essentially rich in carbon compounds, or their self-assemblies are formed due to covalent or non-covalent interactions. Micelles, polymeric nanoparticles, lipid nanoparticles, liposomes, dendrimers, nanogels, and nanoclay particles are a few examples of this class [12, 13].

2. **Hard nanomaterials:** On the other hand, nanomaterials composed of inorganic materials, such as metals and silica, are known as hard nanomaterials. Metallic and bimetallic nanoparticles, metal oxide nanoparticles, magnetic nanoparticles, quantum dots, fullerenes, carbon nanotubes, and mesoporous silica nanoparticles fall under this category [14, 15].
3. **Hybrid nanomaterials:** Recently, researchers are combining the properties of organic and inorganic nanomaterials into new and smart hybrid organic–inorganic (soft-hard) nanomaterials with enhanced catalytic activity, biocompatibility, optical, mechanical, and thermal properties [14].

3 Methods of Synthesis of Nanomaterials

The synthesis of engineered nanomaterials by different techniques falls under one of the two main approaches [7, 16, 17]:

1. **Top-down approach:** It is the destructive method in which bulk material disintegrates into smaller fragments that transform into nanomaterials.
2. **Bottom-up approach:** It is the constructive method in which nanomaterials are formed from the assembling of individual, relatively simpler atomic, and molecular components by nucleation and growth.

These approaches include various physical, chemical, and biological methods, as listed in Fig. 2, for the synthesis of nanomaterials with different desired properties. The physical and chemical methods produce uniform-sized and stable nanomaterials; however, the physical methods require very high pressure and temperature conditions while chemical methods use expensive and toxic materials, such as organic solvents and reducing materials. Therefore, nowadays, extensive research is being focused on the biological methods of synthesis due to several advantages, such as simplicity, safety, less use of toxic chemicals, energy-efficient, and use of inexpensive, easily available, and natural raw materials. Moreover, the nanomaterials synthesized using the biological methods are more biocompatible and useful for applications in medicine, cosmetics, food, and beverage industries [18, 19].

4 Properties of Nanomaterials

The properties of nanomaterials are substantially different from their bulk counterparts owing to their small size. The smaller size of these materials contributes to their higher surface area to volume ratio and the presence of a large fraction of atoms on

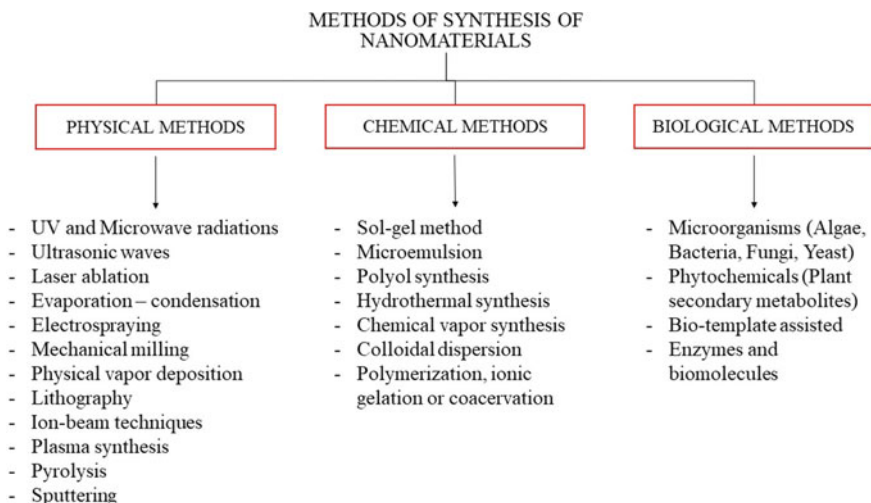


Fig. 2 Different methods of nanomaterial synthesis

the surface. This provides the materials with unique physicochemical properties, as discussed below.

4.1 Catalytic Properties

The smaller size of particles provides them with remarkable physical and chemical properties such as reactivity, catalytic, and absorbance activity. Additionally, electronic structure, number of surface atoms, and the presence of some crystallographic defects on the surface of nanoparticles which plays a key role in their degree of reactivity and catalytic activity. Moreover, the presence/absence of surface charge on the nanomaterials, its nature, and magnitude substantially define their stability, aggregation, agglomeration, colloidal behaviour, and affinity towards different functional groups and the environment. The higher the magnitude of charge (positive or negative), higher will be colloidal stability of the nanoparticles, thus lesser aggregation [4].

4.2 Quantum Confinement Effect

Another peculiar feature associated with these materials is the quantum confinement effect. This effect refers to the physical confinement of electrons and holes into small space and the effect becomes more pronounced when the particle dimensions are extremely small or at the nanoscale dimension [3, 6, 16, 20]. This leads to unique

optical, electrical, and magnetic behaviours when compared to their conventional counterparts [21].

4.3 Optical Properties

Nanomaterials have exceptional linear and non-linear optical properties that differ significantly from their bulk counterparts [22]. The optical properties, such as absorption, adsorption, transmission, fluorescence, reflection, refraction, deflection, and emission of light, depend on the electronic structure of the nanomaterials. Increase in energy level spacing due to the quantum confinement effect and surface plasmon resonance is major contributors of the optical properties of materials at the nanoscale. For example, gold and silver nanoparticles with different morphologies produce different colours [4].

4.4 Electrical Properties

Likewise, as the size of the material reaches nanoscale dimensions, the electrical properties, such as conductivity and resistance, of the bulk materials change significantly. Increase in the energy band gap due to reduced size and quantum effect is eminently responsible for the deviation in these properties of nanomaterials as compared to the bulk particles [4, 23, 24].

4.5 Magnetic Properties

Furthermore, magnetism in nanomaterials is also greatly affected by the small size and surface effects (atoms at the surface have a low coordination number as compared to atoms in the bulk). In some instances, a change in magnetic behaviour of the bulk material may be observed when the dimensions are altered to the nanoscale. This can be witnessed in the case of magnetite (Fe_3O_4), where the bulk material is ferromagnetic while its nanoparticles show superparamagnetic-like-behaviour [25]. Some non-magnetic bulk materials such as platinum, palladium, and gold may exhibit magnetism in their nanofoms due to their small size and quantum confinement effect [20, 26].

4.6 Mechanical Properties

Nanomaterials also exhibit excellent mechanical properties, such as tensile strength, Young's modulus, elasticity modulus, plasticity, fracture toughness, bending strength, hardness, fatigue strength, impact resistance, and rigidity due to their volume, surface, and quantum effects. To improve the mechanical characteristics of a nanomaterial, often nanoparticles with good mechanical properties are added to form a nanocomposite with improved strength, impact resistance, hardness, and other features. The key factors associated with mechanical properties of a nanomaterial include the production process, grain size, grain boundary structure, crystal defects (vacancies, triple junction, dislocation, twins, stacking faults), porosity, chemical composition, and functionalization [27–29]. The bond strength between atoms also affects the elasticity and melting temperature of the nanomaterials. They have lower elastic properties and melting point than bulk materials due to enhanced surface area, grain boundary area, and concentration of defects and decreased bonding energy between atoms [29].

5 Introduction to Soft Nanomaterials

The principle of fabrication is what differentiates a soft nanomaterial from a hard nanomaterial. Hard nanomaterials are usually synthesized by the precipitation of inorganic salts, while the soft nanomaterials are primarily characterized by the self-assembly of their building blocks (organic molecules) into more organized nanostructures. This involves a combination of forces, namely hydrophobic interaction, electrostatic interaction, van der Waals forces, hydrogen bonding, π - π bonding, metal coordination, and host-guest recognition [30, 31]. The energy dissipated by the motion, fluctuations, and orientation of the molecules during their self-assembly into soft nanomaterials is comparable to the thermal energy. The later significantly affects these nanoscale materials due to breaking and re-forming of the weak interactions between the molecules and helps the system to attain thermodynamic equilibrium [32]. The two main types of building blocks of soft nanomaterials are polymer-based and amphiphilic materials. Additionally, biomolecules like lipids, viral proteins, enzymes, peptides, and oligonucleotides also have the property of self-assembling into bio-nanomaterials [31]. The other key features of soft nanomaterials are the presence of zwitter ionic entities, polar, and non-polar regions, the ability to encapsulate other molecules, and a dynamic character due to weak interactions between the building blocks [30]. The major types of soft nanomaterials have been briefly discussed in the following sections.

5.1 Nanogels

Nanogels are three-dimensional soft colloidal hydrogel materials with unique properties that differ greatly from the classic colloids [33, 34]. These hydrogels are typically composed of an organic hydrophilic polymer that is physically and/or chemically cross-linked via covalent or non-covalent interactions into gel networks. These gels swell up strongly in aqueous medium, and the high solvent content leads to fluid-like transport properties while their dimensional stability is attributed to the cross-linking in their structure [35].

5.2 Dendrimers

Dendrimers are monodispersed, synthetic, polymer-based nanomaterials with an ordered and regular, highly branched, 3D structure. These soft materials have peculiar traits, such as structural homogeneity, globular/ellipsoidal shape, high surface reactivity due to the presence of different chemical groups on their surface, and the nature of the internal cavities, that make them good candidates for applications in biosensors, drug delivery, bone and tissue engineering, etc. [36, 37].

5.3 Liposomes

Liposomes are soft, spherical, lipid bilayer membrane constituting organic nanomaterials. They can either be unilamellar, having only a single lamella of membrane or multilamellar, having multiple lamellae of membranes. These particles have an aqueous interior compartment that can be loaded with water-soluble/hydrophilic drugs while the water-insoluble/hydrophobic drugs can be loaded into the membranes. Thereby, liposomes act as good carriers for various drug delivery applications [38].

5.4 Polymeric Nanoparticles

Polymeric nanoparticles are organic nanomaterials derived from natural (cellulose, zein, starch, etc.), synthetic (polycaprolactone, polyethylene glycol, polyvinyl alcohol, etc.), or their combinations. These nanomaterials are widely studied and being researched for their extensive application as delivery vehicles. They can be categorized into nanospheres (matrix systems) and nanocapsules (reservoir systems)

depending on the morphology of the nanoparticle. Nanospheres comprise a continuous polymeric network in which molecules, such as drugs, can either be encapsulated inside or attached onto the surface while nanocapsules comprise of an oily core surrounded by a polymeric membrane, where the drug is usually dissolved in the core or sometimes adsorbed onto the surface [38, 39].

5.5 Vesicles

Vesicles can be defined as closed, spherical, and bilayer structures having dimensions in the nanometre range. These can either be synthesized via self-assembly of amphiphilic molecules or by the polymerization of these self-assembled structures. Vesicles formed from block copolymers, such as poly(styrene)-*b*-poly(acrylic acid), poly(ethylene oxide)-*b*-polycaprolactone, and poly(ethylene oxide)—poly(styrene), are known as polymersomes [40]. Similarly, vesicles formed due to the self-aggregation of amphiphilic metal complexes are termed as metallovesicles. They have the dual advantage of having small hydrophobic cavities acting as nanoreactors as well as the catalytic properties of metal ions [41]. Further, these particles assist in the selection of methods in which reactions can be performed in relatively mild conditions [42].

5.6 Micelles

Micelles are spherical, amphiphilic, self-assembled, nanomaterials consisting of a water-soluble, polar, hydrophilic shell, a non-polar, and hydrophobic core. They generally range from 5 to 50 nm. Micelle formation takes place at certain concentration (minimum micellar concentration) and temperature conditions; below this concentration, the amphiphiles exist as individual entities in the solution [38, 43, 44]. These materials have immense application as carriers for targeted drug delivery. These structures provide a sustained and controlled release of drugs and other loaded macromolecules, provide them with chemical and physical stability, and improve their bioavailability, pharmacokinetics, and tissue distribution [43].

5.7 Microemulsions

Microemulsions are transparent/translucent, homogenous, thermodynamically stable, and less viscous systems that are comprised of two immiscible solvents in the presence of an amphiphile, such as surfactants. The particle size of these emulsions ranges from 10 to 200 nm. Water-in-oil and oil-in-water microemulsions are the two types of microemulsion systems. The key factors determining the type of emulsion

are the ratio of water and oil and the hydrophilic-lipophilic value of the surfactant. Water-in-oil microemulsions are characterized by the dispersion of water droplets in a non-polar solvent medium stabilized by a layer of surfactant. On the contrary, oil-in-water microemulsions are the systems in which oil (water-immiscible liquid) droplets are dispersed in an aqueous medium [45, 46].

5.8 Soft Matter Nanotubes

Soft matter nanotubes are self-assembled organic tubular structures with one dimension in the nano-range. These nanotubes can be formed by bonding between particles belonging to either a single type of component or multiple components. Their size tunable property favours their formation into gels or liquid crystals, dispersion in the matrix, or hybridization with other components of the matrix. These materials have a wide array of applications in every field of science, for example, as nanoreactors, nanochannels, delivery vehicles, sensor, catalyst, energy device, etc. The building blocks of these nanotubes are amphiphiles, i.e. molecules having a hydrophilic head and a hydrophobic tail or bolaamphiphiles, i.e. amphiphilic molecules having two hydrophilic head groups and a hydrophobic tail group [47, 48]. A schematic representation of some of the soft nanomaterials is displayed in Fig. 3.

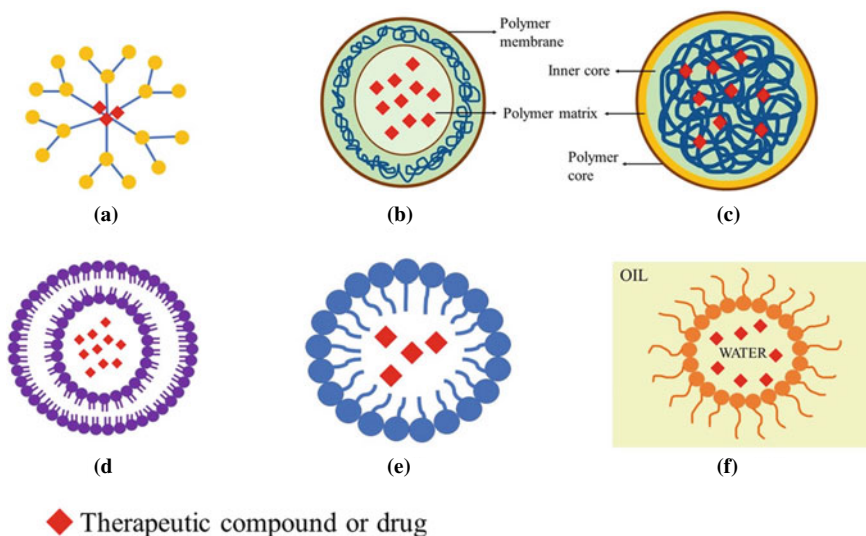


Fig. 3 Different types of soft nanomaterials. **a** Dendrimer, **b** polymeric nanocapsule, **c** polymeric nanosphere, **d** vesicle, **e** micelle, and **f** water-in-oil microemulsion

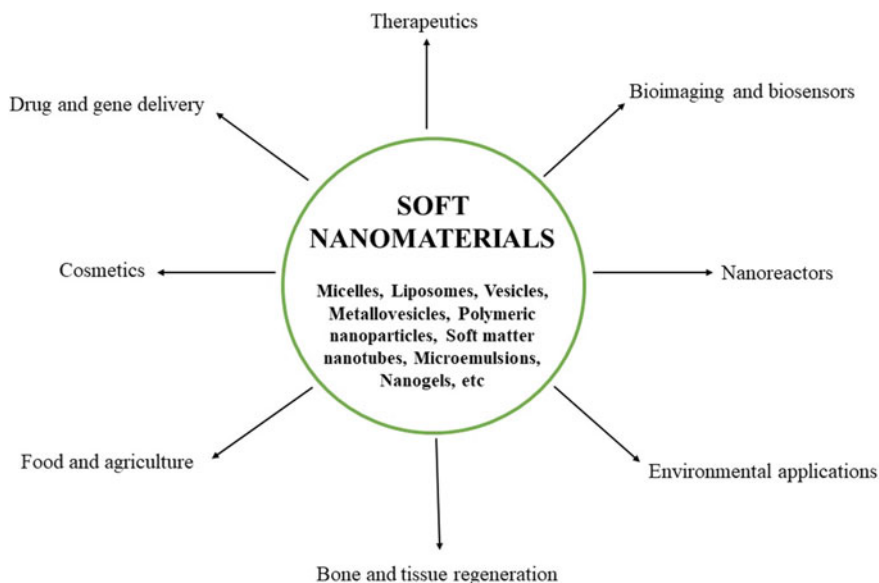


Fig. 4 Applications of soft nanomaterials

5.9 Applications of Soft Nanomaterials

The applications of soft nanomaterials are spread to every field of science (Fig. 4). This can be attributed to their small size, large surface area to volume ratio, surface charge, composition, extraordinary physical, chemical, optical, electrical, magnetic, and mechanical properties. These properties of nanomaterials can be fine-tuned in accordance with the desired applications. In addition to this, soft nanomaterials are biocompatible and less toxic in nature and are therefore good candidates for biomedical applications, such as nano carriers, drug delivery, therapeutics, bioimaging, biosensors, tissue regeneration, and cosmetics. These materials can also be applied in the fields of bioelectronics, food and agriculture, and environmental remediation. This chapter discusses the recent advances in the applications of different soft nanomaterials in various fields of science.

5.10 Drug and Gene Delivery

After administration, a drug must successfully reach its target site, without being degraded in or excreted from the body, to perform efficiently and effectively. Therefore, a number of soft nanomaterials, including polymeric nanoparticles, liposomes,

vesicles, metallovesicles, micelles, metallomicelles, and hydrogels, have been developed and studied as carriers for various drugs, genes, and proteins. Das et al. demonstrated the use of chitosan nanoparticles for the efficient delivery of *Mycobacterium tuberculosis* lipid particles to trigger enhanced antibody and cell-mediated immune response against these particles [49]. Zhou et al. developed pH-sensitive charge-reversal nanocomplex carriers based on the polymers, poly(β -L-malic acid), and polyethylenimine loaded with the anticancer drug and doxorubicin [50]. The complex was then conjugated with the cell penetrating transactivator of transcription (TAT) peptide and encapsulated within polyethylene glycolated 2,3-dimethylmaleic anhydride. At blood pH, the complex is negatively charged with prolonged circulation time and reduced clearance of the nanocomplex from the body. However, at the pH in the tumour microenvironment, the nanocomplex transforms from negatively to positively charged and can now be internalized by the tumours. Li et al. synthesized doxorubicin-loaded halloysite nanotube (HNT) encapsulated by soyabean phospholipid for the efficient delivery of the drug, for both in vitro and in vivo treatment of gastric cancer [51]. A template-assisted synthesis method for poly(ethylene glycol) nanotubes for the delivery of anticancer drug to orthotopic breast tumours was demonstrated by Newland et al. [52]. This method of nanotube fabrication using an anodized aluminium oxide template helped the authors to tune the physical properties of the nanotubes, such as diameter in the range of 200–400 nm and stiffness in the range of 405–902 kPa. Rao et al. prepared gold nanoparticles using curcumin as an anticancer agent on the surface as well as in the lumen of HNTs followed by chitosan coating of the hybrid nanoparticles [53]. They evaluated the near-infrared responsive properties and the pH-responsive curcumin release of the HNT hybrid system and their application as cancer cell-targeted drug delivery agents. Injectable and porous cryogels of laponite using alginate and tetrazine-norbornene were developed for the delivery of various protein drugs, rGM-CSF, IL-2, IL-15, CCL20, and FIT3L [54]. Joshny et al. optimized the synthesis of liposomes for the topical delivery and sustained release of Lornoxicam [55]. A research group has synthesized coordination polymer metallovesicles using $Zn(NO_3)_2$, different non-steroidal anti-inflammatory drugs (NSAIDs) (naproxen, flurbiprofen, ibuprofen, diclofenac, and mefenamic acid), and a bidentate linker [56]. The developed metallovesicles were then used for the loading of the anticancer drug, doxorubicin hydrochloride, and its in vitro delivery to MDA-MB-231 human breast cancer cells along with the NSAIDs. Fan et al. developed a multilamellar vaccine particle system for the efficient in vivo delivery of Ebola virus glycoproteins into C57BL/6 mice [57]. The nanovaccine system was composed of a lipid film (DOTAP + DOBAQ + DOPC) and a toll-like receptor 4 MPLA cross-linked with the biopolymer thiolated hyaluronic acid. The authors were able to achieve 80% protection rate against the virus after a single dose of vaccination. Maiorova et al. developed layer-by-layer polymeric nanocapsules [using poly(allylamine hydrochloride) and poly(styrene sulphonate) on a calcium carbonate template and a lipid nanovector (using amphiphilic phytantriol molecules and pluronic F-127 as stabilizer) for the encapsulation of vitamin B₁₂ [58]. The developed nanosystems could further be used for the targeted delivery of the encapsulated hydrophilic molecule by internal or external magnetic stimuli. Similarly, an

efficient carrier system based on boronic acid-modified polyamidoamine (PAMAM) dendrimers was synthesized for the delivery of 13 cargo proteins, including lysozyme, bovine serum albumin, horse radish peroxidase, Cas-9, trypsin, cytochrome c, etc., into the cytosol of the cells [59]. Further, Zhao et al. fabricated a pH-temperature dual sensitive liposome system, in which the octylamine grafted poly aspartic acid molecules anchored on the coat outside were pH-sensitive, while the self-assembled cholesterol/cationic bionic layer was sensitive to temperature [60]. The liposomes were used to study the targeted delivery of a model drug cytarabine to HepG2 cells. Qu et al. synthesized DNA nanocapsules composed of cytosine-phosphate-guanosine oligodeoxynucleotide vaccine adjuvants for their stabilization and the encapsulation and delivery of various cargo molecules, such as glycogen [61]. These nanocapsules can induce immunogenic effects both as adjuvants and as delivery vehicles. Many research groups have developed zein-based nanomaterials, with or without modifications, for the delivery of a large variety of phytochemicals, such as curcumin [62–64], quercetin [65–67], epigallocatechin gallate (EGCG) [68, 69], myricetin [70], resveratrol [71, 72], essential oils [73–76], and carotenoids [77, 78]. Chen et al. fabricated zein-carrageenan core-shell nanoparticles for the co-encapsulation and delivery of curcumin and piperine [79]. Their group has also developed zein-chitosan nanocomplexes for the co-encapsulation and delivery of curcumin and resveratrol [80].

5.11 Therapeutics

Over the past few years, soft nanomaterials have gained immense popularity in the field of therapeutics as antimicrobial agents, cancer therapies, dental and oral medicine, etc. The key properties that come into play include tunable size and shape, composition, surface modifications, biocompatible, and less toxic nature. For example, Kurczweska et al. developed vancomycin-loaded HNT-Alginate nanocarriers [81]. The antibacterial activity of the system was tested on *Staphylococci* and *Enterococci* bacteria and in vivo toxicity studies on *Acutodesmus acuminatus* and *Daphnia magna* bacteria. Similarly, Zhentan et al. developed a vancomycin-loaded poly(2, (dimethylamino) ethyl methacrylate) hydrogel by reversible addition-fragmentation chain transfer (RAFT) polymerization to treat bacterial infections by *Staphylococcus aureus* [82]. The hydrogel released the antibiotic in response to pH and bacteria by degradation of the hydrogel. Another research group has developed an injectable, thermo-sensitive hydrogel formed by the self-assembly of ABA triblock copolymer, where A represented Catechol functionalized poly(ethylene glycol) and B represented poly{[2-(methacryloyloxy)-ethyl] trimethyl ammonium iodide} [83]. The hydrogel had antimicrobial and antifouling properties and had the ability to self-heal after any damages. Sandri et al. developed HNT-chitosan nanocomposite for the treatment of chronic wounds and evaluated its enhanced

wound healing property in murine rat models [84]. Jiang et al. developed semiconducting PDCDT polymeric nanoparticles as organic nanoagents with dual absorption peaks in NIR-I (650–950 nm) and NIR-II (1000–1700 nm) regions to be used for photothermal therapy [85]. Qin et al. synthesized poly(ethylene glycol)-grafted-chitosan-modified poly(lactic-co-glycolide) nanoparticles for the loading and code-livery of two anticancer drugs—paclitaxel and epirubicin—for synergistic therapy against breast cancer [86]. Another example of soft nanomaterials being used for therapeutics was discussed by Wang et al. [87] They reported the study of a PAMAM dendrimer for the targeted delivery of a proteasome inhibitor drug, bortezomib, for metastatic bone tumours. A cyclic tripeptide sequence (Arg-Gly-Asp) was used as a targeting ligand, bifunctional polyethylene glycol chains were used to improve the blood circulation time, and catechol molecules were used to bind the drug onto the surface of the dendrimer. Drug release from the dendrimer was observed in response to change in tumour acidity (pH-responsive drug release). Yu et al. synthesized poly(D,L,-lactide-co-glycolide) nanovesicles loaded with a nitric oxide donor as an inhibitor of respiration in tumour cells and a photosensitizer for photodynamic therapy [88]. Pandya et al. developed chitosan-tetraphenylchlorin (polymer-photosensitizer) nanoparticle conjugates for the encapsulation and delivery of cytostatic drugs, cabazitaxel, or mertansine [89]. The nanoparticles displayed potential for combinatorial chemotherapy and photodynamic therapy and as contrast agents. Shinde et al. assessed the anticancer activity of carvacrol loaded zein nanoparticles stabilized by lecithin [90]. Similarly, ketoconazole-loaded lecithin-zein core-shell nanoparticles for the treatment of fungal skin infections have also been developed [91]. Chen et al. fabricated high internal phase pickering emulsions (HIPPEs) of enzymatic hydrolysis lignin with soyabean oil for the dispersion of the hydrophobic anticancer compound and curcumin [92]. The emulsion was stabilized using composite nanoparticles composed of enzymatic hydrolysis lignin and chitosan oligosaccharide developed for the loading of a hydrophilic cytarabine drug, Ara-c. The system was shown to co-encapsulate and release both the drug molecules in response to the pH of the tumour microenvironment to provide synergistic cancer therapy. Silk-sericin coated zein nanoparticles embedded in curcumin for the topical delivery of curcumin into the dermis and to exert its anti-dermatitis effects have been fabricated by Zhu et al. [93]. Chen et al. assessed the therapeutic benefits, at the molecular level, of local delivery of chloroquine loaded zein particles for the treatment and management of spinal cord injury [94]. Many research groups are also working on hyaluronic acid-based colloidal polyelectrolyte nanocomplexes as therapeutic agents for breast cancer [95–98], lung cancer [99–101], ovarian cancer [99, 102], colorectal cancer [103, 104], glioma [105], and liver cancer [106]. Shi et al. developed zein-hyaluronic acid nanoparticles to load, protect, and deliver resveratrol [107]. The encapsulated resveratrol was found to show higher antioxidant, antiproliferative, and antitumor activity than free resveratrol.

5.12 As Nanoreactors

Soft nanomaterials such as polyelectrolyte multilayers, microemulsions, micelles, reverse micelles, vesicles, liposomes, and nanogels can work as nanoreactors for the production of nanostructured materials. The type, direction, rate, and efficiency of the same reaction differ immensely when carried out in nanoreactors and bulk solutions. These systems act as reaction vessels in which the reaction volume to produce specific nanomaterials and the particle growth of the obtained nanoparticles can be controlled [35, 108, 109]. Polyelectrolyte multilayers can act as nanoreactors for the synthesis of core–shell colloids, hollow spheres, thin hybrid nanoparticulate films using metal ions, metal alkoxides, metal complexes, and polymer monomers. Wang et al. demonstrated the in situ fabrication of platinum nanoclusters embedded in poly(diallyldimethylammonium chloride) and poly(sodium styrene sulphonate) multilayer film [110]. Jiang et al. have described the synthesis of a polyelectrolyte multilayer-coated hollow mesoporous silica using chitosan and phosphorylated cellulose via layer-by-layer assembly method [111]. The addition of the synthesized material to epoxy resin improved its flame-retarding and fire safety properties. Polyelectrolyte multilayer films using polyacrylamide, polyacrylic acid, and a cationic β -cyclodextrin polymer as coatings on the surface of carboxylated paramagnetic polystyrene particles and ferromagnetic iron oxide (Fe_3O_4) nanoparticles have been synthesized [112]. Kovačević et al. used hydroxyapatite nanoparticles as templates to synthesize poly(allylamine) and poly(acrylic acid) multilayer capsules [113]. Characterization of the synthesized particles confirmed the formation of stable, nano-sized capsules with thin flexible walls. Furthermore, these multilayer colloidal assemblies can also be used in the synthesis of 2D surface arrays as well as 3D microporous materials [114].

Another example of soft material nanoreactors is metallovesicles. Kaur et al. fabricated an amphiphilic surfactant-based copper metallovesicle and assessed its catalytic activity in the synthesis of benzimidazole derivatives in aqueous medium [41]. On the contrary, Shukla et al. developed surfactant-free copper nanoparticle metallovesicles to act as nanoreactors for the production of benzimidazoles via a cascade reaction [42]. Kulshrestha et al. have also synthesized metallovesicles using copper (II)-based amino acids, phenylalanine or valine, and ionic liquid surfactants and used them as nanoreactors for catalyzing the cross dehydrogenative coupling reaction in water [115].

Microemulsions can also be used as templates or nanoreactors for the synthesis of metallic nanoparticles, polymeric nanoparticles, solid-lipid nanoparticles, mesoporous silica nanoparticles, etc. For instance, Tojo et al. synthesized bimetallic platinum–rhodium and platinum–gold nanoparticles using a flexible microemulsion system with a composition of isooctane/tergitol/water [116]. Chin et al. used water-in-oil microemulsion system to synthesize size-controlled cellulose nanoparticles by nanoprecipitation method [117]. The nanoparticles were then used as carrier for the hydrophilic drug methylene blue. Ke et al. developed tumour acidity-responsive

polyprodrug polymersome nanoreactors incorporating ultrasmall iron oxide nanoparticles in the membranes and the enzyme glucose oxidase in the internal water cavities [118]. These nanoreactors activated tumour-responsive cascade reactions for cooperative cancer therapy. Another example of these materials has been demonstrated by Alqarni et al. [119]. They assessed the molecular weight of bis-thyminyl polymers synthesized by photopolymerization using oil-in-water microemulsion, water-in-oil microemulsion, and miniemulsion as nanoreactor systems. They reported that increasing the diameter of the nanoreactors could result in an increase in the molecular weight of the synthesized polymer.

Liposomes are another group of soft nanomaterials that can be used as nanoreactors. Mandal et al. developed a liposome-mimicking niosomal vesicle composed of cholesterol and Brij S-20 surfactant as a nanoreactor for gold nanoparticles [120]. These vesicles also served as an effective vessel for the encapsulation and storing of haemoglobin protein.

5.13 Bone and Tissue Regeneration

Soft nanomaterials have also found their way in the field of bone and tissue regeneration. Organic constituents are combined with other compounds, such as clays, polymers, and drugs to form scaffolds for regeneration. Bonifacio et al. have developed a tri-component hydrogel for soft tissue engineering applications consisting of HNT, polysaccharide gellan gum, and glycerol and studied its in vitro application for human fibroblasts [121]. Chen et al. developed a hyaluronic acid-adipic dihyrazide-G₄RGDS grafted oxidized pectin-based biomimetic and injectable hydrogel system for cartilage tissue regeneration [122]. Similarly, Sionkowska and Kaczmarek fabricated 3D porous nanocomposite blend from chitosan, hyaluronic acid, collagen, and nano-hydroxyapatite for the purpose of bone regeneration [123]. De Silva et al. incorporated cephalixin-loaded HNTs into electrospun alginate-based nanofibrous membrane [124]. The membrane showed excellent antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *S. epidermis*. Tocopherol acetate-loaded transfersome vesicles have been synthesized and their in vitro biocompatibility to fibroblasts and keratinocytes, antioxidant activity, and their wound healing ability were demonstrated [125]. A large number of research groups have assessed the bone and tissue regeneration ability of chitin and chitosan nanofibers [126, 127]. For example, Duan et al. constructed hierarchical structures composed of chitin nanofibers and hydroxyapatite crystals as materials for bone cell adhesion, bone healing, and osteoconduction [128]. Hamidabi et al. developed a nanofibrous mesh composed of chitosan, montmorillonite, and poly(vinyl alcohol) to act as a template for the guided neuron-like differentiation of the stem cells of human dental pulp [129]. The synergistic effects of osteogenic rhBMP-2 and angiogenic rhVEGF₁₆₅ from composite hydrogels incorporating poly(lactide-co-glycolide) and sulphated chitosan on bone regeneration were reported by Cao et al. [130]. Another group has synthesized nanoscaffolds composed of polycaprolactone

and a chitosan derivative for bone replacement applications [131]. Luo et al. fabricated silk fibroin-polycaprolactone blend nanofibers coupled with BMP-2 peptide conjugated polyglutamate with bone tissue regeneration ability and regeneration of calvarial defects [132]. Lee and Kim optimized the synthesis of 3-dimensional porous scaffold mesh composed of nanofibrous collagen struts and Pluronic F-127 for bone tissue engineering [133]. Similarly, Abazari et al. synthesized polyvinylidene fluoride/collagen/platelet-rich plasma composite nanofibers with enhanced osteoinductivity and possible use as a bio-implant for application in bone and tissue engineering [134]. An HNT-TiO₂-Chitosan-Hydroxyapatite composite membrane with enhanced osteoblast adhesion and proliferation properties for guided bone tissue regeneration has also been synthesized [135]. Avani et al. developed a vancomycin-loaded silk fibroin HNT composite scaffolds as a possible treatment for bone infection [136]. Tang et al. demonstrated the osteoporotic bone regeneration capacity, both in vitro and in vivo, of their fabricated scaffold [137]. The scaffold was formed by self-assembling of polyelectrolyte multilayer film coating immobilized with calcitriol in biphasic calcium phosphate. Danti et al. have reviewed the potential of chitin nanofibrils and nanolignin as effective skin regeneration agents [138]. The development of a Laponite hydrogel using TEMPO (2,2,6,6-Tetramethylpiperidine-1-oxyl)-oxidized bacterial culture and sodium alginate for applications in drug delivery, tissue engineering, and biomedical devices has been reported by Wei et al. [139]. Peng et al. reported the preparation of polycaprolactone/gelatin core shell nanocellulose membranes incorporated with magnesium oxide nanoparticles and the application of the as-synthesized membranes for periodontal tissue regeneration [140].

5.14 Bioimaging and Biosensors

Apart from drug delivery and therapeutics, soft nanomaterials have gained immense popularity in the field of bioimaging, such as photoacoustic imaging, fluorescence imaging, magnetic resonance imaging, ultrasound imaging, and as contrast agents for computed tomography. These nanomaterials have controllable dimensions that can be easily tuned for permeability and retention in cells as well as can be easily modified by the grafting of a different ligands for effective binding with target molecules. These characteristics give them an advantage over other nanomaterials for application in bioimaging. Shao et al. synthesized a vitamin C sensing HNT-based composite by functionalizing HNT with the polymer Polyaniline (PANI) [141]. The porous structure enhances the electron transport and interactions between the PANI and Ascorbic acid (AA). Results claimed enhanced composite sensitivity and a low detection limit. Wan et al. developed a bright, organic, and nanofluorophore—pFE—for high performance in the second near-infrared (NIR-II) window [142]. The authors further used pFE for non-invasive in vivo blood flow tracking, 3-dimensional confocal imaging of vasculature, and colour fluorescence imaging for the visualization of tumours in mice. Another research group developed a theranostic nanoassembly with excellent dual MRI contrast activity [143].

The MRI contrast activity in the prepared hyaluronic acid-stabilized redox sensitive polyethylenimine polyplex complex was due to the presence of green-synthesized Mn_3O_4 and Fe_3O_4 nanoparticles. Jeevarathinam et al. synthesized poly(lactic-co-glycolic acid) (PLGA) nanoparticles loaded with paclitaxel-methylene blue conjugates [144]. These nanosystems were used to estimate *in vitro* and *in vivo* drug release via photoacoustic imaging. They were further used for the treatment of an orthotopic colon cancer model via luciferase positive CT26 cells. Xu et al. developed a catalytic hairpin assembly nanoprobe system composed of protamine sulphate with hyaluronic acid and SYL3C aptamer conjugated hyaluronic acid for the *in situ* detection of micro RNA-21 of living circulating tumour cells from whole blood [145]. Sim et al. fabricated hyaluronic acid, protamine, and ferumoxytol-based magnetic nanocomplexes for the labelling of natural killer cells [146]. These labelled cells, after activation, were used to provide MRI-guided natural killer cell therapy to treat solid hepatocellular carcinoma tumours. Furthermore, multifunctional Gadolinium-Ruthenium ligand-based coordination polymer nanospherical multi-modal sensors for the detection of nitroaromatic explosives and trace water in organic solvents have also been synthesized [147]. These nanosensors enabled the simultaneous use of magnetic resonance and fluorescence sensors and can help to broaden the application of magnetic resonance relaxation.

Furthermore, soft nanomaterials can be used either as transduction elements or for signalling and signal amplification in immunosensors. These are affinity or catalytic antibody-based biosensors which have a wide range of applications in biotechnology, research, forensics, defence, environmental monitoring, food safety, and agriculture [148]. For example, Shen et al. devised a gold nanoparticle-dendrimer conjugate for the voltametric immunoassay of α -fetoprotein in human serum [148]. They immobilized the nanoparticle/dendrimer conjugate onto a chitosan treated gold electrode, followed by the immobilization of a ferrocene containing ionic liquid onto the electrode via binding with the dendrimer (G4 polyamidoaminic dendrimer). The authors demonstrated it to be a stable, selective, and reproducible assay that can be used for the detection of cancer biomarkers as well.

Soft nanomaterials can also be used to develop biosensors. The quantum confinement effects acting in these nanomaterials enhance their sensor signals and sensitivity. Further, these materials are thermally stable, have the intrinsic properties of bio inertness and biocompatibility, can themselves be employed as receptors and transducers, and can easily coordinate with metal complexes and form extraordinary details and porous framework, thereby making them a good choice for this application [149]. Zhang et al. devised a silver ion-electrospun alginate nanofibers membrane as a sensor to measure breaths during emotional changes, running, and exercising [150]. On similar lines, Doğaç et al. synthesized sodium ions-alginate nanofibers-planer patterned polydimethylsiloxane-based wearable pressure sensor [151]. Liu et al. developed a Cobalt-porphyrin (TTPP) coordination polymer nanosheet for the fluorescence detection of DNA [152]. Sehit et al. have synthesized highly sensitive and selective biosensors composed of molecularly imprinted polymers decorated with gold nanoparticles for glucose sensing [153] and cancer biomarker detection in human serum samples [154].

Many research groups are working on the application of organic nanomaterials, such as dendrimers, molecularly imprinted polymers, metal–organic frameworks, polymer nanoparticles, nanomachines, nanovesicles, in virus sensing, and tracking. For example, a research group has developed a dendrimer [2,2-bis(hydroxymethyl) propionic acid] doped silver chloride nanospheres via a reverse micelle method with silver ion-selective electrode as a potentiometric immune sensor for the detection of a ss-RNA virus, Enterovirus 71, from serum samples [155]. Barrios-Gumiel et al. synthesized carbosilane dendrons encapsulating magnetic nanoparticles for the detection of HIV-1 strains—R5 and X4 [156]. Nguyen et al. developed coumarin-derived dendrimers as fluorophores targeting envelope 1 of Chikungunya virus for detection via fluorescence-linked immunosorbent assay [157]. Further, Zhang et al. developed a switchable electrochemiluminescence RNA sensing platform for the detection of Zika virus [158]. The platform was composed of a metal–organic gel (in situ loading of graphite-like carbon nitride and post assembly of gold nanoparticles) as the electrode matrix and metal–organic framework (zirconium-based) as the nanotag. Dimethylaminoethyl methacrylate and Material Institut Lavoisier-101 (MIL-101)-based molecularly imprinted polymeric nanoprobe for the detection of Hepatitis A virus through resonance light scattering were designed by Luo et al. [159]. Kim et al. developed Dengue virus (loaded with DiD dye)-polymersomes (encapsulating BODIPY-ceramide dye) hybrid nanovesicles for the real-time tracking of Dengue virus [160]. The DiD dye gave red signals in the endosomes, while the BODIPY gave green signals in the Golgi apparatus.

5.15 Environmental Applications

Human health, economy, and social progress are all connected to the quality of the environment. This necessitates the need to reduce harmful waste, use of biomass and fishery waste for different applications, development of environmental-friendly energy sources, along with reducing carbon emissions. A revolutionary way to adopt is nanotechnology.

Many researchers are working in this field to develop nanomaterials for applications in water treatment, such as removal of dyes, heavy ions, and other wastes from water. For example, Mokhena et al. developed a membrane with electrospun alginate nanofibers and poly(ethylene oxide) blends for the removal of heavy metals, such as Cu(II), from water [161]. Nanofibrillated cellulose-based macroscopic 3D aerogels have also been synthesized for the removal of heavy metals from water [162]. Zhijiang et al. synthesized a nanofiltration membrane composed of electrospun polyhydroxybutyrate/carbon nanotubes coated with calcium alginate hydrogel for the removal of dyes from water [163]. A poly(hydroxyalkanoate) matrix entrapped with chitosan and nanocellulose was fabricated by Soon et al. for the removal of congo red from water [164]. Similarly, Derami et al. synthesized a bacterial nanocellulose composite matrix embedded with mesoporous dopamine nanoparticles and in situ growth of palladium nanoparticles [165]. The nanocomposite was found to be highly

efficient in the removal of different types of dyes, across various concentration and pH factors, from water. Cellulose nanofibers-based aerogel membranes decorated with silver nanoparticles have also been developed for the catalytic discoloration of cationic and anionic organic dyes from aqueous solutions [166]. Sun et al. developed a silver nanoparticle-poly(amic acid) metallovesicle complex for the removal of dyes, heavy metals, and polycyclic aromatic hydrocarbons from water [167]. A research group has developed a water filtration membrane from bacterial nanocellulose and banana peel waste [168]. Yang et al. produced TEMPO-nanocellulose fibre-coated PAN membranes with antifouling activities with possible application in wastewater treatment [169]. Similarly, Hassan et al. have also synthesized thin-film ultrafiltration membranes from cellulose nanofibers for the removal of different pollutants from wastewater [170].

A few other environmental applications of soft nanomaterials have also been cited. Wang et al. devised a lithium chloride/nanofibrillated cellulose/graphene-based hygroscopic aerogel powered by solar energy as a novel strategy for harvesting atmospheric water [171]. Jahan et al. designed a nanocomposite membrane composed of crystalline nanocellulose and poly(vinyl alcohol) for the separation of methane and carbon dioxide [172]. Similarly, such membranes have also been prepared for the separation of carbon dioxide from nitrogen gases [173, 174].

Significant efforts are also being done in the development of nanomaterials from biological materials for the fabrication of novel electronic systems with applications in biomedical fields, wearable electronic devices, as well as generators of energy. Many research groups have synthesized triboelectric and piezoelectric nanogenerator devices based on natural polymers, such as cellulose [175, 176], chitin [177], silk [178–180], amino acid and peptides [181–183], collagen, and chitosan [184], for a variety of applications. Khalil et al. synthesized nanocomposite films composed of nanofibrillated cellulose, polyvinylpyrrolidone, and silver nanoparticles [185]. The films showed remarkable properties such as homogeneity, flexibility, good tensile strength, and electrical conductivity, thereby making them good candidates for future applications as sensitive electronic components. Sun et al. fabricated a transparent, flexible, self-powered, user-interactive wearable triboelectric nanogenerator composed of leaf-moulded microstructured polydimethylsiloxane films and silver nanowires [186]. These nanogenerators can be used for a wide array of applications, including healthcare, energy conversion, environmental applications, and wearable electronics. A research group has developed peptide-based, piezoelectric, unidirectionally polarized, horizontally aligned phenylalanine nanotubes as energy generators in the form of voltage, current, power, and force [187]. Bhakat et al. developed a nanocomposite with electrical properties based on gum arabic and iron oxide (Fe_3O_4) nanoparticles [188]. The conductivity behaviour of the developed bionanocomposite was found to be dependent on the content of the iron oxide nanoparticles. Wang et al. have reported the synthesis and application of an air flow-driven triboelectric nanogenerator composed of nanostructured polytetrafluoroethylene thin films for the self-powered real-time monitoring of human respiratory signals [189]. Further, Šutka et al. have developed highly porous nanostructured films composed of ethyl

cellulose as contact layer material for triboelectric nanogenerators [190]. These nanogenerator devices efficiently converted mechanical energy into electricity. Another research group has fabricated perovskite solar cells based on nanocellulose for application as flexible next-generation electronics [191]. Liu et al. have produced a triboelectric nanogenerator formed by the coating of gold nanofilm on nanostructured poly(tetrafluoroethylene) layers for the development of a flexible and self-powered sensor for endocardial pressure [192]. The sensor can be employed in next-generation implantable sensors for cardiovascular diseases. Calcium chloride-complexed starch-based bio-triboelectric nanogenerators with excellent electrical performance have been synthesized by Ccorahua et al. [193]. A self-powered piezoelectric nanogenerator sensor based on BZT-BCT-P(VDP-TrFE) nanofibers developed by Liu et al. [194].

5.16 Cosmetics

The emerging trends and the increase in the use of cosmetic products have attracted a lot of attention from the field of nanotechnology. This has not only led to improved entrapment efficiency and dermal penetration of the active ingredient of the cosmetic formulation but also to controlled drug release from the products, improved physical stability, enhanced moisturizing capacity as well as better sun protection [195]. Castleberry et al. demonstrated the enhanced dermal accumulation and reduced inflammation at application site by delivering all-trans retinoic acid molecules via polyvinyl alcohol-based nanosystems in *in vitro* and *in vivo* studies [196]. Nanoemulsions of coenzyme Q10 have shown to protect against skin injury induced by UVB radiation [197] and improved skin permeability and anti-wrinkle activity [198]. Su et al. fabricated an oil-in-water nanoemulsion system based on octyldodecanol for the transdermal delivery of ceramide III B [199]. Chen et al. assessed the skincare applications of lipid nanoparticles encapsulating different antioxidants—resveratrol, vitamin E, and EGCG [200]. Similarly, EGCG and hyaluronic acid-loaded nanotransferosomes have also been synthesized for their synergistic UV-protection, anti-ageing, and antioxidant effects [201]. Muzzalupo et al. developed cationic niosomal systems derived from lysine-based gemini surfactants [202]. The niosomes acted as controlled delivery systems when administered parentally while enhanced the percutaneous permeation capacity of the drug when applied topically. A research group has synthesized PAMAM dendrimers for the increased solubility, stability, and skin penetration of resveratrol molecules [203]. Holmes et al. demonstrated increased the *in vitro* permeation of chlorhexidine digluconate into the skin pre-treated with PAMAM dendrimers [204]. Ki et al. have prepared a hybrid composite material composed of a fermented extract of natural products and calcium alginate nanosized hydrogel for application in hair growth [205]. Chitosan nanoparticles have been synthesized as carriers for the skin whitening agents, α - and β -arbutins [206]. Panchal et al. self-assembled halloysite clay into nanotubes (HNTs) and demonstrated their use as carriers for hair dyes as alternatives to chemical hair colouring

treatments [207]. Further, they also reported the use of these HNTs for the topical delivery of drugs onto hair surface. Researchers have also synthesized UV-protecting cosmetic emulsions of annatto and saffron encapsulation within chitosan nanoparticles [208]. Similarly, stable suspensions of organic UV-blocking sunscreen agents with polymeric nanocomposite particles have been fabricated [209]. Leon-Méndez et al. assessed the antioxidant activity of starch microemulsions encapsulating thyme oil, clove oil, and cinnamon oil [210]. Hatahet et al. studied the loading efficiency, delivery, cell interaction ability, antioxidant activity, and toxicity of quercetin loaded liposomes, lipid nanocapsules, and smart crystals [211]. Tokudome et al. evaluated the delivery of hyaluronic acid nanoparticles into skin [212]. The nanoparticles were formed by the polyion complex method with cationic protamine polymer. A self-nano-emulsifying nanovesicular drug delivery system was developed to enhance the topical absorption and antifungal activity of bifonazole [213]. Gupta et al. studied the anti-acne activity of glyceryl monostearate-based solid-lipid nanoparticles loaded with isotretinoin and α -tocopherol acetate [214]. Researchers have also synthesized ascorbic acid hydroxyapatite nanocomposites [215], liposomes [216], and aspasomes [217] for skincare activities. Zhu et al. fabricated zein-hyaluronic acid colloidal nanoparticles encapsulating tetrahydrocurcumin for its topical application to improve its cutaneous bioavailability and anti-photoaging activity [218]. In addition to this, zein nanoparticles encapsulating EGCG by nanoprecipitation method have also been developed [219]. The synthesized nanoparticles showed positive antioxidant, anti-tyrosinase, and photoprotective activities, thereby boosting the main biological properties associated with sun protection and skin pigmentation.

5.17 Food Industry

Nanotechnology is also being significantly used in the food industry as preservatives, carriers of antimicrobial, antifungal, and antifouling agents, food packaging films, emulsifiers, stabilizers, bakery industry, dairy industry, and production of functional foods. Several bio-based compounds and their derivatives, individually and/or combined with other compounds, are being used in the food industry for the processing of these materials for food products. These materials are biodegradable, sustainable, biocompatible, economical, eco-friendly, and non-toxic. Additionally, they have improved properties as well as can be used as carriers for active ingredients [220]. The various biological materials being used in this regard include, but are not limited to, cellulose, lipids, waxes, chitosan, sorbitols, carrageenan, vitamins, proteins, phytochemicals, starch, and gum arabic, as discussed in Table 1.

Cellulose, chitosan, their nanoforms, and their derivatives from bacteria, plants, and animals are immensely used in the food industry in bakery [221–223], meat industry [224, 239, 240], edible coatings [225], packaging films [226–228, 235, 236], emulsion stabilizer [229, 230], for delivery of bioactive compounds [231, 232], as functional ingredients in foods [233, 234], and to improve the shelf-life of food products [237, 238]. Edible starch nanocomposites from different sources, such as

Table 1 Nanoformulations of different biological materials and their application in food industry

S. No	Biomaterial	Nanoform	Application	References
1	Cellulose	Microcrystalline cellulose	Reduced fat content	[222]
2	Cellulose	Carboxymethyl cellulose nanoform	Edible coating for enhancing quality and extending postharvest life of avocado fruit	[225]
3	Cellulose	Cellulose nanofibre	Water resistant and antibacterial film for food contact packaging	[226]
4	Cellulose	Nanocellulose	Emulsion stabilizer	[229, 230]
5	Cellulose	Nanofibrillated mangosteen cellulose	Pickering emulsion for the encapsulation of vitamin D ₃	[231]
6	Cellulose	Cellulose nanofibrils	Structural components of ice cream	[233]
7	Chitosan	Nanochitosan and/or chitosan nanoparticles	Edible coatings on fruits, vegetables, and meat products and their preservation	[235–240]
8	Starch	Cassava starch nanocrystals	Preservation of Huanggan pears	[241]
9	Starch	Starch nanoparticles	Carrier of bioactive compounds	[247–252]
10	Starch	Starch nanocrystals	Stabilizers	[253–255]
11	Proteins	Zein nanoparticles	Carrier of bioactive compounds	[256–262]
12	Proteins	Soy protein isolate	Pickering nanoemulsion	[263]
13	Proteins	Whey protein isolate nanofibers	Coating for preservation on salted duck egg yolks	[265]
14	Proteins	Casein nanoparticles	Biopolymer-based bilayer film	[267]
15	Proteins	Soy protein isolate nanoparticles	Pickering emulsion stabilizer	[269]
16	Lipids	<i>Artemisia annua</i> oil nanoliposome	Edible coating on cherry tomato	[270]
17	Lipids	Candeuba wax solid-lipid nanoparticles	Quality maintenance of guava fruit	[271]
18	Lipids	Satruja plant essential oil nanoencapsulation	Effect of coating on lamb meat	[275]
19	Lipids	Betanin nanoliposomes	Fresh beef preservation	[276]

cassava [241, 242], mung beans [243], sugar palm [244], and potato [245, 246], have also been developed as packaging materials. In addition to this, starch nanomaterials have been used as carriers for various bioactive compounds [247–252] and as stabilizing agents [253–255]. Moreover, many proteins and their nanostructures have been incorporated in the food industry. These proteins can be sourced from both plants as well as animals. For example, zein, an amphiphilic protein obtained from corn has

been used as a carrier for many hydrophobic compounds and improved their antioxidant activities, including curcumin [256, 257], lutein [258], quercetin [259, 260], resveratrol [261], and fucoxanthin [262]. Similarly, Ju et al. synthesized a pickering emulsion based on soy protein isolate and anthocyanin complex nanoparticles for the efficient encapsulation and delivery of anthocyanin [263]. Other applications of these proteins can be found in the meat industry [264], dairy [265], cheese industry [266], and prevention of spoilage of foods [267–269]. Similarly, lipid-based nanoemulsion, nanoliposomes, and solid-lipid nanoparticles have been extensively used for the preservation and increasing the shelf-life of fruits and vegetables [270–274], meats [275–277], and dairy products.

5.18 Agriculture

To meet the growing needs of the population as well as to protect the environment, it is important to practice sustainable agriculture. This necessitates the use of greener compounds for crop improvement and protection, such as natural compounds, plant secondary metabolites, and biocompost, as alternatives to agrochemicals. Nanoformulations of these compounds show improved stability, thereby providing better efficacy and action on pests [278]. Working in this direction, researchers are developing soft nanomaterials such as polymeric nanocapsules, microemulsions, nanodispersions as nanobiopesticides, nanofertilizers, or as carriers to be used in agriculture. For example, Pascual-Villalobos et al. assessed the activity of 10 different essential oils and their nanoemulsions against the bird cherry-oat aphid (*Rhopalosiphum padi* L.) [279]. The antifungal activity of carbendazim was found to be enhanced when released from chitosan-pectin nanoformulation as compared to pure compound [280]. Also, the nanoformulation of the fungicide was found to be safer for germination and root growth of seeds of various plants. Choudhary et al. fabricated copper-chitosan nanoparticles and reported enhanced antioxidant, antifungal, growth, and disease resistance in maize plants [281]. Kottegoda et al. synthesized hydroxyapatite nanoparticles as a source for the slow release of urea, to maintain yield and reduce the amount of urea being given [282]. Furthermore, the hydroxyapatite particles also acted as a source of phosphorus. Liang et al. developed poly(styrene-methacrylic acid)-avermectin-catechol nanoparticles inspired by mussel avermectin as nanobiopesticides [283]. The developed nanoparticles showed remarkable adhesive property on foliage and better indoor toxicity to pests, as assessed on cucumber and broccoli. Chauhan et al. synthesized chitosan nanocapsules for the encapsulation and slow release of the fungicide, hexaconazole [284]. The nanoformulation was found to be less toxic as compared to the commercial pesticides. Guar gum-based hydrogels were developed by Thombre et al. increased the water holding capacity and porosity of the soil and behaved as a good soil conditioning material [285]. Chitosan nanoparticles have been reported to significantly improve the yield of barley plants while decreasing the drought stress [286]. Akalin and Pulat

reported an increase in the performance of the wheatgrass plant after the application of zinc-loaded carboxymethyl cellulose-carrageenan hydrogels, suggesting their use as controlled fertilizers in agriculture [287]. Khan et al. synthesized a fertilizer based on nanozeolites saturated with macronutrients and studied the nutrient uptake capacity and release study of the prepared nanofertilizers [288]. Hao et al. synthesized and stabilized zein nanoparticles as carriers for hydrophobic pesticides [289]. Similarly, da Cruz Silva et al. synthesized oil-in-water nanoemulsions based on the essential oils, thymol, eugenol, geraniol, and methanone [290]. The antibacterial activity of these emulsions was assessed against *Xanthomonas* strains that cause the citrus canker disease.

6 Conclusion

Nanotechnology is an ever-growing field with a wide array of applications in every field of science. Soft nanotechnology deals with the design, synthesis, and applications of soft organic and organometallic nanomaterials. Their small size, high surface area to volume ratio, extraordinary physical, chemical, optical, and magnetic properties, biocompatibility, and less toxic nature make them valuable materials for the future. Soft nanomaterials are present abundantly in the nature, such as nano cellulose, nanoclay, virus particles, vesicles, micelles, and liposomes. Synthetic soft nanomaterials derived from these natural particles, or mimicking them, or from synthetic components are also being produced, for example, polymeric nanoparticles, synthetic nanoclay particles, soft matter nanotubes, biomimicking micelles, vesicles, and liposomes. These natural and synthetic nanomaterials have been employed in drug delivery, as carriers, therapeutics, bioimaging, biosensors, tissue engineering, environmental applications, etc. However, with the growing advancements and research in technology, there is yet a lot more to understand and learn about these materials and to utilize them with their full potential.

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Biological Nanomaterials and Their Development



Yogita Karki, Smriti Sneh Verma, and Farheen Naz

Abstract Biological nanomaterials, also known as biomaterials, are materials derived from or inspired by biological systems, such as proteins, nucleic acids, and viruses. This chapter provides an overview of the synthesis, characterization, and applications of biological nanomaterials. We begin by discussing the properties and synthesis methods of these materials, including genetic engineering, chemical modification, and self-assembly. Next, we describe their characterization techniques, such as electron microscopy, X-ray crystallography, and circular dichroism. The chapter also explores the various applications of biological nanomaterials, including in drug delivery, tissue engineering, biosensors, and biocatalysis. Moreover, we highlight the challenges associated with their large-scale production and commercialization, such as immunogenicity, stability, and regulatory issues. Finally, the chapter concludes with a summary of the current state of research and suggests possible directions for future work in this exciting field.

Keywords Biological nanomaterials · Biocatalysis · Chitosan · Fibroin · Silica · Synthetic bionanomaterials · Nanocellulose

1 Introduction

The word ‘nanotechnology’ has its origin from the Greek word ‘nano’ meaning ‘tiny’ and is one thousand millionth of a meter. The technology that is related to the study of molecules that have range between 1 and 100 nm and makes it practically approachable and available is known as ‘nanotechnology.’ Richard Feynman, an American physicist and Nobel Prize laureate, was the first one who during a lecture introduced

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the concept of nanotechnology in 1959. For the first time, the word nanotechnology was used by Norio Taniguchi in 1974.

The nanomaterials which have biological origin are continuously used in diverse fields as they have huge potential due to their being biocompatible, non-toxic, and biodegradable in nature. These nanomaterials which have biological origin are known as bio-nanomaterials. Bio-nanomaterials have diverse properties such as biological, chemical, mechanical, physical, and catalytic properties which can be detected using techniques such as microscopy and spectroscopy.

The size of the bio-nanomaterials plays an important role in their functioning [1]. The bio-nanomaterials small size proves to be more efficient in different applications such as in drug delivering as the small size particle can travel more conveniently than large size particles. The small size bio-nanomaterials are being continuously designed as smaller size enhance the properties of the bio-nanomaterial.

The recent advantages in the biological nanomaterials are the use of green-based approach for the synthesis of bio-nanomaterials. Microorganisms, plants, and agricultural waste are being used for the synthesis of biological nanomaterials. The different plant organs (such as leaf, stem, seed, and root) have been used as these are environmental-friendly and have low toxicity levels. For example, the roots of coriander, *Platycodon grandiflorum*, were used for the production of Fe–Ag–Pt nanoparticles [2]. The extracts from the fruit of Chinese wolfberry have been used to produce Au–Ag [3]. The fungi when in vicinity of metal ions produce biomolecules such as anthraquinones or naphthoquinones used for creating metal particles [4]. The banana peels have been utilized for the production of CdS alloy [5], and *Antigonon leptopus* (a useless weed) has been utilized for the production of Au–Ag nanoparticles [6].

The bio-nanomaterials are classified as organic-based bio-nanomaterials, synthetic-based bio-nanomaterials, and biological nanomaterials on the basis of their source of origin.

2 Organic Bio-nanomaterials

Organic bio-nanomaterials are a class of nanomaterials that include nanoparticles made of polymers such as chitosan, silk fibroin, and poly (lactic-co-glycolic) acid (PLGA) with diverse use in biological fields. Organic bio-nanomaterials have been continuously under ongoing research due to their huge potential for various biomedical use. Organic bio-nanomaterials are recently being used for diagnostic imaging techniques, cancer therapies, and sustainable drug administration.

Polymeric-based, carbon-based, silica-based, and metallic-based are mostly used classes of organic bio-nanomaterials in diverse fields (Fig. 1).

(A) Polymeric-Based Organic Bio-nanomaterials

Organic nanoparticles such as chitosan, silk fibroin, and PGLA are in continuous research and use as they have huge potential in the biomedical field due to their

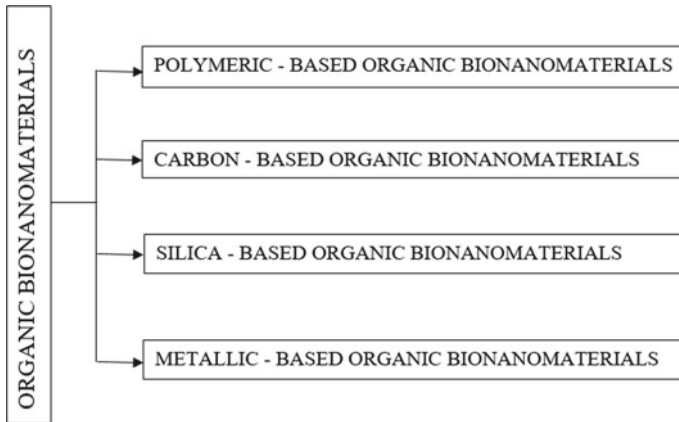


Fig. 1 Different class of organic bio-nanomaterials

non-toxic nature. The side effects caused by these polymers are minimum, so they are being continuously researched for their potential use in the biomedical field.

(1) Chitosan

Chitosan is one of the most abundant natural polymers and can be easily extracted and utilized in different domains. Being a biocompatible, biodegradable, and non-toxic polymer, it is considered to be very sustainable and renewable. Chitosan has been continuously used as a coating agent for a lot of metal nanoparticles. The chitosan coating of the metal nanoparticles has been useful as a carrier of drugs [7] and control release of the drugs [8].

The chitin deacetylation leads to the formation of glucosamine and n-acetyl glucosamine which constitutes the main structure of chitosan [9]. The key factors that have a major influence on the properties of chitosan are its molecular weight (MW) and degree of deacetylation (DDA) [10].

1(a) Properties of Chitosan

- (a) Antimicrobial property—Chitosan exhibits antimicrobial properties as during acidic conditions the positive charge chitosan interacts with the biomolecules' negative charge residues on the bacterial cell's surface [11]. This antimicrobial property of chitosan has been utilized in biomedical applications. The molecular weight of the chitosan determines its ability to penetrate the bacterial membrane as a low molecular weight chitosan has been effective to permeate the bacterial membrane better than a high molecular weight chitosan [12].
- (b) Antioxidant property—Free radicals are molecules that are unstable and have high reactivity and are thus linked with a lot of health problems [13]. Chitosan mimics the antioxidants as a scavenging agent for free radicals and thus helps in the prevention of free radicals formation [14].

- (c) Tumor growth inhibiting property—Chitosan has been utilized as a tumor growth inhibitor [15]. Chitosan is effective to inhibit the tumor growth by preventing tumorigenesis, inducing tumor cell apoptosis, and inhibiting tumor metastasis. The molecular weight and the degree of deacetylation of the chitosan are important factors that are known to exhibit the anti-tumor activity of chitosan. The chitosan with a high degree of deacetylation and low molecular weight show better anti-cancerous activity [16].
- (d) Biocompatible property—The chitosan affects the formation of the metal nanoparticles as the chitosan which is a cationic polymer electrostatically interact with nanoparticles which are negatively charged. The absorbance of the chitosan on the surface of nanoparticles enhances the ability of bio-nanomaterials to carry the drugs and also enhances the biocompatible nature of the nanoparticles [17]. Chitosan has been shown to increase the formation of AgNPs as it was also observed that at high chitosan concentrations, the size of the AgNPs also decreased.

1(b) Recent Applications of Chitosan in Drug Delivery System

1. The drugs are entrapped to the chitosan coated metal nanoparticles for their effective delivery into the body system [18]. An example is the delivery of doxorubicin (DOX) using the chitosan-copper oxide (CS-CuO) nanoparticles into the cancer cells [19].
2. Gold nanoparticles (AuNPs) have been synthesized using the chitosan's reducing ability. The chitosan-coated gold nanoparticles (CS-AuNPs) were able to effectively load insulin, and this increases the insulin delivery into the body. The application of the CS-AuNPs in insulin delivery to the body shows potential for the control of the postprandial hyperglycemia [20].
3. The increase in resistance of different bacterial species to drugs has been a concerning issue since last decade. The CS-AuNPs have been effective as bactericidal molecules as these proved to be efficient in inhibiting bacterial strains [21]. The chitosan molecules being positively charged in nature interact efficiently with the negatively charged membrane of the bacteria (Fig. 2).

(2) Silk Fibroin

Silk fibroin is being used widely as a bio-nanomaterial due to its non-toxic properties. The silk fibroin is used extensively in the biomedical field due to efficiency as a safe

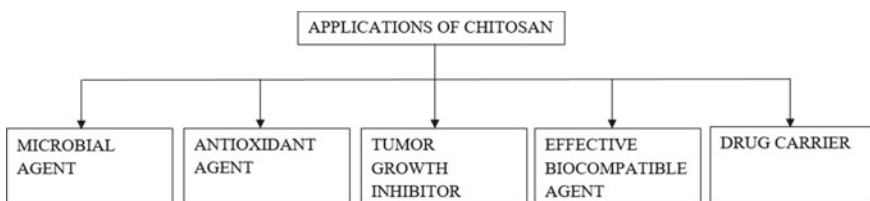


Fig. 2 Applications of chitosan in biomedicine

drug delivery system. Silk fibroin can be used at the nanoscales as nanoparticles and nanofibers. Sericin and fibroin are two proteins that are the main components of silk fibroin. The ability of silk fibroin to get shaped into different scaffolds has been used in drug delivery and the regeneration of skin and tissues.

The structural unit of silk fibroin consists of two fibroin filaments with a covering of sericin [21]. The glycine (43%), alanine (30%), and serine (12%) constitute the most repetitive sequences in the primary structure of the silk fibroin with [22]. The Food and Drug Administration (FDA), USA, has given its approval for silk fibroin for use in the medicine. The sericin component of the silk fibroin is not used in the medicine as it has been related to generate immunogenic response after administration in the body [23].

The silk fibroin can be formed into a variety of materials at the nanoscales, micro-scales, and macro-scales such as nanofibers, nanoparticles, hydrogels, microspheres, and silk fibroin sponges. The textile industry is the major consumer of silk as it contains properties such as luster, softness, and lightness. By combining the silk solution with a porogen (such as salt or sugar crystals, polymer or mineral beads), silk fibroin sponges can be created. Silk fibroin sponges can be used as scaffolds for bone tissue regeneration due to their macroporous properties that can be tuned to promote the development of new vascularized bone tissue [24].

Silk microspheres can be made in several ways. Encapsulation in fatty acids to form emulsions, phase separation of silk from another polymer such as poly (vinyl alcohol) (PVA) [23], or addition of potassium phosphate to aqueous silk solutions [25] are some of the ways to form silk microspheres. Silk microspheres has its application in the medication delivery system as silk microsphere has use in the controlled release of the contents, and this can be achieved by controlling the rate at which the encapsulating material breaks down its contents [26, 27].

The hydrogels have mechanical properties that makes it similar to soft tissues of the body. This is utilized in the field of regenerative medicine [28] and tissue engineering [29]. Silk has been used as an important substance for the fabrication of microneedle systems used in drug delivery, and for efficient drug delivery, other materials such as insulin [30] and vaccines [31] have been used to prepare these microneedles.

2(a) Applications of Silk Fibroin

Since silk is a foreign body, a mild inflammatory response is usually observed upon administration. This immunogenic response is associated with the presence of sericin in the material [32]. However, no immunogenicity was found when using materials composed of silk fibroin [33].

The applications of silk materials in the biomedicine are attributed to their biocompatible nature, biodegradable nature, and mechanical robustness. For the skin burn wounds, silk materials have been found to generate a rapid re-epithelialization, and studies have revealed that improvement in wound healing was observed with electrospun silk materials functionalization with silver sulfadiazine and epidermal growth factor (EGF) [34]. The use of silk fibroin in drug delivery has been successful. The

drug used as a treatment agent for age-related macular degeneration, bevacizumab has been used with silk hydrogels for its release at the target site [35].

The antibacterial application of the silk materials has been demonstrated by functionalizing them with silver nanoparticles by using UV irradiation in silk solutions [36]. The bone regeneration has also been achieved with AgNPs loaded silk hydrogels [37].

3 Carbon-Based Organic Bio-nanomaterials

Carbon-based nanomaterials have been in continuous use recently due to their various applications in the biomedical field. The various sources of carbon-based nanomaterials include graphene oxide (GO), carbon nanotubes (CNTs), fullerene, and graphene quantum dots (GQDs) as allotropes of carbon [38]. Graphene is the most common and popular allotrope of carbon, making it an ideal candidate for drug delivery due to properties such as its extremely high surface area and chemical purity [39]. Graphene shows good compatibility with different biological materials, fluorescent dyes, and therapeutic agents. This makes it a potential candidate for diagnosis purposes of medical conditions such as cancer, and in vivo imaging.

3.1 Applications of Carbo-Based Nanomaterials

3.1.1 Carbon-Based Nanomaterials as Biosensors

- (a) Carbon-based nanotubes have been used as biosensors due to their high conductivity, sensitivity, chemical stability, and aspect ratio [40]. The electron-transfer rate of carbon-based nanotubes being fast in nature makes them have huge applications in biosensing [41].

An example of carbon-based nanotubes being used in medicine is the use of carbon nanotube non-woven fabrics (CNTFs). The CNTFs have been used as a sensor of glucose from a solution of glucose oxidase-impregnated polyvinyl alcohol [42]. Carbon-based nanotube-based electrochemical biosensors have been used for the detection of nitric oxide [43] and sensors of epinephrine [44].

- (b) Graphene oxide-based nanoparticles have applications as biosensors [45] that can transduce a specific reaction to the target molecules due to fluorescence, electrochemical reactions, and Raman scattering. The single and double-stranded DNA can be sensed using graphene oxide-based nanoparticles as elective electrochemical sensors [46, 47]. Graphene field effect transistors (GEFTs) have been used for the design of label-free DNA biosensors. These graphene field effect transistors functionalized with single-stranded probe DNA serve as sensitive biosensors with a detection limit of 1 fM for 60-mer DNA oligonucleotides [48].

- (c) Graphene quantum dots have been used as biosensors in the medical industry for disease diagnosis purposes. The graphene quantum dots show better sensitivity and selectivity for the detection of biological molecules such as DNA, proteins, glucose, and RNA due to their electrochemiluminescence, photoluminescence, and electrochemical properties [49, 50].

3.1.2 Carbon-Based Nanomaterials as Drug Delivery

- (a) Carbon-based nanotubes for drug delivery have been very efficient due to their dynamic properties such as their morphology that enables them to penetrate (non-invasive) into the biological membranes [51]. The carbon nanotubes' inner hollow cavity is used for drug loading, and this method is ideal for drug release into the system as it has less impact from the physiological conditions. Examples of carbon-based nanotubes as efficient drug delivery vehicles include doxorubicin [52], paclitaxel [53], and oxaliplatin [54] for cancer treatments.
- (b) Graphene oxide-based nanoparticles for drug delivery

The graphene-based nanoparticles are based on the properties of graphene such as the availability of π electrons in graphene and graphene's large surface area.

The doxorubicin (DOX) in high amounts has been loaded into graphene (phospholipid monolayer coated), and it was observed that acidic pH favored more release of doxorubicin in comparison to a basic pH [55]. Doxorubicin (hydrophilic) and indomethacin (hydrophobic) have been loaded on poly-N-isopropyl acrylamide (PNIPAM) grafted GO (GPNM) via π - π interaction, H-bonding, and hydrophobic interaction. The free radical polymerization process (FRPP) was used to covalently link PNIPAM with GO [56].

3.1.3 Graphene quantum dots as drug delivery

The graphene quantum dots have been used for the delivery of drugs due to their oxygen-rich surface and a small lateral size single atomic layer.

It makes it highly suitable for drug delivery loading and enhances its stability. The graphene quantum dots have a fluorescent property, and this property is utilized to trace the drugs delivered into the system [57]. A drug delivery system has been designed using graphene quantum dots-conjugated gemcitabine-loaded HSA nanoformulation where albumin has been used to deliver gemcitabine into tumor cells [58]. Graphene quantum dots loaded with doxorubicin conjugated with Cy5.5 dye via a cathepsin D-responsive (P) peptide have been developed that showed enhanced penetration of the drug through tissues and the uptake of the drugs by the cells. Blue fluorescence was observed in the cells that were treated by GQD-P-Cy confirming the efficient drug delivery and confirming its biocompatible nature [59].

4 Silica-Based Organic Bio-nanomaterials

The applications of mesoporous materials as bio-nanomaterials have been increasing continuously due to their distinct pore sizes, pore volumes, and large surface area such as carriers for the controlled release of bioactive ingredients. The mesoporous silica materials show excellent drug-loading capacity and are also used to encapsulate molecules. The encapsulation of materials for safe use in medical applications shows its biocompatible nature [60].

The synthesis of mesoporous silica involves the incorporation of surfactants into silica precursors (such as tetraethyl orthosilicate—TEOS or sodium orthosilicate— Na_2SiO_6) under basic conditions in alcoholic solutions (NH_4OH or NaOH). The alcoholic solution hydrolyzes the silicate and surrounds the spherical micelles which then undergo hydrothermal treatment so that the self-assembly of silicate micelles can take place in the form of cylinders [61].

The morphology of the mesoporous silica nanomaterials affects their biocompatible nature as the dimensions of the mesoporous silica nanoparticles affects different biological parameters such as their distribution in the body. It has been researched that the smaller silica nanoparticles circulate in the blood for longer durations [62].

Silica nanoparticles with a size of 110 nm were administered from different routes (hypodermic, intravenous, oral administration, and intramuscular). This study aimed to check the effect of the mode of administration of the nanoparticle on its biodistribution, elimination, and toxicity. The results showed that the intramuscular and hypodermal routes of administration showed slight inflammation at the site of injection while the target organs did not show any histopathological abnormalities on all four administration routes [63].

The toxicity levels of silica were also studied by different researchers. One such study was aimed to check the toxicity of silica nanoparticles in the dermal area. The study involved colloidal silica nanoparticles of 20 nm which were applied for 90 days on the skin to check their toxicity levels. The study also checked for internal organ damage (with a 2000 mg/kg dose of silica nanoparticles), and the results showed no damage in the internal organs and toxicity in the rats [64]. The toxicity levels of the silica nanoparticles can be reduced and the biocompatibility of the silica nanoparticles can be enhanced by optimizing the physiochemical factors such as particle sizes and surface charges.

4.1 Applications of Silica-Based Nanomaterials

The silica-based nanomaterials show a wide range of applications in the biomedical domain such as in drug delivery, vaccines, and in cell imaging. As drug delivery molecules, mesoporous silica nanomaterials are considered ideal as these can be used for the containment of drugs and their protection with successful drug delivery. An example of a mesoporous silica nanomaterial used for drug delivery is MCM-48 silica

which is utilized for the fast transport of drugs. The drugs used with MCM-48 that have been successfully delivered to their target sites are ibuprofen and erythromycin [65]. It was also observed that the pore size when decreased resulted in a reduced release rate of the drug.

The use of mesoporous silica nanomaterials in the diagnostic field has gained success due to their imaging susceptibility. A study showed that the functionalization of targeted ligands with mesoporous silica nanomaterials showed imaging susceptibility at the target site due to magnetic resonance contrast agents (nanomaterials-based) [66].

5 Metallic-Based Organic Nanomaterials

The metallic-based organic nanomaterials in the form of metal or metal oxide-supported nanomaterials have been on the rise due to their therapeutic properties. These nanomaterials can be categorized into

- (1) Metal-based nanomaterial (such as gold, copper, titanium, and silver-based nanoparticles).
- (2) Metal oxide-based nanomaterial (such as silver oxide, and titanium dioxide).
- (3) Metal oxides and metal-based doped nanomaterial (such as ZnO doped with Mg).
- (4) Metal–organic framework nanomaterials (such as Zn-based metallic organic frameworks).
- (5) Metal sulfides nanomaterials (such as AgS, CuS, FeS, and ZnS-based nanomaterials).

Metal-based nanoparticles such as gold nanomaterials have gained more recognition lately due to their low toxicity levels. The gold-based nanomaterials also show a high attachment to biological molecules and can be easily prepared [67]. The silver nanoparticles show antimicrobial properties, and this is utilized against microbes and other viruses. This antimicrobial property of silver nanoparticles has made it a useful agent in the textile industry [68]. The metal oxide-based nanomaterials such as TiO₂ are effective against different infectious disease transmission [69].

Metal-based nanomaterials such as zinc oxide-based nanomaterial exhibit safe properties that are utilized in photo-oxidation and photo-catalysis in a variety of biological fields [70].

The antimicrobial property of metal-based nanoparticles has been due to the positive surface charge on the metallic nanoparticle that interacts with the negative charges on the bacterial membrane surface. This results in the bactericidal ability exhibited by the metallic nanoparticles, and this antimicrobial property is strongly influenced by the shape of the nanoparticles [71].

6 Synthetic Bio-nanomaterials

The synthetic class of bio-nanomaterials includes the peptide nucleic acid (PNA). The PNA is synthesized by removing the phosphate backbone with a pseudopeptide backbone and has the ability to hybridize with neutral nucleic acids. The purines and pyrimidines in the PNA are connected to its N-(2-aminoethyl) glycine backbone by methyl carbonyl linkages [72]. This backbone allows the PNA to be resistant to the enzymatic degradation, and this structural property of PNA is utilized in the biomedicine [73].

The nanoparticles and PNA complexes have been used as biosensors. The surface-coated fluorescent nanoparticles used as biosensors have been used for live imaging of the RNA molecules and a high surface to volume ratios of the PNA-nanoparticles complex increase the biosensor-based detection [74].

The ability of the PNAs to be able to bind to specific nucleic acids is utilized in cancer therapies. The PNAs can be designed as cancer drugs and used for nucleic acid delivery to the specific cells. For example, the microRNAs have been used cancer therapy as target nucleic acids for PNAs-based cancer drugs [75]. The silicon nanowires labeled with PNA have been used as biosensors for the detection of miRNAs in the cancer diagnostics [76].

7 Green-Based Bio-nanomaterial

Green nanotechnology is the application of nanotechnology to improve the sustainability of processes that have harmful environmental effects. It also refers to the usage of nanotechnology-related products to improve sustainability. Making environmentally friendly nanoproducts and utilizing nanoproducts to promote sustainability are part of it. Green nanotechnology aims to create nanomaterials and products that don't affect the environment or people's health, as well as nanoproducts that solve environmental issues. It creates nanomaterials and nanoproducts using already-existing principles of green chemistry and green engineering [77].

The phrase 'green synthesis of nanomaterials' describes the production of various metal nanoparticles using bioactive materials such as plant matter, microbes, and a variety of biowastes like vegetable waste, fruit peel waste, eggshell, agricultural trash, and so on.

7.1 Classification of Green Nanomaterials

The order of dimensions to which a nanomaterial's structure extends determines its classification. The dimensions of an electron are limited to one, two, or three [78] (Fig. 3).

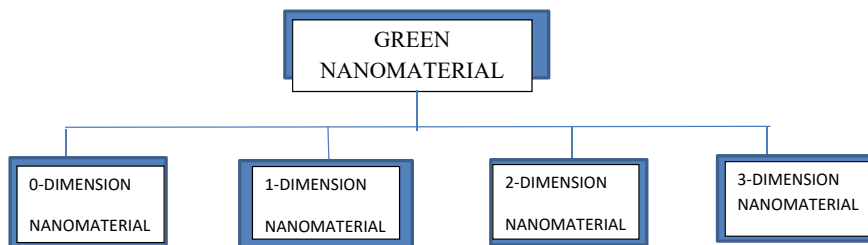


Fig. 3 Classification of green nanomaterials

(1) **Zero-Dimensional (0D) Nanomaterial**

The most fundamental and symmetric shapes are those with zero dimensions, such as spheres and cubes, having nano-dimensions along all of the axes of x , y , and z and polygon. Examples of this include semiconductors like quantum dots and metallic nanoparticles like gold and silver class, with spherical shapes and dimensions between 1 and 50 nm.

(2) **One-Dimensional (1D) Nanomaterial**

These nanostructures will have one dimension that extends beyond the nanometer range, as seen in metal and metal oxide nanowires, nanorods, and nanotubes. Although these materials are only a few micrometers long, the diameter is measured in nanometers [79].

(3) **Two-Dimensional (2D) Nanomaterial**

Nanosheets or nanofilms with two dimensions lie outside the nanometer range in nanomaterials like nanofilms and thin film multilayers. The surface area of nanoscale films could be many square micrometers, yet the thickness is still the same in nanoscale. In 2D, there are fewer forms and varieties of inorganic nano-objects class.

(4) **Three-Dimensional (3D) Nanomaterial**

Objects with a cumulative size in the micrometer or millimeter range but with nanometric characteristics like confinement on the nanoscale spaces, or those created by the regular assembly and arrangement of nanoscale components can be referred to as '3D nano-systems.' With all dimensions greater than nano, they nonetheless have peculiar molecular and bulk characteristics that reveal their component parts. Nanocrystals with three dimensions are created by arranging 0D spheres, 1D rods, or 2D plates resulting in unique superstructures, like the box-shaped graphene or the platinum mesostructured films.

7.2 Introduction to Green Synthesis

Natural reducing agents, such as polysaccharides or plant extract, bacteria, and fungi are examples of biological microorganisms that can be employed for the synthesis of nanoparticles.

7.3 Meaning of Biological Synthesis

The environmentally friendly and green technique of biosynthesizing metallic nanoparticles from microorganisms like bacteria, actinomycetes, fungi, and algae. The combination of depending on the situation, nanoparticles may be intrinsic to the cell or a reaction from the outside where the nanoparticle product is located.

7.4 Synthesis Based on Plant Extract

The method for using plant extracts to create nanoparticles is straightforward, in that: The extract is combined with a metal salt solution at various temperatures and kept constantly moving and occasionally exposed to ultrasonic or microwave irradiation for a specified amount of time. Metal ion biogenic reduction to base takes place in a single step. Metal moves quickly and can operate at ambient temperature and pressure; therefore, that scaling up is simple to do. The reducing agents found are secondary plant chemicals [80].

The metabolites are chemically categorized as co-enzymes, alkaloids, tannins, and terpenoids. Various plant species' extracts have been used to create synthetic; alternatively, to metallic nanoparticles, live plants have also been employed [81].

7.5 The Advantages of Green Synthesis When Compared to Conventional Process

The environmentally friendly, more affordable, and simpler green synthesis of metal nanoparticles is a safe replacement for traditional chemical and physical processes that produce good results that don't need sophisticated equipment or complicated reagents [82].

7.6 Utilizing Green Synthesis to Create Metallic Nanoparticles

According to a preliminary study, the following herbs (leaf and fruit) are abundant in biomolecules that can be used to create nanoparticles.

7.6.1 Coconut Leaf

The coconut plant, or *Cocos Nucifera*, has pinnate leaves that are 4–6 m, (13–20 ft) long, with pinnae measuring 60–90 cm. Its capacity for free radical scavenging, antioxidant, and antibiotic properties are all heavily researched. The coconut leaf extract's total phenol content (TPC) ranges from 0.59 to 2.22 mg/g. Phenolic compounds have the ability to reduce in a green manner.

7.6.2 Jackfruit Leaf

Jackfruit, or *Artocarpus heterophyllus*, is a popular fruit in India, while some features such as having dark green, alternating, comparatively big, and oval-shaped leaves are characteristic of Southeast Asia, which have immature shoots that are strongly lobed.

7.6.3 Indian Gooseberry Fruit

Indian gooseberry (amla), also known as *Phyllanthus emblica*, was first discovered in India. Amla fruit extract and each of its constituent components have been demonstrated to have an antioxidant effect. Vitamin C, a water-soluble antioxidant that scavenges free radicals, is abundant in amla. Amla includes a number of other active ingredients, including polyphenols, flavones, tannins, ellagic acid, derivatives, flavonols, and anthocyanins [83].

7.6.4 Night Flowering Jasmine Leaf

The popular name for the *Nyctanthes arborist* is the night flowering jasmine tree. It is a medicinal plant with a broad range of biological activities, a leaf growing in India and other tropical and subtropical regions. Additionally, leaves contain an alkaloid called acanthine. Mannitol, astringent, and resinous are also present in leaves. Leaves also contain components, including tannic acid, sugar, methyl salicylate, and a minuscule amount of volatile oils.

8 Silver Nanoparticles

Since they display a variety of bactericidal and fungicidal actions, silver nanoparticles, which belong to the class of noble metal nanoparticles, have attracted attention. They are commonly used in a number of consumer items, including plastics, food, fabrics, pastes, soaps, and more. Typically, synthetic compounds used as reducing agents are used to create silver nanoparticles, which later, during the usage of the product, cause a variety of biological concerns due to their general toxicity, even at low concentrations of residual quantities. In biological compounds obtained from plant sources in the form of extracts and employed in 'green synthesis,' feasible, alternative, and superior reagents have been discovered. Aqueous leaf production of silver nanoparticles is one example. *Azadirachta indica* extract is used as a capping and reducing agent; it is well rounded, with a diameter of 34 nm, which is spherically shaped. After 15 min of reduction without the use of hazardous chemicals, silver ions are produced. The silver nanoparticles were active against both Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria. Silver nanoparticles are created using a precursor called silver nitrate and leaves three plant extracts: *Musa balbisiana* (banana), *A. indica* (neem), and *Ocimum tenuiflorum* (black tulsi), as a reducing and stabilizing agent, have been achieved. *E. coli* and *Bacillus* sp. were significantly more resistant to the antibacterial effects of silver nanoparticles, in relation to both unprocessed plant extracts and silver nitrate. Silver nanoparticle-treated moong bean (*Vigna radiata*) and chickpea (*Cicer arietinum*) seeds demonstrated quicker and more effective germination, indicating silver's low toxicity Nanoparticles [84].

9 Nanofibers Green Synthesis

Due to their high surface area and membrane-like structure, nanofibers created utilizing environmentally friendly solvents or naturally occurring biodegradable polymers have found a niche application in medical devices for controlled drug release and wound healing structure. Electrospun nanofibers mats have been produced utilizing hydroxypropyl cellulose (HPC) alone or by addition of fiber-forming polymer to improve the mechanical qualities of the nanofiber mats, using poly (vinyl alcohol) (PVA) or polyvinylpyrrolidone (PVP). Favorable characteristics, such as heat stability and PVA or PVP's aesthetic appeal and mechanical characteristics substantially improved and increased by the incorporation of HPC. Drug loading on these nanofibers enabled medication release that is sustained when assessed in vitro [85].

10 Application and Sources of Green Synthesis and Green Nanomaterial

The use of green nanotechnology and nanomaterials is extremely widespread. It is of immense importance as engineering and science advance into a new era. The vastness, inventiveness, and futuristic outlook of human civilization will all be the precursors to the real emancipation of science on a worldwide scale. The engineering field of green nanomaterials is currently undergoing extensive study and emancipation. Challenges in the fields of green nanotechnology, green nanomaterials, and the future of nanotechnology science are all pallbearers for a transformative period in science and engineering. Green nanoparticles come from a wide variety of sources. Plant extracts, biopolymers, vitamins, proteins, peptides (such as glutathione), sugars, and other plant-based compounds are only a few of the chemical compounds that nature gives us that work as reducing agents (e.g., glucose and fructose). Recently, the field of biomedical applications, such as medication and gene delivery, has emerged as an exciting prospect for forward-thinking research. Another class of natural resources utilized for the manufacture of metal nanoparticles is biopolymers. These polymeric carbohydrate molecules are accessible for the mass synthesis of nanoparticles since they have already been used in a variety of applications [86–91].

11 A Green Nanomaterial—the Nanocellulose

Nanocellulose is cellulose with a nanoscale structure. This includes cellulose nanofibers, micro-fibrillated cellulose, nanocrystalline cellulose, and bacterial nanocellulose, all of which refer to cellulose with a nanostructure created by bacteria. A very promising field of science and technology today is the enzymatic processing of nanocellulose. Nanocellulose's characteristic makes it a promising and significant material for various uses, and it has the potential to create a thriving industry [86, 92, 93].

12 Scientific Advances in the Field of Green Nanomaterial and Green Nanotechnology

The wonders of modern science and technology are green nanotechnology and green nanomaterials. Huge scientific changes are occurring in the fields of green engineering, green chemistry, and nanotechnology. With a clear focus on the advancement and emancipation of science, technology, and engineering, the authors in this part explain the scientific and engineering success in the fields of green nanotechnology, green nanoengineering, and green nanomaterials [94–96].

Glaser [97] provided an insightful discussion on green chemistry using nano-catalysts. Since nanomaterials may be designed at the nanoscale, they are anticipated to be a potential area for green chemical catalysis. Since they have a greater surface area and have been proven to exhibit catalytic properties, nano-catalysts are highly valued as materials. New and innovative process candidates, nano-catalysts are hailed for their higher activity, improved stability, durability or recycling potential, and cost-effectiveness.

Chemical catalysis and reaction engineering are currently undergoing new revisions. These novel catalysts are potential clean energy choices for fuel cell applications, hydrogen generating applications, and hydrogen storage applications. The topic of green nanoparticles and how environmentally friendly they are as a biotherapeutic approach was covered by Nath et al. [98]. Nanomaterials engineering and technology are moving quickly forward, crossing one bold boundary after another [98].

Due to their special qualities and potential uses in a variety of fields, including drug administration and therapy, green nanoparticles have received a great deal of interest in the scientific and engineering community for decades. Green nanotechnology offers ways to reduce the risk associated with manufacturing nanoparticles and employing them to reduce the creation of chemical intermediates.

A relatively new and expanding field of inquiry is nanotechnology. It is the newest cutting-edge development in science and technology today. Nanotechnology is the study of materials at the nanoscale, between 1 and 100 nm, where special phenomena can be seen and new uses can be imagined. As nanotechnology advances into new fields and offers up more windows, technology, engineering, and science are enshrined and envisioned [99].

The use of plant extracts in the green synthesis of gold nanoparticles is one of the promising methods for producing environmentally friendly nanomaterials for applications for environmental preservation and biology. The chemistry of natural goods is a modern scientific miracle. Proanthocyanidins, or functionalized gold nanoparticles, were created in this study using a hydrothermal process. UV and visible spectrophotometry were used to characterize the produced gold nanoparticles (UV-vis) [100].

Green nanotechnology and nanomaterials are currently on the cutting edge of tremendous scientific renewal. The worldwide scientific establishment is currently being destroyed by environmental catastrophes and global warming, leaving the globe in shock and awe [101].

Environmental biotechnology and chemical engineering both currently occupy the same space in the midst of profundity, prophecy, and revelation. This chapter emphasizes the complexity and breadth of the subject of environmental sustainability.

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Synthesis, Properties, and Characterization of Biological Nanomaterial



Sarvat Zafar

Abstract This chapter explored the various biological methods for creating nanostructured materials, including their properties and characterization techniques. Biological approaches are gaining popularity in the synthesis of nanomaterials because of their sustainability, cost-effectiveness, speed, non-pathogenic nature, environmental friendliness, ease of scaling up for large-scale synthesis, and lack of need for high pressure, temperature, or toxic chemical components. Furthermore, these nano-sized materials are used safely and effectively for human therapeutic purposes and have distinctive dimensions with a large surface area, chemical stability, and greater binding density, making them promising for applications in diverse areas such as food processing, drug delivery, cosmetics, pharmaceuticals, chemical industry, mechanics, wastewater purification, and catalytic properties. In addition, nanomaterials are characterized by their surface morphology and compositional structure using various techniques such as energy-dispersive X-ray spectroscopy (EDS), dynamic light scattering (DLS), atomic force microscopy (AFM), Raman spectroscopy (RS), Fourier transform infrared (FT-IR) spectroscopy, and scanning and transmission electron microscopy (SEM/TEM).

Keywords Nanomaterials · Biological synthesis · Properties · Characterization

1 Introduction

The field of science and technology has witnessed remarkable advancements and innovative breakthroughs, leading to an encouraging potential among the international scientific community to explore into new facets of nanotechnology. At its core, nanotechnology entails the manipulation of matter at the scale of nanometers (nm), where any one of its dimensions falls within the range of 1–100 nm [1]. Particles fabricated at the nanometer scale exhibit a variety of distinctive properties, such

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as optical, magnetic, and electrical characteristics, owing to wide-range surface area, high surface energy, and quantum confinement [2]. These unique physico-chemical attributes have led to the limitless application of nanoparticles in various fields, such as food industry [3], medicine [4], cosmetics [5], electronics [6], and the chemical industry [7]. The production of nanomaterials can be accomplished through a range of methods, such as physical, chemical, and biological techniques [8–10]. These physico-chemical and biological pathways for synthesizing nanoparticles (NPs) can be broadly categorized into two groups, namely the top-down approach and the bottom-up approach. The top-down approach encompasses processes that involve the production of nanoparticles by reducing their size, whereas the bottom-up approach involves creating nanoparticles from building blocks such as atoms and molecules [11, 12].

Several physical methods are commonly employed for synthesizing NPs, including inert gas condensation [13], laser ablation [14], electric arc discharge [15], and the radiofrequency plasma method [16]. Nevertheless, physical methods require a significant amount of time to achieve thermal stability, consume substantial energy, increase the environmental temperature around the source material, and may also require large spaces for equipment such as tube furnaces [17]. Thus, physical synthesis routes are considered insufficient for producing nanoparticles. A major drawback of chemical synthesis methods for nanoparticles is their reliance on harsh reducing agents like sodium borohydride, sodium citrate, and organic solvents [18], which pose toxicity and environmental concerns [19]. Consequently, biological synthesis methods are favored over physical and chemical routes for synthesizing nanoparticles. The nanoparticles' fabrication through biological method involves the utilization of various microorganisms, including bacteria [20], fungi [21], algae, and plants [22–24]. However, the use of microorganisms for this purpose is often hindered by two significant drawbacks. Firstly, the process is time-consuming, leading to low productivity rates. Secondly, the use of microorganisms for large-scale nanoparticle synthesis poses a potential pathogenic concerns, and the maintenance of such cultures can be a challenging task [25, 26].

Green synthesis of nanomaterials refers to the use of plant materials or components to biologically reduce metal ions to their elemental form, producing nanoparticles in the size range of 1–100 nm [2]. In comparison to alternative methodologies, the green synthesis technique is recognized for its elevated efficacy, simplicity, and economic viability. Furthermore, it possesses the added advantage of facile upscaling for larger-scale applications [27]. Moreover, unlike nanoparticle synthesis mediated by microorganisms, the green synthesis process obviates the need for maintaining large-scale cultures and eliminates the associated biohazard risk [28, 29]. The process of biological synthesis has been utilized to synthesize a diverse array of nanomaterials, such as Ag [30], Au [31], Pd [32], Fe [33], and ZnO [34]. Polyphenols, terpenoids, and polyols are phytochemicals that have been identified as the primary agents responsible for the reduction of metal ions to nanoparticles in plant extracts [10]. The nanomaterials synthesized through green approach exhibit notable properties, including antimicrobial activity [35], antioxidant potential [36], and catalytic activity [37], which are attributed to the phytochemicals involved in their reduction

process. Due to their exceptional properties, they are applicable in a wide range of fields, such as pharmaceuticals [38], drug delivery [39], cosmetics [40], food [41], and enzyme industry [42]. Currently, the worldwide research community is actively exploring additional potential applications of nanoparticles.

1.1 Methodology for the Biological Synthesis of Nanomaterial

In 1959, the concept of advanced nanotechnology was first introduced by Richard Feynman [43]. This emerging technology focuses on the synthesis of materials at the nanoscale and exploring their distinct physico-chemical attributes. The field of nanotechnology has undergone a significant surge in development, which has paved the way for its utilization in numerous fields such as electronics [44], drug delivery systems [45], food packaging [46], pharmaceuticals [47], optics [48], chemical industry [49], mechanics [50], solar energy capture [51], catalytic processes [10], wastewater purification [52], and hydrogen production [53].

The global research community is currently involved in the development of eco-friendly methods for producing highly effective products that are also environmentally sustainable. To achieve this goal, researchers are exploring the use of green nanotechnology and biotechnology [54, 55]. One-step synthesis of nanomaterials using green technology results in materials with enhanced stability, exceptional properties, and dimensions that eliminate the need for harsh reaction conditions such as high temperature, pressure, and pH levels. This approach to nanomaterial synthesis is considered environmentally friendly [56].

1.2 Techniques to Synthesize Nanoparticles

The synthesis of nanomaterials can be accomplished through either the top-down or bottom-up methods. All methods for synthesizing nanoparticles, whether physical, chemical, or biological, can be classified into one of these two approaches.

1.2.1 Top-Down

The top-down method involves breaking down a bulk material into smaller particles by employing different lithographic techniques, including grinding, sputtering, and milling [14].

1.2.2 Bottom-Up

The bottom-up method involves the synthesis of nanoparticles by self-assembling atoms into nuclei, which then increase in size to form particles at the nanoscale through a range of chemical and biological techniques [57].

2 Approaches for Nanoparticle Synthesis

2.1 Physical Approach

Several physical strategies are commonly utilized for the fabrication of nanoparticles, including laser ablation [58], electrospraying [59], high-energy ball milling [60], laser pyrolysis [61], and evaporation–condensation [62]. Other physical methods include the atomization [63], arc discharge method [8], annealing [64], and metal sputtering [65]. Physical techniques such as evaporation–condensation have proven successful in synthesizing a variety of nanomaterials, including silver, Au, fullerene, and lead sulfide (PbS) [66]. The absence of solvent contamination in the prepared thin films and the uniform distribution of nanoparticles are advantages of physical approaches that differentiate them from chemical methods [67].

2.2 Chemical Approach

Chemical approaches for nanoparticle synthesis are numerous and typically involve techniques such as the microemulsion, hydrothermal synthesis, sol–gel method, chemical vapor synthesis, and polyol synthesis. Chemical reduction is the most commonly employed method for synthesizing nanoparticles, utilizing both organic and inorganic reducing agents like NaBH_4 . Other reducing agents, including hydroquinone, sodium citrate, gallic acid, and elemental hydrogen, are also utilized in this process. The synthesis of nanoparticles through chemical reduction reactions is commonly carried out in a solution phase, resulting in colloidal properties of the product. The phenomenon of co-precipitation, which encompasses reduction, nucleation, growth, coarsening, and/or agglomeration, underlies these processes [68]. While chemical reduction is a widely used method for nanoparticle synthesis, its drawbacks include the toxicity of the reagents involved and the generation of non-eco-friendly by-products.

2.3 Biological Approach

The generation of NPs in an environmentally sustainable manner involves the use of biological approaches. This entails using bacteria, fungi, or plants and necessitates a solution containing metal ions and a biological reducing agent (Fig. 1) [69]. The stabilizing and capping agents are often present in cells as reducing agents and other components, thereby eliminating the need for external addition of these agents during nanoparticle synthesis via biological methods. These reducing agents are naturally occurring and widely distributed throughout biological systems.

3 Synthesis of Nanoparticles Using Green Methods

As previously noted, there are various methods for generating nanoparticles, such as physical, chemical, or biological routes. However, these approaches pose toxicity issues and environmental concerns. The physical method demands a significant amount of space and generates substantial heat, resulting in elevated environmental temperatures surrounding the source material. Likewise, chemical methods utilize hazardous chemicals and solvents that can result in significant harm to the environment. The requirement for an alternative method in nanoparticle synthesis led to the emergence of the concept of green nanotechnology. This eco-friendly and cost-efficient approach has gained considerable significance in recent times. Several nanoparticles produced using green nanotechnology have been successfully employed in diverse fields.

Green nanotechnology refers to the utilization of biotechnological techniques and biological pathways involving bacteria, fungi, or plants, to produce nanoparticles or nanomaterials that are environmentally friendly and free of toxic substances

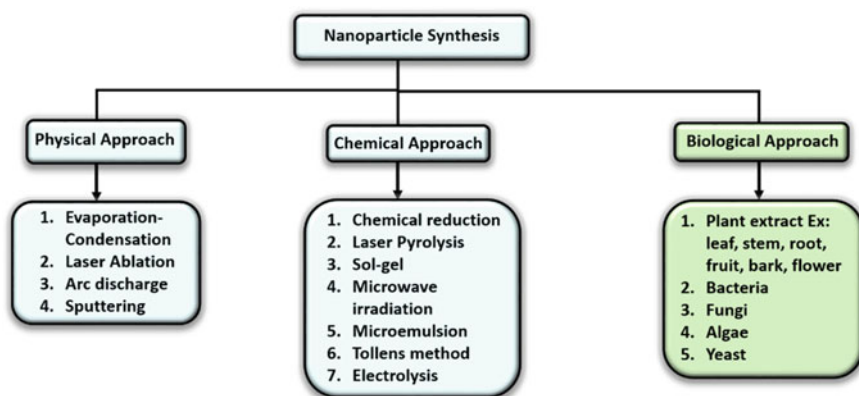


Fig. 1 Different techniques for the synthesis of NPs

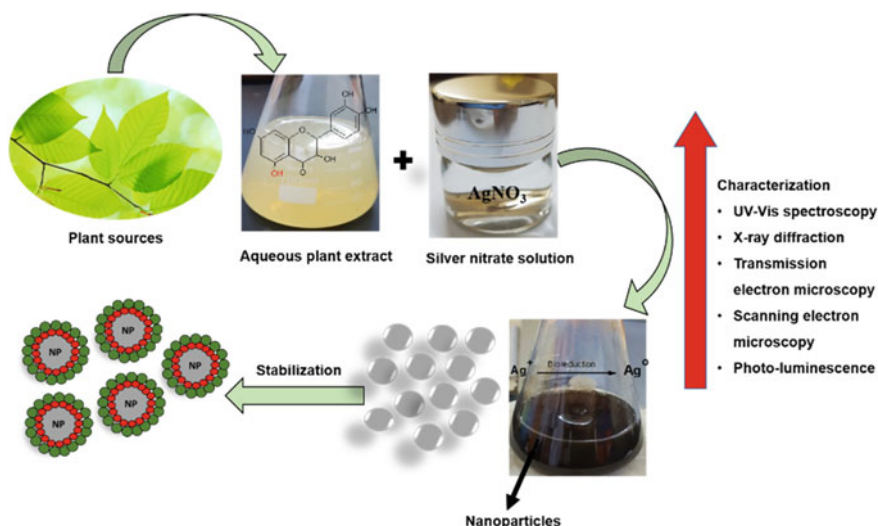


Fig. 2 Biological synthesis of nanoparticles using phyto-constituents

(Fig. 2). This chapter will provide an in-depth examination of the different biological pathways employed in the generation of nanomaterials.

3.1 Bacteria-Mediated Method

Bacteria have emerged as a promising means of synthesizing metallic nanoparticles, particularly silver and gold, due to their inherent ability to produce a range of inorganic materials both intra- and extracellularly. Despite the well-known biocidal properties of silver, certain bacterial strains have developed resistance to it, allowing them to accumulate substantial quantities of silver on their cell walls, accounting for up to 25% of their biomass by dry weight. These bacteria could potentially have industrial applications in the extraction of Ag from ores. The AG259 strain of *Pseudomonas stutzeri*, which was first discovered in a silver mine, was the first to exhibit the ability to produce silver nanoparticles through bacterial synthesis [70–72]. The current understanding of the biosynthesis mechanism for silver nanoparticles (AgNPs) involves the involvement of the nitrate reductase enzyme, which transforms nitrate into nitrite. NADPH-dependent nitrate reductase present in bacteria can simplify the process of in vitro synthesis of Ag by eliminating the need for additional processing steps typically required in other methods [73]. In a study, it was found that *E. coli* DH5 α mediated the intracellular biosynthesis of Au nanoparticles from chloroauric acid. The resulting NPs displayed mostly spherical shape, as well as triangular and quasihexagonal shapes. These nanoparticles were also found

on the surface of the bacterial cells, which facilitated the direct electrochemistry of hemoglobin and other proteins [74].

3.2 *Algae-Mediated Method*

Numerous reports have shown that algae can be beneficial in the synthesis of nanoparticles. One such example is the use of *Spirulina platensis*, a blue-green algae, for the production of gold nanoparticles mediated by proteins. The gold nanoparticles produced showed a homogeneous size distribution, with an average diameter of about 5 nm. Their antibacterial efficacy against *Bacillus subtilis* and *Staphylococcus aureus* was also tested [75]. A recent report has revealed that *Sargassum wightii*, a brown seaweed, can produce stable and evenly dispersed gold nanoparticles within the 8–12 nm size range. This was confirmed using multiple analytical techniques, including UV–visible spectroscopy, transmission electron microscopy, and X-ray diffraction analysis [76]. In addition, studies have reported the biosynthesis of gold nanoparticles, as well as EPS-Au and Si–Au bionanocomposites, using diatoms such as *Navicula atomus* and *Diadesmis gallica* [77].

3.3 *Fungi-Mediated Method*

The utilization of fungi in the synthesis of metallic NPs has been reported due to their unique characteristics, including high tolerance toward metals, exceptional metal binding capacity, and a bioaccumulation ability that is comparable to that of bacteria [78–80]. Various fungal species, including *Colletotrichum sp.* [81], *Fusarium sp.* [82], and *Phanerochaete chrysosporium* [83], have been utilized for NPs synthesis, as reported in the literature. The use of fungi for nanoparticle generation holds certain advantages over other microorganisms, owing to the rapid growth and ease of handling and fabrication in laboratory settings. Moreover, the fungal mycelial network has been shown to withstand a range of conditions, including flow pressure and agitation in bioreactors. The biosynthesis mechanism of NPs in fungi differs from that of other microorganisms, as fungi secrete a substantial amount of enzymes that aid in the reduction of metal ions, thus enabling the formation of metallic nanoparticles [84]. Recent reports suggest that extracellular enzymes, such as naphthoquinones and anthraquinones, may also contribute to the reduction process during nanoparticle synthesis [85, 86].

In a study by Syed et al. [86], extracellular NP fabrication was observed using the thermophilic fungus *Humicola species*. The researchers found that the cell filtrate is reacted with Ag^+ ions, resulting in the catalytic bioreduction of Ag ions and subsequent nanoparticle generation.

3.4 *Yeast-Mediated Method*

Yeast, a unicellular eukaryotic microorganism, has been utilized primarily in the production of semiconductors. Specifically, the yeast species *Candida glabrata* was employed to synthesize monodispersed, spherical CdS quantum crystallites that were peptide-bound and measured 20 Å in size, while *Schizosaccharomyces pombe* produced wurtzite hexagonal CdS crystals that were approximately 1–1.5 nm in size during the mid-log phase [87]. *Torulopsis sp.* has also been identified as a promising candidate for the efficient intracellular production of lead sulfide (PbS) nanocrystallites, with dimensions ranging from 2 to 5 nm, which are stored within the vacuoles of the organism. The nanoparticles synthesized using yeast have been employed in the fabrication of an ideal diode, highlighting their potential for practical applications [88, 89].

3.5 *Engineering Nanoparticles Using Biomolecular Templates*

The potential use of viruses, nucleic acids, and cell membranes as templates for NPs' fabrication has been extensively investigated. Of these biomolecules, DNA has emerged as a highly suitable template due to its strong affinity toward transition metal ions. Its biomolecular properties make it an excellent candidate for both nanoparticle synthesis and templating. In a recent study, DNA was employed as a template for the production of Au nanostructures using an electroless photolytic method. The nanoclusters obtained from the aforementioned study had dimensions ranging from 10 to 40 nm, whereas the diameter of the nanostructure was between 40 and 70 nm. Additionally, the resulting nanostructure exhibited resistivity similar to that of pure metal. Electrical characterization revealed that the synthesized gold nanostructures exhibited continuous and Ohmic behavior with minimal contact resistance between the electrodes [90]. Biological membranes have been widely explored as templates for the synthesis and engineering of NPs, taking advantage of their ultrafine pores. One study reported the formation of AuNPs using a rubber membrane derived from *Hevea brasiliensis* as a preservative during the bioreduction of Au⁺³ in a solution maintained at 80 °C [91]. Using viruses as templates is an alternative approach to achieve consistent size and morphology of synthesized NPs, as the hollow cavities within their structures can be utilized for this purpose [92, 93]. Certainly, the utilization of M13 bacteriophage as a template for the formation of ZnS and CdS quantum dots has been reported [94, 95].

3.6 Plant-Mediated Method

The utilization of aqueous extracts from various plants as both reducing and capping agents in the production of metallic NPs has been reported. This method has been deemed advantageous over microbial synthesis due to the ease of cell culturing and maintenance, faster reduction rates, and the production of stable NPs. Plants are widely regarded as an essential source of bio-green methodologies, particularly with regard to the synthesis of nanoparticles. Biological synthesis has gained considerable attention due to its many advantages, including cost-effectiveness, speed, non-pathogenicity, environmental friendliness, and the ability to scale up for large-scale synthesis. This method involves the use of living organisms or their byproducts, such as enzymes, to synthesize various materials, including nanoparticles. Biological synthesis offers numerous benefits over traditional methods, including the ability to use mild reaction conditions, which minimizes the usage of harmful chemicals and reduces the generation of hazardous waste. Additionally, this method can be easily scaled up to meet commercial demand.

A wide variety of plants, including their different parts such as leaves [96], stems [97], flowers [98], fruits [99], roots [100], and seeds [101], have been employed in the biological synthesis of metallic NPs [57]. Plant extracts are rich in various secondary metabolites, including proteins, enzymes, amino acids, polysaccharides, saponins, phenolic intermediates, terpenoids, vitamins, and alkaloids as shown in Fig. 3. These phytochemicals can serve as effective reducing agents for the bioreduction of metal ions into metallic NPs. For instance, α -Fe₂O₃ NPs were synthesized using *S. cordifolia* [102] aqueous plant extract, while zirconia nanoparticles were synthesized from *Euclea natalensis* [103] plant extract.

Furthermore, *Centella asiatica* [104] plant extract was used for the biosynthesis of iron oxide NPs, and the leaf extract of *Prosopis juliflora* [105] was utilized to derive ZnO NPs. Additionally, *Fumariae* herba [106] extract was involved for the biosynthesis of platinum NPs, which demonstrated excellent catalytic activity toward organic dyes. *Blumea eriantha* [107] extract was used to derive silver and iron NPs, while *Punica granatum* [108] fruit peels' extract was used to produce zinc oxide NPs, which showed significant cytotoxicity and antibacterial activities. Likewise, the tuber extract of *Coccinia abyssinica* [109] was utilized to produce zinc oxide nanoparticles, which displayed significant antimicrobial and antioxidant characteristics. The research presented highlights the possibility of utilizing natural extracts as a viable and environmentally conscious alternative for producing nanoparticles in a sustainable manner [110].

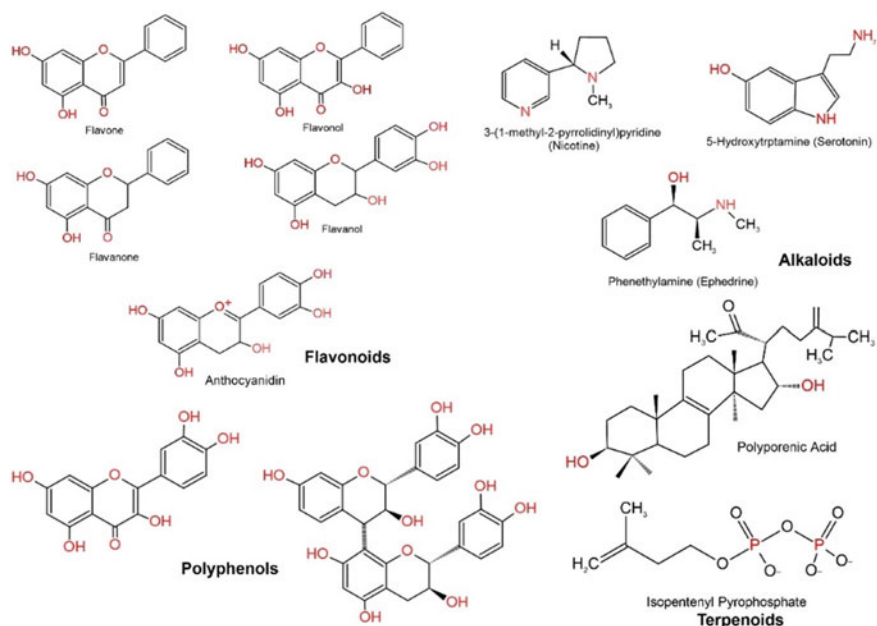


Fig. 3 Phytochemical constituents in the plant extract [10]

4 Factors Influencing the Biological Synthesis of Nanomaterials

Various factors, such as pH, temperature, and reaction time, have a substantial impact on the formation and stabilization of nanoparticles utilizing plant-based entities. These factors are critical in determining the properties and characteristics of biogenically synthesized NPs.

4.1 pH Level of the Reaction Medium

The formation of nanoparticles is significantly influenced by the pH level of the reaction medium, as reported in various studies [111]. Variation in hydrogen ion concentration has been found to significantly impact the size and morphology of NPs. It has been observed that lower pH levels result in the production of larger particles, while higher pH values tend to yield smaller particles [112]. According to a study, *Avena sativa* produced large rod-shaped gold NPs at a pH of 2, whereas smaller NPs were formed at pH levels of 3 and 4 [113]. Likewise, the synthesis of spherical AgNPs using bark extract of *C. zeylanicum* was favored at higher pH values of 5 and above [114].

4.2 Temperature of the Reaction Medium

The synthesis of metallic NPs is notably affected by temperature, particularly in terms of the resulting size and shape of the NPs. For instance, the synthesis of AuNPs using leaf extract of *Cymbopogon flexuosus* indicated that the formation of nanotriangles was more favorable at lower reaction temperatures. Conversely, higher reaction temperatures led to the formation of more spherical nanoparticles alongside the nanotriangles [115].

4.3 Synthesis Methodology

Numerous techniques exist for synthesizing NPs, including physical, chemical, and biological methods, each with its own unique set of benefits and limitations. Among these techniques, the biological approach is particularly attractive due to its eco-friendly and non-hazardous characteristics. As a result, nanoparticles produced through biological synthesis are often considered more desirable than those produced through other synthetic routes [1].

4.4 Pressure

The impact of pressure on the size and shape of metallic NPs is a key parameter during synthesis. Studies have shown that under ambient pressure conditions, biochemical agents can rapidly reduce metal ions, implying that pressure can significantly influence the synthesis of NPs [116].

4.5 Reaction Time

Numerous studies have indicated that the duration of incubation in nanoparticle reaction media is a crucial factor that significantly influences the quality and morphology of the synthesized nanomaterials [117, 118]. The properties of the nanoparticles can be significantly influenced by variations in the incubation time, as well as by factors such as light exposure, synthesis method, and storage conditions [119, 120]. Prolonged incubation times can lead to aggregation or shrinkage of nanoparticles, which may negatively impact their potential [121].

5 Physico-chemical Properties

As previously discussed, nanoparticles possess a range of physico-chemical properties that render them unique and well-suited for diverse applications. These properties include large surface area, optical activity, chemical reactivity, and mechanical strength.

The subsequent section will provide a detailed explanation of the importance of these properties.

5.1 *Optical and Electronic Properties*

The optical and electronic properties of nanoparticles, particularly noble metal nanoparticles, are closely interconnected. These noble metal NPs exhibit size-dependent optical attributes and demonstrate a distinct extinction band in the UV-visible spectrum, which is not observable in bulk metal. The phenomenon is primarily attributed to the localized surface plasmon resonance (LSPR) effect, resulting from the collective excitation of conduction electrons triggered by photons with a constant frequency. The maximum wavelength of the LSPR is influenced by several factors, such as the size, shape, and spacing of nanoparticles, as well as the dielectric properties of both the nanoparticles and their surrounding environment. This environment includes the substrate, solvents, and any adsorbates present [122]. The distinct colors observed in stained glass doors/windows can be attributed to the presence of gold colloidal NPs which impart a rusty appearance, while silver NPs generally appear yellow. These NPs possess free electrons on their surface, specifically d electrons in the case of Au and Ag, that are capable of facile transport within the nanomaterial. Interestingly, the mean free path for both Ag and Au is approximately 50 nm, which is larger than the size of the NPs for these materials. Consequently, scattering from the bulk is not expected upon interaction with light, instead these NPs undergo a standing resonance condition known as LSPR, which is accountable for the distinct colors observed in these materials [123].

5.2 *Magnetic Properties*

Magnetic nanoparticles have attracted considerable interest among researchers in various fields, including magnetic fluids, data storage, heterogeneous and homogeneous catalysis, biomedicine, magnetic resonance imaging (MRI), and environmental remediation, such as water decontamination. According to previous research, nanoparticles demonstrate superior performance when their size is less than a critical threshold of 10–20 nm [124]. At this size range, the magnetic characteristics

of nanoparticles become dominant, making them extremely useful and applicable in various fields [125].

5.3 Mechanical Properties

The unique mechanical characteristics exhibited by nanomaterials have sparked research on their potential uses in various essential fields, including tribology, surface engineering, nanofabrication, and nanomanufacturing. The mechanical characteristics of nanoparticles can be precisely assessed by analyzing various parameters, such as stress, strain, elastic modulus, hardness, friction, and adhesion. Additionally, the mechanical behavior of NPs is influenced by factors such as surface coating, coagulation, and lubrication [126]. NPs exhibit distinct mechanical properties in comparison to microparticles and bulk materials. Attaining precise control over the mechanical attributes of NPs and their surface interactions is crucial in enhancing material removal and improving surface quality. In order to achieve successful outcomes in various areas involving nanoparticles, it is crucial to have a comprehensive grasp of their fundamental mechanical characteristics.

5.4 Thermal Properties

Metal nanoparticles are highly regarded for their exceptional thermal conductivities, surpassing those of fluids in their solid states. At ambient temperature, copper exhibits a thermal conductivity that is approximately 700 times higher than water and 3000 times greater than engine oil. Similarly, oxides like alumina display thermal conductivities greater than water. Consequently, suspensions of solid particles in fluids are anticipated to exhibit considerably improved thermal conductivities in comparison to traditional heat transfer fluids. Nanofluids are created by blending solid particles that are nanoscale in size with liquids like water, oils, or glycol. These fluids are anticipated to display enhanced characteristics in contrast to standard heat transfer fluids and fluids that comprise particles at the macroscopic scale. Particles possessing a substantial overall surface area are favored as heat transfer occurs predominantly at their surface. Additionally, a greater surface area contributes to the stability of the suspension. Recent studies have indicated that nanofluids comprising copper or alumina oxide NPs dispersed in ethylene glycol or H₂O display considerably enhanced thermal conductivity [127, 128].

6 Characterization

Energy-dispersive X-ray spectroscopy (EDS), dynamic light scattering (DLS), atomic force microscopy (AFM), Raman spectroscopy (RS), Fourier transform infrared (FT-IR) spectroscopy, and scanning and transmission electron microscopy (SEM/TEM) are among the commonly employed techniques for characterizing nanoparticles. These techniques facilitate the investigation of crucial NPs characteristics such as size, shape, structure, and surface morphologies [129].

6.1 Structural Characterizations

The analysis of structural properties typically entails the utilization of various techniques, including X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), Raman spectroscopy, Brunauer–Emmett–Teller (BET), zeta size analyzer, and surface area analysis. X-ray diffraction is a prominent technique used for characterizing nanoparticles, especially with regard to their structural characteristics. XRD is capable of revealing crucial detail about the phase identification of the crystalline nanomaterials, as well as providing a rough estimate of their size through the application of the Debye–Scherrer formula. Notably, XRD has been successfully utilized for the identification of both single and multiphase nanoparticles. These findings have been corroborated in prior research by Khan et al. [130] and Ullah et al. [131].

Energy-dispersive X-ray spectroscopy is frequently employed in conjunction with TEM for determining the elemental composition of nanoparticles, providing an approximate percentage by weight. In practice, EDX is utilized by focusing an electron beam on a single nanoparticle via SEM or TEM, thereby enabling the acquisition of insightful information regarding the nanoparticle under observation [132].

X-ray photoelectron spectroscopy (XPS) is widely regarded as a highly sensitive technique for determining the precise elemental ratios and bonding nature of elements within nanoparticle materials. The surface sensitivity of XPS makes it a valuable tool for conducting comprehensive profiling studies, which aim to evaluate the composition and variations in composition throughout the depth of a material. As such, XPS is an important tool for characterizing nanoparticle materials and provides valuable insights into their structural and compositional properties. Wang et al. [133] employed X-ray photoelectron spectroscopy and scanning transmission electron microscopy (STEM) spectroscopies, aided by SESSA software, to quantify the coating of nanoparticles.

According to [134], surface-enhanced Raman spectroscopy has become a highly effective method for analyzing vibrational conformations due to its ability to enhance signals through the surface plasmon resonance phenomenon. In a related study, Ma et al. [135] utilized the SERS method to investigate the vibrational properties and

phonon modes in nano-sized and quantum dots of TiO_2 , PbS, and zinc oxide nanoparticles. The researchers assumed that the enhanced spectra observed in semiconductor systems could be ascribed to the plasmonic resonances present within the nanoparticles. This underscores the potential of SERS as a valuable tool for characterizing the vibrational properties of nanoparticles.

6.2 Particle Size and Surface Area Characterizations

Various approaches are available for elucidating the size of nano-sized materials, including XRD, SEM, TEM, atomic force microscopy (AFM), and dynamic light scattering (DLS). While SEM, TEM, XRD, and AFM are capable of providing precise information on particle size [136], the zeta potential size analyzer and dynamic light scattering can be particularly useful for determining NPs size at extremely low levels. Thus, a combination of techniques may be necessary to obtain a comprehensive understanding of the size of NPs in a given sample.

In addition to differential scanning calorimetry (DSC), nanoparticle tracking analysis (NTA) represents a relatively novel and specialized technique that can prove helpful for biological components, such as proteins and DNA. Through the NTA approach, nanoparticles in liquid media can be visualized and analyzed by relating their Brownian motion rate to particle size. This technique offers the advantage of determining size distribution profiles for NPs within a size range of 10–1000 nm in a liquid phase [137]. Consequently, NTA can serve as a valuable complement to other nanoparticle size characterization techniques, particularly when applied to biological samples. Due to the significant surface area of nanomaterials, various applications have been proposed. To assess this area, the Brunauer–Emmett–Teller (BET) has emerged as the most appropriate method. This approach operates on the fundamentals of adsorption and desorption, as well as the BET theorem, in order to quantify the surface area of NP materials [138]. By determining the surface area of nanomaterials, the BET technique can provide valuable information about their properties and potential applications.

6.3 Optical Characterizations

In the investigation of photocatalytic applications, the characterization of optical properties is a crucial aspect, and photochemists have invested significant efforts toward developing a thorough understanding of this technique to elucidate the fundamental mechanisms of photochemical processes. The characterizations primarily rely on the established Beer–Lambert law and fundamental principles of light, both of which are widely accepted within the field of photochemistry [139]. Optical techniques provide valuable insights into the absorption, reflectance, luminescence, and phosphorescence attributes of NPs. The fact that metallic and semiconductor NPs

exhibit unique colors is widely recognized, making them highly suitable for photo-related applications. Optical instruments such as ultraviolet–visible (UV–Vis) spectroscopy, photoluminescence (PL), and the null ellipsometer are widely used in the study of the optical properties of NP materials. The UV/vis-diffuse reflectance spectrometer (DRS) is a highly versatile device that enables the measurement of key optical properties, including absorption, transmittance, and reflectance. Although absorption and transmittance are often considered complementary techniques, DRS is especially valuable for solid samples. This method is widely accepted for its accuracy in determining the bandgap of various nanomaterials, including NPs [140].

Besides UV spectroscopy, photoluminescence (PL) is an invaluable method for investigating the optical properties of photoactive nanomaterials. This method offers complementary insights into the absorption or emission traits of the materials. As such, it can provide important insights into charge recombination and the half-life of excited materials in their conduction band, making it beneficial for various imaging and photo-related approaches [141]. Furthermore, the PL technique has demonstrated efficacy in determining several key properties of NPs, including layer thickness [142], doping levels [143], and the presence of defects and oxygen vacancies [144]. These capabilities make it a versatile and valuable tool for study nanomaterials, particularly in the context of their optical properties.

6.4 Morphological Characterizations

The investigation of the morphological features of NPs is a key aspect of their characterization since morphology strongly influences many of their properties. The morphology of NPs can be investigated using various techniques, but among them, TEM, SEM, and polarized optical microscopy (POM) are considered the most important. This microscopic techniques enable the determination of critical parameters including shape, size, and surface properties of NPs, making them essential tools in the study of nanomaterials.

The SEM operates on the principle of electron scanning and offers a wealth of information on NPs at the nanoscale level. Numerous studies in the literature have demonstrated the utility of this technique not just for examining the morphology of nanomaterials, but also for evaluating the dispersion of NPs in bulk or matrix. The dispersion of single-walled carbon nanotubes in the matrix comprising poly(butylene) terephthalate and nylon-6 was investigated using the SEM technique [145]. This study has demonstrated the ability of SEM to reveal information about the distribution of nanomaterials within the matrix, including the extent of their dispersion.

TEM is another electron-based technique that offers valuable insights into the morphological features of NPs at various magnifications, providing information on bulk materials. This method has been broadly used to inspect the different morphologies of gold NPs. Figure 4 displays TEM micrographs depicting silver NPs morphologies obtained from date fruit extract [30].

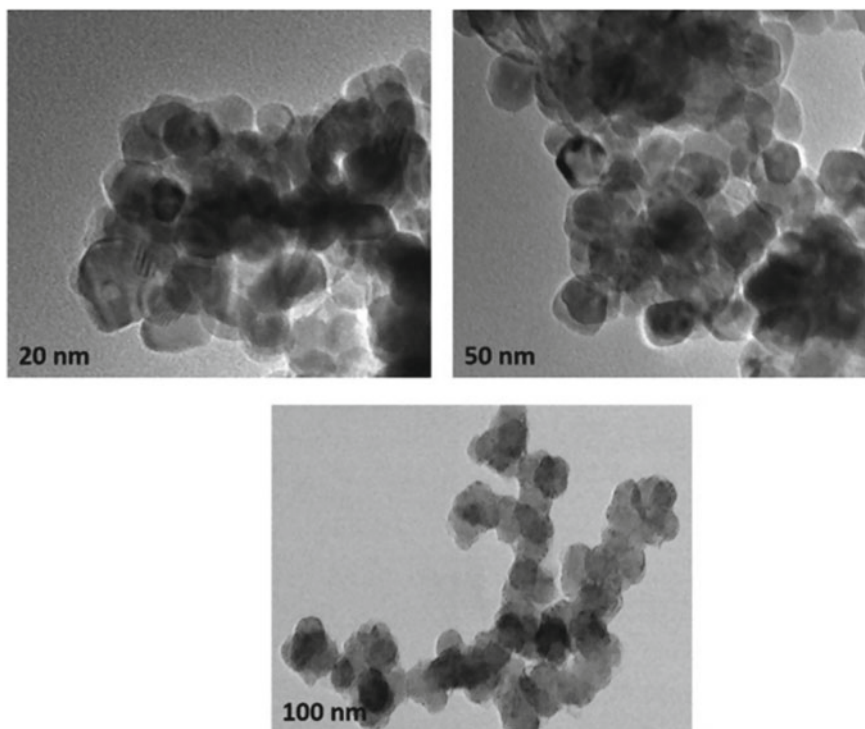


Fig. 4 TEM images of nanoparticles using date fruit extract, highlighting the different morphologies of the nanoparticles [30]

7 Conclusion

This chapter has explored the various biological approaches for synthesizing nanostructured materials and highlighted their unique properties and characterization techniques. The increasing popularity of biological approaches for nanomaterial synthesis is driven by their sustainability, cost-effectiveness, non-pathogenic nature, environmental friendliness, and ease of scaling up for large-scale synthesis, making them an attractive alternative to traditional methods. Additionally, these nano-sized materials possess unique attributes such as a large surface area, higher binding density, and chemical stability, which make them promising for various applications, including food processing, cosmetics, drug delivery, pharmaceuticals, chemical industry, mechanics, wastewater purification, and catalytic properties. Overall, this chapter provides valuable insights into the rapidly growing field of biological methods for the synthesis and characterization of nanomaterials.

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Antimicrobial Potential, Drug Delivery and Therapeutic Applications of Bio-nanoparticles in Medicine



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Abstract A nanoparticle (NP) is a tiny particle with ranging in size from 10 to 100 nm. Bionanomaterials have a remarkable potential as ‘magic bullets’ mainly produced from plants, bacteria, fungi, etc. Green synthesized of nanomaterials are powerful and significant tool defending from the unsafe effects of medicine in addition to overcoming the obstacles to access of the drug in targeted tissues and dealing with drug resistance effectively. In recent era, the designing of bio-nanoparticles and extensive use in numerous biomedical applications like as anti-cancerous, antibacterial, and site-specific drug delivery systems has become the top-priority research goal. Nanoparticles are used in the field of medicine as a powerful weapon due to their stability, inert nature, high dispersity, non-cytotoxicity, and biocompatibility. The current chapter specifically emphasizes the applications of bio-nanoparticles in the field of medicine.

Keywords Bio-nanoparticle · Green synthesis · Antimicrobial · Anti-cancerous · Drug discovery

1 Introduction

Nanotechnology is an interdisciplinary field that bridges various disciplines like biological and physical sciences that result in the development of new technological era. Nanotechnology is an emerging scientific areas which playing a vital role in our daily lives and have a wide ranging multiple applications such as medicine,

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drug delivery, environmental remediation, information technology, energy conversion, and agriculture [1]. Nanomaterials (usually ranging 1–100 nm) are attaining great importance in the field of science and technology and with advancement in medical expertise role of nanoparticles also expanded. Nanomaterials have resourced curiosity in the field of applied sciences from material science to biotechnology [2]. Nanotechnology is alteration of materials in which other ingredients are incorporated using different techniques like chemical, biological, and physical methods. The purpose of alteration of material is to make new substance which can be applied in different fields with enhanced characteristics and specialized functionalities.

As conventional methods chemical and physical methods are commonly used methods for synthesis of nanomaterial but these methods are expensive and are not environment friendly well as due to production of cluster of hazards material/products [3]. Therefore, it's urgently required to develop new methods for synthesis of nanomaterials. Currently, biosynthesis of nanoparticles is recognized as feasible and facile alternative methods and acknowledged as a safe, environment friendly, and economically cheap alternative methodology. For this scientists moved toward biological synthesis and various organisms like unicellular and multicellular are used to generate nanomaterial both intracellularly and extracellularly [4]. This significance has led to the need to progress in the development of environment friendly, sustainable and safe nanomaterials by incorporating the principles of green chemistry during their synthesis and in their applications [5]. Nanomedicine is the branch of medicine which uses to cure and prevent various illness using nanoscale materials. The nanoscale medicine use in different applications such as diagnosis, drug delivery, sensory, and actuation purposes in a living being [6]. The existing chemotherapeutic agents are broadly used worldwide, but they are eliminated due to expensiveness, high toxicity, various incidental effects, rise of drug resistance, and poor specificity. So, it is imperative to learn substitute therapies, tools, and medicine to overcome the current challenges [7]. Nanomedicine is the most significant field of nanotechnology using the molecular knowledge of human body and applied for diagnosis, prevention, and treatment of various diseases. The outline of this discussion majorly focuses the role of bio nanoparticles in medicine.

Globally, food borne diseases are an alarming threat caused by different pathogenic bacteria, and nearly 30% people of industrial countries are suffered in food borne diseases every year. These diseases are result of intake of contaminated food by bacteria, fungus, or toxins. During handling, process like harvesting and transportation food can be adulterated. *Escherichia coli*, *Salmonella* sp., *Campylobacter* sp., *Listeria* sp., and Clostridia are most dominant bacteria responsible for food borne diseases [8].

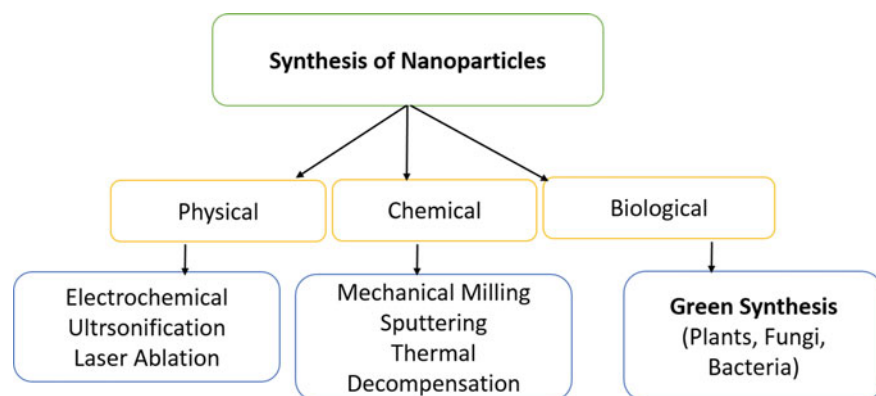


Fig. 1 Synthesis methods of nanoparticles

2 Synthesis Techniques for Nanoparticles

Nanomaterials are widely synthesized and studied because of their outstanding medicinal properties in different fields like cancer and antimicrobial. Nanoparticles remarkable potential influenced by their structural shape has been extensively investigated, and many studies have done to synthesize nanoparticles using different techniques like biological, chemical, and physical [9]. The biological methods of bio-nanoparticle have benefit utilizing microorganisms, plants, and plants extract over other methods because of environmentally friendly, energy efficient, and cost-effective. For example, microorganisms are referred as promising bio-factories for bionanomaterial production and their precise physicochemical features make them a new generation antibacterial agent. For synthesis of bionanomaterials green material act as both stabilizing and reducing agents [10].

Globally, green synthesis of nanoparticles from plants extract or plants products is getting huge importance due to a cluster of bioactive reducing metabolites and their abundant aptitudes. Especially, plants are more prefer for synthesis of nanoparticles compared to algae and bacteria because plants are more renitent to metal toxicity. So, biological source offers a great alternative for synthesis of nanoparticles [11] (Fig. 1).

3 Role of Bio-nanomaterials Against Microorganisms

At the turn of the twentieth century, infectious diseases were the leading cause of death across the globe. The widespread use of antibiotics during the past century has greatly contributed to the decline in infectious disease-related mortality and morbidity. But antibiotic resistance has reached a crisis point in recent years; rendering many of the most essential antimicrobial drugs currently used in the clinic

are ineffective. The problem of bacteria acquiring resistance to antimicrobials has prompted numerous attempts to either find novel medicines or chemically change existing antimicrobial treatments. The creation of resistance among microbiological pathogens is occurring at an alarming rate, and there is no guarantee that new antimicrobial treatments will be created soon enough to keep up [12, 13].

Recent developments in nanoscience and nanotechnologies have allowed for the incorporation of nanoparticles into the design of antibacterial and antibiofilm agents. To speed up the delivery of drugs and antibiotics, “nanocarriers” made from nanostructured materials can be used. Antibacterial and antibiofilm capabilities have been found in many different types of nanomaterials. In the presence of nanoparticles, synergistic systems can arise that combine two or more antimicrobial drugs, and smart on-demand treatment modalities can be constructed. This is due to the fact that nanoparticles themselves may be antibacterial or possess other useful properties [14, 15]. Because of their extensive applicability, sustainability, and low cost, nanoparticles manufactured from renewable resources (bionanomaterials) continue to garner interest from academics and business. Oxygen barrier, Young modulus, biodegradability, tensile strength, water swelling capacity, and compatibility with other materials like viscosifier and emulsifier are only few of the many useful qualities of bionanomaterials [16].

Antibacterial applications of nanotechnology have shown remarkable success, offering encouraging hope for the future of antibiotic-free methods. Because of their unique structures, nanomaterials can be used for a wide range of applications. Bionanomaterials’ physiochemical properties can be precisely controlled, including their size, surface chemistry, and shape. Aside from their inherent antibacterial activity (through cell membrane destruction or nutritional scarcity), the resulting functional materials also exhibit light-assisted antibacterial action and immunomodulation [17].

Second natural compounds for bacterial suppression or as adjuvants in vaccine formulations can be more effectively delivered via bionanomaterials due to the improved permeability, controlled release, and targeted bacterial absorption that these materials provide. Last but not least, bionanomaterials can be tailored to have a wide range of bactericidal capabilities, reducing the possibility that bacteria would develop resistance to them. In order to create viable antibiotic alternatives, it is critical to understand how the physiochemical properties of nanomaterials affect their antibacterial efficacy and mechanism [18].

Nanomaterials have been labeled as a promising new class of antibacterial agents due to research into and proof of their ability to suppress infections *in vitro* and *in vivo*. There may be no short-term or immediate risks associated with antibiotic NPs, but the question of whether or not they pose long-term dangers remains open [19]. Recently, the creation of new nanomaterials having antibacterial properties has been a hot topic of discussion. Whether it be on specific types of nanomaterials like carbon, metal/metal oxide, liposome, and polymer-based materials, or on specific antibacterial applications like antibacterial coatings, biofilm inhibition, and fighting

antibiotic-resistant pathogens, there are a number of excellent reviews that summarize the antibacterial properties and corresponding bacterial killing mechanisms of nanomaterials [20, 21].

The focus of scientific inquiry has switched over the past decade from the prevention of antibiotic resistance to the discovery of new medicines for prevalent bacterial diseases. Clearly, antibiotic-free alternatives offer a fresh perspective on how to address the issues of antibiotic overuse and resistance. But most information on alternatives to antibiotics comes from a medical or biological perspective. Relying on multifunctional nanomaterials to disseminate the antibiotic-free concept has been given little consideration [22].

Antimicrobial resistance (AMR) has emerged as a major threat in healthcare settings and beyond. Antibiotic-resistant bacterial infections are expected to increase by about 9% worldwide in 2020 compared to 2019 according to a report published by the World Health Organization. The global prevalence of antimicrobial resistance (AMR) has prompted calls for novel approaches to drug delivery and the identification of additional antimicrobial drugs that can be used to combat drug-resistant bacteria and halt the spread of AMR [23] (Fig. 2).

Synthetic chemistry, the multichannel device (iChip), and artificial intelligence have all contributed to the development of novel antibiotics, allowing for the development of potent treatments that can kill off even the most drug-resistant bacteria. A breakthrough in antibiotic development has been thwarted by a number of factors, including the potential for toxicity, a decrease in financing, and the risk of drug resistance [24]. Currently, various well-known pathogenic bacteria like *S. aureus*,

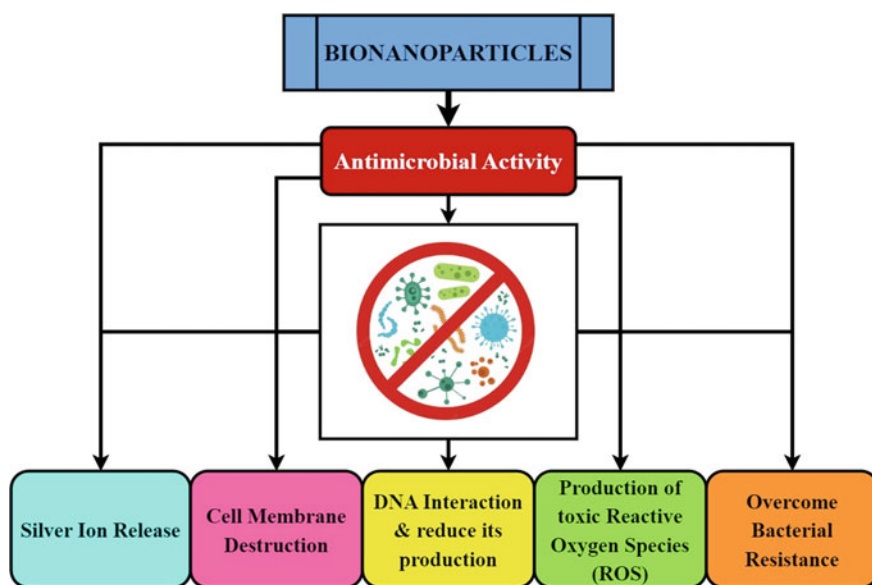


Fig. 2 Role of bio-nanoparticles against bacteria

K. pneumonia, *E. coli*, and *Pseudomonas* spp. are reported against most commonly used antibiotics agents. Silver nanoparticles were synthesized from extract of wild ginger plant and found to be very effective against multidrug resistant oral bacteria [25].

Discovering new, effective antibacterial medications that work in a way that is different from existing antibiotics is, thus, a challenging yet appealing task. Significant effort has been put into the study of and development of antimicrobial peptides, bacteriophages, probiotics, and nanomaterials for the treatment and prevention of potentially fatal bacterial infections. It's crucial to find ways to combat the growth of AMR while also preventing the current AMR process from rendering new antibacterial medications useless [26].

As our understanding of nanoscience and technology has grown, we have found that certain nanoparticles (NPs) exhibit higher efficacy in antibacterial characteristics than antibiotics primarily derived from microorganisms or natural sources. For instance, NPs' enhanced interaction and permeability to bacterial cell membranes may lead to a wide variety of antibacterial effects, including bactericidal efficiency [9]. Nanotechnology offers the possibility of engineering the structure and activity of NPs, leading to potentially increased bactericidal ability with reduced biotoxicity. The fact that some antibacterial nanoparticles can actually cause bacterial drug resistance is reason enough to keep looking for effective antibacterial nanomaterials that don't produce drug resistance and are instead based on a unique antibacterial action mode [27, 28] (Table 1).

4 Role of Bionanomaterials in Vaccine

The use of nanotechnology has increased significantly in recent years across many fields. The application of nanoproducts has also received attention from various fields of medicine and healthcare [29]. A biological procedure known as vaccination uses antigenic materials to stimulate a person's immune system to produce antibodies against a particular infection. The best method for preventing infectious infections and conditions that can lead to cancer is vaccination [30]. It has been demonstrated that nanomaterials can help in viral infection prevention, diagnosis, and therapy [31]. Nanomaterials with antimicrobial or self-sterilizing capabilities have received the most attention in research on the viral transmission prevention through the cleaning of surfaces, such as protective equipment. Silver and copper, which are naturally antimicrobial substances, have been proven to be effective against SARS-CoV-2 [32, 33]. Nanotechnology platforms are extremely useful in the design of contemporary vaccinations and have accelerated the development of novel candidate vaccines for clinical testing. In order to overcome lymph nodes, mucosal barriers, tissue, and epithelial barriers (gastrointestinal, airway, nasal, etc.), nanoparticles can be given via intramuscular, intranasal, oral, and subcutaneous routes [34, 35] mRNA and DNA vaccines can be delivered by nanoparticles into cells, where they cause antigens expression. In subunit vaccinations, nanoparticles can also target immune

Table 1 Source of origin and antimicrobial potential of bio-nanoparticles

Bionanomaterial	Organism	Origin	References
CuO-Cum	i. <i>Escherichia coli</i> ii. <i>Staphylococcus aureus</i> iii. <i>Shigella dysenteriae</i> iv. <i>Streptococcus pneumoniae</i>	<i>Curcuma longa</i>	
AgNPs	<i>Escherichia coli</i>	<i>Moringa oleifera</i> leaves	Asif et al. [8]
AuNPs	SARS-CoV-2	Antibody	Ghaemi et al. [42]
ZnO-MPs	<i>E. coli</i> <i>P. aeruginosa</i>	Micelles	Wang et al. [22]
TiO ₂ -NPs/MPs	i. <i>E. coli</i> (O157:H7) ii. <i>S. aureus</i> iii. <i>Pseudomonas fluorescens</i> iv. <i>Listeria monocytogenes</i>	Curcumin	
Al ₂ O ₃ -NPs	i. Microalgae ii. <i>Chlorella sp.</i> iii. <i>B. subtilis</i> iv. <i>E. coli</i> v. <i>Pseudomonas aurigenosa</i>	Muntingia Calabura	

CuO-Cum—Copper oxide-curcumin nanomaterials

AgNPs—Silver nanoparticles

AuNPs—Gold nanoparticles

CM-NPs—Cell membrane-camouflaged nanoparticles

ZnO-NPs/MPs—Zinc microparticles/nanoparticles

ZnO-NPs—Zinc nanoparticles

TiO₂-NPs/MPs—Titanium dioxide nanoparticles

Al₂O₃-NPs—Alumina bio-nanoparticles

cells selectively to deliver antigens directly. The wide range of antigenic variations that may be packed into nanoparticles (via encapsulation, chemical conjugation, or physical trapping), combined with an adequate antigenic demonstration, gives them a viable alternative to conventional methods in vaccine development [36, 37]. In the nanosystem, the virus antigen can either be encapsulated during vaccine production or conjugated to the nanocarriers surfaces for delivery alongside adjuvant [38, 39]. An adjuvant, which can boost immune responses, provide better protection against pathogens, and decrease the amount of antigens required for protective immunity, is essentially added to the vaccine formulation because many recombinant and synthetic antigens are not very immunogenic [30]. The primary benefit of vaccine nanocarriers is that they are on the same size scale as many biological systems, such as viruses, and are therefore more effective (including SARS-CoV-2).

Because of the COVID-19 pandemic, mRNA vaccines have gained prominence in the biotechnology and pharmaceutical sectors. The lipid nanoparticle delivery

systems development, which serve roles as adjuvants and in the vaccine reactogenicity as well as efficiently expressing the mRNA-encoded immunogen following intramuscular administration, is in part responsible for the current success of mRNA vaccines in SARS-CoV-2 clinical trials [40]. The nanotechnology industry can make a substantial contribution to the fight against coronavirus illness in 2019. The strategies that have been studied to inactivate coronavirus often involve the contact of the virus's outer layer with nanomaterials, resulting by a reduction in virus infection or complete eradication of the virus. When this occurs, a nanomaterial with antiviral and hydrophobic properties can interact with the surface of the virus [41]. Nanomaterials made of carbon play a substantial and active part in the fight against COVID-19. These nanomaterials, which have excellent antimicrobial, and antiviral properties in particular, are the best options against COVID-19 in biosensors for diagnosis, drug delivery, airborne virus filtration, antiviral coating, and facemasks. They also include carbon quantum dots, fullerene, grapheme, graphene oxide, and carbon nanotubes [42, 43]. One of the most important nanomaterials with successful biomedical applications are metal-based nanoparticles because they can act as efficient drug delivery systems and allow for the observation of stimuli-responsive properties and distinctive abilities of some kinds (for example, gold or magnetic nanoparticles) after in vivo organization to the human body utilizing noninvasive clinical imaging [44]. Despite extensive preclinical and clinical research on metal-based nanoparticles (NP) for the detection, diagnosis, and treatment of different infections, certain worries about the applications' safety in medicine are still being raised [45]. Due to their harmless qualities, functionalized metal-based nanoparticles with various types of biocompatible materials are being researched as a potential solution to this issue.

Synthesis and natural polymer-based nanoparticles with exceptional attributes, such as adjustable properties, practical synthetic procedures, and strong biocompatibility, make promising candidates for biomedical applications [46, 47]. In vivo delivery, viral delivery systems, and controlled viral vaccines release are only a few biological applications that make use of these sorts of nanomaterials with biosafety features [47, 48]. It is possible to provide viral vaccinations in the form of DNA, mRNA, or protein, all of which are quickly enzymatically destroyed once they enter the bloodstream [49–51]. However, several nanoparticles have been used for effective nucleic acid delivery; among these, lipid nanoparticles (LNPs) are a therapeutically advanced one that has received FDA approval [52]. The versatility of the platform and the quick manufacturing capabilities of mRNA-LNP vaccines are its main advantages. However, there are several options to consider when creating the ideal mRNA-LNP vaccination in terms of efficacy, stability, and toxicity [53] (Fig. 3).

5 Nano-based Drug Delivery Systems

Currently, various latest techniques have been emerged to ensure maximum availability of natural-based active compounds and therapeutic agents to its site of target against several diseases [54]. However, there is need to address various challenges to

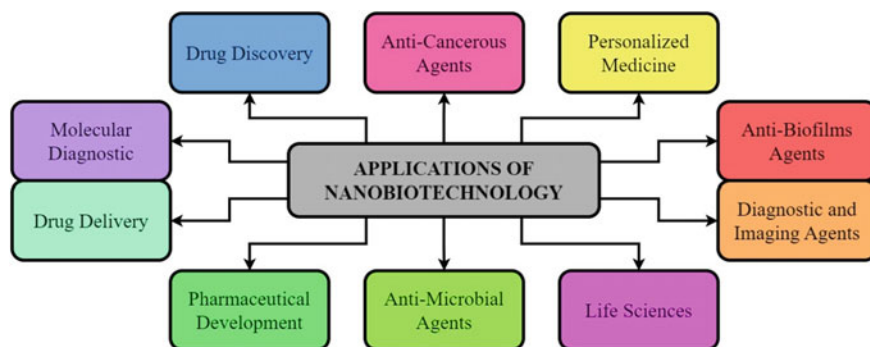


Fig. 3 Application of bio-nanoparticles in medicine

synthesize latest technology like nano-based drug delivery systems to facilitate effective delivery of medicine to its target location. With progression of drug designing and drug delivery system and development of nanomedicine, different traditional clinical diagnostic and therapeutic procedures have been explored to enhance the drug specificity. With the passage of time, different routes of drug administration have been discovered to ensure the delivery of drugs at specific location which decrease the toxicity and increase the bioavailability of drugs [55].

Nanomedicine has become most fascinating area of research and previously in last two decades a lot of research has led to the filling of 1500 patents with completion of several clinical trials. The selection of bionanomaterials for delivery of drug relies on the physical and chemical features of drugs. Recently, nanoparticles and natural bioactive compounds use in combination has become very captivating and growing rapidly. Especially, its role is very appealing and has several benefits when natural bioactive compounds used for treatment of several diseases like cancer. For example, in case of caffeine and curcumin autophagy whereas cinnamaldehyde, carvacrol, curcumin, and eugenol showed the antimicrobial properties [56]. The incorporating nanoparticles increase bioavailability, targeting, and controlled release of drug. For example, encapsulation of thymoquinone (*Nigella sativa* bioactive compound) with lipid nanocarrier increases its sixfold bioavailability in comparison to free thymoquinone.

6 Applications of Nanomaterial in Treatment of Cancer

Cancer is a chronic disease that accompanies many complications that indicate a dire need of development of anticancer treatment which can target individual and bulk tumor cells. In modern time's prevalence of this lethal disease is increasing tremendously, hence it is important to invent targeted drugs to control cancer disease. Nanoparticles have been used effectively in treating different cancers like lung cancer,

breast cancer, and prostate gland cancer. Nanoparticles have ability of attachment with metals, minerals that proves effective against the deadly cancerous tissue. Cancer is an alarming disease and recent treatment options proving ineffective due to toxicity effect [57].

NPs exert their action by absorbing light energy and converting into heat that further target and kill definite cancerous cells. Usually, chemotherapy is considered as the major therapy in treatment process of cancer however targeted NPs has been proven to be more effective in delivering chemotherapeutic drugs by increasing drug delivery and overcoming the adverse effects allied with orthodox chemotherapy. Cancer cells in liver carcinoma of human can be destroyed even via minute concentrations of TiO₂ NPs by involving the mechanism of by oxidative damage of DNA damage and apoptosis [58].

Gold nanoparticles are getting the prime intention for their use in treatment of cancer as they have many properties. They possess property of adhering with many proteins and drugs. Gold nanoparticles possess strong potential to target cancer cells through over expressions of receptors on the cell surface. Drugs loaded with NPs have greater tendency of penetration that also surge the therapeutic concentrations of chemotherapeutic agents in brain cancer [59].

Along with treatment NPs are equally effective in diagnostics of tumor cells [60]. AgNPs were synthesized from leaves of *T. officinale* and aqueous extract of orange peel, which found to therapeutically active against liver cancer (HepG2) and rat glioma tumor C6 cells, respectively [57, 61].

Many side effects are associated with anticancer drugs like patients taking anastrozole, usually use for breast cancer, mostly experience osteoporosis and bone fracture, and these side effects can be prevented by giving this drug in conjugation with SeNPs that exhibit the strong potential of NPS synthesized through green method in cancer treatment [62]. There is a strong need of developing the drugs that are hydrophilic in nature with minimum adverse effects and development of a carrier drug delivery system to deliver higher concentrations of anticancer drugs at target site. However, with such advancement in research still limitations are found in treating cancer. To overwhelm these hurdles, effective target drug delivery systems may be appropriate solution [63].

Ginsenoside possesses many therapeutic properties; desolvation method was used to prepare BSA-CK nanoparticles by entrapping ginsenoside with bovine serum albumin (BSA). The resultant synthesized BSA-CK nanoparticles (NPs) showed higher hydrophilicity and stability as well as anti-inflammatory effects. Cytotoxic effects of the BSA-CK NPs and standard CK were also evaluated against different cell lines HaCaT, skin cell line, A549, lung cancer cell line, HepG₂, liver carcinoma cell line and the HT29, colon cancer cell line where the BSA-CK NPs presented significant therapeutic activity in vitro. It can be considered as a potential drug carrier in cancer treatment [64]. Multidrug resistance phenomenon is a major obstacle in chemotherapy. Currently, identified zinc oxide nanoparticles inhibit proliferation of cancer and able to target many types of cancers. Green synthesized doxorubicin loaded zinc oxide nanoparticles regulate Bax and Bcl-2 expression in breast and colon carcinoma [63].

Flavone base natural anticancer Chrysin (ChR) was synthesized from AgNPs and AuNPs in a greener route without addition of toxic excipients. Synthesized NPs from ChR had strong potential of reducing Ag^+ and Au^{3+} into their nano-forms that showed size and shape uniformity, along with improved surface chemistry. Significant cytotoxicity was reported with green synthesized nanoparticles than ChR alone against two different breast carcinoma cell lines (MDA-MB-231 and MDA-MB-468) [65]. Exopolysaccharides obtained from fish-intestine-associated bacterial strain reported to have remarkable ability of reducing materials of iron base and converting them to iron oxide nanoparticles (FeONPs), hence increasing their cytotoxic potential in human epidermoid carcinoma cells [66]. Potential applications of green nanomaterials include magnetically responsive drug delivery in cancer therapy, bio-imaging, and photo-thermal therapy [67].

In spite of many applications, there are many challenges that need to be overcome. Many amino acids, polysaccharides, flavonoids, alkaloids, vitamins that are used in the metal NPs' medium method, their residues remain stick to surface of metal, even after washing and purification. Similarly, in microbial synthesis, there lot of microorganisms involving saprophytes and even pathogenic microbes such as *E. coli* are utilized as a bio-source for preparation of metal NPs have various health hazards. *Aspergillus niger*, *Aspergillus flavus*, and *Fusarium solani* have also been used in biosynthesis of metal NPs [68, 69]. Another drawback is the protein corona effect, when the nanoparticle enters the biological system, adsorption of proteins on the colloidal NPs' surface occurs which can alter biological fate of NPs. Green nanomaterials could emerge as trending agents in near future for cancer therapeutics and diagnostics [70].

7 Role of Nanoparticles in Food Industry

World population expansion is occurring abruptly in last few decades which lead to revolutionized in the field of food industry. Recently, bio-nanotechnology has arisen as an emerging technology in the field of food industry and role of nanoparticles in food industry has been demanded globally. The role of bio-nanoparticles has become appealing due to non-toxic nature and stability in high temperature and pressure. The use of nanoparticle contributes to maintain the shelf life, quality, and freshness of food especially incorporation during packaging [71]. Nanoparticles in food industry work into food nanosensing contributed in food processing and food packaging to prevent from microbial growth and food nanostructured improved food quality and safety by preventing from environment contamination. Various kind of nanoparticles like Ag, TiO_2 , ZnO, magnesium oxide (MgO) etc., are used in food industry to stop unwanted growth of bacteria [72, 73] (Fig. 4).

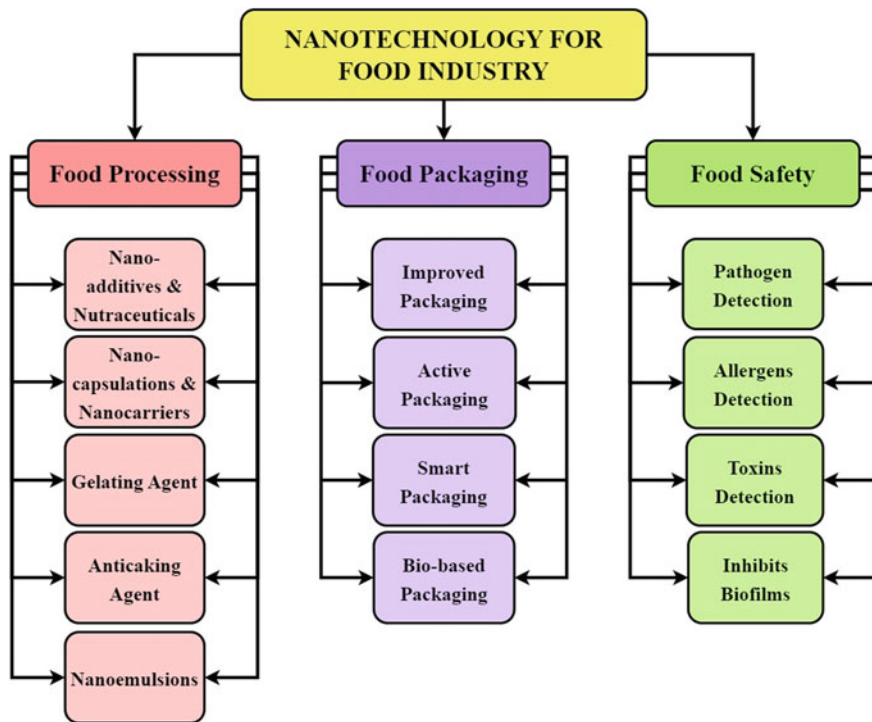


Fig. 4 Role of nanoparticles in food industry

8 Conclusion

Due to continuous innovative research and abundant use, biotechnology has emerged as a revolutionary field over the last decade and the rise in nanotechnology has increased its popularity in science and technology. Recently, due to low cost, short production time and safety makes biological products like plants and microorganisms an appealing platform for nanoparticle synthesis. The great biocompatibility and unique role of bionanomaterials make them ideal candidate in the field of medicine like diagnosis, drug delivery systems, anti-cancerous, and antimicrobial potential. The cooperation of dissimilar disciplines is required to develop novel biomaterial-based approaches, and this innovation may lead to the invention of something new in future with remarkable potential for the prevention and treatment incurable diseases. It can be inferred on the base of research conducted in last decade that in future, nano-biotechnology will become an indispensable phase of our daily life. Lastly, although nanoparticles have very important therapeutic applications in medicine, but toxicity studies acquire a greater understanding of this captivating and capable technology [74]. It would be fair to say that in the future nano-biotechnology will

play an excellent and unique role in the treatment of human diseases and the study of human physiology.

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Composite Nanomaterials and Their Development



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Abstract Composite nanomaterials, consisting of two or more different materials, have gained significant attention in recent years due to their enhanced physical, chemical, and mechanical properties. This chapter provides an overview of different types of nanocomposites and their synthesis and potential uses. We begin by discussing the properties and synthesis methods of these materials, including chemical synthesis, physical mixing, and in situ growth. The chapter also explores the various applications of composite nanomaterials, including in catalysis, energy storage, sensors, and environmental remediation. Furthermore, we highlight the challenges associated with their large-scale production and commercialization, such as scalability, reproducibility, and cost-effectiveness. Finally, the chapter concludes with a summary of the current state of research and suggests possible directions for future work in this exciting field.

Keywords Nanocomposites · Polymer-based nanocomposites · Metal-based nanocomposites · Coating applications · Ceramic-based nanocomposites

1 Introduction

Composite nanomaterials are a class of materials that consist of two or more distinct materials combined at the nanoscale [1]. The combination of different materials at the nanoscale leads to unique properties that are not found in the individual components. Composite nanomaterials can be classified into several categories based

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on their structure, composition, and properties. One of the most common types of composite nanomaterials is the polymer-based nanocomposites. In these materials, nanoparticles such as clay or carbon nanotubes are dispersed in a polymer matrix to enhance the mechanical, thermal, or electrical properties of the polymer [2]. Another type of composite nanomaterial is the metal oxide-based nanocomposites, where metal oxides such as titanium dioxide or zinc oxide are combined with other materials to create novel properties such as photocatalytic activity or high surface area [3]. Carbon-based nanomaterials such as carbon nanotubes and graphene are also commonly used in composite nanomaterials. These materials have high strength, thermal, and electrical conductivity and can be used to reinforce other materials or to create new properties such as increased conductivity in polymers. Composite nanomaterials have a wide range of applications in various fields, including energy storage, catalysis, biomedical engineering, and environmental remediation. For example, composite nanomaterials can be used to create lightweight and durable materials for use in aerospace and automotive applications, or to develop new catalysts for more efficient and sustainable chemical reactions [4]. In biomedical engineering, composite nanomaterials can be used to create drug delivery systems with improved efficacy and reduced toxicity. Overall, composite nanomaterials represent a rapidly evolving field of research with immense potential for new materials and applications. Composite nanomaterials are materials composed of two or more distinct materials at the nanoscale, where at least one of the components has a dimension less than 100 nm. These materials can be made by combining nanoparticles or nanofibers of different materials to create a material with unique properties that are different from the individual components [5].

The properties of composite nanomaterials can be tailored to meet specific application requirements by adjusting the composition, size, and shape of the constituent materials. The combination of different materials can lead to novel properties such as increased strength, flexibility, and electrical conductivity, and improved thermal stability, and optical properties. Composite nanomaterials have a wide range of applications in various fields, including electronics, energy, health care, aerospace, and construction. For example, composite nanomaterials can be used as high strength and lightweight materials in the aerospace industry, as highly conductive materials in the electronics industry, and as drug delivery vehicles in the healthcare industry. The development of composite nanomaterials requires a multidisciplinary approach that combines knowledge and techniques from chemistry, physics, materials science, and engineering [6]. Researchers need to understand the properties of the individual components, the interactions between them, and the mechanisms that govern their behavior at the nanoscale. Overall, composite nanomaterials have the potential to revolutionize various fields by enabling the development of new and innovative materials with tailored properties. However, there are also challenges associated with the production, characterization, and application of these materials, which require further research and development [7]. Nanocomposites can be classified as polymer-based or non-polymer-based nanocomposites as shown in Fig. 1.

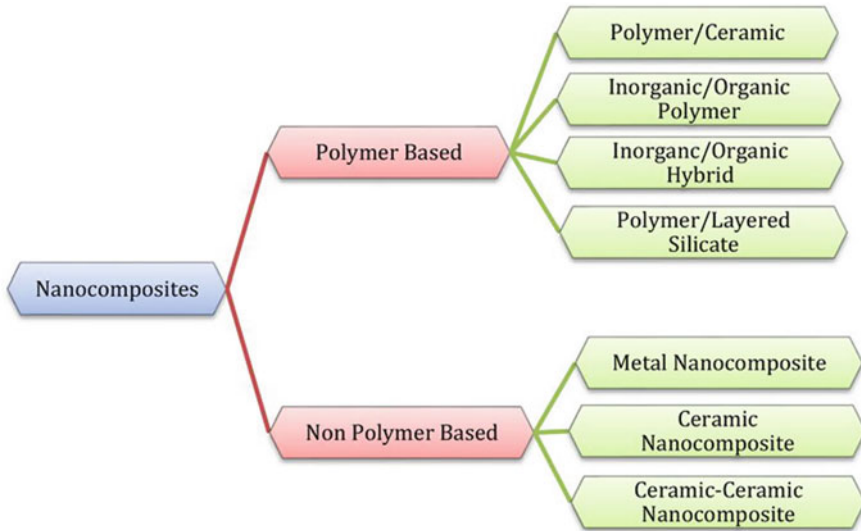


Fig. 1 Classification of nanocomposites into different categories [8]

2 Polymer Nanocomposites

Polymer-based nanocomposites are a class of materials that have received significant attention over the past few decades due to their unique properties and potential applications. These materials are composed of a polymer matrix, which can be a thermoplastic or a thermoset polymer and nanoparticles that are typically less than 100 nm in size. The nanoparticles used in polymer-based nanocomposites can be inorganic materials such as clays, silica, metal oxides, or carbon-based materials such as carbon nanotubes, graphene, or fullerenes [9]. These nanoparticles have unique physical and chemical properties that can be exploited to enhance the properties of the polymer matrix. The preparation of polymer-based nanocomposites involves the dispersion of the nanoparticles within the polymer matrix. This can be achieved using various methods such as melt mixing, solution mixing, and in situ polymerization. In melt mixing, the nanoparticles and polymer matrix are melted together and mixed to disperse the nanoparticles uniformly. In solution mixing, the nanoparticles are dispersed in a solvent, which is then mixed with the polymer matrix. In in situ polymerization, the polymer matrix is formed in the presence of the nanoparticles [10].

The addition of nanoparticles to the polymer matrix can improve the mechanical, thermal, and electrical properties of the resulting nanocomposite. For example, the addition of clay nanoparticles to a polymer matrix can increase its stiffness and strength, while the addition of carbon nanotubes can increase its electrical conductivity. The improvement in properties is due to several factors, including the high surface area of nanoparticles, the large aspect ratio of some nanoparticles, and the

strong interfacial interactions between the nanoparticles and the polymer matrix [12]. Polymer-based nanocomposites have a wide range of applications in various industries. In the aerospace industry, they can be used to produce lightweight and strong materials for airplane components. In the automotive industry, they can be used as high-performance tires, brake pads, and engine parts. In the packaging industry, they can be used as gas barrier films and coatings to improve the shelf life of food products. In the biomedical industry, they can be used as scaffolds for tissue engineering and drug delivery systems [13].

However, there are also some challenges associated with the production and use of polymer-based nanocomposites. One of the major challenges is achieving a uniform dispersion of nanoparticles within the polymer matrix as shown in Fig 2. Poor dispersion can lead to uneven properties and reduced performance. Another challenge is the potential toxicity of some nanoparticles, which can be harmful to human health and the environment. Careful consideration must be given to the selection and handling of nanoparticles to minimize their impact on health and the environment [14]. Finally, polymer-based nanocomposites are a promising class of materials that offer unique properties and potential applications in various industries. The development of efficient and scalable methods for the preparation of these materials, along with careful consideration of their potential impact on health and the environment, will enable their successful commercialization and widespread use in the future.

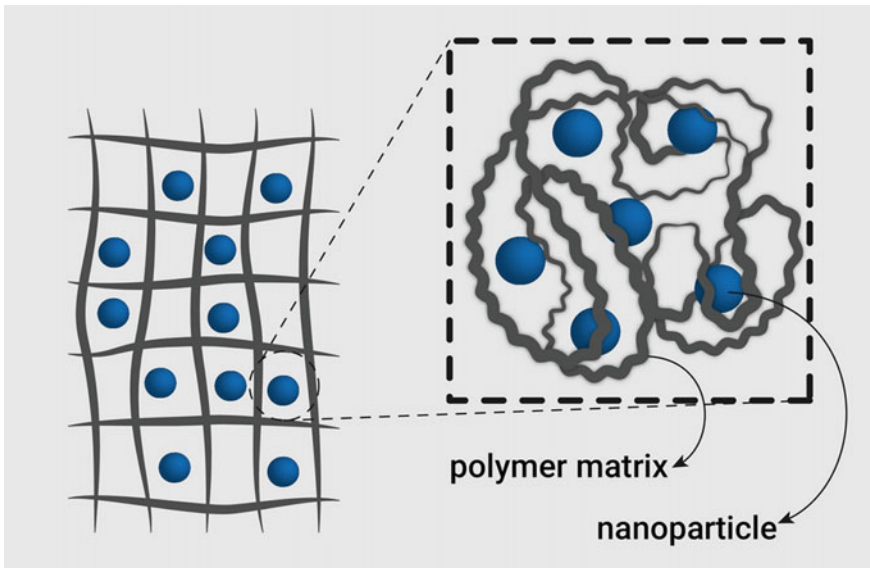


Fig. 2 Polymer nanocomposite consists of a polymer matrix (black lines) and any other substance as reinforcement material or filler (blue symbols) [11]

3 Non-polymer Nanocomposites

Bimetallic nanoparticles have been extensively studied in the form of either alloy or core–shell structures, as they exhibit improved catalytic properties and advancements in optical properties related to individual and differentiated metals [15]. These nanoparticles possess various unique characteristics, including superplasticity, lower melting points, increased strength and hardness, improved magnetic properties, increased electrical resistivity, and more. Non-polymer-based nanocomposites are another type of material that can be classified into metal/metal nanocomposites, such as Pt-Ru nanocomposites.

On the other hand, ceramic-based nanocomposites are defined as composites with more than one solid phase, where at least one phase has dimensions in the nanoscale range (<50–100 nm). These composites exhibit combined magnetic, chemical, optical, and mechanical properties and are exemplified by hydroxyapatite/titania nanocomposites. These types of nanocomposites are characterized by better toughness, increased ductility, increased strength, and hardness [16–18]. Figure 3 shows the oxide and non-oxide sol–gel processes for synthesis of polysiloxane and polysilylcarbodiimides, respectively.

4 Ceramic–Ceramic-Based Nanocomposites

The non-polymer-based nanocomposites can be also classified as ceramic/ceramic nanocomposites which can be used in the area of artificial joint implants for fracture failures and it could promptly reduce the cost of surgery and would extend the mobility of the patient. The life span would increase by 30 years, if the use of zirconia-toughened alumina nanocomposite implants is used effectively. The other example of ceramic/ceramic nanocomposites is calcium sulfate-biomimetic apatite nanocomposites [20].

The most promising prospects of both metal-based nanocomposites and ceramic-based nanocomposites are in the application of areas in dentistry in which the non-polymer-based nanocomposites or the inorganic materials that is metal or ceramics such as calcium phosphate, hydroxyapatite, and bioactive glass nanoparticles are very advantageous in alveolar bone regeneration and enamel substitution [21].

The development of composite nanomaterials involves several steps, including the selection of materials, synthesis, and characterization of the composite material. Here is an overview of the typical process:

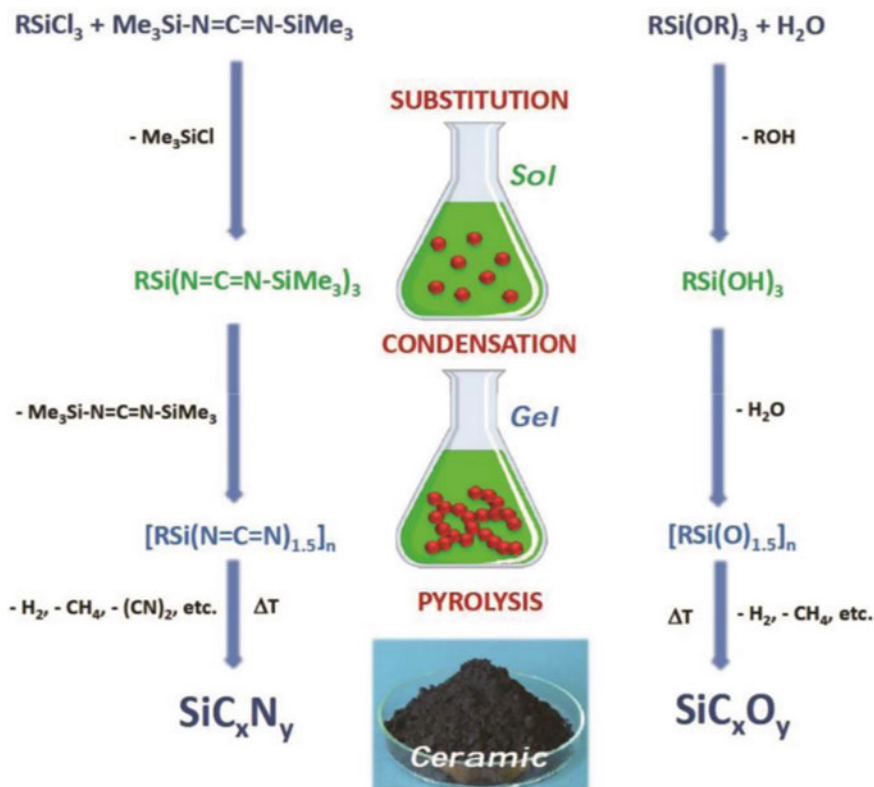


Fig. 3 Comparison between the non-oxide sol-gel process for the synthesis of polysilylcarbodiimides and the oxide sol-gel process for the synthesis of polysiloxane [19]

5 Material Selection and Development

The first step in developing composite nanomaterials is to select the appropriate materials that will be used as the constituents of the composite material. The properties of the materials should complement each other and result in desirable properties for the composite material.

5.1 Synthesis

There are various methods for synthesizing composite nanomaterials, including physical mixing, chemical deposition, and in situ growth. The synthesis method chosen will depend on the materials being used and the desired properties of the composite material. For example, physical mixing can be used to create a composite material

by mixing two different types of nanoparticles together [22]. On the other hand, chemical deposition can be used to grow one material onto the surface of another material to create a composite material.

5.2 Characterization

Once the composite nanomaterial has been synthesized, it needs to be characterized to understand its properties. Common characterization techniques for composite nanomaterials include electron microscopy, X-ray diffraction, and spectroscopy. These techniques can provide information about the size, morphology, and crystal structure of the composite material [23].

5.3 Property Optimization

After the composite material has been synthesized and characterized, it may be necessary to optimize its properties for a specific application. This can be achieved by modifying the composition or structure of the composite material.

5.4 Application Development

Finally, the composite nanomaterial can be used in various applications depending on its properties. For example, a composite nanomaterial with high electrical conductivity could be used in electronics, while a composite nanomaterial with high strength and stiffness could be used in aerospace.

Overall, the development of composite nanomaterials requires a multidisciplinary approach that combines knowledge and techniques from chemistry, physics, materials science, and engineering. The process can be time-consuming and complex, but the potential benefits of composite nanomaterials make it an area of active research and development. There are several methods for synthesizing composite nanomaterials, each with its advantages and limitations [24]. Here are some of the common methods used for synthesizing composite nanomaterials:

5.5 Chemical Co-Precipitation

In this method, the nanoparticles are synthesized in situ by co-precipitation from a solution containing precursors of the different materials. The resulting nanoparticles are then mixed together to form a composite material. This method can result in a

homogenous distribution of nanoparticles, but it may also result in the formation of unwanted phases [25].

5.6 Electrospinning

This method is used to create nanofibers by electrostatically spinning a solution of polymers and nanoparticles. The resulting nanofibers can be collected and used as a composite material. This method can create a homogenous distribution of nanoparticles, and the resulting nanofibers can be used in various applications, including filtration and tissue engineering.

5.7 Sol-gel Method

This method involves the formation of a gel from a solution of precursors that are then dried to create a solid material. The addition of nanoparticles to the precursor solution can result in a composite material. This method can be used to create complex shapes and structures, and it can result in a homogenous distribution of nanoparticles.

5.8 Chemical Vapor Deposition

In this method, one material is deposited onto the surface of another material through chemical reactions in a vapor phase. This method can create a homogenous distribution of nanoparticles, and it can be used to create thin films and coatings [26].

Overall, the synthesis of composite nanomaterials requires careful consideration of the properties of the individual materials, the desired properties of the composite material, and the method used to synthesize the material. The resulting composite material can have unique and tailored properties that can be used in various applications. The synthesis of composite nanomaterials involves combining two or more different types of nanomaterials to create a material with unique properties. There are some more methods for synthesizing composite nanomaterials, including physical mixing, in situ growth, and surface modification. Here is an overview of these methods.

5.9 Physical Mixing

Physical mixing involves the simple mixing of two or more types of nanomaterials to create a composite. The resulting composite will have a heterogeneous structure, with the individual components dispersed throughout the material. Physical mixing is a relatively simple and low-cost method, but it can be challenging to control the distribution and interaction of the different components within the composite [27].

5.10 In Situ Growth

In situ growth involves growing one type of nanomaterial onto the surface of another type of nanomaterial. This can be achieved through a variety of methods, such as chemical vapor deposition, electrochemical deposition, and sol-gel techniques. In situ growth can produce a more homogeneous composite structure, with the two components intimately intertwined. However, it can be challenging to control the growth process, and the resulting composite may have limited compositional flexibility.

5.11 Surface Modification

Surface modification involves modifying the surface of one type of nanomaterial to enable the attachment of another type of nanomaterial. For example, the surface of a metal nanoparticle can be modified to enable the attachment of a semiconductor nanoparticle. Surface modification can provide precise control over the composition and structure of the resulting composite, but it can be challenging to achieve a high degree of control over the attachment process [28].

Overall, the choice of synthesis method will depend on the specific requirements of the composite nanomaterial, such as composition, structure, and properties. The development of composite nanomaterials requires a multidisciplinary approach that combines knowledge and techniques from chemistry, physics, materials science, and engineering.

6 Potential Uses of Nanocomposites

Nanocomposites have been gaining momentum in recent years, and their applications are growing rapidly, according to research [8]. It is expected that within the next 10 years, the worldwide production of nanocomposites will surpass 600,000 tons. This growth is expected to occur in various regions and can be attributed to

their numerous benefits and applications in different fields. Specifically, nanocomposites are expected to see growth in six key areas, including superior strength fibers and films, UV protection gels, drug delivery systems, new fire retardant materials, anti-corrosion barrier coatings, and lubricant and stretch paints. These applications demonstrate the versatility and potential of nanocomposites in various industries, and their increasing production and use is a testament to their potential to enhance performance and improve products across different sectors.

7 Conclusions

The field of nanocomposites has become increasingly important in the development of new materials for advanced applications, thanks to the rapid growth of nanotechnology in recent years. Nanocomposites are a versatile class of materials that offer a high level of integrated association, making them suitable to fulfill the growing needs of multifunctional materials. The creation of macroscopic engineered materials obtained through nanolevel structures is a multidisciplinary field that combines scientific knowledge with technological aspects. These materials are well-suited to meet the emerging demands arising from scientific and technological advances. The outstanding potential of nanocomposites can be seen in the massive investments made by many companies and governments throughout the world. As a result, nanocomposites are expected to have a significant impact on the world economy and business, benefiting industrial sectors like electronics and electrical industry, chemical industry, transportation sectors, healthcare organizations, and above all, the protection of the environment. Nanoparticles can be treated with green agents to modify their surface properties for specific applications, resulting in improved microstructural properties such as exfoliation, compatibility, and thermal stability. The optimization of polymerization conditions during the preparation of nanocomposites is essential to maximize output while minimizing cost. The effect of nanocomposite composition on developed microstructures during preparation activities should also be studied in detail. Nanocomposites can be prepared using materials like polymer blends along with melt blending technologies, allowing the advantages of the individual materials' properties and their coaction to be developed. Flexible batteries can be made using nanocomposites.

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Advancements and Challenges in Synthesizing Colloidal Semiconductor Nanocrystals by Hot-Injection Method



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Abstract Synthesis of semiconductor nanocrystals through solution-based approaches has turned out huge interest among researchers. Out of other methods, preparation of colloidal semiconductor nanocrystals through hot-injection method is intensively investigated owing to its versatility. Importantly, the structure, shape and size of the nanocrystals can be precisely tuned with respect to the precursors and temperature. This influence a lot on the composition, physical, and chemical properties of the synthesized nanocrystals. Using hot-injection synthesis approach, the nanocrystals are prepared either in aqueous medium or in organic solvents. The acidic or basic nature of surface metal atoms integrate the ligand interaction and hence stability of the nanocrystals in solution is governed. Furthermore, with respect to the reaction time intervals and type of precursors, the absorption and emission spectra of the nanocrystals can be tuned. Diverse range of inorganic nanocrystals such as metallic nanostructures (ex: Ag, Au, Pt, Pd) metal-chalcogenide semiconductor nanocrystals (ex: CdS, ZnS, CdTe, CdSe), metal-oxide nanocrystals (ex: TiO₂, CeO₂), metal phosphides, metal nitrides and metal halide perovskite nanocrystals (RNH₃PbX₃ and CsPbX₃, where R = alkyl group and X = Cl, Br and I) are prepared using this method and their structural, optical and morphological properties are evaluated. Interesting features such as polytypism, different phase formation, surface charge and ligand metal interaction are dealt with respect to the reaction conditions. In this view, this chapter discuss about the advancements of hot-injection approach in synthesizing different group semiconductor nanocrystals, challenges and it's future perspectives.

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1 Introduction

Inorganic semiconductor nanocrystals (NCs) or quantum dots (QDs) are intensively studied in the last four decades due to their exciting structural optical properties when they are reduced to smaller size [1–5]. Hence, synthesizing semiconductor NCs using appropriate methodologies is also governed with different aspects. Out of others, solution-phase synthesis of inorganic semiconductor NCs has reached new dimension in the recent years [6–9]. Although several ways are possible to carry out the synthesis in solution, it is important to know how the NCs are functionally modified. Through modification on the NCs surface using different organic molecules and inorganic compounds, it is possible to apply the NCs for several kind of applications. Depending on the functionalization, the NCs are fabricated as thin films to harvest photons from ultraviolet (UV) to near-infrared (NIR) region for the optoelectronic applications. In order to efficiently manage the carrier transport, it is essential to fabricate the NC films as well-ordered assembly with very good inter-connectivity. When we fabricate the NC films, several factors are affecting the assembly such as method of deposition, solvent, concentration of ligands, nature of ligand molecules and effect of annealing. In order to fabricate high quality NC films, it is essential to concentrate on the synthesis method which result in highly crystalline NCs with narrow size distribution. In this point of view, synthesizing semiconductor NCs in solution is interested because of the easy approach and possibilities for the large scale production. The experimental space, equipment, time and other required utilities for the solution-based synthesis are quite simple and convenient. Methods such as hydrothermal [10], sol–gel [11], solvothermal [12], co-precipitation [13], sonochemical [14] and colloidal approach [15] are generally used to prepare the semiconductor nanocrystalline materials in solution. Several kind of precursors, from ionic to covalent compounds are investigated in all these methods to prepare the nanocrystalline materials with specific functionality. Despite the preparation method, control of growth, morphology, size, and functionality of the NCs for different applications are the essential parameters. In this view, colloidal hot-injection method has emerged as one of the successful approaches to synthesis of narrow size, single crystalline NCs [16–18]. From moderate temperature (~ 100 °C) to extremely higher temperature (up to ~ 300 °C), this method is extensively used to prepare inorganic semiconductor NCs with different structure, morphology and functionality. Importantly, UV harvesting metal-oxide NCs (ex: TiO_2 , ZnO), visible light sensitive metal-chalcogenide NCs (ex: CdTe , CdSe), near-infrared (NIR) harvesting QDs (NIR QDs) (ex: PbS , PbSe) could be prepared using this method. Also, the prepared NCs in this method could be deposited on the conducting substrates through methods such as spin-coating, dip-coating, spray-deposition, layer-by-layer deposition (LBL) and doctor blade method. Different group inorganic compounds such as metallic nanostructures [19],

metal-oxides [20], metal-chalcogenide nanostructures [21], metal halide perovskite NCs [22] and their alloyed/core–shell nanostructures are prepared by colloidal hot-injection method. Also, fabrication of perovskite, metal-chalcogenide nanostructures with polymer is also achieved through hot-injection method [23, 24]. Moreover, different sectors such as bio, magnetic, optoelectronic and thermoelectric are enriched with the nanomaterials developed through hot-injection method. In order to stabilize the prepared NCs, organic molecules called ‘ligands (or) organic linkers (or) capping agents’ are used to passivate (or) adhere the NCs surface. These ligands are typically long, short-chain and having different polarity in order to interact with the NC surface [25–27]. The interaction between surface atoms and ligands and also the solvent atmosphere are the most important parameters for the stability and other physical, chemical properties of the dispersed NCs. Besides, purification of the prepared NCs is an important stage to achieve excess ligand-free NCs and their assembly. It is possible to prepare strongly quantum-confined semiconductor NCs [i.e. QDs] through hot-injection method. The influence of physical parameters, ligands, polarity of the solvents used for the purification and surface modification on the NCs lattice is quite sensitive on the final assembly of the prepared NCs. Other advantages such as upscaling nanomaterials, fabrication of core–shell assembly, phase transfer from aqueous to organic medium, wavelength tuning by external doping are possible in hot-injection method. Thus, a very good controllability with reproducibility can be achieved through hot-injection synthesis method and this could be used for several kind of applications. Here, the gradual addition of the precursors at high (or) low temperature concisely arrange the atoms and with respect to the synthetic conditions, the properties of the NCs are tuned. From the spherical shaped NCs, different morphologies such as nanorods, nanowires, nanoplatelets, nanosheets, cuboctahedra and hierarchical shaped nanostructures can be achieved through this method. Importantly, the size of all these morphologies could be precisely managed through controlling reaction parameters. Thus, colloidal hot-injection method has become an indispensable synthetic approach in the nanochemistry research area. In this regard, this chapter work discussing about the achievements and challenges in the synthesis of semiconductor nanocrystals through colloidal hot-injection method. The fundamental principle, experimental scheme and reactor assembly of this method are analysed. Furthermore, the developments in colloiddally synthesized different class metal chalcogenide nanostructures, metal-oxide nanocrystals and recently developed all-inorganic perovskite nanostructures are discussed in detail.

2 Hot-Injection Method—Basic Principle and Experimental Assembly

The synthetic revolution in II-IV, I-III-VI₂ and III-V group semiconductor NCs and newly emerged metal halide perovskite NCs is excellently achieved through hot-injection method and lot of scientific innovations are demonstrated accordingly [28–30]. In hot-injection method, the precursors in solvent(s) are rapidly injected into the another precursor in hot-coordinating solvents. The nucleation burst takes place once the precursors are injected into the solution and depending on the concentration of the precursors, the growth kinetics differs. The stabilization of NCs is achieved either through electrostatic or by steric interaction. In this method, the growth of the NCs is explained through La-Mer plot which describes the NCs growth after nucleation [31, 32] (Fig. 1). According to this model, upon injection of the precursor, the nucleation burst generate atoms in solution and this immediately tend to nucleation. Nucleation at this stage lead to formation of ultra-small size NCs which further guide towards NCs growth. At this stage, growth of the NCs begins through a diffusion process. Here, the NCs attain a critical size called ‘magic size’ in which the precisely arranged smaller number of atoms of NCs show superior stability [33–35]. The formation mechanism of magic size clusters is described through several possible concepts namely, (a) fusion (b) template-assisted growth and (c) layer-by-layer assembly [33]. The consequent growth of NCs takes place through Ostwald ripening, in which the exploitation of smaller NCs leads to bigger size during prolonged reaction period [36, 37]. To achieve the monodisperse from the polydispersity, NCs undergo another process, called digestive ripening [38]. Hence, the NCs growth is achieved through three stages namely, (i) supersaturation, (ii) nucleation and (iii) growth through diffusion. Teunis et al. have proposed that together with these three steps, surface ligation, i.e. adsorption of ligand molecules on the NCs surface also the fourth step in the growth [33]. A recent study on the growth of metal halide perovskite NCs also confirms this surface ligation stage [39]. Although La-Mer model fit for the most of the semiconductor NCs, highly ionic semiconductor NCs, for example metal halide perovskite NCs are seems to be an exceptional. Because of their extreme ionicity and rapid chemical reaction, the formation mechanism of the cesium lead halide perovskite NCs, i.e. CsPbX₃ NCs (where X = Cl, Br and I) and hybrid lead halide perovskite NCs, i.e. CH₃NH₃PbX₃ NCs (where X = Cl, Br and I) is not much explored. The next important step after the preparation of NCs is purification. Because most of the NCs are synthesized in the presence of highly unsaturated fatty acids and higher boiling point solvents, the excess ligands and solvents and the by-products formed in the reaction should be removed. The selection of solvent for the purification is on the basis of the interaction of surface ligands. Solvents with different kind of polarity are used for the precipitation of the prepared NCs [40, 41]. In addition, with polarity, the solvent also influences on the final assembly and optical properties of the NCs. For instance, if the excess surface ligands are removed by the purifying solvent, the surface may lose some of the ligands. In such case, the optical properties, in particular the photoluminescent (PL)

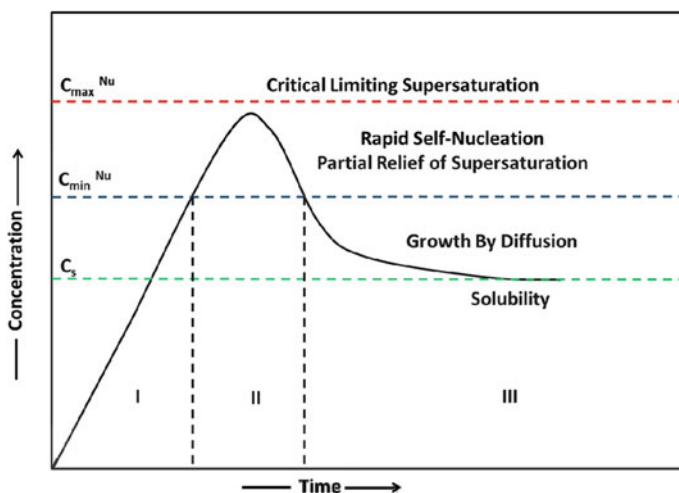


Fig. 1 La-Mer model describing the growth of NCs. Reprinted with permission from Ref. [31] Copyright 1950@American Chemical Society

properties [PL intensity, photoluminescent quantum yield (PLQY)] of the prepared NCs are severely affected and luminescence is quenched [42, 43]. The quenching in PL properties can be recovered by surface treatment process or by forming a shell. When a bad solvent is added into the nanoparticles solution, the precipitation takes place and the NCs are separated out through centrifugation. With respect to the type and chain length of the purifying solvent, the resultant NCs may have influence on the device performance.

The preliminary work on colloidal hot-injection method was reported during the year 1993 by Brus and Bawendi for the preparation of cadmium chalcogenide NCs (CdX , where $X = \text{S}, \text{Se}$ and Te) using organometallic solvents [44]. Strongly coordinating trioctyl phosphine (TOP) and trioctyl phosphine oxide (TOPO) were used in this experiment to achieve smaller size nanocrystallites with narrow size distribution. This report laid a foundation for the further developments in synthesizing different class of semiconductor NCs using hot-injection method. The experimental arrangement of synthesizing NCs using hot-injection approach is typically a Schlenk line setup, which consists of a three-neck flask, a condenser, a nitrogen cylinder and a vacuum pump system. At first, the flask is degassed completely and circulated with nitrogen (N_2) or argon (Ar) for an inert atmosphere. This help to avoid oxidation with the air-sensitive precursors and to carry out the reaction without any issues. Then, the precursor in hot-coordinating solvent(s) is injected rapidly into the solvent(s) which consists of anionic (or) cationic precursor to form NCs in solution. In general, a transformation of colour is often observed as an indication of NCs formation. Temperature play key role in decomposing the precursors at the critical point, which also control the growth and shape of the resultant NCs in solution. For the solvents, amines with different chain length are mostly exploited for

the preparation of semiconductor NCs and they critically influence on the optical properties [45]. Although phosphine group compounds such as TOPO and TOP were dominating initially, phosphine-free solvents and ligands are currently used to prepare numerous type of nanocrystalline materials. Specifically, different class of NCs are prepared through oleylamine (OAm), octadecylamine (ODAm), and hexadecylamine (HDAm) [28]. Since amines are having high boiling point, their ability to form highly crystalline NCs through decomposition is much interested. Furthermore, they also influence on the NCs surface through their binding ability which critically influence on the morphological properties. Similarly, oleic acid (OA), a long-chain aliphatic fatty acid is the widely used carboxylic acid compound along with amines in hot-injection method [46]. Along with OA and OAm, an additional non-coordinating solvent, 1-octadecene (1-ODE) is always preferred. 1-ODE is a highly stable, low-cost solvent and with low-hazardness, this solvent also help to dissolve most of the precursors at high temperature. However, it is found that 1-ODE could polymerize at high temperature and form poly(1-octadecene) which cannot be removed through typical purification methods [47]. The growth of NCs is generally monitored through spectral position of the absorption and emission spectra. For this, aliquots of the sample are taken at different time intervals and analysed. Recently, there is a significant development in the analysis of NCs growth in solution. For example, it is possible to monitor the growth of NCs through in situ diffraction measurements. For example, the experimental arrangement for the in situ monitoring of growth of the $\text{Cu}_2\text{ZnSnS}_4$ NCs is given in Fig. 2 [48]. In the case of aqueous synthesis, short-chain thiols such as thioglycolic acid (TGA) and mercaptopropionic acid (MPA), quaternary ammonium salts such as hexadecyl ammonium bromide (HTAB) and cetyltrimethyl ammonium bromide (CTAB) are widely used [49, 50]. These ligands not only stabilize the NCs, but also influence on the NCs assembly and charge transport properties. Although most of the preparation procedures are dealing halide and oxide kind of precursors, there are some experimental evidences using single-source precursors [51]. The decomposition of these precursors at high temperature leads to the formation of ultra-small NCs, which further allow the growth. Thus, careful selection in precursors and ligands for a reaction could accelerate to achieve high quality NCs with excellent optical properties. Based on the discussed growth mechanism, several group nanocrystalline semiconductors are prepared using hot-injection synthetic strategy. Specifically, luminescent nanomaterials belong to cadmium chalcogenides (ex: CdSe, CdTe), cadmium-free chalcogenides (ex: InP, ZnS), cesium lead halide perovskite NCs (CsPbX_3 , X = Cl, Br, I), hybrid lead halide perovskite NCs ($\text{R}_3\text{NH}_3\text{PbX}_3$, R = alkyl cation, X = Cl, Br, I) are synthesized using hot-injection method. The optical properties could be precisely tuned by optimizing the reaction conditions and we can synthesis NCs with emission from ultraviolet (UV) to near-infrared (NIR) region. This indeed helpful to achieve luminescent NCs for light emitting diodes (LEDs) and solar window applications.

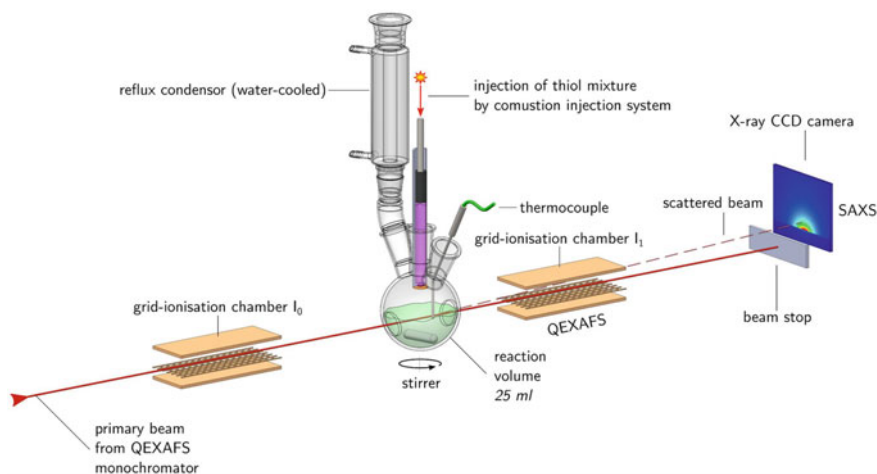


Fig. 2 Experimental arrangement of the in situ monitoring of the growth of the colloidal $\text{Cu}_2\text{ZnSnS}_4$ NCs through SAXS. Reprinted from Ref. [48] Copyright 2021 @American Chemical Society

3 Synthesis of Inorganic Semiconductor Nanocrystals by Hot-Injection Method

3.1 Role of Ligands and Solvents in Morphological Evolution

As discussed, ligands (or) capping agents are adhering on the NCs surface and depending on their interaction, the growth direction is restricted. Further, organic ligands and solvents are playing important role in the decomposition of precursors to controlling the size, shape and phase of the NCs [52–54]. It is important to wisely select the suitable ligands and solvents to synthesis NCs with narrow distribution. The solvents used in hot-injection method are belongs coordinating and non-coordinating category. Most of the non-aqueous-based synthesis of NCs in this method carries use of coordinating solvents such as OAm, OA and a non-coordinating solvent, 1-ODE [55–57]. These solvents decompose the precursors at high temperature to form NC lattice. Apart from the growth, solvents/ligands influence a lot on the phase formation of the NCs [58]. Here, the ligands sterically influence on the growth of the NCs which result in different phase and morphologies. For instance, colloiddally prepared copper selenide (Cu_2Se) NCs using TOP resulted mixture of two phases while with OAm only one phase [50]. While in the case of aqueous synthesis of semiconductor NCs, the stability of the resultant NCs relies on the type of surface ligands. Generally, water soluble short-chain ligands are used during the NCs preparation and they are useful for solution-processed applications. Some ligands are also used as precursor for the NC formation. Thiols with longer chain length are serving this role and they are helpful in synthesizing sulphide NCs. For example, 1-dodecanethiol (1-DDT), a

long-chain thiol which also serve as ligand is used to synthesis binary, ternary and quaternary copper chalcogenide NCs [28, 60]. At higher temperature, decomposition of 1-DDT generate sulphide (S^{2-}), which essentially lead to the formation of metal-sulphide NCs [61, 62]. In addition to passivation, ligands and solvents may also undergo an isomeric transformation and can form a shell to passivate the surface [63]. With respect to the nature of binding, ligands are classified as L-, X- and Z-type. The elaborative discussion about these ligands could be seen elsewhere [25, 64]. Sometime, the by-product formed in the reaction may act as a ligand. It is observed that in the presence of OAm, carboxylic acid formed in the reaction could serve as a ligand [63]. The generally applied selection rule in the NCs synthesis is Pearson's rule of hard soft acid base theory (HSAB). According to this rule, soft acids will prefer to bind towards soft base while hard acids will prefer to bind with hard base [65, 66].

Although organic ligands are proved as versatile for the capping purpose, inorganic ligands have also been investigated to achieve colloidal NCs with excellent properties. Halides, pseudohalides, halometallates such as NaCl, NH_4I , NaN_3 and molecular metal-chalcogenide complexes (MCCs) are found to be useful in stabilizing colloidal NCs and maintaining superior optical properties [67–69]. Kovalenko et al. have found that negatively charged MCCs, such as (SnS_4^{4-} , $Sn_2S_6^{4-}$, $SnTe_4^{2-}$, AsS_3^{3-} , MoS_4^{2-}) are useful in removing the ligands of core/shell CdSe/ZnS NCs and metallic Au NCs [70]. Importantly, MCC (here, $Na_4Sn_2S_6$) capped Au NCs showed high conductivity over $f > 1000 \text{ S cm}^{-1}$, which show the promising direction of this approach. The same research group further demonstrated use of hydrogen selenides (HSe^-), hydrogen telluride (HTe^-) and their elemental ligands (Se^{2-} , Te^{2-}) to cap CdSe and CdSe/ZnS core/shell NCs [71]. Besides, the short-chain thiocyanate (SCN^-), chloride (Cl^-) and sulphide (S^{2-}) ligands are quite useful in improving carrier transport of $Cu_{2-x}Se$ NC films [72]. They are indeed quite useful in achieving NC films with excellent electrical properties. When inorganic ligands are used in the reaction, the cationic or anionic species could influence on the growth as observed in the case of cadmium chalcogenide [73, 74] and copper chalcogenide NCs [75, 76]. These species sterically influence on the growth pattern of the NCs and control their thickness or size/shape. Usually, this inorganic ligand capping strategy is achieved through ligand-exchange, which is discussed in this chapter separately. The schematic diagram of inorganic ligand passivation using HBF_4 treatment in the case of CdSe and CdSe/ZnS core/shell NCs and their corresponding UV-visible, PL and IR spectra are represented in Fig. 3.

3.2 Influence of Precursors in the Reaction

Precursors play remarkable role in hot-injection method to synthesize NCs with excellent structural and optical properties. By carefully choosing or designing the precursor, the properties of the NCs can be modified. Most of the reports in hot-injection synthesis of semiconductor NCs are halides, nitrates and

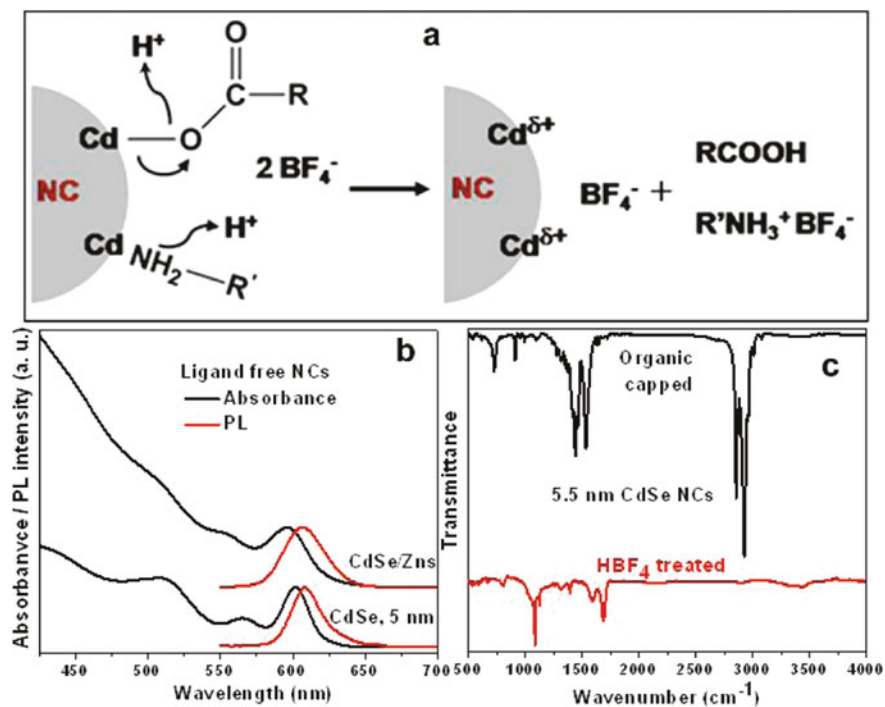


Fig. 3 a Schematic representation of removal of organic ligands from the CdSe NCs using HBF_4 treatment b UV–visible and PL spectra of the ligand-free CdSe and CdSe/ZnS core/shell NCs and c FTIR spectra of the HBF_4 treated and untreated CdSe NCs. Reprinted with permission from Ref. [71]. Copyright 2011@American Chemical Society

acetates based precursors. By changing or modifying the ratio between the precursors, it is possible to tune the phase, structure and morphology of the NCs. In the case of ZrO_2 , it is found that when zirconium (IV) bromide is used as the precursor, very smaller NCs are obtained compared with the NCs obtained using zirconium chloride (ZrCl_2) precursor [77]. Similar kind of size variation is also observed in the case of PbS, ZnS, CdS and MnS NCs [78]. Apart from molecular halides and covalent compounds, single-source precursors are playing vital role in synthesizing monodispersed NCs through hot-injection method. Here, dithiocarbamates, xanthates, diselenophosphinates, semicarbazones are the widely used metal-complex single-source precursors. These single-source precursors are quite useful in synthesizing metal phosphides and selenides such as CoP , Co_9S_8 [79], Sb_2Se_3 nanorods, SnSe nanosheets [81] and BaTiS_3 nanorods [82]. Out of other metal-complexes, dithiocarbamates are the leading complex ligands in the preparation of metal-sulphide NCs through hot-injection method. Shen et al. used metal-dithiocarbamate complex to synthesize several kind of metal-sulphide NCs such as Ag_2S , ZnS, CdS QDs and SnS nanosheets, Bi_2S_3 and Fe_7S_8 nanoplates [83]. By modifying the reaction temperature and solvents/precursors ratio, the authors cleverly tuned the size

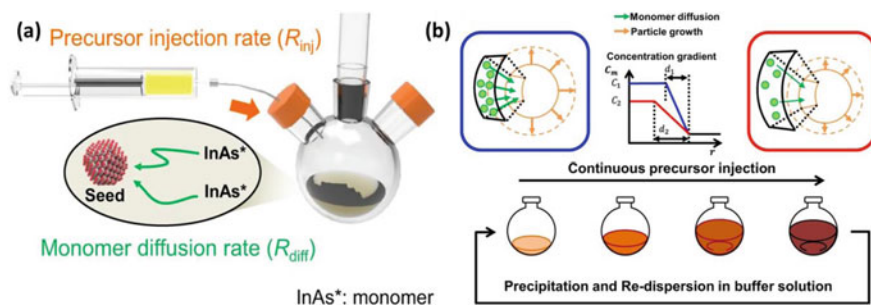


Fig. 4 a Schematic diagram of continuous injection of InAs clusters into the InAs seeds b diffusion dynamics controlled growth of InAs QDs. Reprinted from Ref. [86]

and morphology of the prepared products. Depending on the precursor type, the spectral position of the NCs is influenced. For instance, it is observed that use of gallium oleate (Ga-oleate) precursor to synthesize InP QDs lead to red shift in UV–visible (450–525 nm) and PL spectra due to the formation of core/shell (i.e. InP/GaP) assembly whereas blue shift is observed when $\text{Ga}(\text{acac})_3$ is used [84]. This is because of the formation of alloyed InGaP nanostructures shift the spectral position towards blue. This show that selection of suitable precursor is important to achieve semiconductor NCs with excellent properties. Zhao et al. used InCl_3 and pnictogen chloride (As, Sb)-OAm as precursors to prepare InAs, $\text{InAs}_{1-x}\text{Sb}_x$ and InSb QDs [85]. The authors achieved QDs with precise control in size with the controlled stoichiometry. Importantly, the reaction temperature is extremely lower here (3 °C per minute) and this approach seems to be a favourable to synthesize III-V group QDs. Kim et al. explored that it is the concentration gradient between the solution and QDs which determines the size of the InAs QDs [86]. The schematic representation of the precursor injection in hot-injection method to synthesize InAs QDs is given in Fig. 4.

3.3 Influence of Physical and Chemical Parameters

Physical and chemical properties are hardly influencing in hot-injection synthesis method. By modifying temperature, pH, reaction time, precursor injection time interval, volume of the solvent, amount of the ligands and ratio between the precursors, it is possible to control the reaction, phase, morphology and size of the NCs. Unlike other methods, control of physical and chemical properties through hot-injection synthetic approach is more feasible. Even a small variation in the reaction could be recorded and their influence on the NCs can be measured. The size of the NCs could be precisely tuned in this method by simply altering physical and chemical parameters. Also, it is possible to achieve different morphologies from nanodots to nanosheets through controlling the reaction conditions. For example, in the case of

halide perovskite NCs, the high temperature ($\sim 270\text{ }^{\circ}\text{C}$) results in nanocubes whereas same amount of precursors at low temperature ($\sim 120\text{ }^{\circ}\text{C}$) results in nanoplatelets [87–89]. Ou et al. precisely tuned the spectra and composition of the $\text{Cu}_2\text{ZnSnS}_4$ NCs through incorporating selenium (Se) [90]. The monodispersed $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ NCs obtained in this approach possessed nearly spherical shape with the band gap 1–1.5 eV. Similar kind of spectral alteration is possible in other ternary chalcogenide nano-semiconductors such as CuInS_2 , CuInSe_2 , AgInS_2 and AgInSe_2 . Similarly, the ratio between the precursors significantly influence on the morphology of the NCs. Joo et al. varied ratio of the precursors to prepare CdS, PbS, MnS and ZnS NCs [83]. Here, the authors achieved different morphologies which includes rods, bipods and tripods (CdS NCs), and bullet shape (MnS NCs). In this study, it is found that the size of the CdS NCs could be varied (6, 8 and 9 nm) by simply varying the ratio between PbCl_2 and sulphur. Similar to this, instead of OAm, Wang et al. used ODA as solvent and successfully achieved different kind of metal-sulphide nanomaterials [91]. Here, in the case of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ NCs, by increasing the concentration of Cd^{2+} , the emission was tuned from blue to red. Moreover, variation in ratio between Cd^{2+} and S^{2-} resulted in NCs with different morphologies (nanoneedles, nanotripods and nanorectables). Instead of injecting sulphur in OAm, a one-pot approach is adopted to synthesize wide-variety of metal-sulphide NCs and this strategy is usually carried out in the presence of a long-chain alkanethiol [92, 93].

3.4 Purification of Colloidal Semiconductor Nanocrystals

Purification plays important role in achieving semiconductor NCs with excellent properties and stability. Since hot-injection method involves with solvents and ligands, it is necessary to eliminate the excess ligands and solvents after the completion of reaction. In order to remove the excess ligands, solvents and by-products, purification is carried out in the presence of anti-solvents. Ligands can rely on the NCs surface through either physisorbed or surface bound state depending on the surface metal atoms. The excess organic ligands on the NCs and the by-products formed during the reaction are effectively removed using suitable anti-solvents. Here, depending on the size, the bigger NCs are precipitated at first and smaller NCs remains in the mother solution. This is collected through another cycle of purification and the resultant solid is recovered through centrifugation. This is further redispersed in a suitable solvent and the cycle is continued until the excess ligands are fully removed. It is important to reduce the physisorbed ligand density using multiple cycles without affecting the PL properties. Among the purification strategies, ‘size-selective precipitation’ is quite familiar where extremely smaller size NCs (often called as ‘QDs’) are extracted [94, 95]. The selectivity and volume of the anti-solvent for the purification, centrifugation speed, ligands interaction with the NC surface, pH of the medium and polarity of the anti-solvent are critically influencing on the purification and final assembly of the NCs. With different innovative approaches, recently, remarkable

developments have been achieved in the purification of NCs. Other than ultracentrifugation, separation of NCs is carried out through membrane-based dialysis techniques [40]. Here, the excess ligands are allowed to pass through a membrane from a higher concentration area to lower concentration area and the resultant solution would have purified NCs. Chromatographic techniques such as size-exclusion chromatography and gel-permeation chromatography (GPC) are widely used to separate the NCs from solution [96–98]. Once the NCs are purified, they are redispersed in a suitable polar (or) non-polar solvent and the stability of the resultant colloidal solution is monitored. Depends on the polarity of the solvent, pH and dielectric constant of the medium, the NCs stability is affected [99]. Since multiple purification influence on the optical properties of the NCs due to the removal of ligands, it is essential to monitor the absorption and emission spectra in order to understand the intensity variation. In general, purification cycle partially (or) completely removes conventional OAm and OA ligands and due to the strong binding ability of phosphine ligands, it is less influenced. Since phosphine ligands are L-type ligands, multiple purification could affect their bonding with the NCs. It is found that methanol deteriorate CdSe QDs surface during multiple washing and reduce the PL properties while ethanol helps to retain the PL properties [42]. In this case, it is identified that the removal of TOPO from the surface is faster than the removal of stearic acid (X-type ligand). This implies that role of purifying solvent is different with respect to the type of ligand. In the case of metal halide perovskite NCs, purification significantly affect the PL properties. Among the solvents with different polarity, methyl acetate, methyl acetate and tertiary-butanol are found to be efficient in the removal of excess ligands and further stabilization of the halide perovskite NCs [100–102]. A pictorial representation of influence of different solvents on the purification of CsPbBr₃ NCs and PL properties is given in Fig. 5.

Other than anti-solvent-based purification, ligands removal can also be achieved through methods such as calcination and plasma treatment. Calcination is a process where the NCs are heated at high temperature to evaporate the organic content. For this purpose, thermally degradable ligands are used [103]. However, thermal treatment of removing ligands leaves organic carbon residue and this hinders the charge transport properties [104]. Also, plasma treatment of NC films is found to be eliminating the organic ligands from the NC surface. Plasma treatment is depend on the size of the ligands which makes the interparticle distance closer or far away. When plasma treatment is carried out, care should be taken on the type of the gas used for the plasma. It is observed that degradation of ligands with Co–Pt NC assembly takes place when plasma is generated through nitrogen and hydrogen whereas it is preserved when plasma is generated by oxygen [105]. When plasma is carried out in the presence of Ar, OAm and OA ligands could undergo polymerization and because of this, the stability of the NC films increases [106, 107]. In few cases, it is observed that the thermal treatment of removing ligands affect the catalytic properties of the NCs [108, 109]. Recently, gel permeation chromatography (GPC) has emerged as potential approach to purify colloidal NCs. In this approach, the NCs are allowed through a column of the packing medium (ex: polystyrene beads), which remove the ligands efficiently. This is because the highly porous polystyrene is useful for

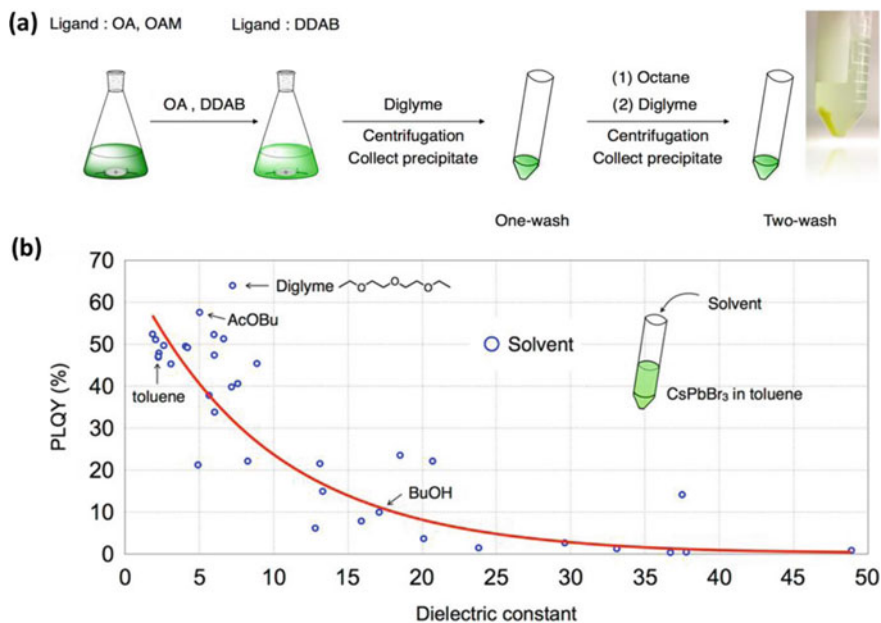


Fig. 5 **a** Schematic representation of surface treatment of CsPbBr₃ NCs using didodecyl dimethyl ammonium bromide (DDAB) and **b** influence of solvents in PLQY of CsPbBr₃ NCs with respect to the dielectric constant value. Reprinted with permission from Ref. [102]. Copyright 2018@American Chemical Society

the absorption of excessive ligands which are ultimately collected. Kessler et al. used undec-10-ene-1-thiol (UDT) ligand to treat PbS NCs [110]. Here, the surface treated NCs were purified using GPC and corresponding properties were analysed. The authors found that GPC method was efficient in removing free UDT and native oleate ligands. The characteristics of this method and the schematic representation of the purification process is given in Fig. 6.

4 Influence of Hot-Injection Method on the Synthesis of Metal-Oxide, Metal-Chalcogenide Semiconductor Nanocrystals

Although metal-oxides possess complicated surface chemistry, synthesizing metal-oxide nanomaterials through hot-injection approach has been identified as suitable for the solution-processed device fabrication applications. Here, the high temperature synthesis is carried out through non-hydrolytic sol-gel approach and generally OAm, OA and TOPO are employed as solvents. Cozzoli et al. prepared colloidal TiO₂ nanorods using OA as solvent in the presence of titanium-tetra-isopropoxide

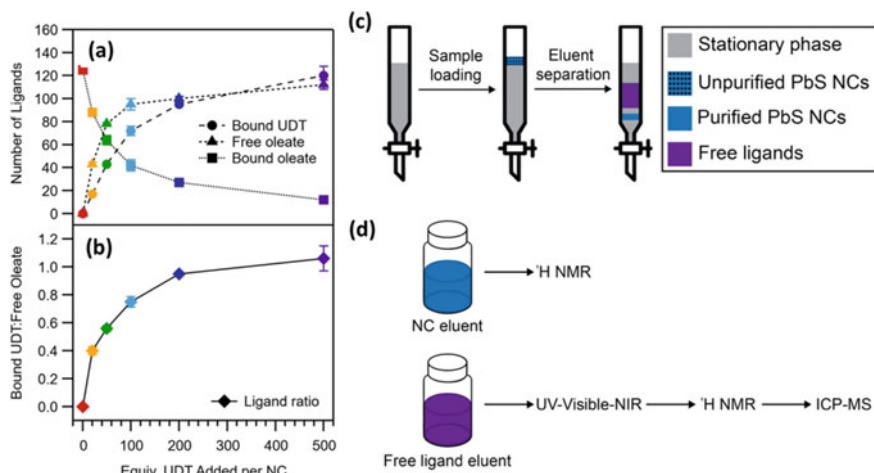


Fig. 6 **a** Bound UDT, free oleate, bound oleate ligands integrated from NMR spectra **b** bound UDT to free oleate ligands ratio calculated from number of each ligand **c** schematic representation of purification of UDT treated NCs using GPC and **d** characterization techniques used to analyse the NCs eluent and free ligand eluent. Reprinted with permission from Ref. [110]. Copyright 2022@American Chemical Society

(TTIP) [111]. Here, the nanorods were prepared at 110°C. Interestingly, when TiF_4 is mixed with TiCl_4 and used as a source, depending on the ratio, it is observed that the resultant TiO_2 NCs phase varies. Gordon et al. adopted this approach and prepared TiO_2 NCs with different morphologies (size from 10 to 100 nm) [112]. Here, the authors achieved blue coloured TiO_2 owing to the deficiency of the Ti^{3+} . Since these insulating ligands are often problematic for charge transport, they are usually removed through facile ligand-exchange to fabricate NC films. Basina et al. have observed that depending on the injection temperature, the size of the $\text{Fe}/\text{Fe}_3\text{O}_4$ core/shell nanomaterials is found to be varied [113]. Usually, a high temperature is required to decompose the precursor for the formation of metal-oxide NCs through hot-injection method. Jana et al. prepared Fe_3O_4 NCs through decomposition of iron-oleate metal-complex at 300 °C [114]. By altering the reaction conditions, the authors achieved Fe_3O_4 NCs with 8–30 nm size. Also, extension of this approach to MnO , NiO , Co_3O_4 , ZnO NCs resulted in interesting morphologies with control of size.

For the metal-chalcogenides, aqueous synthesis of cadmium chalcogenide nanomaterials, CdS , CdSe and CdTe are much studied for several promising applications such as optoelectronics, fabrication of polymer nanocomposites, bio-imaging and counterfeit currency identification [115, 116]. Synthesis of cadmium chalcogenide nanomaterials through hot-injection method was firstly carried out through toxic phosphine solvents [44] but after the development of aqueous strategy, use of short-chain thiol ligands are found to be useful to achieve highly crystalline, monodispersed NCs [117]. From the literature, it is known that CdTe NCs are prepared

using NaHTe as tellurium precursor and this method has produced very smaller size (below ~ 10 nm) NCs under controlled conditions [118]. In this case, thiol ligands TGA, MPA, mercaptosuccinic acid (MSA) and glutathione are found to be efficient in providing long-term stability in water [119, 120]. Similar to cadmium chalcogenides, binary sulphide compounds such as bismuth sulphide (Bi_2S_3), iron sulphide (FeS_2), nickel sulphide (NiS_2), manganese sulphide (MnS_2) and their corresponding selenides are prepared and characterized. In some of the binary sulphides, for ex: Cu_{2-x}S , FeS_2 , the phase and composition of the NCs are found to be strongly dependent on the reaction conditions [121, 122]. Joo et al. prepared different class of metal-sulphide NCs by injecting sulphur in OAm into the metal-oleate complex [78]. Also, quaternary copper chalcogenides belong to the kesterite group such as $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ NCs are synthesized using hot-injection method and their dispersion in various organic solvents is found to be useful for the optoelectronic device fabrication. Here, a high temperature reaction of Cu, Zn and Sn precursors in the presence of OAm and 1-ODE ultimately result in a metal-oleate complex formation [55, 56, 123–125]. In most of the cases, sulphur in OAm is used to generate sulphide (S^{2-}) which is injected into the metal-oleate mixture [126, 127]. In some cases, bis-trimethyl silyl halides are also used to prepare sulphide-based NCs by hot-injection method [128, 129]. The schematic representation of the synthesis of $\text{Cu}_2\text{ZnSnS}_4$ NCs by hot-injection method is given in Fig. 7.

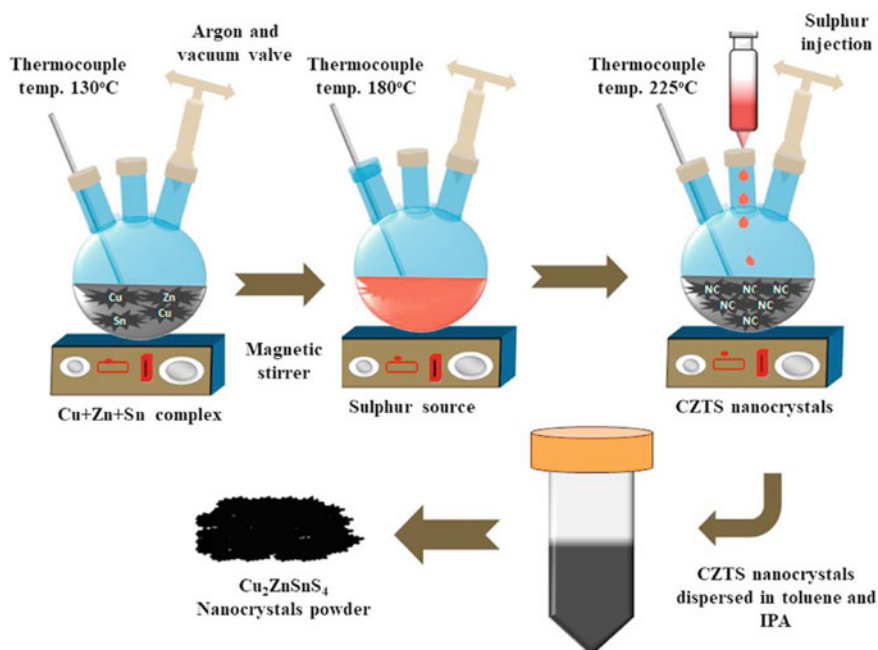


Fig. 7 Schematic diagram of the preparation steps of colloidal $\text{Cu}_2\text{ZnSnS}_4$ NCs through hot-injection method. Reprinted from Ref. [127]

5 Significance of Hot-Injection Method on the Synthesis of Metal Halide Perovskite NCs

Metal halide perovskite NCs with the general formula $APbX_3$ ($A = Cs^+$, $CH_3NH_3^+$ and $X = Cl, Br$ and I) are the currently examined promising materials for the future generation optoelectronic devices. Compared with traditional semiconductor nanocrystalline materials, the luminescence characteristics of these nanomaterials are found to be superior and possessing high PLQY [130, 131]. Research on metal halide perovskite NCs has reached its zenith within the short duration due to the impressive development in synthetic approaches. Specifically, hot-injection approach has proved as potential method to synthesis different class metal halide perovskite nanomaterials. In this view, compared with hybrid lead halide perovskite NCs, all-inorganic lead halide perovskite NCs (ex: $CsPbX_3$) have attracted much attention. Remarkable synthetic achievements have been made in the synthesis of halide perovskite nanomaterials using this method. During the year 2015, synthesis of $CsPbX_3$ NCs through hot-injection method was reported [132] and shortly after that seminal work, several works were demonstrated to prepare $CsPbX_3$ NCs with different morphologies such as nanocubes, nanoplatelets, nanowires, nanorods and nanosheets [133–135]. Because of the ionic surface, selection of ligands and controlling physical parameters are important in synthesizing metal halide perovskite NCs. Most of the synthesis routes describe that by altering the chain length of the organic ligands, varying the reaction conditions, and modifying precursor ratio, it is possible to synthesis these morphologies [136]. The ionic $CsPbX_3$ NCs are highly sensitive with ligands, solvents, atmosphere and externally added compounds. Because of this, the traditionally used OAm and OA ligands are critically influencing on the phase, morphology of the $CsPbX_3$ NCs. Although through hot-injection method we could able to synthesis wide variety of nanocrystalline perovskite materials, the exact formation mechanism of these NCs is not much explored due to the extreme fast reaction time (in secs). Because of the weak binding ability with $CsPbX_3$ NCs, OAm and OA are easily removed during purification and so surface treatment help to achieve high PL properties [137–139]. Investigations are firmly confirming that the carrier life-time and PLQY of these NCs is highly improved after surface treatment. Although several ligands and solvents are attempted, OAm and OA are dominating in preparing these ionic compound NCs by hot-injection method. Recently, it is inferred that phosphine compounds are imparting high stability over OAm and OA ligands in metal halide perovskite NCs [140, 141]. Other than $CsPbBr_3$ NCs, their counterparts such as Cs_4PbBr_6 and Cs_2PbBr_5 NCs are also synthesized through hot-injection method and their physical and chemical properties are evaluated [142]. Together with lead halide perovskite NCs, significant milestones have achieved in the synthesis of lead-free halide perovskite NCs through hot-injection method. Specifically, layered perovskite nanostructures based on $Cs_3Sb_2I_9$, $Rb_3Sb_2I_9$ are showing promising results [143]. In specific, colloiddally prepared lead-free halide perovskite nanomaterials such as $CsCu_2I_3$ and $Cs_3Sb_2Br_9$ are showing excellent photoluminescence properties and delivering promising results for the fabrication of optoelectronic

devices [144, 145]. Nanomaterials of other perovskite compounds such as CsEuCl_3 , Cs_4SnBr_6 , $\text{Cs}_3\text{Bi}_2\text{X}_9$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have also emerged as potential candidates for diverse applications [146]. Besides, hot-injection synthetic method based lead-free double perovskite nanocrystals with different morphologies are also showing interesting structural and optical properties which could be used for several purposes. These analyses are featuring that hot-injection method is playing a major role in the preparation of different group metal halide perovskite nanomaterials and their counterparts for potential applications.

6 Post-treatment (or) Surface Passivation, Core/Shell Nanostructures, Ligand-Exchange, Ion-Exchange and Doping Strategies of Semiconductor Nanocrystals Prepared by Hot-Injection Method

While purifying the as-synthesized NCs, they usually lose some ligands due to the polarity of purifying solvent and so loss in PL properties is observed. This is common in all kind of semiconductor NCs and the physical and chemical characteristics of the luminescent NCs are degraded with multiple purification. The loss of ligands mainly cause surface traps on the NCs and so the luminescent properties are severely affected [147]. It is imperative to maintain the PL properties of QDs in order to apply them for potential lighting devices, for example, LEDs. Other than losing ligands, the NCs would obviously have unsatisfied bonds (called 'dangling bonds') on the surface. To maintain the luminescent properties in NCs, it is essential to carry out surface treatment which recover or improve the PL properties. This surface treatment is generally carried out by organic molecules, incorporation of metal ions, and by ionic compounds. Surface passivation of the colloiddally prepared NCs could be achieved through facile treatment approaches. By passivating selective sites on the NCs surface, the optical properties of the NCs can be improved. This is realized in chalcogenide as well as metal halide perovskite NCs [148, 149]. Passivation of metal halide perovskite NCs using different compounds is studied by several research groups since because of the ionic nature, the surface ligands easily lose and hence the surface treatment is essential to fabricate defect-free metal halide perovskite NC films. Several kind of halides, ionic compounds and organic molecules are exploited for the surface treatment and they are useful to improve the functional characteristics of the NC films [139, 150]. In the case of PbS NC films, lot of reports are describing about the surface treatment using molecular halides to improve the carrier transport properties for solar cell applications [151, 152]. Similarly, halides and organic molecules treated CsPbX_3 NC films are resulting in high PLQY. For example, when CsPbBr_3 NC films are treated by PbBr_2 , the PLQY reach to near-unity [153]. Likewise, 1-DDT treated colloidal CsPbBr_3 NCs solution show near-unity PLQY [154] due to the formation and consequent passivation of thiolate and thioethers. These investigations clearly reveal about the promising avenue of the surface treatment

processes on the colloiddally synthesized NCs. In the case of InP QDs, it is found that surface etching with fluoride significantly improve the PLQY [155]. Here, instead of corrosive HF, use of ionic liquid compounds such as BF_4^- , PF_6^- are found to be efficient in enhancing the PL properties. This is because of the surface dangling bonds are passivated by fluoride (F^-) ions. These fluoride compounds are also found to be effective with metal halide perovskite NCs and improving the PLQY significantly [156]. Other than these, metal ion passivation on the colloiddally prepared NCs also incredibly improve the optical properties.

Ligand exchange is a facile, efficient process where the long-chain insulating ligands of the NCs are replaced by highly conductive, short-chain ligands. This process is also used to transfer the NCs from aqueous to organic medium and vice-versa. In hot-injection method, most of the synthesis protocols are based on the use of highly unsaturated, poorly conductive or insulating ligands such as OAm, OA, 1-ODE. To fabricate efficient NC films for charge transport, it is necessary to replace the long-chain ligands by short-chain ligands. These ligands may either completely or partially exchanged in liquid or in the solid-state. For this, the short-chain ligands are dissolved in a solvent and the fabricated NC film is dipped for some time to exchange the native ligands and this process is repeated for several times. It is important to note that preservation of NCs shape, size and structural integration should be undertaken while exchanging the native ligands. This process ultimately eliminates the insulating ligands and the NCs are fabricated with the conductive, short-chain ligands. This impact on the carrier transport of the NCs and in particular for solar cells, this process is highly efficient [58]. Ligand exchange is usually carried out in solution or in solid-state. In solution, the aqueous synthesized NCs could be transferred to organic medium through a facile phase transfer ligand exchange process. For example, aqueous synthesized thioglycolic acid (TGA) capped CdSe nanoparticles can be transferred to organic medium through an exchange ligand, 1-DDT [157]. Despite multiple purification, removal of OAm from the NCs surface is found to be difficult when it is bonded with Cd^{2+} and Pb^{2+} . In contrast, removal of 1-DDT and poly-vinyl pyrrolidine (PVP) from the Pd NPs surface is found to be difficult compared with the OAm capped NPs [158]. In this case, the ligand exchange is claimed as partial one. For the lead chalcogenide nanocrystalline materials, ligand exchange is carried out in the presence of mercapto propionic acid (MPA) and 1,2-ethanedithiol. Several reports deal about the use of these ligands to treat PbX_2 ($\text{X}=\text{S},\text{Se}$) QD films and its critical influence on the performance of the quantum-dot sensitized solar cells (QDSSCs) [159]. Other than organic short-chain ligands, inorganic ligands like thiocyanate (SCN^-), tetrafluoro borate (BF_4^-) [160], S^{2-} [161], HS^- , Se^{2-} , HSe^- , Te^{2-} , HTe^- , TeS_3^{2-} , OH^- , NH_2^- [71], oxoanions such as PO_4^{3-} , MoO_4^{2-} [162], metal-chalcogenide complex (ex: Cu_7S_4^-) [68, 70], and alkali metal-chalcogenide complexes (ex: K_2S , K_2Te and Na_2S) [163] are found to be efficient in stabilizing the NCs in solution. In few cases, it is found that depends on the NC-ligand combination, the conductivity (p-type or n-type) is determined. Jiang et al. carried out an interesting approach to prepare ternary semiconductor chalcogenide selenide and sulphide NC films [164]. The authors prepared Cu_{2-x}Se and CuInSe_2 NCs (~ 16 nm size) by capping molecular chalcogenide complexes $\text{In}_2\text{Se}_4^{2-}$ and

$\{\text{In}_2\text{Cu}_2\text{Se}_4\text{S}_3\}^{3--}$ and upon annealing at 500 °C, the corresponding ternary and quaternary metal-chalcogenide NC films are formed. Although metal-chalcogenide complexes are doing efficient passivation, they unfortunately create a high defect density on the NCs surface, which is a demerit for the lighting applications. Another potential method to remove the NC surface ligands is ‘ligand-stripping’. In this approach, a stripping agent is used to remove the ligands. This stripping agent destabilize the NCs by removing the native ligands and induce the aggregation activity. Out of others, tetrafluoroborate (BF_4^-) ions are the widely studied ligand-stripping agent for the colloidal NCs prepared by hot-injection method [160]. Researchers have also demonstrated the active role of Meerwein’s salt and trialkyloxonium salts in removing native ligands of colloidal NCs [165]. However, ligand-stripping approach is successful only with few systems and so careful selection of ligands would be beneficial for the fabrication of efficient NC array.

Self-assembly is one of the salient characteristics of the solution-processed semiconductor NCs. Here, NCs self-assemble in solution or in films through electrostatic interaction of ligands. Self-assembly in semiconductor NCs is motivated through ligands, light, solvents and deposition methodologies. In specific, excess ligands, electrostatic interaction of ligands and self-organization of ligands are the ways to induce the NC superlattice structures [166]. The interaction between two NCs influence on the energy level and so optical properties are varied. Here, the distance between one NC to another is usually determined by the length of the ligand. Depending on the ligand, i.e. short-chain or long-chain, the self-assembled NC array is influenced and so different structures can be achieved. Self-assembly has been realized in different kind of chalcogenide, metal-oxide and halide perovskite NCs [167–169]. The key requirement of self-assembly is monodispersity in NCs and so hot-injection method plays vital role in forming superlattice structures. Readers are advised to go through some of the potential review articles in order to understand about the principle and applications of the self-assembly of the colloiddally prepared NCs [170–172].

Ion-exchange is a commonly used strategy in hot-injection prepared II-VI, III-V, I-III-VI group semiconductor NCs [173, 174]. Here, the cations in a NC are ligated with the ions present in the solution, resulting different optical and structural, morphological properties. Compared with the bulk solids, the exchange rate in the nanoscale is so rapid, hence influencing a lot on the composition and properties of the NCs. Also, this process is reversible with respect to reaction conditions. Reduced activation barrier, preferential solvation of the incoming ion, difference in the lattice stability are influencing cation-exchange severely. Son et al. investigated the effect of cation-exchange in CdSe NCs [175]. Here, the ion-exchange is carried out in the presence of AgNO_3 to achieve Ag_2Se NCs. The instantaneous colour change implies the rapid ion-exchange and the reverse conversion is achieved in the presence of $\text{Cd}(\text{NO}_3)_2$. Interestingly, here the authors observed that the crystal structure and morphology of the ion-exchanged NCs are dependent on the size and shape of the synthesized NCs. Similar to the cation-exchange, recently, metal halide perovskite NCs are executed with anion-exchange in which the halide is replaced by another halide in solution or in solid-state [176, 177]. As a result, the structural and optical

properties are varied and this is much useful for the spectral management. Cation-exchange of CsX to CsPbX₃ NCs has been observed in metal halide perovskite NCs and this implies the comfortability of perovskite lattice for ion-exchange [178]. This ultimately result in a change in the peak position of absorption and PL spectrum, which is useful for the fabrication of LEDs and solar cells.

Formation of core/shell assembly is one of the important strategies to improve the PL properties of semiconductor NCs. As we know, the as-synthesized NCs will have surface defects due to the incomplete passivation of ligand molecules. These defects can be removed or minimized through organic or inorganic passivation. In core/shell structure, NC surface is passivated by a nanoscale layer of another semiconductor to improve the PL properties. The growth of this shell layer is monitored through the UV-visible and PL spectra, which generally show a red shift under growth. Core/shell NC assembly is achieved in different class of semiconductor NCs, and especially in the II-VI and III-V group nanocrystalline semiconductors it is much investigated [179, 180]. When CdS NCs are additionally passivated by CdTe NCs, their PL properties are greatly improved [181]. Similarly, it is observed that when InP QDs are passivated through zinc sulphide (ZnS) by hot-injection method, the luminescence properties are found to be improved. Likewise, the same kind of approach is found to be resulting an improved PLQY in CuInS₂/ZnS core-shell NC assembly [182, 183]. In few cases, ternary layer passivation such as InP/ZnSe/ZnS [184] and InP/GaP/ZnS [185] are also attempted and excellent stability with improved PL properties are achieved. Through this multishell growth, PLQY even reached to 92% (for the InP/ZnSe/ZnSe) which is much useful for the wide colour gamut display applications. The preparation steps associated with the formation of InP/GaP/ZnS core/shell NCs are schematically given in the Fig. 8. Recently, without any passivation, such impressive PLQY has been achieved in metal halide perovskite NCs through hot-injection synthesis method.

Doping with the metal ions generally help to improve the optical properties of the semiconductor NCs [186]. Other than optical properties, doping generally influence on the structural and magnetic properties. Doping in semiconductor NCs is generally carried out in the presence of transition metal ions, noble metals and rare earth ions [187]. Compared with other elements, doping with manganese (Mn) and copper (Cu) is widely studied in traditional semiconductor and metal halide perovskite NCs owing to their strong influence on the physicochemical properties [188, 189]. Other than modifying spectral position, metal ions can also influence on the morphology of the NCs. For example, Li et al. used aluminium salt, Al(NO₃)₃·9H₂O during the preparation of Cu_{2-x}Se nanocubes [190]. It is found that the addition of this salt influence on the morphology of the prepared nanocubes without diffusing into the lattice. The authors concluded that the Al³⁺ ions promote the crystal growth of Cu₃Se₂ nanocubes in a specified direction. In few cases, it is observed that the metal ions passivate the NCs and improve the PLQY. Doping is found to be useful in metal halide perovskite NCs since transition metal ions and rare earth ions doping are found to be helpful to achieve near-unity PLQY [191]. For example, CsPbI₃ NCs doped with Ni²⁺ ions deliver near-unity PLQY [192]. Here, the dopants are added in synthesis once

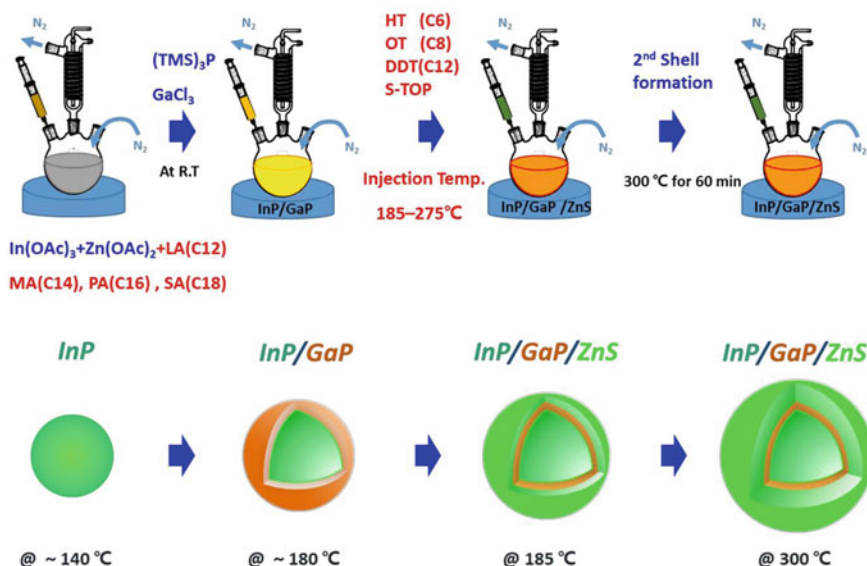


Fig. 8 Preparation steps followed in the core-shell structured InP/GaP/ZnS nanoparticles through hot-injection method. Reproduced from Ref. [185], *Nanomaterials*, published by MDPI, Switzerland, 2020. Link: <https://doi.org/10.3390/nano10112171>

the NC lattice formation takes place. These results are predicting that it is possible to achieve the desired properties through doping by means of hot-injection method.

7 Upscaling in Hot-Injection Method

Large scale synthesis of semiconductor NCs through hot-injection route is important for the industrial applications. Carefully designed glass apparatus with special inert gas circulation arrangement is used for the gram scale preparation of the NCs. It is possible to achieve semiconductor NCs in gram scale and a typical experimental arrangement for the preparation of CdSe NCs and CdSe/CdS/ZnS core/shell NCs and their corresponding morphological and optical analysis are given in Fig. 9 [193]. By injecting selenium precursor in 1-ODE into the metal-carboxylate/1-ODE mixture, Flamee et al. achieved high reaction yield (80–85%) in the case of CdSe, CdSe/CdS and ZnSe NCs [194]. Similarly, diphenylphosphine (DPP)/1-ODE assisted synthesis resulted in highest yield (23.5 g) in the case of PbSe QDs [195]. Although phosphine ligands are dominating in hot-injection method, phosphine-free solvents are also showing promising directions. These kind of solvents are typically used for a non-injection-type ‘one-pot’ synthesis approach [196]. Recently, there are promising experimental results have come out in developing perovskite QDs for the future generation lighting devices [197, 198]. Specifically, the AI-guided

modular manufacturing of lead halide perovskite QDs has shown promising direction in commercializing these materials for future applications [199]. For the large scale production, automated or continuous flow synthesis approach is followed in industry. There are few initiatives undertaken to establish the industrial upscaling of QDs in the private sectors like Nanoco technologies (U.K), Quantum Science (U.K), UbiQD Inc (USA), Avantama (Switzerland), etc. and their use for the commercial applications such as Quantum dot light emitting device (QLED) television technology, crop growth is demonstrated. These developments are indicating the potential pathway of hot-injection method for the development of modern electronic devices.

Upscaling colloidal hot-injection method for the industrial purpose is generally carried out through microfluidic reactor arrangement. This field is currently growing in different directions and interesting results are explored in different group of semiconductor NCs. Importantly, microfluidic reactor has more control over traditional method in achieving the good quality NCs. Here, the NCs are synthesized through heaters and fluid control arrangement which essentially result in finely tuned NCs. The important feature of microfluidic synthesis is achieving NCs through continuous flow reactor through continuous feeding of the precursors. The size of the synthesized NCs or QDs in this method is varied by controlling the reaction time. Here, an immiscible carrier phase is introduced with the reaction phase where the liquid-to-liquid flow production takes place [200]. Advantages such as efficient mixing, high heat and mass transfer, high surface-to-volume ratio, temperature control, varying the composition of the NCs through continuous injection, efficient injection and mixing of precursors to achieve homogeneity, continuous production of NCs and low-reagent consumption emphasis are making this method as more efficient to prepare several kind of compound NCs [201, 202]. The typical experimental arrangement of a multichannel droplet reactor is given in Fig. 10 [203].

8 Challenges in Synthesizing Semiconductor NCs Using Hot-Injection Method

The discussion in this chapter clearly reveal about the promising results in achieving highly monodispersed semiconductor NCs through hot-injection method. Although this method has proved to be a potential approach in synthesizing semiconductor NCs under controlled conditions, there are few existing challenges could be seen. Since this synthetic approach is carried out in the presence of organic ligands, the possibility of oxidation is quite high and this hurdle the fabrication of NC layers for the long-term applications. The steric hindrance provided by these ligands is an another issue and due to this, the space between the ligands create voids on the NC surface, which act as the defect centres. This ultimately reduces the optical performance of the NCs and so the device performance is affected. Furthermore, these organic ligands may direct crack formation in NC films which deteriorate the device performance. Also, influence of such ligands on the different facets of NCs for the

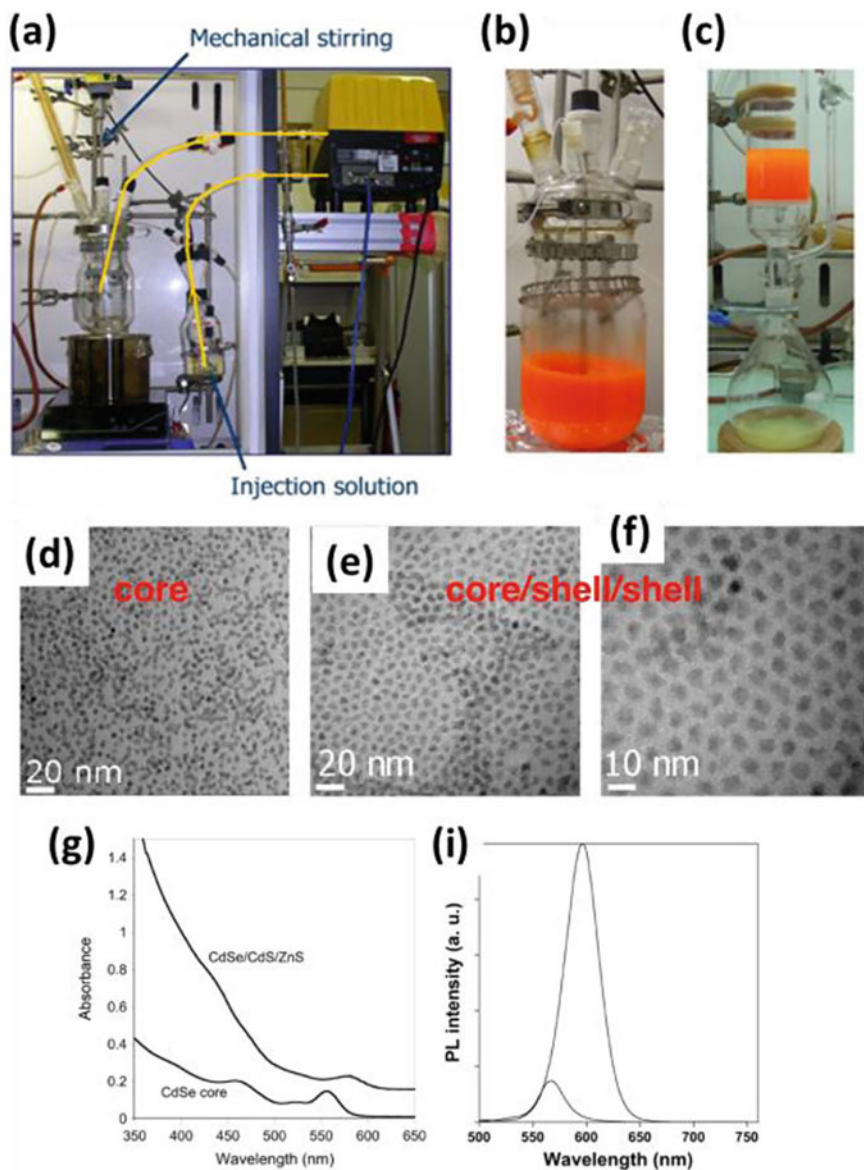


Fig. 9 a Experimental arrangement for the gram scale synthesis of CdSe NCs b appearance of CdSe/CdS/ZnS core/shell/shell NCs in the 2 L reactor c purification assembly of the prepared NCs and d–i corresponding morphological and optical analysis of the NCs. Reprinted from Ref. [193]

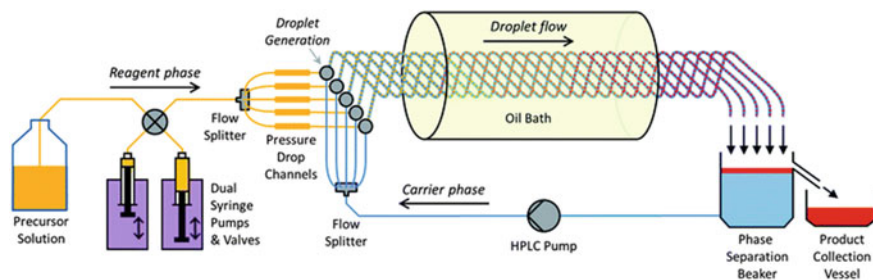


Fig. 10 Schematic diagram of the multichannel droplet reactor to synthesis semiconductor nanocrystals. Reprinted with permission from Ref. [203]

large scale preparation is not yet explored. Moreover, the reaction mechanism of semiconductor NCs of all classes is not well established and it should be discussed in order to understand critical concepts. Especially, the growth mechanism of halide perovskite NCs is still lacking and this may hamper their future generation optoelectronic device applications. Additionally, controlling the phase conversion in different kind of the chalcogenide NCs is still need to be much studied. The theoretical aspects of colloidal semiconductor NCs in accordance with experimental results are still lacking and considerable attention should be paid in this view. In the case of metal halide perovskite NCs, although hot-injection synthesis provides different morphologies, it is still challenge to prepare NCs with monodispersity. Besides, solubility of the selenide and telluride precursors in aqueous medium is challenging compared with the sulphide precursors and this limit the preparation of water soluble NCs in a large scale. The large scale synthesis of highly monodispersed NCs is another challenge and this still need further analysis. Preparation of large scale core/shell assembly is another challenging issue to achieve high quality, highly luminescent semiconductor NCs. Also, high volume purification of semiconductor NCs is appeared as critical in handling the wastes and also several cycles of purification are required to remove the excess ligands. This is challenging in terms of mass production but advancements in the synthetic protocols are expected to deliver a fruitful solution. Although heterostructures of semiconductor NCs are showing outstanding optical properties, it is challenging to understand the interface and it still prevents further progress in this area. Still, advanced characterization studies in colloidal semiconductor NCs are in their preliminary stage and future developments are expected to pave a way for the further improvement in this area.

9 Other Solution-Based Synthetic Approaches of Semiconductor NCs

Other than hot-injection method, semiconductor NCs could be prepared through hydrothermal, solvothermal, co-precipitation and sol–gel methods. Synthesizing NCs using all these methods under optimized conditions result in monodispersed NCs with different functionalities in the presence of organic ligands. In the case of hydrothermal and solvothermal methods, the reactions are carried out under the controlled atmosphere, normally at high pressure. In the case of solvothermal method, amine and polyols (ethylene glycol, glycerol, etc.)-based solvents are widely used to integrate the NCs assembly and to redisperse the NCs in different solvents. Several kind of morphologies are achieved through these methods and their applications for the energy devices are studied. In the case of sol–gel method, mostly semiconductor metal-oxides are studied especially titanium-di-oxide (TiO_2) and Zinc oxide (ZnO). Several research articles are dealing about the sol–gel synthesis of TiO_2 and ZnO NCs at room temperature for the photovoltaic and photocatalytic applications. Strategies such as sensitization of organic dyes and QDs and doping with transition elements are helping to expand the spectrum of these metal-oxide NC layer for PV applications. Similarly, co-precipitation method also helps us to achieve semiconductor NCs at room temperature. Oxide nanomaterials such as Fe_2O_3 , SnO_2 are mostly prepared using co-precipitation technique. Here, the precipitation of metal in the form of hydroxide takes place with the help of a base. This method is highly productive with high yield and hence applicable for the large scale production. However, challenges such as controlling the size, shape and crystallinity limit this method for other applications.

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Advances in Hybrid Energy and Power Density-based Supercapatteries



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Abstract The utilization of renewable resources can only be feasible to today's advance electronics when equipped with apt energy storage devices. The batteries and supercapacitors have captured the energy market, but the run for smart electronics still challenging. The issues like high energy storage capacity of electrodes, capacity retention, chemical and mechanical stability during long term cycling of charge/discharge have been limiting utilization of supercapacitors. While shortcomings in batteries are high cost, unsafe, leakage, low power density. To overcome these issues in batteries and supercapacitors are assembled in a single platform. In this context, researchers or industries are focusing on the advance the supercapatteries with high energy and power densities. Recently, a wide range of nanomaterials are explored for the application as electrode in hybrid energy storage devices due to their unique features. Such electrodes and electrolytes in supercapatteries will be discussed in this chapter. An extensive survey will be done to summarize on operational parameters for better electrochemical performances of the supercapatteries to be implemented in the consumer electronics.

Keywords Batteries · Supercapacitors · Supercapatteries · Electrodes · Electrolytes · Hybrid energy storage device

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1 Introduction

Over the decades, global energy scenario has been evolved gradually. However, in recent years energy demands has been increased due to high economic growth as well as expansion of energy intensive industrialization. Fossil fuel depletion is another major reason due to which is why meeting the energy demand became problematic; as a result, dependency on renewable energy sources is keep increasing day by day. Production of energy from such clean and effective energy sources is not the only point of concern but also developing and maintaining the storage system is required to continue the uninterrupted supply. Scientific communities from different part of the world are focusing on constructing high performance energy storage as it has enormous application scope in applications such as electric vehicles, laptops, tablets, mobiles phones, and various electronic devices. Utilization of electrochemical energy storage devices has shown promising outcomes existing electrochemical energy storage devices such as supercapacitors (SCs), batteries, and fuel cells that have shown remarkable effectiveness and reliability when integrated with renewable energy sources [1–3]. Researchers are putting efforts to improve the performance of these devices by modifying the designs and raw materials of the device. However, several drawbacks of these systems still remained. For example, batteries have demonstrated high specific energy densities, but they have failed to ensure adequate power densities and thermal stability. In addition, increased flammability, electrolyte, and electrode damage are other problems that have been raised. On the other hand, SCs are the devices which have shown high specific power, promising lifespans cycle, and swift charging and discharging rate capability-like benefits [4–6]. However, insufficient energy density is been observed in SCs which has restricted their utilization in different applications. So, to bridge the performance gap between SCs and batteries, a hybrid energy storage device named supercapattery is introduced.

Supercapatteries is a battery–supercapacitor (as shown in Fig. 1) hybrid device which is generally developed using a high energy density battery-type electrode as positive electrode and a high-power capacitive non-Faradaic (EDLC) electrode used as the negative electrode. The particular aim to construct the device is to study combinational effect of the non-capacitive and capacitive charge storage mechanisms in a single device. So, it can be easily inferred that to evaluate the performance of supercapattery, significant experimentation is required to study the activities of electrode materials [7–13]. Parameters such as economical synthesis, porosity, strong redox activity, number of electrochemically active sites, chemical and thermal stability, are the crucial ones to consider when employing particular electrodes in supercapattery devices. For instance, carbon-based materials, transition metal phosphates, phosphides, sulfides, oxides, hydroxides, and metal–organic frameworks, etc., are frequently utilized electrodes which we will elaborately discuss in upcoming sections of this chapter. Apart from electrode materials, electrolytes also have crucial role to study the supercapattery performance. The interaction of electrode and electrolyte in terms of charge movements has important impact on the device stability as well as on the resulted energy and power densities. Usage and electrochemical effect along

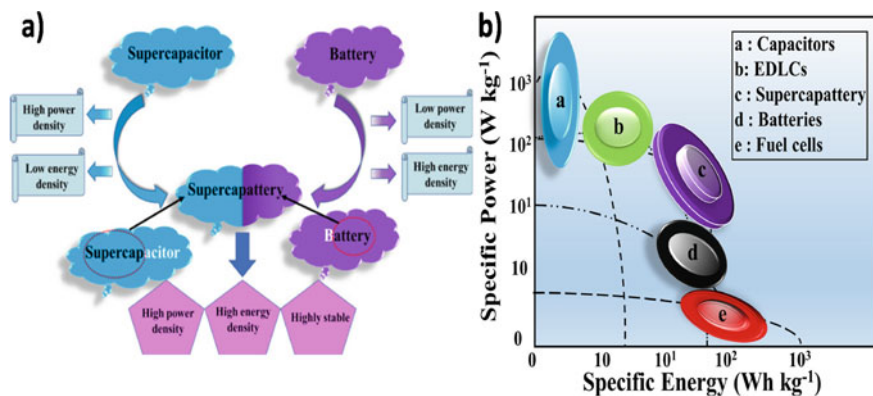


Fig. 1 a Merging of battery and supercapacitor technology, b Ragone plot demonstrating the comparison among different energy storing devices. Reproduced from Ref. [14]. Copyrights (Elsevier, 2022)

with stability of popular electrolytes like Na_2SO_4 , K_2SO_4 , KOH , etc., will also be included in the further discussion of this chapter. In this chapter, we will be focusing on the basic working of supercapattery and the electrode–electrolyte combinations suggested in different studies. Additionally, we will illustrate the device performances reported in literatures to briefly portray the current state of supercapattery research which will indeed be a useful approach for the upcoming researchers.

2 Electrodes in Supercapatteries

2.1 Methods and Materials of Electrodes in Supercapattery

2.1.1 Sonochemical Method

The sonochemical technique is a facile cost-effective process through which the synthesis of the high surface area nanostructures can be efficiently obtained. Using either volatile or non-volatile precursors, the synthesis of materials can be done using sonochemistry, through different mechanisms. In this technique, very high heat treatment can be avoided, to prevent declining of the surface area [15]. Basically, in this process, precursor materials are stroked by sound waves, and bubbles are formed due to the associated energy developed during the interaction between the sound wave and precursors in the reaction mixture. Because of the acoustic cavitation, these bubbles grow and break immediately. Variation in temperature and pressure is observed due to this formation and disintegration of the bubbles which eventually generates materials with enormously short-timed crystallization. It is important to understand that precursor materials gain kinetic energy in the reaction which leads

to interaction between reacting molecules, and hence, different morphologies with uniformly distributed nanostructures are formed depending on the intensities of sound waves.

Iqbal et al. employed the simple sonochemical technique to synthesize strontium phosphide [16]. Strontium carbonate and disodium hydrogen monophosphate were utilized in the study to prepare the material. In the strontium carbonate solution, disodium hydrogen monophosphate was added dropwise under continuous sonication along with the usage of distilled water. Afterward, at 25 °C for 1 h 30 min, the sonication process was properly maintained where the ultrasonic wave level was set at 30%. Finally, through centrifugation and multiple times distilled water washing, strontium phosphide was obtained and composited with polyaniline via physical blending, used as an electrode. In a few more studies, Iqbal et al. utilized an almost similar synthesis route with little modification to prepare the strontium phosphide and used it as a supercapattery electrode [17, 18]. Duraisamy et al. prepared anisotropic nano/micro rectangular shape $\text{Co}_3(\text{PO}_4)_2$ using sonochemical synthesis where disodium hydrogen phosphate anhydrous and cobalt (II) chloride hexahydrate was used as starting material [19]. However, in this study, the sonication amplitude was high comparatively (70%), and the reaction temperature was maintained between ~ 55 and 65 °C for four separate time periods of sonication (10, 60, 120, and 180 min). Sonicated samples for 10 and 60 min exhibited more irregular shapes compared to the samples sonicated for higher time periods (120 and 180 min). Similarly, the synthesis of supercapattery electrode materials like MoSe_2 nanosheets, manganese tungstate (MnWO_4) microflowers, etc., is done using sonochemical synthesis [20, 21].

2.1.2 Hydrothermal Method

Hydrothermal synthesis, a solution reaction-based technique, is one of the most frequently employed synthesis procedures. This technique has numerous benefits such as a wide range of operating temperatures and pressures, adequate yield (minimum loss of materials), stable operation, economical approach, etc. Due to its inexpensive nature and optimum production, this technique can be easily scaled up. Morphologies like nanotubes, nanorods, nanosheets, nanoparticles, hollow nanospheres, etc., have been achieved using this synthesis method [22]. Apart from the conventional hydrothermal, a combination of microwave, sol-gel, mechanochemical, electrochemical, etc., techniques individually with hydrothermal processing was found to be much faster, cleaner, and more precise to explore different morphology of diverse range of materials [23]. Recent studies have modified this method by altering different parameters to make the operational systems more efficient and obtain favorable outcomes.

Arunpandiyam et al. reported $\text{BiVO}_4/\text{FeVO}_4:r\text{GO}$ synthesized via hydrothermal method using $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as precursors which were allowed to stir for 30 min and then NH_4VO_3 , 1 g of urea, and 2 mL of polyethylene glycol were allowed to mix for 30 min under stirring. The resulting solution was transferred to an autoclave and reacted at 180 °C for 24 h the precipitate was

collected and washed with deionized water and dried overnight. Finally, the resulting powder was calcined at 500 °C for 4 h, the as-synthesized material was utilized as the cathode material for supercapacitor using redox active electrolyte as shown in Fig. 2a. The electrochemical performance showed a significant increase in energy density and power density (Fig. 2b). Sankar et al. synthesized carbon-coated cobalt ferrite (CoFe_2O_4) spherical nanoparticles by using cobalt chloride, iron(III) chloride-like precursors and using two-step hydrothermal approach [24]. Precursors mixed with distilled water and sodium hydroxide were autoclaved and kept for 12 h at 180 °C. Later it was washed with distilled water and ethanol and dried. Afterward, to form the carbon-coated form CoFe_2O_4 , a particular amount of glucose solution (CoFe_2O_4 to glucose ratio 2:1) was utilized to disperse CoFe_2O_4 and again autoclaved and kept for 12 h at 150 °C. Lastly, washed, dried, and carbonized for 180 min at 450 °C under an argon atmosphere to obtain the final product. Raghavendra et al. hydrothermally treated the mixture of starting materials such as cobalt (II) acetate, Thioacetamide, and Copper Chloride Dihydrate at 120 °C for 12 h to synthesize CuS/CoS [25]. Along with the starting materials, ultrasonicated Ni foam, Urea, and Acetic Acid were used which actually formed Ni foams deposited with CuS/CoS , and then the resultant was dehydrated, dried, and annealed for 180 min at 250 °C. Nano-petal or packed sheets-like morphology was observed in the formed CuS/CoS , and such electrode morphology is suitable to obtain high access to the electrolyte. Manikandan et al. [26] developed $\text{NiS}_2@\text{NiV}_2\text{S}_4$ nanoflakes (2D polycrystalline phase) using NH_4VO_3 and NiCl_2 at 180 °C for 16 h. Then, via centrifuging black precipitate was obtained, and it was dried at 70 °C for 12 h. To obtain the final composition, the dried substance was annealed at 400 °C for 180 min under an argon atmosphere. MXene became a popular material for energy storage in recent times. Liu et al. [27] carried out etching Al atomic layer of Ti_3AlC_2 to prepare MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) and then mixed nickel chloride, thiourea, and ammonia to synthesize MXene/ NiS composite through the hydrothermal method at 180 °C for 12 h. The composite was prepared with different NiCl_2 ratios (0.8, 0.4, and 1.1 mmol) where different morphologies were observed. The important feature to notice in the composite formed is that NiS did prevent MXene sheets from being stacked and collapsed which eventually acted favorably to achieve better electrochemical performance in the assembled supercapacitor device. Other than that, hydrothermal synthesis is also utilized for the synthesis of silver cobalt sulfide, nickel phosphide-polyaniline, and nickel silver sulfide (NiAg_2S) like binary composites which were utilized as supercapacitor electrodes [28–30].

2.1.3 Sol–Gel

Owing to the ability to produce unique characteristics and properties, the sol–gel technique is utilized to synthesize high-quality structures with wide size variations [31]. This bottom-up technique can be easily used to obtain narrow particle size distribution and pure structures. It has been seen that nanosized porosity can be achieved through this method by optimizing the drying conditions of the gel which finally resulted in a larger specific surface area. Basically, through several steps,

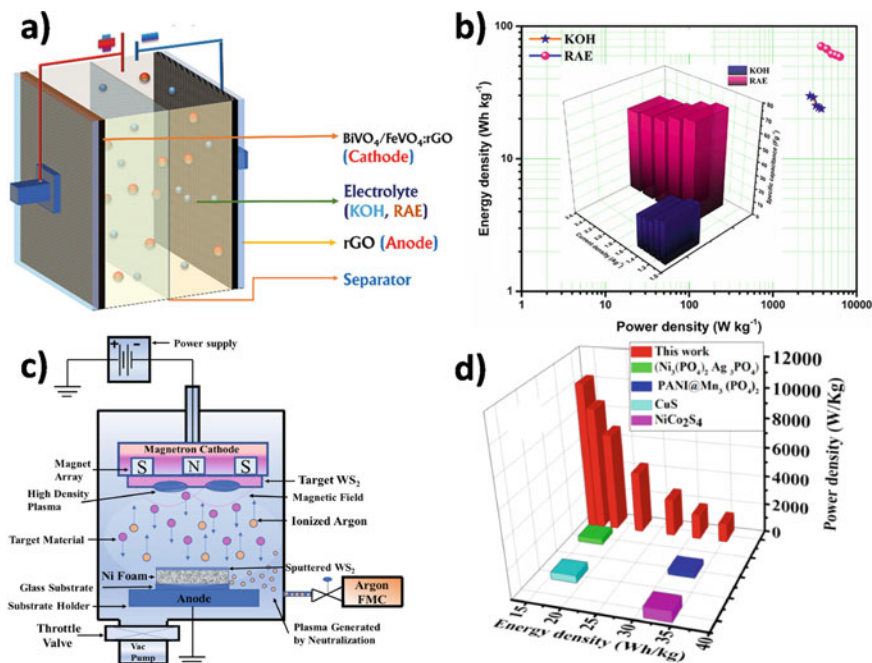


Fig. 2 **a** Schematic representation of the deposition of WS₂ via magnetron sputtering, **b** specific energy and power delivered via device compared previously reported work. Reproduced from Ref. [37, 38]. Copyrights (Elsevier, 2022) (ACS, 2022)

this technique can be used to form compounds/composites which are homogeneous solution preparation, sol formation, and gel formation. Additionally, this method is useful in preparing complex shapes, high-purity products, low-temperature synthesis, uniform compound formation, high reactivity, etc.

Ramasubbu et al., [32] reported Co-MOF (Co₃(BTC)₂ (BTC—1, 3, 5 benzenetricarboxylic acid)), Titanium(IV) isopropoxide to produce TiO₂ aerogel/Co-MOF composites. In short, glacial acetic acid was mixed with titanium (IV) isopropoxide and hydrolyzed, and the synthesized MOF was added which was then kept under stirring for a whole day. Afterward, the whole sol solution was gelatinized after being exposed to ammonia vapors for 30 min. The wet gel was immersed in DI water at 50 °C for 24 h. In the composite formation, the authors assumed that MOF particles may attach to the surface of TiO₂ aerogel matrix or it may occupy the aerogel pores. In another study, Elumalai and the group explored a modified sol–gel technique to synthesize nanostructured spinel cobalt oxide (Co₃O₄) [33]. In the preparation, cobalt nitrate was used as a major precursor and as a complexing agent cetyltrimethyl ammonium bromide (CTAB) surfactant was used. The solution was mixed with distilled water and urea was sonicated and kept stirring at 55 °C for 240 min until gel is formed and then dried it overnight. To obtain the final compound, the dried outcome from the oven was annealed in a muffle furnace at 350 °C in the air for 240 min. From the SEM,

it was revealed that the grains (of average size ~ 150 nm) are highly agglomerated with nearly spherical shapes. Similarly, sol-gel was utilized to produce CeNiO_3 , $\gamma\text{-KCoPO}_4$ nanocrystals, and different layered double hydroxides to enhance the supercapattery performances [34–36]. Alam et al. prepared WS_2 through a different approach of magnetron sputter coating as shown in Fig. 2c, through this method highly pure (99.99%) WS_2 was synthesized due to the high purity, the electrochemical performance was much high even when compared to bimetallic sulfides (Fig. 2d). Other than these wet chemical approaches, co-precipitation, soft template, sacrificial template routes, additive-free synthesis etc., are also utilized for the supercapattery electrode preparation. However mostly due to simple and inexpensive benefits, hydrothermal has been the most explored route.

2.2 Mechanism in Performance of Supercapatteries

The capacity of charge storage for an electrode is one of the most critical parameters to evaluate an electrode material over a potential window. Generally, this can be used to correlate the electrochemical performances of various device. The researchers in the field of energy storage are actively looking for new electro-active electrode materials for enhancing the charge storage ability of the device. The charge storage in the conventional capacitors is temporary polarization induced in the dielectric itself. In the EDLC, dielectric medium is replaced by the electrolyte which follows charge accumulation via electrostatic force. The use of electrolytes turns the supercapacitors by providing ion rich solution and improving conduction of both ions and electrons. The surface charge storing of the EDLC electrode is estimated in specific capacitance (C_f). The porous carbon-based materials are usually used as EDLC electrode materials, providing channel for an uneven surface distribution of ions and enlarges the surface area. Thus, the porosity aids physical absorption process at electrode/electrolyte interfaces. The chemical adsorption, predominantly a Faradic reaction takes in charge transfer between the active electrode materials and ions depending on the potentials. Even carbon-based materials in the form of sheets (graphene, reduced graphene oxide), nanotubes (multiwalled/single walled carbon nanotube), amorphous (carbon aerogel, carbon sponge) etc., are also explored. The most striking work is recycling wastes to carbon-based materials and developing high yield devices. Unlike the EDLC materials, the charge storage for pseudocapacitors with redox peaks and battery-type electrode are analyzed in terms of specific capacity (C_s). The intrinsic energy storage for electrode is usually standardized by mass (gravimetric capacitance), area (areal capacitance), or volume (volumetric capacitance). It has been perceived that the charge storage is highly affected by electrode material loading on current collector, thickness of active material, dimension of the device, nature of electrolyte used. The chemical absorption in a pseudocapacitor differs from the redox reaction of the battery-type electrode in degree of intercalation and activation energy of electrode material. The slow interaction in battery-type material stores higher energy than a fast intercalation process. The valuation of specific capacity of

the electrodes benefits in choosing a proper electrode material for impeccable hybrid energy storage devices.

3 Various Designed Supercapatteries

Fascinatingly, the supercapatteries can be designed as per the necessities to power consumer electronics. The devices can be of various forms such as working electrodes, current collectors, and separators. To realize the scaling feasibility for fabrication of hybrid device in certain aspects such as cost, size, electrochemical performance and eco friendliness, the following approaches are being in the market.

3.1 Compact/Non-stretchable Devices

Owing to the provisions of energy storage devices in compact electronics, there is a quest for non-stretchable, solid and eco-friendly power sources engineered in a cost-effective manner. The flexible device fabrication is mainly altered by quality of current collector (solid and mechanically strong such as stainless steel or carbon rod), attachment of electrode materials to the current collector by deposition or coating, and separator with electrolyte between two electrodes. There is a scope to design various types of compact devices such as flat, cylindrical or box configuration, among others. Certain challenges the compact devices have to face are corrosion/reaction of current collector with electrolyte, leakage of electrolytes, and limit of size to power output ratio, packaging of device components, issues to overcome.

3.2 Flexible/Stretchable Devices

The flexible/stretchable devices appear as a solution for the aforementioned issues; moreover they fit into the wearable electronics. It allows for flexible, lightweight, stretchable, and eco-friendly power sources engineered in a cost-effective manner. The flexible device fabrication is mainly altered by flexible current collector such as carbon cloth or thin films and separator with few drops of electrolyte or gel electrolyte between two electrodes. There is a scope to design various types of flexible devices such as paper-like configuration, porous-/sponge-like configuration, and textile-like configuration.

Among the battery-type electrodes involving intercalation/deintercalation mechanism, metal oxides have been widely explored not only because of the intrinsic properties of it but also due to the less cost of transition metals and simple synthesis method. Direct growth of iron oxide on graphene sheets was reported by Qu et al. which provides the composite with highly active sites. Compared to other metal

oxides, Fe_3O_4 possesses high negative potential which makes it suitable for using as anode material for supercapacitors and combined with the graphene which possess high surface area and conductivity, the composite exhibits excellent electrochemical performance. The calculated energy density based on the weight of the cathode and anode was 31 W h kg^{-1} (assuming 50% of the total weight might account for the electrodes) which is higher when compared to any commercial EDLC or lead acid batteries and Ni-MH battery [39].

Chang et al. proposed an asymmetric supercapacitor with two different materials with high and low work function as positive and negative electrodes. Since MnO_2 has the high work function, it is chosen as positive electrode and MoO_3 with lower work function as negative electrode this extends the operating potential window up to 1.9 V. The asymmetric supercapacitor shows a high energy density of 42.6 W h kg^{-1} at a power density of 276 W kg^{-1} which is higher than any other asymmetric supercapacitors reported. Also the device exhibited good electrochemical performance even at higher current density [40]. Following the work of Qu et al. [39], Guan et al. reported a similar work with Fe_2O_3 decorated on carbon nanotube framework (CNT) supported on graphite foam (GF). The three electrode tests performed shows pseudocapacitive behavior. With a areal capacitance of 470.5 mF cm^{-2} which is higher than the GF-CNT, this is also due to the coating of Fe_2O_3 by atomic layer deposition method (ALD). The full cell was assembled using GF-CNT@ Fe_2O_3 //GF- CoMoO_4 which exhibits an energy density of 74.7 W h kg^{-1} at a power density of 1.4 kW kg^{-1} with a very high cycling stability of 95.4% retention after 50,000 cycles at a high current density of 7 A g^{-1} [41].

Even though single metal oxide provides good performance, there are some disadvantages for each metal, to overcome this bimetallic oxides were reported by combining two metal oxides and gaining a new property through synergistic effect. Vijayakumar et al. reported a spinel-type CuCo_2O_4 supported on Ni foam synthesized through facile hydrothermal approach. The as-synthesized sample exhibited flower-like morphology which enhanced the specific capacity up to 645 C g^{-1} . Also the initial capacity retention was about 109% after 2000 cycles. Due to these properties, this material might be a suitable candidate for positive electrode in supercapacitors [42]. Further to enhance the synergetic effect, Huang et al. reported a ternary metal oxide $\text{Ni}_x\text{Co}_y\text{Mo}_z\text{O}$ with the ratio of 1:2:2 synthesized through hydrothermal method and the material exhibits high areal capacitance of 2.94 F cm^{-2} also a hybrid device was assembled using the as-prepared material as positive electrode an activated carbon as negative electrode. The device shows a wider potential window of 1.8 V with high energy density of $22.02 \text{ W h kg}^{-1}$ at a power density of 3.50 W kg^{-1} [43]. Following this work, the group also reported a quaternary metal oxide using metal as Ni, Co, Mo, and Cu. The as-prepared material exhibited high capacity of $0.78 \text{ mA h cm}^{-2}$ and the assembled hybrid device showed a maximum energy density of 4.60 W h kg^{-1} at a power density of 0.21 kW kg^{-1} [44].

Since the conductivity of metal oxides are less, materials with better conductivity was needed. Pawar et al. reported a mixed metal sulfide with $\text{Cu}_2\text{S-Ag}_2\text{S}$ synthesized through successive ionic layer adsorption and reaction technique (SILAR). The as-prepared electrode exhibited high specific capacity of 772 C g^{-1} and good

electrochemical stability of 89% capacity retention after 2000 cycles. The assembled device exhibited good specific energy of $0.241 \text{ kW h kg}^{-1}$ at a specific power of 5.357 kW kg^{-1} [45]. Wang et al. reported Ni_3S_4 synthesized through simple two-step hydrothermal technique the compound had a spinel structure with rose-like morphology. The three electrode cell showed a high specific capacitance of 1797.5 F g^{-1} with 22.66% of the performance attributing to the capacitive behavior. A hybrid device was assembled using the electrodes as $\text{Ni}_3\text{S}_4//\text{AC}$ which shows high energy density of $18.625 \text{ W h kg}^{-1}$ at a power density of 1500.2 W kg^{-1} also the device maintained high retention of 93% over 5000 cycles [46].

Liu et al. reported different metal sulfides coated on NiCo_2S_4 in a core-shell morphology. The metal sulfides being Co, Cu, Ni, and Mo were grown in situ on carbon cloth. Among them $\text{Co}_9\text{S}_8\text{-NiCo}_2\text{S}_4$ shows better energy storage capabilities with high specific capacity of $337.78 \text{ mA h g}^{-1}$ among which 27.4% is contributed to the capacitive behavior as shown in Fig. 3a. Subsequently, a flexible solid state hybrid supercapacitor was assembled for the same material using gel electrolyte as shown in Fig. 3b which exhibits a high specific energy of $56.44 \text{ W h kg}^{-1}$ and high specific power of 8153 W kg^{-1} [47]. To further increase the active sites by incorporating heterostructured material, NiCoP@CoS the performance was increased, Xu et al. reported this 3D tree-like core shell nanoarrays grown on nickel foam which exhibited high specific capacitance of 1796 F g^{-1} with an exceptionally high stability of 91.4% after 5000 cycles at higher current density of 10 A g^{-1} . Further, the assembled asymmetric supercapacitor with activated carbon as negative electrode achieved high energy density of 35.8 W h kg^{-1} at a power density of 748.9 W kg^{-1} [49].

Since the chalcogenides showed excellent electrical conductivity theoretically, the focus of research toward chalcogenides increased. Ye et al. reported a mixed phase of NiSe and ZnSe . This hybrid structure was prepared by coelectrodeposition method on nickel foam making it binder free electrode. The electrode exhibited high specific capacity of $651.5 \text{ mA h g}^{-1}$ at 1 A g^{-1} and the capacity dropped quickly with increase in current density as shown in Fig. 3c, d. The asymmetric device was assembled using the active material as positive electrode and activated carbon as negative electrode. The device delivered a high energy density of 44.4 W h kg^{-1} at a power density of 800 W kg^{-1} which is high compared with previous literature (Fig. 3e) [48]. Further, Zardkhoshoui et al. reported CuCo selenide synthesized via a simple hydrothermal method. The as-prepared material showed a hollow sphere-like morphology which showed a high capacitance of 1775.4 F g^{-1} which is higher than the CuCo oxide. The material was further used as positive electrode for hybrid supercapacitor with negative electrode as activated carbon which delivers a high energy and power density of $53.86 \text{ W h kg}^{-1}$ and 800 W kg^{-1} [50].

Even though electrode material plays a critical role in determining the specific capacitance and stability, some other factors like ionic conductivity, potential window also relies on the electrolyte being used. Zhang et al. reported a hybrid supercapacitor with a high energy density by different approaches like optimizing the electrodes as well as adding a redox mediator in the electrolyte to provide more capacity. $\text{K}_3\text{Fe}(\text{CN})_6$ was added in neutral aqueous Na_2SO_4 electrolyte. The device exhibited high energy density of 62.9 W h kg^{-1} at a power density of 984 W kg^{-1} . The device

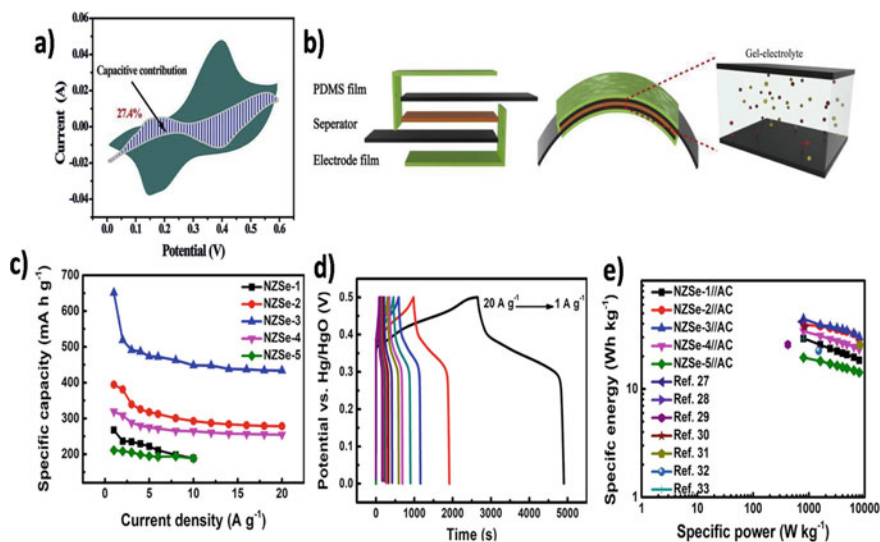


Fig. 3 **a** CV curves with the capacitive fraction shown by the shade region, **b** schematic diagrams of the hybrid supercapacitor based on the $\text{Co}_9\text{S}_8@\text{NiCo}_2\text{S}_4/\text{activate carbon (AC)}$ electrodes and PDMS films, **c** specific capacity of the NZSe hybrid electrode with various Ni/Zn ratios, **d** GCD curves of the NZSe-3 hybrid electrode, **e** comparison of Ragone plots with literature. Reproduced from Ref. [47, 48]. Copyrights (ACS, 2020) (Elsevier, 2020)

exhibited high cycling stability of 96.8% retention after 10,000 cycles with a wider potential window of 2.4 V [51].

Wong et al. reported ionic liquid-based electrolyte using EMIMBF₄/AN, the ionic conductivity decreased with the increase in the concentration. The assembled EDLC device showed high energy density 74.2 W h kg⁻¹ and a maximum power density of 17.5 kW kg⁻¹. Wu et al. reported EMIMBF₄ electrolyte using high porous carbon which shows high energy density of 107 W h kg⁻¹ at a power density of 94 W kg⁻¹ also an all solid state symmetric supercapacitor shows high specific capacitance for 180 F g⁻¹ using EMIMBF₄/PVDF-HFP gel polymer electrolyte. Huang et al. reported a self-healable hydrogel electrolyte suitable for flexible high energy density supercapacitor. The ionic conductive hydrogel used was SPMA-Zn:ZnSO₄/sodium alginate/polymethyl-acrylic acid which shows a working voltage of 0–2.2 V with high energy density of 164.13 W h kg⁻¹ with a power density of 1283.44 W h kg⁻¹ with a good cyclic stability of 95.3% retention after 5000 cycles at high current density of 10 A g⁻¹ [52]. Sandhiya et al. reported Na₂MoO₄ incorporated gel polymer electrolyte which shows higher capacitance of 714 F g⁻¹ which is 2.4 times higher than the normal electrolyte using H₂SO₄ the symmetric supercapacitor device exhibited high energy density of 23 W h kg⁻¹ [53]. Han et al. reported zwitterionic natural polymer hydrogel electrolyte for zinc ion hybrid supercapacitor which shows a wider potential window of 2.4 V with high energy density of 286.6 W h kg⁻¹ at a power density of 220 W kg⁻¹ [54]. Yang et al. reported a flexible quasi solid state zinc

ion hybrid supercapacitor using poly(vinyl alcohol)/montmorillonite/ $\text{Zn}(\text{ClO}_4)_2$ gel electrolyte which operates at wider temperature ranges from -50 to 80 °C and also it delivers a ultrahigh energy density of $190.3 \text{ W h kg}^{-1}$ at a power density of 89.8 W kg^{-1} [55]. Park et al. reported a water in salt electrolyte with redox active mediators which widens the potential window up to 3 V also the device reached a maximum energy density of 36.7 W h kg^{-1} and a maximum power density of 26.5 kW kg^{-1} [56].

4 Challenges in Supercapatteries

Despite of a series of progress made in supercapacitors since the nineteenth century, it has been challenging task to provide a unfailing application for the advance technology for energy storage devices [57–60]. Looking into past records of supercapacitor developments and its practical usage, in 1957 the first electrochemical capacitor was developed by General Electric's H. I. Becker and then by Robert A. Rightmire came with new technology patented by a Japanese company Nippon Electric Company (NEC). In 1975 NEC first commercialized the electrochemical capacitors in market. PSCap (9 in., 2 feet, 200 V, energy up to 45 kJ) was started for diesel locomotives engines in mid of 1990s. Later, Panasonic designed many models such as Goldcap for solar-based wristwatch, spirally wound capacitor UpCap (2000 F, 2.3 V) for hybrid electric vehicles. In current era, the market ecosystem consisting Maxwell, Tecate, CA-XX, ELNA Co. LTD., and Murata are seriously involved in developing the hybrid energy storage devices for automotive industry, rail system, grid units, emergency door-openings, spacecraft, wearable technologies, etc. Even the supercapacitors are engineered in combination with fuel cells and LiBs which afford the peak power and reduced an energy pressure on fuel cell or LiBs. The graphene-based lightweight supercapacitors (specific capacitance of $150\text{--}550 \text{ F/g}$) were designed for rapid charging/discharging in a wearable electronics. Concurrently, the cost of production per farad of supercapacitors was dragging its usage in small electronics. But in current survey, it is found that the cost has been drastically reduced, i.e., 3 kF ultracapacitor (\$5000/10 years ago) is now fixed at only \$50. By 2022, the supercapacitor market is projected to USD 2.18 billion, at a compound annual growth rate (CAGR). It is also reported that the hybrid capacitors are estimated to develop with highest CAGR during forecast period. The growth toward low-cost, low resistance, high voltage, and capacity deemed possible supercapacitors for applications in various sectors, but penetrating to a wide range of today's industrial domains is quite difficult. The market demands a solution for abating energy and power density and an evident charge storage. The manufactures are struggling in voltage management with stacking of device prototypes, apropos durability of the device, hasty self-discharge rates, and power implementation with the size of device. In fact, tangible issues arise when transfer from laboratory to the industry level productions, i.e., development of supercapacitors system sizing (stack in parallel or series) the device to add up current or voltage. A voltage drop due to resistance is often overlooked that consequence in

low performance of the device. It is noteworthy that high operating potential window of hybrid energy storage device reduces the cost as well as boosts the outcome for various applications. Further, intrinsic technology of hybrid energy storage devices demands hybrid electrode with high surface area, metal oxides with high storage capacity, long cyclability, and fast current response to meet the goal. The powering in short-long term devices can only be come by combined contribution of appropriate electrode, electrolyte, and separator usage. The potential electrode materials can be one of feasibilities to achieve the benchmark of 100% sustainable energy. The major advantage of fabricating NiO-based device is easy tuning of its properties and high storage ability as aforementioned. In various researches, it has been revealed that the NiO-based devices delivered a high energy and power densities with reliable stability and safety in handling for commercial electronics.

5 Summary

Supercapatteries are promising hybrid energy storage devices which have great potential for large-scale applications. This combinational assembly of battery and supercapacitor can deliver adequate level of energy and power densities which is comparably high than the individual electrochemical devices (batteries and SCs). In this chapter, we discussed about different electrode materials and their versatile characteristics such as electrical conductivity, excellent surface area, short ion/electron diffusion length, porous structure. These properties greatly impacted the fabricated supercapattery devices. Especially, employing nanostructured carbon materials and metal oxides have shown great electrochemical activities for such devices. In addition, we have also discussed about several electrolytes utilized for supercapatteries. Better redox activity of such electrolytes can favor the electrodes to achieve higher performances. That is why equal importance must be provided for selecting both the electrodes and electrolytes to create an efficient and compatible system. In the previous sections we have mentioned the complete mechanism involved in supercapattery to illustrate the role of both electrodes and electrolytes. With examples of different recent studies and pinpointing their energy and power capacities, a clear picture of the ongoing research approaches was portrayed. Although, this technology has been enhanced over the past few years, still creative strategies are required to develop, to make this system eco-friendlier, cost efficient and achieve better performance, so that we can implement such technology in commercial scale. Additionally, large-scale development of supercapatteries using existing equipment for commercial supercapacitors and batteries is another idea which might be possible and more consideration needs to be given upon that.

6 Future Scope

With the combination of high-power non-Faradaic electrodes and hybridization of high energy Faradaic electrodes, supercapatteries are generally developed which have shown an excellent balanced output of power density as well as energy density. So, the role of electrode in supercapattery is one of the major factors required to be consider, as further modifying its structure and properties will be useful to get efficient and stable device performances. In recent years, nanoscale electrode materials are frequently recommended by researchers as using such materials exhibits excellent surface area, porosity, and diffusion length for electrolyte ions get shorter. Additionally, several nanoscale materials have demonstrated great conductivity which in turns proven favorable to achieve great electrochemical activity. Thus, utilizing efficient and cost-effective synthesis and application of nanoscale materials can enhance the performance of supercapatteries. Carbon-based materials can be an efficient choice as electrodes. Significant electrochemical performance improvement can be obtained using hybridization of nanostructured carbon materials with redox-based electrodes. So, investigating different hybrid/composite materials in the device will be efficacious. Exploring waste biomass materials for producing carbon or other promising materials is another attractive aspect which can be used for supercapattery electrodes. Already there are several studies which used biomass feedstocks like, plant/animal residues and even functionalized the derived materials for favorable applications in battery and SCs electrodes. Apart from electrodes, to enhance the electrochemical performance of supercapatteries, choice of electrolytes has a great influence. Excellent ionic conductivity of electrolytes can lead to stable activity, higher energy and power densities under relatively higher humid environment and under broad operating temperature range (from -40 to 85 °C) [2, 10]. Novel choices like water-in-salt, hydrate-melt electrolytes can be used in supercapatteries which could result in safer workability of device as well as excellent operating potential. So, it is important to consider every part of supercapatteries as appropriate device arrangement will be useful in developing flexible, lightweight, and cost-efficient device which can impact the future electronics devices and also larger applications such as EVs.

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The World of Green Nanomaterials and Their Development



Tamer A. Sebaey and Tabrej Khan

Abstract Nanotechnology is a highly versatile and innovative scientific field that has vast applications in various domains such as medicine, electronics, and modern manufacturing. It holds tremendous potential to revolutionize our lives, society, and the global economy. However, most of the materials and techniques currently used in this technology are nonrenewable and generate harmful waste. To address these challenges, green chemistry and green technology approaches can significantly influence the future development of nanotechnology. Several researchers have extensively explored the use of natural materials, nanoparticles, and the development of naturally harmless synthetic processes. While many green nanomaterials are already in use, from laboratory to commercial scales, they still face significant challenges. The pressing demands of today's world call for the development of sustainable and eco-friendly practices in green chemistry, green nanotechnology, and green engineering. This chapter delves into the recent advancements and challenges in the application of green nanomaterials. It emphasizes the concept of sustainability science and how it intersects with green nanotechnology and green nanomaterial applications. The authors' well-researched efforts are sure to open up new avenues of knowledge in the fields of green nanomaterials, nanoscience, nanotechnology, and green chemistry over the next few decades.

Keywords Green nanotechnology · Nanomaterial · Sustainability · Engineering · Chemistry · Vision

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1 Introduction

Green nanotechnology and organic chemistry are poised for a new era of scientific innovation and progress. As climate change, global warming, and dwindling fossil fuel reserves present significant challenges to environmental and petroleum engineering, novel approaches are required. Unfortunately, the technology currently available offers limited solutions to the complex scientific issues associated with heavy metal toxicity in drinking water, which affects people in both developed and developing nations worldwide. Therefore, environmentally friendly chemicals, green nanotechnology, and environmental nanomaterials are increasingly crucial [1]. At this crucial juncture in history, the fields of nanotechnology, green chemistry, and green engineering have immense potential to address global scientific challenges. As science and technology continue to progress, it is imperative that we rise to meet these challenges. Currently, nanotechnology and green engineering are often viewed as opposing forces. However, it is becoming increasingly clear that they can work hand in hand to create sustainable solutions. One such pressing concern is environmental remediation, which has garnered significant attention in the scientific community. As we face the devastating consequences of environmental degradation, it is essential to leverage the power of nanotechnology and green engineering to develop effective and sustainable strategies for remediation. By embracing the synergies between nanotechnology, green chemistry, and green engineering, we can tackle significant global challenges and create a better future for all [2]. The tremendous scientific determination, passion, and understanding of human needs, coupled with the potential of nanotechnology, will play a crucial role in advancing science and technology globally. This article aims to define scientific innovation in the areas of nanotechnology, green nanomaterials, and green chemistry. Additionally, the author emphasizes the significance of comprehending water and wastewater treatment, as well as other aspects of industrial pollution control. As civilization continues to evolve and grow, it is vital to leverage the latest scientific advancements and technologies to improve our quality of life sustainably. The fields of nanotechnology, green nanomaterials, and green chemistry hold immense potential to contribute to this goal. However, it is equally critical to address the pressing concerns surrounding water and wastewater treatment and the broader issue of industrial pollution control [3].

This volume highlights recent breakthroughs in nanotechnology, environmental nanomaterials, and eco-friendly chemistry, aimed at expanding the boundaries of science and technology, in contrast to idealistic approaches that are being overtaken by the rapid pace of scientific progress [4]. Science and engineering are at a critical juncture, where innovation, vision, and scientific divination intersect. Nanotechnology and green engineering offer promising solutions to complex scientific challenges, including global warming, environmental engineering, and petroleum engineering obstacles [5]. The main goal of this section is to pave the way for future breakthroughs in green nanotechnology, as well as explore topics such as heavy metal poisoning and environmental sustainability. However, global warming poses

a serious threat to scientific progress and human civilization. Environmental disasters, such as arsenic-contaminated drinking water in developing and industrialized nations, continue to occur worldwide. Material science is a remarkable achievement of modern civilization [6].

As a result, there is a critical need for global research initiatives in water technology and green nanotechnology, as well as a long-term plan for deploying green nanomaterials. Engineering and science are being pushed to their limits by nanotechnology, space technology, and nuclear technology [7]. Environmental and energy sustainability are critical as society advances [8]. The author highlights the significance of the field of nanotechnology environmental engineering and science, and alternative energy technology in the true resolution of science and technology research challenges in this chapter. This chapter is a call to action for the coming generations of engineers, scientists, and citizens [9].

2 Green Nanomaterial Sources

With science and engineering advancing into a new era, the importance of utilizing green nanomaterials and green nanotechnology cannot be overstated. Human civilization's vastness, ingenuity, and futuristic vision of material science will lead to true scientific liberation. Currently, green nanomaterials are undergoing significant engineering research and development [2]. The challenges of green nanotechnology, green nanomaterials, and the future of nanoscience herald a new era in science and engineering. Green nanoparticles may be obtained from a number of different sources. Natural sources such as plant extracts, biopolymers, vitamins, proteins, peptides (e.g., glutathione), and sugars (e.g., glucose, fructose) can serve as reducing agents for green nanoparticles. Among these, plant derivatives have received the most attention [10]. A significant scientific breakthrough has been the use of plant extracts, biopolymers, and other natural substances as reducing agents to produce metal nanoparticles. These nanoparticles have a range of applications in electronics and medicine, including medication and gene transfer. Biopolymers, which are polymeric carbohydrate molecules, have already been used in various applications and are ideal for large-scale nanoparticle production [11].

3 A Green Nanomaterial

Let us take an example of nanocellulose, a nanostructured cellulose, is a promising material for various applications, with cellulose nanofibers, microfibrillated cellulose, nanocrystalline cellulose, and bacterial nanocellulose being the primary types. Enzymatic treatment during its production is a rapidly developing area of study and technology. The unique properties of nanocellulose make it a valuable material with the potential to contribute to a thriving industry [12] (Fig. 1).

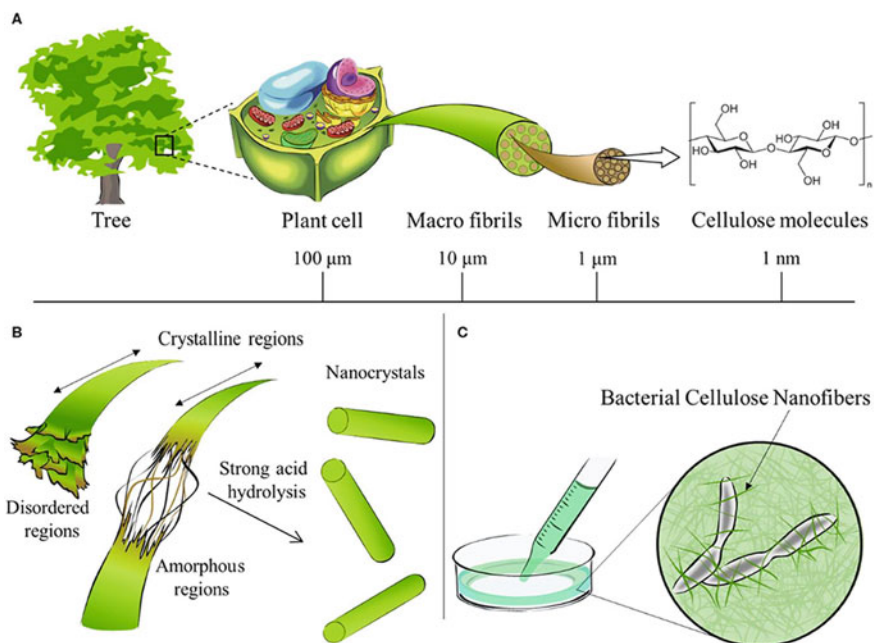


Fig. 1 Cellulose contained in plants or trees has a hierarchical structure from the meter to the nanometer scale, as shown in (a). A schematic diagram of the reaction between cellulose and strong acid to obtain nanocellulose is shown in (b). Bionanocellulose cultured from cellulose-synthesizing bacteria is shown in (c) [13]

4 Green Nanomaterial Processing Systems

Green engineering, green chemistry, and green nanotechnology are urgently needed as environmental processing systems undergo extensive renovation. With the world facing the consequences of global warming and the depletion of fossil fuel sources, science and technology must rise to the challenge of these massive scientific disasters [14]. To meet critical demands such as freshwater purification, water consumption, subsurface treatment, and integrated water resource management, the scientific community requires visionary and ingenious solutions. Green chemistry and nanotechnology are two emerging fields that offer potential solutions. Green nanotechnology encompasses both green chemistry and green engineering, and it aims to predict and maintain sustainability in the environment, particularly through nanoscience and nanotechnology [8]. The chemical industry plays a crucial role in the global economy and anticipates advancements in science for new materials, renewable energy, environmental protection, and energy-efficient processes. Green chemistry is at the forefront of this movement, offering environmentally friendly products, life-saving drugs, sustainable agricultural chemicals, renewable energy solutions, efficient chemical engineering, and innovative materials [6]. Scientists

and engineers have recognized that sustainable management of natural resources is crucial to meet future development and economic needs, driven by humanity's rapid and innovative accomplishments in the twentieth and twenty-first centuries [15]. Green processing methods are revolutionizing the course of scientific advancement, particularly in the field of green chemistry. The importance of green nanotechnology in global scientific development is emphasized in this chapter. The authors highlight the significance of green process engineering and systems, which will pave the way for new scientific advancements and the realization of environmentally sustainable chemistry and nanotechnology [16].

5 Green Nanomaterials and Green Nanotechnology

Nanotechnology that is environmentally friendly and environmental nanomaterials are the scientific and technical marvels of the day. Significant scientific breakthroughs are taking place in the fields of nanotechnology, green engineering, and green chemistry. In this section, the authors elaborate on the scientific and technological accomplishments in the fields of green nanotechnologies, green nanoengineering, and green nanomaterials, with the single goal of advancing and liberating the fields of science, technology, and engineering [2]. The use of green chemistry with nanotechnology catalysts has been thoroughly investigated. Nanomaterials are substances that are expected to be a viable topic for green chemical catalysis due to their ability to be engineered at the nanoscale. Nanocatalysts are highly prized materials because of their increased surface area and catalytic capabilities. Because of their enhanced activity, greater stability, durability, recycling potential, and cost-effectiveness, tiny catalysts are being promoted as novel and unique procedure options [17]. Chemical catalysis and reaction engineering are being revitalized. These innovative catalysts might be employed in renewable energy applications such as hydrogen synthesis, hydrogen storage, and fuel cell applications. Plastic cycle conversion technology, biofuels for transportation, reaction kinetics in the pharmaceutical industry, the future of green chemistry, the relevance of the green innovation index, and stratospheric chemistry technologies are all discussed by the author [18]. In this study, the author also emphasized the present quantity of publications in the disciplines of the field of nanotechnology, including nanomaterials, nanoenergy, and green chemistry. Green nanoparticles and their environmental friendliness as a biotherapeutic therapy, nanomaterials technology, and engineering are all rapidly evolving, leapfrogging one novel boundary after another.

As nanotechnology progresses into new sectors and opens up additional scientific doors in the next few years, technology, engineering, and science are being institutionalized and envisioned. In exchange for making nanomanufacturing processes less energy- and resource-intensive, the basic principles of green chemistry applied to nanoscience and nanotechnology require, if at all feasible, the use of renewable energy sources. (a) the use of cost-effective precursors, (b) the minimization of carcinogenic reagents and solvents, (c) the reduction of experiments that are highly

risky, (d) the use of a small number of reagents, (e) the minimization of reaction steps that lead to waste [19]. Green nanotechnology and therapies, green nanomaterials in therapeutic usage, therapeutic nanoparticle platforms, inorganic nanoparticles, and the broad field of green nanoparticles were all thoroughly covered by the writers. The world of nanoparticle technology and engineering will be completely reimagined as the use of nanoparticles in biological sciences, medical science, and biomedical engineering expands into new knowledge dimensions. The European Commission Report (2009) went into great length on the problems, prospects, and goals of green nanotechnology applications. This study deliberates and discusses in minute detail a critical assessment of possibilities and hazards. Materials created using nanotechnologies are beginning to be used and reimagined in many sectors of human life (cosmetics, textiles, fabrics, paints, packaging, meals, and so on) [20]. Mankind's vast intellectual capacity, tenacity, and determination will all pave the way for the true freedom of nanotechnology today. Nanotechnology, biological sciences, and biotechnology are all linked these days. Many supporters of nanoscale research believe that as its uses expand, this industry will become greener and more sustainable. Environmental science and technology, as well as energy sustainability, are at the peak of scientific investigation right now. Nanotechnology and sustainability are intricately intertwined nowadays. At this important juncture of vision and innovation, civic society must gather knowledge on many aspects of rising nanotechnology growth and development, notably green engineering, and environmentally friendly technology [21]. The accomplishments of environmentally friendly science, the rigorous academia of nanotechnology, and the needs of human society are true forerunners toward a new visionary age in technology and engineering (European Commission Report 2009). The following topics are carefully outlined by the authors of this study: Green nanotechnology application challenges, goals, and possibilities.

- (i) Environmental, health, and safety studies, as well as hazardous waste management.
- (ii) Regulatory status (European Commission Report 2009).
- (iii) NGO guidelines on sustainability assessment of nanotechnologies.

The writers of this work thoroughly investigated the vision of nanotechnology applications in the ever-expanding accomplishments of science and engineering. Today's scientific wonders include nanotechnology and nanoengineering. The authors of this paper looked at water purification, renewable energy generation, waste management, and environmental rehabilitation [22]. The use of nanotechnologies and materials, as well as their implications on biodiversity, ecosystems, and human health, were also considered in this research (European Commission Report 2009). This study also investigates regulatory regimes and options for guaranteeing the safe and responsible future of nanotechnologies, with an emphasis on green nanotechnologies. The environmental and health effects of nanomaterials are fundamental pillars of this well-researched work (European Commission Report 2009). The twenty-first century's environmental concerns are broad and varied. Climate change, overdependence on fossil fuel supply, excessive harvesting of resources that are renewable, and the consequences of Western economies are the most pressing

environmental engineering challenges today. Similarly, as science moves toward a new scientific period and a new knowledge dimension, two fields are being extensively emphasized: chemical technology and petroleum engineering. (2009 European Commission Report) [23]. Nanotechnology is the next revolution in technology. This study's authors comprehensively discuss the success, originality, and scientific feasibility of nanotechnology applications to human civilization. With scientific foresight, the green synthesis of gold nanoparticles was carefully investigated. The green manufacturing of gold nanoparticles using plant extracts is one of the viable ways for developing environmentally friendly nanomaterials for biological applications and environmental protection applications. The chemistry of natural products is a modern scientific marvel [24]. This study used a hydrothermal approach to create proanthocyanidins, which are functionalized gold nanoparticles. The gold nanoparticles that were generated were characterized using UV–vis spectrophotometry. The findings demonstrated that functionalized gold nanoparticles had high removal rates for heavy metal ions and dye. Gold nanoparticles are among the most intensively explored nanoparticles of noble metals due to their multiple applications in catalysis, electrical devices, medicine, and physical chemistry [25]. In this study, the researchers investigated the use of pomegranate peel water extract as both a reducing agent and a capping agent in the hydrothermal synthesis of gold nanoparticles. The vast domains of scientific confirmation and technical vision are important for nanoparticle applications in human civilization. The authors of this paper extensively explain why nanoparticles and environmental engineering are crucial for future scientific growth [26]. Green nanoparticles and their research and development ventures into a sustainable future with great scientific knowledge. Nanotechnology is one of the most significant technological discoveries of the twenty-first century. In terms of the application of nanoparticles to human civilization today, the technological and scientific perspective is vast. Nanomaterials and artificial nanomaterials are true scientific triumphs in modern civilization. Nanotechnology has the scientific ability to significantly modify lives and the overall economic condition of the human race, with applications ranging from electronics to biomedical engineering, improved industrial technologies, and cosmetics. However, present nanomaterials and techniques are not only reliant on nonrenewable technologies but also create hazardous byproducts [27]. As a consequence, there is a higher demand for sustainability in the environment and a better grasp of environmental science and engineering. This research looks at present advancements and future opportunities in green nanotechnology and green nanomaterials. The challenges and vision of nanomaterials and artificial nanomaterials are novel, and they must be imagined and explored as science progresses. In the past few decades, nanomaterials have shown incredible improvement in performance in a wide variety of applications, including medical, energy, the environment, and engineering for manufacturing. Advanced manufacturing tools, human factor engineering, and technology management are required in today's science, engineering, and technology [28]. The research's researchers highlight the accomplishments of green nanomaterials as well as the scientific creativity of nanomaterials applications in green nanomaterials and green customized nanomaterials applications. Chemical engineering, process technology, and environmental engineering are now related to

nanotechnology in a variety of scientific domains. Current green nanotechnology techniques usually involve the use of natural sources, nonhazardous solvents, and energy-efficient tools in the synthesis of nanomaterials. This chapter goes into great detail regarding the scientific issues surrounding nanotechnology [29].

6 Management of the Environment, Sustainability, and a Visionary Future

The broad domains associated with environmental engineering and management are increasingly vital for scientific progress and academic quality. Today, the governance of the environment and sustainable development are intricately connected. The visionary views of Dr. Gro Harlem Brundtland, former Prime Minister of Norway, on “sustainability” must be reimaged and modified as time passes. Management of the environment for long-term growth based on scientific and technological knowledge [30]. Environmental management is a large and fast-growing scientific and technological topic. Today, human scientific advancement is at a crossroads of vision and scientific innovation. Today, academic rigor is defined by environmental management and sustainable development. Barrow aims to provide a comprehensive and comprehensible introduction. In modern human society, basic human needs such as water, electricity, food, and shelter are greatly ignored. Environmental engineering and management are rapidly evolving; they are becoming increasingly important in an expanding number of human activity sectors and are crucial to the achievement of environmentally friendly growth. The provision of basic human needs like water and energy is vital to the growth of human civilization and the accuracy of science. [31]. Water purification and wastewater treatment are currently being approached with extreme prudence, scientific innovation, and scientific fortitude. Environmental management in general assumes a multidisciplinary approach, which might be difficult to achieve in an orderly manner because appropriate enabling frameworks are still being developed. In this book, the author defines environmental management theory, principles, and essential ideas, the management of the environment approaches—standards, monitoring, modeling, auditing, and framework cooperation—are all covered. In the quest for science and technology, the author was fully aware of the needs of environmental management as well as environmental and energy sustainability [32].

7 Nanotechnology and Sustainability

Today, the science of “sustainability” is beset by technical hurdles and immense scientific challenges. Today’s futuristic research questions are in nanoscience and nanotechnology. The pallbearers of a new visionary period in nanotechnology and

green engineering are scientific articulation and inventiveness [8]. Environmental protection, as well as a deep scientific vision of environmental engineering and chemical engineering, will all play a significant role in uncovering the scientific truth of nanoscience and nanotechnology. As society and science advance, the provision of essential human necessities such as food, water, energy, electricity, and shelter becomes increasingly important [33]. The field of nanotechnology is a scientific marvel. In a similar vein, water purification research is being put to the test as nations throughout the world confront the wrath of heavy metal drinking water and groundwater pollution. As a result, a collaborative effort by scientists, engineers, and civil society is required. With the passing of history and time, the visionary remarks of Dr. Gro Harlem Brundtland, former Prime Minister of Norway, on sustainability must be readdressed and reenvisioned. Green engineering and environmental engineering science are now inextricably connected. As a result, there is an enormous demand for green nanomaterials and sustainable solutions in modern human civilization. Nuclear science and space technology are rapidly advancing, crossing one threshold after another. Similarly, nanotechnology is on the verge of a new beginning [34].

8 Green Nanomaterials, Nanotechnology, and Sustainability: Future Research Directions

Nanotechnology is green, and its potential uses are rapidly evolving. The scientific endeavor and comprehensive reflection in the field of green nanotechnology must be reformed with the march of civilization and rigorous academia. Future green nanomaterials research should concentrate on more inventive applications of sustainable green nanomaterials as well as the proper implementation of the preservation of the environment for the advancement of humanity [35]. Environmental protection is today at an intersection between catastrophic tragedy and profound scientific thought. The supply of clean drinking water has gotten much too little attention in investigations. As a result, green nanotechnology and green nanomaterial applications in water purification are the way of the future. With frequent natural disasters, global warming, and the depletion of fossil fuel sources, the human environment is both demanding and, in some eyes, terribly dismal. As a result, as civilization advances, chemical process engineering, environmental engineering, and petroleum engineering must be restructured [36]. Future nanotechnology study and development initiatives should be aimed toward improved energy liberation and environmental sustainability. Water purification and industrial wastewater treatment are present and future requirements of human society. As a result, long-term and practical solutions to human scientific and academic rigor are urgently required. Future research should concentrate on increasing environmental sustainability applications for greater emancipation and greater realization of infrastructure development and holistic sustainable development. Pollution control, heavy metal pollution mitigation in groundwater, and catastrophe mitigation are critical scientific imperatives for human society's growth [37].

Sustainability and nanotechnology research directions must be sound and environmentally safe in today's scientific world. Human factor engineering, reliability engineering, and systems science should be investigated alongside green nanomaterials and applications for nanotechnology. Nanomaterials' science of the environment problems face a wide range of challenges today. Environmental sustainability and industrial hazard management are presented as issues. The authors go deeply into these essential issues of environmental engineering and green nanomaterial applications. The focus of research should be commercial-scale production. Then there will be more scientific truth and more profound scientific judgment [38]. The condition of sophisticated substance and green materials research is promising and far-reaching. Green materials and sustainability will intersect to develop new intelligent substances and nanomaterials. The research program and its vast scientific imagination must be reformed in order to perform breakthrough green materials research. The key thrust area of vision is the utilization of green nanomaterials in the development of humanity. This chapter will surely usher in a new era in the study of green materials. Scientific understanding will reach new heights if sustainability is integrated with new domains of environmentally conscious technology [39].

9 Conclusions

Today, the intersection of society, scientific advancements, and research endeavors presents profound thoughts and scientific challenges. Green nanotechnology, green nanomaterials, and the field of green engineering are approaching scientific maturity, as the world's ecology is threatened by advancing science and engineering. Heavy metal toxicity in drinking water remains a massive problem with limited technological solutions, and green nanomaterials must be employed to address this issue. Sustainable development in energy, environment, society, and economy is crucial, as humanity moves toward a new economic system with long-term development and provision of basic human needs such as water, food, energy, power, housing, and education. Water research and technology are essential for achieving these goals and will drive new ideas in the fields of nanoscience and nanotechnology. The real redemption of science and engineering today will rely on human determination, enlightenment, and ambition, along with the urgent needs of sustainability. This will herald a new beginning, a new chapter, and the development of a new scientific and technological era for humanity.

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Available Synthesis Methods of Green Nanomaterials, Their Properties, and Characterization



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Abstract Metal nanoparticle synthesis has recently gained significant attention due to its unique physical and chemical properties such as mechanical strengths, high surface area, optical properties, low melting point, surface plasmon resonance, good antibacterial properties, and magnetic properties. It thus has broad applications in photography, biotechnology, anticancer, catalysis, antimicrobial agents, and agriculture. Green synthesis is recognized as the most significant approach for the purpose of our environment, and green nanotechnology is gaining relevance in recent times as an alternative cost-effective, eco-friendly, efficient, and non-toxic method. Many natural capping and reducing agents, such as plants, fungi, and algae, are employed to manufacture these environmentally benign nanoparticles. The green synthesis of nanoparticles using plant extracts is cost-effective, offers reducing agents and natural capping, provides stability. The unique approach for producing green nanoparticles and their characterization is briefly discussed in this book chapter.

Keywords Green nanoparticles · Characterization · Synthesis · Plant · Microorganism · Properties

1 Introduction

The field of nanoscience and nanotechnology has become one of the most rapidly developing research topics in multidisciplinary fields. A few examples include electronics, cancer treatment, biotechnology, catalysis [1], cosmetics, environmental remediation [2], the space industry, drug delivery [3], anticancer medication delivery, and materials science [4]. Nanotechnology is an emerging interdisciplinary field bridging the disciplines of biology, chemistry, pharmaceuticals, physics, material

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science, medicine, and engineering [5]. In addition, nanoparticles have attracted considerable interest due to their unusual physicochemical and morphological properties, such as shape, ultra-small size, and size distribution. In addition, they have interesting thermal, magnetic, optical, and mechanical properties. For the synthesis of various nanomaterials, a variety of conventional and traditional techniques have been reported. Two primary techniques (i.e., bottom-up and top-down) and several chemical and physical strategies have been reported for the manufacturing of nanomaterials. Chemical processes reported for the synthesis of nanomaterials involved the use of harmful reducing agents such as NaBH_4 and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ [6]. In addition, due to a complicated degradation mechanism, many harmful chemicals used for the synthesis of nanomaterials remain in the environment for many years [7]. On the other hand, physical processes for the synthesis of nanomaterials require high temperature and pressure. In order to solve all of these issues, scientists have developed a new field of study promoting sustainable development: green nanotechnology. Green nanotechnology refers to the ability of natural substances to minimize risks to the environment and the health of living organisms, and it involves the replacement of existing products with new nanomaterials that are more cost-effective and eco-friendly [8]. Between 2004 and 2013, the use of environmentally friendly nanotechnology resulted in a 7% reduction in the release of hazardous waste, including methyl isobutyl ketone, hydrochloric acid, and trichloroethylene [9]. There are many applications for nanoparticles that are indirectly related to green nanotechnology. Some examples of these applications include the use of nanocomposites to reduce the weight of vehicles, the creation of self-cleaning nanoscale surface coatings, the extension of the life of batteries, and the creation of self-cleaning light-emitting diodes, etc. [10]. Microorganisms, biodegradable polymers, vitamins, carbohydrates, and plant extracts have served as reductants and capping agents in the biosynthesis technique for production of nanomaterials [11]. In addition to being economical, biocompatible, and green, the biosynthesis technique is also environmentally friendly [12]. Also, plant-based nanomaterial synthesis is utilized on a global basis. During the manufacture of nanoparticles, phytochemicals such as alkaloids, terpenoids, saponins, and polyphenols found in various plant parts serve as surfactants or reducing agents. As a result of the presence of natural organic components in the plant extract, green nanoparticles have a stronger adsorption effectiveness than chemically manufactured nanoparticles. In addition to plants, bacteria and fungi have been employed for the synthesis of nanomaterials. Microorganisms and fungi are gaining favor as nanofactories due to their ability to reduce metal cations into metallic nanoparticles [13]. Metallic nanoparticle with different structures and sizes have been effectively synthesized by altering the reaction parameters, such as temperature, pressure, oxygenation, pH, and incubation time [14, 15]. Using microorganisms, various kinds of metal nanoparticles such as Ag, Au [16] and Cd [14, 15] and metal oxides of ZnO [17] and CeO_2 [18] have been investigated. Different types of characterization techniques are used to obtain structural information about nanomaterials, such as FT-IR, SEM, TEM, XRD, AFM, XPS, EDAX, and DLS. This chapter will provide the reader with a complete overview of green nanotechnology and green synthesis techniques. Various

types of eco-friendly nanomaterials and their characterization methodologies have also been covered.

2 Plant and Plant Derivative-Based Synthesis

Many researchers are interested in plant-based approaches because of the advantages of employing plant materials to biosynthesize nanoparticles, such as their availability, variability, eco-friendliness, and sustainable methodologies [19, 20]. Plants are capable of absorbing, hyperaccumulating, and degrading metallic oxides present in the environment [21]. Recently, certain organic chemicals found in plants have been used as practical biological factories to reduce environmental contamination. However, it is essential to find a balance between scalability, cost, and applicability when fabricating nanoparticles. Fabricate nanomaterials using plant extracts as reducing agents provides an economical pathway. Different parts of the plants, such as flowers, roots, leaves, stems, calluses, seeds, and peels, can be used for the fabrication of nanomaterials [22–24]. The plant extracts' source influences the nanoparticle's properties due to the fact that different extracts contain different organic reducing agents. Alkaloids, terpenoids, and phenolic chemicals are only a few examples of water-soluble plant metabolites which can act as reducing agent. In phenolic compounds, hydroxyl and ketonic groups have chelation properties that enable them to bind to metals. Eco-friendly nanoparticles offer improved control over size, shape, and stability (Fig. 1).

3 Microorganism-Based Synthesis

The ecologically friendly nature of microorganism-based nanoparticle synthesis attracts significant attention in comparison to conventional techniques. The eco-friendly processes involve the use of both prokaryotic and eukaryotic microorganisms. Nanoparticles containing metal and metal oxide can be generated utilizing either extracellular or intracellular methods. To produce nanoparticles, a variety of microorganisms, including bacteria, fungi, and yeast, are utilized. Intracellular nanoparticles are more likely to be monodisperse than extracellular ones. Optoelectronic, sensor, and bioimaging are only a few of the commercial applications that heavily rely on extracellular nanoparticle. By using an intracellular process, nanoparticles inside the surface of cells are generated using metal ions trapped on their surfaces. Enzymes found in the cytoplasmic membrane, a component of the cell wall, are used in reduction processes. Although nanoparticle recovery is highly expensive, it is feasible to control the size and structure of nanoparticles via intracellular processes. The intercellular approach requires the use of cell lysis to release nanoparticles from microorganisms, unlike the extracellular method. Consequently, it takes longer time and

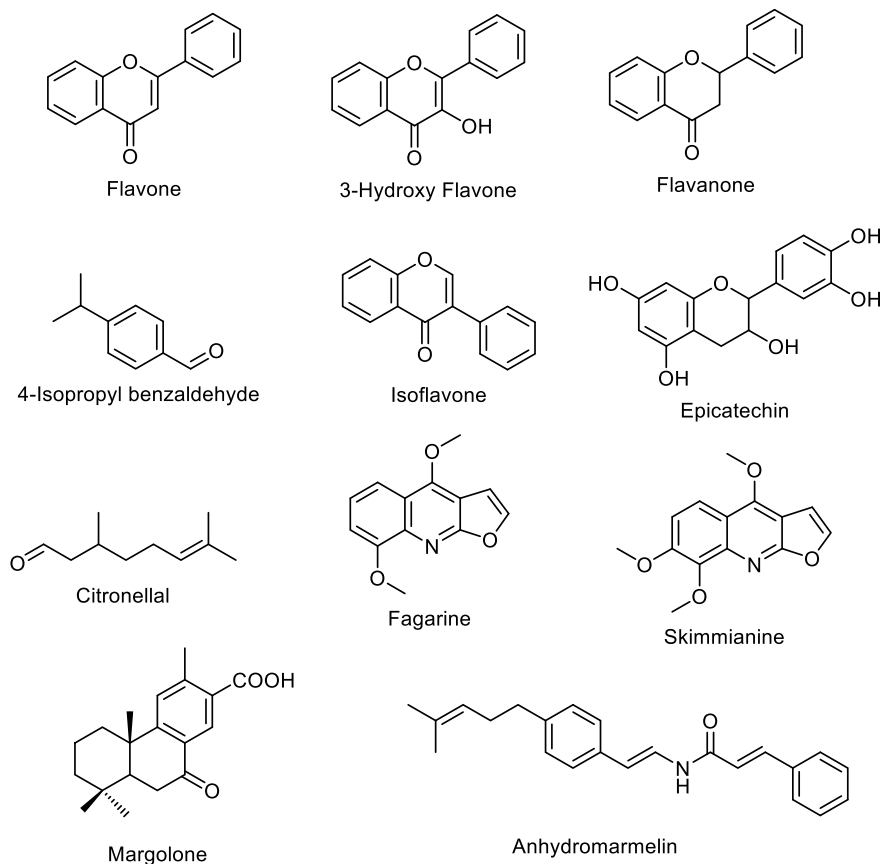


Fig. 1 Structures of various bioactive compounds present in the different parts of plant

expensive than the extracellular phenomena. A room temperature is used in microorganism based nanomaterial synthesis and consequently it is more effective, employs fewer hazardous chemicals, and is readily accessible [25]. Proteins, peptides, and genes are examples of natural capping agents which are used to prevent nanomaterials to agglomerate, thus helps to provide stability of nanomaterials [26]. In the extracellular environment, enzymes play a significant role in the reduction of metal ions that are electrostatically bonded to the surfaces of microorganisms. On the other hand, metal ions diffused within the cell and reacted with enzymes to generate nanoparticles in the intracellular process [27] (Tables 1 and 2).

4 Microwave-Based Synthesis

During microwave synthesis, a sample is exposed to electromagnetic (microwave) irradiation. Microwave irradiation enables greener and faster heating of nanomaterials since it requires less energy. In order to carry out a microwave-assisted synthesis, the samples are to be synthesized in a microwave reactor at frequencies ranging from 300 to 900 MHz. The microwave uses less energy and enables faster heating for nanoparticle formation. The microwave method provides greater control over morphology, size, and dispersion than other techniques [28]. Using the aqueous extract of the plant *Salvia aegyptiaca* and microwave-assisted techniques, the ZnO nanoparticles were synthesized with a size of less than 80 nm [29]. The biggest issue with the microwave method is that it makes minimal product due to small size of the reaction vessel. Multi-mode microwave units are needed to improve the microwave-based method so that it can be used on a large scale. Iron oxide nanoparticle with yield more than 80% was synthesized from a solution of $\text{Fe}(\text{acac})_3$ in anhydrous benzyl alcohol, through microwave-based synthetic method [30]. In order to improve the quality of biodiesel, zinc nanoparticles were manufactured using banana com extract [31]. Microwave-assisted technique also reported synthesis of Ag nanoparticles using aqueous leaf extract of *Melia azedarach*. The production of the spherical gold nanoparticle was accomplished through the use of a microwave process that used the peel extract of *Annona squamosa* L [32]. These technologies are used a lot to make a wide range of nanomaterials, and they have an exciting future ahead of them.

5 Solvent-Based Synthesis

Synthetic processes that use solvents are an important part for the synthesis of nanomaterials. Water is thought to be the best and most effective and easily accessible solvent for synthesis procedures [33]. Sheldon's comment is referred to as "the selected solvent is not a solvent, and if a solvent is significantly more valuable than water, then it can be considered ideal." Water has been used as the finest solvent for nanomaterial synthesis due to widespread interest in nanoscience and technology. For example, at room temperature, bi-functional chemical agents such as gallic acid are used to prepare Ag and Au nanoparticles [34]. The green route technique is made up of two mechanics. As a solvent, either natural extract or water may be preferred. In this context, both routes have been explained. The discussed contents provide greater insight into green routes, toxic and non-toxic components, and the utilization of non-conventional resources obtained from nature. Ionic and supercritical liquids are examples of such developing bases. Ionic liquids include ions with a sharp melting point of less than 100 °C. Ionic liquids were used to create a variety of metallic nanoparticles such as Ag, Au, and Pt. The capacity of an ionic solution to act

as both a protecting reagent and a reducing agent, simplifies the process of nanomaterial synthesis [35]. These can either have a hydrophobic nature or a hydrophilic one, depending on the cations or anions that are involved. If a component has a propensity to exhibit ionic tendency, then it will also function as a catalyst in the reaction. The features stated below comprise the advantages of ionic solvents over other solutions. (i) Numerous organic polar chemicals, metal catalysts, and gases dissolve readily in ionic solutions. (ii) Ionic solutions are thermally stable, allowing them to operate across a larger temperature range. Most solutions melt at room temperature and break down above 400 °C because they can endure a range of temperatures. (iii) The miscibility properties can be altered by altering the nature of the anions and cations occluded with them and (iv) non-coordinating polar alcohols/solvents [36]. Regardless, their polarity was comparable to alcohol. (v) The vapor pressure of ionic solutions is much lower than that of volatile solvents, so they do not evaporate at ambient temperatures as volatile solvents do. (vi) Ionic liquids have a dual character due to the presence of both anions and cations. Ionic solutions' biodegradability makes them unsuitable for metallic nanomaterial production. A biodegradable novel and ionic solution was developed to overcome these disadvantages. A common solvent liquid can also become a supercritical liquid at pressures and temperatures above its critical point. In the case of a supercritical liquid, solvent characteristics such as density, viscosity, and thermal conductivity are correspondingly altered. CO₂ is the most available supercritical, non-toxic, inert fluid. Since water has a critical temperature of 646 K and a pressure of 22 MPa, it may also be an effective solvent for various reactions.

6 Properties of Green Nanoparticles

It has been shown on several occasions that the incorporation of plant extracts for the preparation of nanoparticles results in a process that is non-detrimental to the natural environment [83–86]. Nanoparticles are an excellent choice for its use in the field of therapeutics, which prioritizes the use of materials that are clean and devoid of hazardous impurities. It has been noted that the size and morphology of the particles may be controlled by the minerals, vitamins, carbohydrates, proteins, and amino acids that are present in the plant extract [87]. Despite this, the nanoparticles that were generated from the plant extract are being tested for a limited number of applications. In contrast to their counterparts which were generated physically or chemically, nanoparticles prepared through green methods have shown superior performance in a variety of tests. Photosynthesized nanoparticles are now being considered for various investigations in different fields of study. Biocatalysis, antiviral action, anticancer activity, antimicrobial activity, DNA labeling, molecular imaging, food additives, biosensors, drug delivery, agriculture, cosmetics, coatings, and other applications are among the most common uses of the green nanoparticles.

Table 1 Synthetic methods of nanoparticles from different plant extracts

S. No.	Nanoparticle	Plant origin	Size (nm)	Morphology	References
1.	Silver	<i>Acalypha indica</i>	21–30	Spherical	[37]
2.	Silver	<i>Brassica juncea</i>	5–35	Spherical	[38]
3.	Silver	<i>Citrus limon</i>	< 50	Spherical/ Spheroidal	[39]
4.	Silver	<i>Carica papaya</i>	65–80	Spherical	[40]
5.	Gold	<i>Avena sativa</i>	10–20	Rod shaped	[41]
6.	Gold	<i>Coriandrum sativum</i>	7–58	Triangular, truncated triangular, decahedral, spherical	[36]
7.	Gold	<i>Cymbopogon flexuosus</i>	201–500	Spherical/ Triangular	[42]
8.	Iron oxide	<i>Medicago sativa</i>	5–10	Crystalline	[43]
9.	Zinc oxide	<i>Sedum alfredii</i>	50–55	Hexagonal, pseudospherical	[44]
10.	Tin oxide	<i>Lycopersicon esculentum</i>	4–5	Spherical	[45]
11.	Palladium	Cotton balls	10–15	Spherical	[46]
12.	Cerium oxide	<i>Datura metel</i> L.	5–15	Spherical	[47]
13.	Copper oxide	<i>C. paniculatus</i>	2–10	Spherical	[48]
14.	Iron	<i>Cinnamomum verum</i> bark	20–50	Spherical	[49]
15.	Copper	<i>Ginkgo biloba</i>	15–20	Spherical	[50]
16.	Zinc oxide	<i>Prosopis juliflora</i>	31.80–32.39	Irregular	[51]
17.	Platinum	<i>Nigella sativa</i> L.	1–6	Spherical	[52]
18.	Platinum	<i>Prosopis farcta</i> fruits	3.5	Irregular	[53]
19.	Titanium oxide	<i>Mentha arvensis</i>	20–70	Spherical	[54]
20.	Titanium oxide	<i>Syzygium cumini</i>	11	Spherical	[55]
21.	Nickel oxide	<i>Tamarix serotina</i>	10–14	Cubic	[56]
22.	Nickel oxide	<i>Raphnus sativus</i>	13–52	Cubic	[57]

(continued)

Table 1 (continued)

S. No.	Nanoparticle	Plant origin	Size (nm)	Morphology	References
23.	Cobalt oxide	<i>Citrus limon</i>	46–56	Pyramid like	[58]
24.	Cobalt oxide	Fenugreek	6–20	Spherical	[59]
25.	Selenium	<i>Aloe vera</i>	7–48	Spherical	[60]

6.1 Biological Properties

6.1.1 Antibacterial Properties

Jakub Siegel and colleagues carried out studies on the antibacterial effects of green-produced AgNPs. When compared to the control samples, which consist of bacteria that had been incubated in glycerol or physiological saline solution for either 6 or 24 h, the growth of *Staphylococcus epidermidis* and *Escherichia coli* were completely inhibited in the presence of AgNP4–6 after 24 h (for both 6 and 24 h incubated samples). The fact that AgNP4–6 was able to sustain its ability to limit the development of both bacterial strains even after 30 and 48 h of growth which confirm the potent bactericidal action of AgNPs. During the course of the experiment, no sign of growth inhibition of *E. coli* in the presence of AuNP4–6 or AuNP9–12 for any of these compounds. When compared to the control samples, it was discovered that AuNP4–6, but not AuNP9–12, was able to limit the development of *S. epidermidis*, and the effect lasted for the whole 48 h testing period. Throughout the course of the experiment, any growth inhibition of *E. coli* occurred regardless of the size of the AuNPs. On the other hand, AuNP4–6 was successful in preventing *S. epidermidis* from expanding its population [88].

Asem A. Mohamed and his colleagues used a technique known as the microbial reduction percentage method to evaluate the antibacterial activity of cotton textiles which were loaded with various forms of ZnO-NPs. Although the deposition ratio of nanorods on cotton fabrics was lower than that of hexagonal ZnO-NPs, the results showed that the antibacterial activity generated from cotton fabrics coated with nanorods was higher than that obtained from hexagonal ZnO-NPs. In the case of cotton textiles loaded with hexagonal and nanorod ZnO-NPs, the decrease in the bacterial viability were found to be in the ranges of 72.4–79.7% and 76.3–84.3%, respectively. There is a correlation between the morphology of the ZnO-NPs and their antibacterial activity [89].

6.1.2 Antifungal Properties

Javed Iqbal and his colleagues explored the antifungal potentials of iron oxide nanoparticles (IONPs) by testing them against various fungal strains by utilizing disk-diffusion techniques. The results of their research were positive for the antifungal properties of the IONPs. After being grown in 100 mL flasks containing sabouraud

Table 2 Synthetic methods of nanoparticles from different microorganisms

S. No.	Nanoparticle	Origin	Size (nm)	Morphology	References
1.	Silver	<i>Bacillus brevis</i> (NCIM 2533)	41–68	Spherical	[61]
2.	Silver	<i>Lactobacillus casei</i> WK2G-3A	0.7–10	Spherical	[62]
3.	Silver	<i>Lactobacillus fermentum</i> E10-15	1.4–10	Spherical	[62]
4.	Gold	<i>Paracoccus haeundaensis</i> BC74171 ^T	20.93 ± 3.46	Spherical	[63]
5.	Gold	<i>Escherichia coli</i>	~ 10	Spherical	[64]
6.	Palladium	<i>Citrobacter</i> bacterial species	11–16	Dendritic shaped	[65]
7.	Palladium	<i>Cupriavidus metallidurans</i> CH34	20–40	Dendritic shaped	[66]
8.	Magnesium oxide	<i>Burkholderia rinojensis</i>	26.7	Spherical granular shape	[67]
9.	Copper	<i>Shewanella loihica</i>	10–16	Spherical	[68]
10.	Copper	<i>Botryococcus braunii</i>	10–70	Elongated spherical and cubic	[69]
11.	Copper oxide	<i>Lactobacillus casei</i> subspecies	30–75	Spherical	[70]
12.	Copper oxide	<i>Streptomyces pseudogriseolus</i> Acv-11 and <i>S. zaimyceticus</i> Oc-5	78	Spherical	[71]
13.	Titanium oxide	<i>Streptomyces</i> species HC1	43–67	Spherical	[72]
14.	Titanium oxide	<i>Halomonas elongata</i>	104.63	Spherical	[73]
15.	Iron oxide	<i>Lactobacillus fermentum</i>	10–15	Spherical	[74]
16.	Iron oxide	<i>Bacillus cereus</i> strain HHM1	29.3	Spherical	[75]
17.	Zinc oxide	<i>Pseudomonas putida</i>	25–45	Spherical	[76]
18.	Zinc oxide	<i>Xylaria acuta</i>	40–55	Hexagonal	[77]
19.	Platinum	<i>Fusarium oxysporum</i>	~ 25	–	[78]
20.	Platinum	<i>Botryococcus braunii</i>	86.96	Monodisperse	[79]
21.	Iron	<i>Trichoderma</i> species and <i>Rhizopus stolonifera</i>	100	–	[80]
22.	Cerium oxide	<i>Fusarium solani</i>	20–30	Spherical	[81]
23.	Cerium oxide	<i>Aspergillus niger</i>	5–20	Cubical and spherical	[82]

dextrose liquid medium, the various fungal spores were placed in a shaking incubator at 37 °C for a period of 24 h. The optical density of the liquid cultures was brought up to 0.5. After the preparation of the samples, the SDA medium was then autoclaved before being put onto Petri dishes that had already been sanitized. Using an autoclaved cotton swab, fifty milliliters of broth culture were distributed on a petri plate with SDA medium in order to produce a homogeneous lawn of fungal strains. Each disk had 10 mL of IONPs loaded onto it. Amp B was used as the positive control, while DMSO was used as the negative control. In addition, fungal plates were subjected to an incubation period of 24 h at 37 °C, during which time zones of inhibition were noted at regular intervals. Different concentrations of IONPs ranging from 46.875 to 1500 mg/mL were used in the experiments [90].

6.1.3 Anticancer Properties

The HepG2 cells were subjected to various dosages of IONPs ranging from 5.47 to 700 mg/mL for a period of about 24 h, which resulted in inhibitions of HepG2 cells that were dose-dependent. The effects of *Rhannella gilgitica*-mediated IONPs on the HepG2 cancer cell line revealed a high potential for anticancer activity, as shown by our research. At a dosage of 700 mg/mL, the IONPs caused a death rate of 89%; however, the anticancer impact of the IONPs decreased as the concentration of the compound decreased. The IC₅₀ value that was found was 14.30 mg/mL, which indicated a high level of potency [90].

6.2 Physical Properties

6.2.1 Antioxidant Properties

The antioxidant activities of IONPs were investigated, and the antioxidant nature of IONPs was assessed at concentrations ranging from 1 to 200 mg/mL. At a concentration of 200 mg/mL, the highest levels of total antioxidants, measured in terms of the ascorbic acid equivalents per mg, were found. The total anti-oxidant capacity (TAC) has shown that IONPs possess a strong antioxidant nature in relation to reactive oxygen species (ROS), due to the fact that the leaf extract of *R. gilgitica* was used in this investigation as a powerful reducing and capping agent. It is well accepted that some flavonoids can scavenge ROS that are present on the surface of IONPs. The antioxidant potential of the IONPs discovered in *R. gilgitica* was found to be quite high and was shown to be concentration dependent. As the concentrations decreased, the reducing power also did as well. At a 200 mg/mL concentration, the reducing power was measured to be at its highest point (59%). At a 200 mg/mL concentration, IONPs were observed to have a strong capacity for DPPH radical scavenging, with a percentage of 78.36%. It is possible to conclude that the use of *R. gilgitica*

results in the reduction and stabilization of IONPs due to the presence of some kind of antioxidant ingredient [90].

6.3 Optical Properties

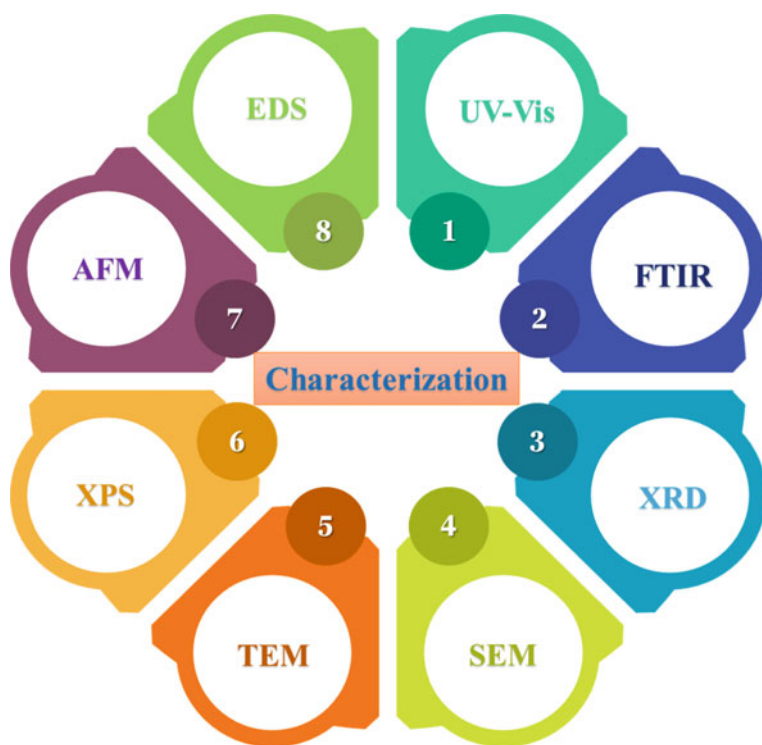
Silver nanoparticles were synthesized using an environmentally friendly process. R. Sarkar and his colleagues discovered that the matching nanoparticle exhibited some optical characteristics. It has been discovered that the colloidal silver nanoparticles that were generated emit photoluminescence at room temperature [91].

The optical sensor was used to determine the level of copper sensitivity shown by these biosynthesized nanoparticles. It was determined that the sensitivity of the medium toward the concentration of copper ions was 0.249/mM for D2 and 0.624/mM for D8, respectively. Therefore, as a result of the obtained antimicrobial and optical properties, it is suggested that obtained AgNPs, which were synthesized by M. R. Bindhu and co-workers, be utilized in water purification for the purpose of inhibiting the growth of bacteria and determining the concentration of heavy metals in water [92].

6.3.1 Electrochemical Properties

Voltammetric methods, namely CV and SWV, were used to analyze the reversibility of electron transfer and assess the electro-catalytic capabilities of ZnO nanoparticle films deposited on a glassy carbon electrode. The ZnO nanoparticles display excellent electrochemical behavior and are thus regarded to be a potential electrocatalyst for use in electrochemical applications. This was the finding that N. Matinise and his colleagues investigated. The influence of scan rate (ν) on the electrochemistry of ZnO-NPs was investigated, and the electrochemical performance of the material is determined by analyzing the peak current during a cathodic and anodic scan, respectively. The decreased peak current has been shown to grow linearly with scan rate, indicating a diffusion-controlled electrolyte ion transport kinetic at the interface and nanoparticle stability [93].

7 Characterization of Green Nanoparticles



The physicochemical properties of green nanoparticles are chemical composition, size, morphology, molecular weight, stability, purity, and solubility. These physicochemical properties are characterized by different spectroscopic techniques, such as UV–Vis absorption spectroscopy, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), etc.

UV–Vis spectroscopy is used to characterize the optical properties of metal oxides and bioconjugates of inorganic and organic nanoparticles. The absorbance spectra are useful to identify the optical behavior of the nanoparticles in the UV–Vis region. It can be used as a primary method to determine the concentration and size of nanoparticles.

The dynamic light scattering technique involves scattering of light by nanoarchitectures with a low concentration of materials in order to avoid multiple scattering effects. It is used to analyze nanoparticles with a size of 0.1 to 10 nm. DLS can be used to determine the aggregation state and hydrodynamic diameter of nanoparticles in solution.

FT-IR is used to detect the functional group in organic compounds, which gives information on how the rotation and vibration of molecules are affected by infrared radiation. From the FT-IR spectra, researchers are able to obtain information about the intensity of the adsorption as well as the wavelength of the molecule.

XRD is an excellent tool and gives information about the lattice parameters, particle size, crystalline structure, and the nature of the phase of nanoparticles. Comparing the peaks with reference patterns available at the International Centre for Diffraction Data (ICDD) can provide information about the sample composition. There are two types of XRD present; one is the powder diffraction method using a wavelength-independent angle of diffraction that alters the angle of diffraction. Second is the Laue method, in which the wavelength of the X-ray does not change but the angle of diffraction is.

By using transmission electron microscopy (TEM) and scanning electron microscopy (SEM), nanoparticles can be characterized by their morphology and size. The TEM and SEM techniques are fundamentally distinct from one another due to the fact that the former determines internal morphology in addition to diffraction patterns, while the latter provides information about the surface morphology of a material. With either methods, we get a two-dimensional image of the samples that shows the size and orientation of the particles.

The composition of nanoparticles is determined with the use of an X-ray non-destructive technique known as EDS. An electron microscopic technique is used to determine the material's composition, microstructure, and elemental spectra through SEM and TEM.

XPS is primarily employed to analyze the surface properties of nanoparticles. This can include using the binding energy and intensity of the photoelectron peak to figure out the composition and oxidation state of the elements.

In thermogravimetric analysis (TGA), nanoparticles are tested for their thermal stability, moisture content, and volatile substances on their surfaces.

Selected area electron diffraction (SAED) is an electron diffraction technique that is used inside a TEM to study nanoparticles defects and crystal structure.

The atomic force microscopy (AFM) is a scanning probe microscopy technique that provides information about roughness, size, surface texture, morphology, surface area, and volume distribution. Because the AFM image is a three-dimensional picture, we can use it to figure out the width of the nanoparticles.

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Green Nanotechnology: A Roadmap to Long-Term Applications in Biomedicine, Agriculture, Food, Green Buildings, Coatings, and Textile Sectors



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Abstract As the result of the growing world population, the availability of resources is decreasing. Creating new non-polluting technologies is essential for the long-term prosperity of human society. Eco-friendly and sustainable technologies can be developed with nanotechnology, which will benefit humans and the environment. In green nanotechnology (biosynthesis), nanomaterials and nanoparticles are formed through biogenesis. Biomedical, nutrition, environmental remediation, coating, textile, and agricultural fields are some of the many applications of green nanotechnology. Many regulatory processes rely on green nanotechnology due to its small size. Better biological diagnosis, better quality of food, agriculture input reductions, better absorption of soil nanoscale nutrients, environmental cleanliness, and clean energy supply are some of the many potential benefits of green nanotechnology. Green nanoscience and technology can address current and future problems in the biomedical and food industries as well as society. These include issues of sustainability, sensitivity, and human welfare. The areas discussed in this chapter include biomedical, food, environmental remediation, coatings, textiles, and agriculture.

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Keywords Green nanotechnology · Human health · Food and agricultural applications · Coating and textile applications · Environmental remediation

1 Introduction

According to Bhainsa and D'souza [27] and Shahverdi et al. [192], nanotechnology is primarily concerned with objects, materials, and devices that have a diameter of less than 100 nm (nm). Nanomaterials have gained prominence over the past decade in medical, pharmaceuticals, agriculture, coating industries, energy production, nanostructured electrodes in batteries, communication technology devices, and food and textile industries [43, 49, 186].

Despite the many applications and benefits of synthetic nanoparticles, their synthesis is expensive and their by-products are environmental hazards [132]. Therefore, scientists and researchers are showing keen interest in green nanoparticle synthesis [153]. A green nanotechnology is an approach that uses renewable resources as opposed to physical and chemical nanotechnology [6, 117, 164], because it is less expensive, less energy-consuming, eco-friendly and causes no harm to humans [5, 10, 98, 205] (Fig. 1). Biological materials are used in the production of nanomaterials in green nanotechnology [16, 26, 63, 163, 195, 198, 205] (Fig. 1).

The field of green nanotechnology is an important subset of green chemistry and green engineering. This minimizes power and fuel consumption wherever possible [220]. In green chemistry, there are 12 principles (Fig. 2) which are being used by Scientists, engineers, and chemists worldwide because they produce less harmful chemical products and by-products [11, 12, 124, 148]. Aside from synthesizing sustainable nanoparticles [155], green nanobiotechnology also saves raw materials, energy, and water, reduces greenhouse gases, stops adverse effects before they occur, and contributes significantly to environmental and climate protection [103, 220, 242].

Fig. 1 Main goals and materials used for green nanotechnology

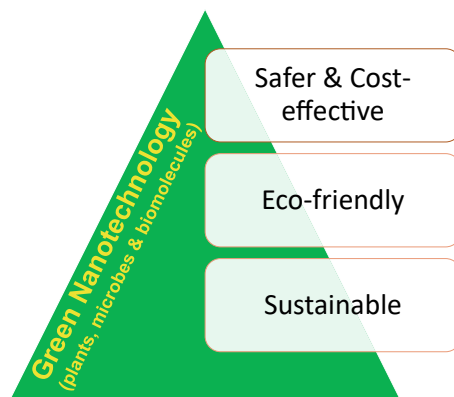


Fig. 2 Green chemistry principles for green nanotechnology

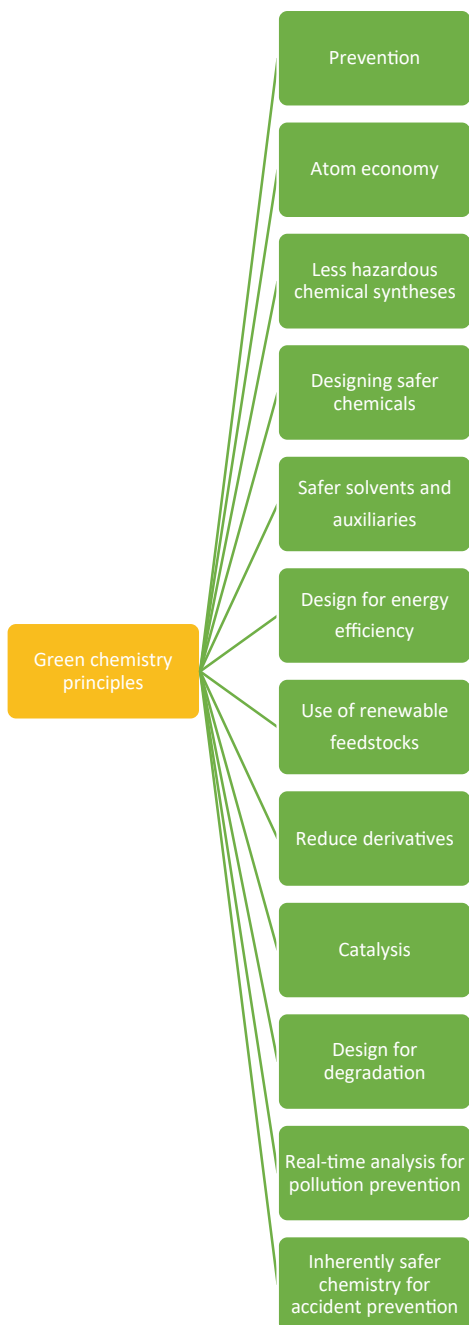


Figure 3 shows green nanotechnology applications which may involve in cosmetics, nanofabrication, bioengineering, energy production, green building constructions, medicines and drugs, nanobiotechnology, optical engineering, agriculture, food and coating industries, etc. [220]. To make a conclusive assessment, green nanotechnology requires a complete process assessment like any other industrially manufactured product [18, 25].

To eliminate or greatly reduce pollution, as well as to foresee and lessen the environmental repercussions of the manufacturing chain, green nanotechnology relies on the design and use of non-toxic nanomaterials [104, 204]. Other applications of green nanotechnology include photocatalysis, solar cells, fuel/bio-fuel cells, and cleaner production [78, 96, 168]. Furthermore, green nanotechnology applications include the conversion of diesel soot into carbon nanomaterials which can be used to recycle industrial wastes [30, 142]. In this chapter, we have elaborated the applications of green nanotechnology in different fields.



Fig. 3 Applications of green nanotechnology in various sectors

2 Green Nanotechnology and Its Applications

According to Anastas and Warner [11, 12] and Karn and Bergeson [112], green nanotechnology aims to develop and produce goods that are environmentally sustainable. Its primary objective is to inform readers about nanoparticles and their numerous useful and potentially harmful properties. Furthermore, negative impact on health and ecosystem can be reduced through nanotechnology, which has a wider societal benefit. Thus, green nanotechnology contributes from selection of raw materials to safer release to the environment [202].

2.1 Green Nanotechnology in Biomedical Applications

Treatment and prevention of many diseases could be revolutionized by biomedical nanotechnology [143]. Opportunities in the near future include the discovery of infectious microorganisms and viruses and the detection of molecules that are associated to the development of many diseases like cancer, diabetes, and neurological diseases. Nanoparticles with the ability to react to external stimuli would be useful in the delivery of cancer medications [7, 20, 47, 64, 88, 126, 134, 167, 174, 183]. In addition to medical implants, biomaterials can be used to create scaffolds for grafts. Non-specific macromolecules could be prevented from adhering to nanostructured surfaces created by this method. Biocompatibility of materials can be improved by controlling surface characteristics at the nanoscale.

There is currently a paucity of information on the pharmacological dangers linked with this technique, despite it is being widely available. Structures can take on entirely new features when scaled down to the nanoscale. A particle's aggressive or kidney-damaging actions appear to be best predicted by its minuscule size, which is mostly determined by its chemical composition. All medical technology applications (Fig. 4) must have a risk management plan in place. Afterward, we will take a look at some of the possible medical applications of nanomaterials and nanoparticles. Biocompatibility, implants, cardiology, cancer [42, 102, 158, 199], and theranostics are just a few of the many diagnostic and therapeutic uses for "nanorobots" and other forms of nanomedicine. Last but not least, the dangers to human health and ethical issues are discussed in detail [170, 171, 175].

In the field of drug delivery, nanomaterials and nanoparticles are useful tools. There are a number of nanomaterials that can be used to destroy cancer cells because of their unique mechanical, electrical, electronic, thermal, and optical properties [176, 202]. Due to their extraordinary size, optical and electrical capabilities, and comparatively low cost and ease of manufacturing, quantum dots have found utility in medical imaging applications. Physicochemical and biological properties of dendrimers can be enhanced through their small size (5 nm) and can pass via cell membranes, tissues,

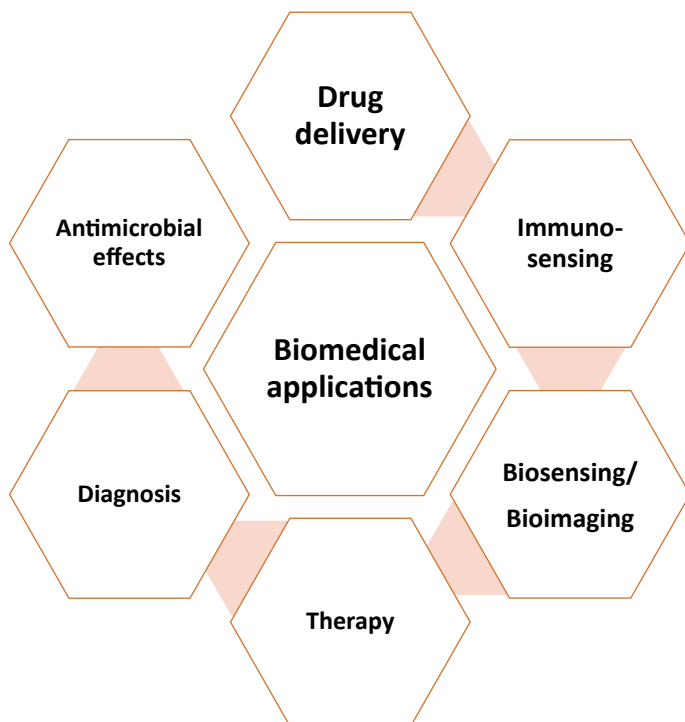


Fig. 4 Biomedical applications of green nanotechnology

and vascular pores. Nanomaterials can be used in protein, RNA, and DNA structure detection by using fluorescent markers for resonance imaging improvements [194, 202].

2.2 Agricultural Applications of Green Nanotechnology

The food and feed sectors have always relied on agriculture for supply and generation of raw materials. Population growth and the scarcity of natural resources (such as farmland and water) encourage agricultural development that is more profitable and environmentally friendly [109, 149, 236].

It is essential for the elimination of poverty and hunger that agricultural development takes place. As a result, we must take a risk in order to advance agricultural growth. This global mainstream has people living in poverty and in rural areas where agricultural expansion is less effective [166]. More recently, food and nutrition security have become a central part of cutting-edge scientific research. The objectives of agricultural development should include factors such as social inclusion, health, climate change, energy, ecosystem processes, natural resources, and good

governance, [236]. As a result, sustainable agriculture increases the likelihood of eliminating poverty and hunger in the real world [213].

Incontrovertibly, the future of agriculture depends on the implementation of cutting-edge techniques like nanotechnology. In agricultural systems, the increasing use of smart nanotools has the potential for revolutionizing agricultural practices and reducing or eliminating their environmental impact [133, 189].

Nanotechnology plays a crucial role in sustainable agriculture by regulating nutrients and productivity via water quality [91, 149] and pesticide monitoring [165]. A general assessment of the health and environmental hazards posed by nanomaterials is impossible due to their wide range of properties and activities [165]. In agriculture, nanotechnology research also influences sustainable development. Soil fertility can be maintained, agricultural resources can be effectively managed, drugs can be effectively delivered, and this technology has proven to be effective. Risk assessments are continuing in several fields, including those dealing with biomass and agricultural wastes, food processing and packaging, and more [76]. It has recently become common practice to use nanosensors for environmental monitoring in agriculture because of their robustness and speed [106].

Microorganisms use nanoparticles to directly catalyze the destruction of toxic chemicals and waste products, making the process more effective. Hazardous compounds and toxins are broken down by organisms in agricultural soils and waters. Bioremediation (using beneficial microorganisms), phytoremediation (using plants), and mycoremediation are other commonly used terms (fungi and mushrooms). As a result, bioremediation can be used to safely and effectively remove heavy metals from soil and water using microorganisms [60]. As a result, agricultural bioremediation encourages long-term approaches to remediation that restore soil to its natural state. Consider using the nano–nano interaction to improve agricultural soil sustainability by removing potentially harmful components [60, 106]. Microbes are undeniably important in sustaining soil health, the environment, and agricultural productivity [145]. As a result, the introduction of modified NPs (chemical or green) should constantly be evaluated on a regular basis to ensure environmental stewardship in the agricultural sector (Fig. 5).

Although nanofertilizers (Table 1) have been widely available on the market in the past decade, the majority of agricultural fertilizers have not been developed by major chemical companies. Several types of nanofertilizers are available, including “nanozinc, silica, iron, titanium dioxide, core–shell quantum dots, and gold nanorods.” Its quality is further enhanced by the fact that it was released under strict supervision. Over the past decade, researchers [59, 239] have focused on the potential benefits of using metal oxide nanoparticles in agriculture. As a result of zinc deficiency in alkaline soils, agricultural productivity has been limited [180].

In the near future, nanomaterials will be used to protect crops and produce food. In agricultural fields, NPs play a crucial role in controlling insect pests and host pathogens [121]. The development of a novel nanoencapsulated pesticide formulation with slow release properties has been reported recently [29]. Increasing the effectiveness of active ingredients by preventing their premature degradation for longer periods of time is the primary way to achieve crop protection due to the development

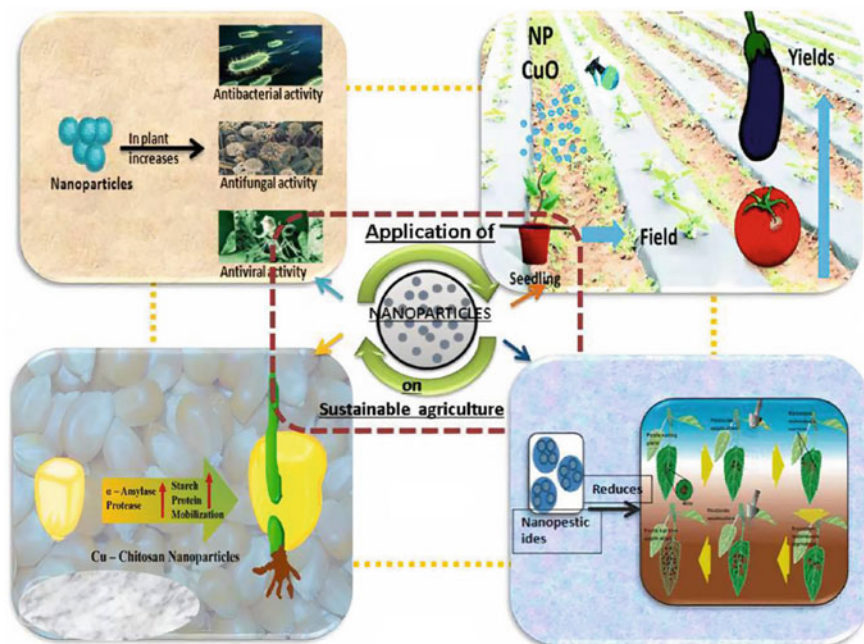


Fig. 5 Applications of green nanotechnology on sustainable agriculture [166]

Table 1 List of nanofertilizers and their composition [166]

Nanofertilizers	Composition
Nano-Gro™	Plant growth regulator and immunity enhancer
Nano-green	Extracts of corn, grain, soybeans, potatoes, coconut, and palm
Nano-Ag Answer	Microorganism, sea kelp, and mineral electrolyte
Biozar nanofertilizer	Combination of organic materials, micronutrients, and macromolecules
Nano max NPK fertilizer	Multiple organic acids chelated with major nutrients, amino acids, organic carbon, organic micro nutrients/trace elements, vitamins, and probiotic
Master nano chitosan organic fertilizer	Water soluble liquid chitosan, organic acid and salicylic acids, phenolic compounds
TAG NANO (NPK, PhoS, Zinc, Cal, etc.) fertilizers	Proteino-lacto-gluconate chelated with micronutrients, vitamins, probiotics, seaweed extracts, humic acid

of environmentally friendly nanoencapsulated insecticides [160], which has resulted in a decrease in pesticide doses and human exposure. There is a growing interest in developing non-toxic and environmentally friendly pesticide delivery systems in order to improve global food production and minimize the adverse effects on the environment [29, 55, 90, 110].

The quality of chemicals delivered to biological processes can be improved using nanoencapsulation, which is similar to microencapsulation. Nanoscale pesticides have recently been marketed as “microencapsulated pesticides” by some chemical companies [89]. Microencapsulated pesticides from Syngenta (Switzerland), “Subdew MAXX Karate ZEON, Osprey’ Chyella, Penncap-M, and BASF” are all suitable for use at the nanometer scale. “Primo MAXX, Banner MAXX, and Subdue MAXX” are all Syngenta products sold in Australia. These are nanoscale emulsions, despite the fact that they are commonly referred to as microemulsions in the marketplace. As a result, the distinction between microemulsion and nanoemulsion is kept as thin as possible. Agrochemicals and organic NPs are commonly formulated using this method [89].

Biosensor development will continue to be influenced by nanotechnology because of its many advantages. The unique properties of nanomaterials can greatly enhance the performance and sensitivity of biosensors [77], but it has also prompted the development of numerous new transduction technologies [190]. Utilizing nanomaterials streamlines the development of numerous (bio)sensors, including nanosensors and other nanosystems essential for biochemical analysis [77, 190, 221]. Mycotoxins, which are present in many different foods, can be detected fast and easily with (bio)sensors help [190].

2.3 Green Nanotechnology in Food Industry

Future food production will be significantly affected by nanotechnology. Food additives and food packaging are the primary uses of nanoparticles in the food industry. The most important differences between the two types of packaging are that additives can be used to enhance the flavor or texture of food, while packaging can help to prevent rotting and increase the quality of the product by minimizing gas flow during packaging [157].

Antimicrobial food contact surfaces, including containers, cutting boards, and freezers, are now being manufactured commercially using nanotechnology [210]. Sugars and proteins serve as a target recognition group for nanostructures used in food biosensors [38]. Foodborne pathogens and other contaminants can be detected and tracked using these biosensors. Environmentally protective encapsulation systems can benefit from nanotechnology as well. As a flavor and an antioxidant, it can be used in the formulation of food products as well [105]. While reducing the concentration of these substances, the goal is to increase their activity and efficiency [95]. Nutraceutical delivery systems and controlled release mechanisms are increasingly being investigated as the practice of adding new ingredients to foods [135]. All food production and processing could benefit from nanotechnology, but many of the techniques are prohibitively expensive or impossible to put into practice commercially. New functional materials and food formulations, as well as micro and nanoscale processing, product development, and storage development, are all areas in the food industry that can benefit from nanoscale techniques [156].

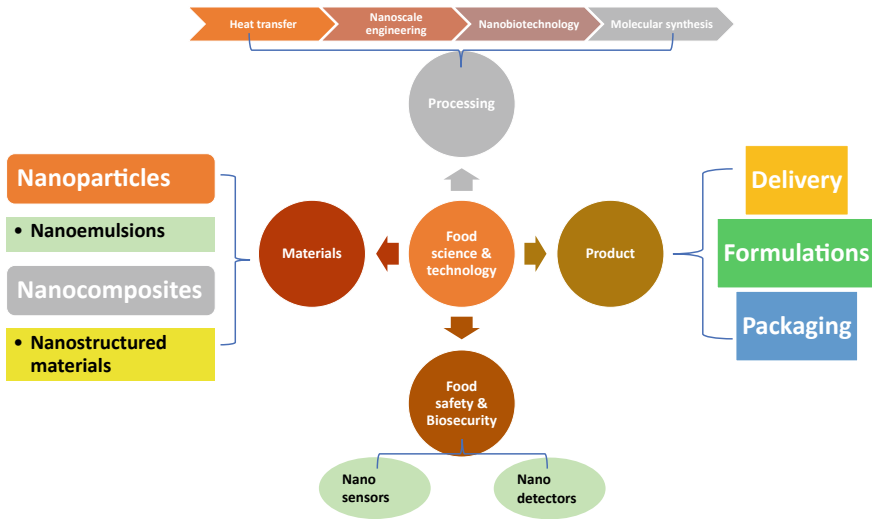


Fig. 6 Applications of green nanotechnology in food processing and technology [171]

A reduction in the risk of certain diseases, such as cancer, may be one of the physiological benefits of bioactive chemicals present in some foods. In the gastrointestinal system, nanotechnology is capable of improving transport characteristics, solubility, and long-term absorption by reducing particle size [41]. Ingredients like “omega-3 and omega-6 fatty acids, probiotics, prebiotics, vitamins, and minerals” are used in food nanotechnology [223]. A number of nanoparticles have been developed to ensure the safety of food products, including “micelles, liposomes, nanoemulsions, biopolymeric nanoparticles, and cubosomes” [71, 131, 152, 232]. Nanotechnology’s applications in the food industry are illustrated in Fig. 6.

As of today, most of the nanotechnology research is concentrated in the fields of electronics, medicine, and automation. The topic of nanoparticles being unintentionally or purposefully introduced into food is a common one when discussing nanotechnology and food [39, 177, 216, 219]. Risks and benefits of using nanoparticles are that very little is known about their bioaccumulation and toxicity [97].

There are numerous applications for the incorporation of nanoparticles into food contact materials. TiO_2 pigment nanoparticles remain UV absorbent after becoming transparent. The absorption of UV radiation must be minimized in transparent wraps, films, or plastic containers. By using nanoclays, gas diffusion can be reduced and shelf life can be extended.

Additionally, food preservation is critical to the food industry’s success. When exposed to foodborne pathogens, nanosensors, such as a system composed of hundreds of fluorescent nanoparticles, can fluoresce in a various forms of colors, allowing in order to detect food spoilage. By using nanosensors, it is possible to detect pathogens in hours or minutes rather than days [28], given the vital necessity of time in food microbiology. In packaging materials, nanosensors can be used

as “electronic tongues” or “noses,” detecting the compounds that are emitted when food is spoiled [82, 125]. Microfluidic nanosensors [17] can also be used to detect infections quickly and accurately in real time and with great sensitivity.

Devices with nanometer- to millimeter-scale moving parts, known as NEMS (nanoelectromechanical systems), are already being employed in the food analysis sector as development tools for food preservation technology. One of the numerous benefits of using micro and nanotechnologies (MNTs) in food technology is the ability to carry about instruments that respond quickly, are inexpensive, and can communicate intelligently at multiple frequency levels. MNTs are ideal for food safety and quality since they are able to identify and manage any contamination packing or storage conditions [34].

The food industry’s nanotechnology R&D is heavily focused on food packaging and regulation [31]. In spite of public concerns about nanotechnology, the food packaging industry continues to develop products utilizing this technology. According to Fletcher [75], the global market for food and beverage packaging nanotech products will reach \$20.4 billion by 2010. Despite increased marketing, researchers have found success in the realm of food and food products by applying nanotechnology [39]. Due to concerns around prospective food labeling and consumer health, nanotechnology has not yet been applied to the realm of food. Researchers in the Netherlands have developed nanopackaging, which detects when food is going bad and releases a preservative to extend its shelf life. One of the most fascinating emerging trends in the food sector is the use of nanopackaging to both improve food safety and lengthen its shelf life. The world has already adopted other, less dramatic (but more useful) innovations in nanopackaging [17, 32, 33].

2.4 Green Nanotechnology in Environmental Applications

Nanomaterials have been utilized to clean contaminated water, which includes heavy metal ions, organic and inorganic solvents, and a wide range of microorganisms [14, 123]. The affinity of nanomaterials for non-degradable pollutants has led to the development of nanomaterials for environmental cleanup and site remediation. Adopting eco-friendly building principles can reduce or eliminate environmental pollutants [8]. All forms of water contamination can be effectively removed by using nano-adsorbents such as “clay, zeolites, metals, metal oxides, polymeric membranes, porous nanofibers, and zero-valent iron” [188, 224]. As part of their irradiation-based degrading and mineralizing process, AOPs rely on semiconductor-based photocatalysts (natural and artificial) that are ecologically safe [215].

Nano-treatment reduces the amount of pollutants in the environment compared to earlier cleanup procedures [22]. Health and environmental problems can be prevented, reduced, and mitigated using nanotechnology [99]. As nanotechnology advances in environmental protection technologies, new solutions will be available to manage and remove pollutants in the atmosphere, groundwater supply, and surface

water. Traditional techniques of cleansing will also benefit from this advancement [193].

In situ treatment with nanotechnology is a time and money-saving alternative to traditional methods [58]. Treatment of polluted areas with nano-based remediation technology can cut costs, speed cleaning, and virtually remove the need to dispose of or treat contaminated soils [85, 86]. Advanced research and development are looking into the possibility of using nanomaterials to efficiently filter out environmentally harmful contaminants [203, 237]. Recently, many nanomaterials, such as “nanoscale zeolites, metal–metal oxides, carbon nanotubes, dendrimers, and metal-polymer doped nanoparticles,” have been studied for potential applications in nanotechnology [22, 161]. Nanomaterial oxides used on site, in addition to surface and groundwater cleanup, are effective for cleaning up non-aqueous phase fluid (NAPL) spills from subterranean oil tanks [50, 65, 94, 179].

Environmentally friendly products and processes can be developed using nanotechnology, which is central to green nanotechnology [62]. According to Maksimovic and Omanovic-Miklicanin [140], these technologies are primarily designed to be environmentally friendly and have a minimal impact on human health and the environment. Wastewater treatment using catalysts, adsorbents, and membranes based on nanotechnology is more environmentally friendly [214]. A high surface-to-volume ratio (SVR) makes nanoparticles promising for use in environmental purification and restoration [57]. Many researchers are working to create novel nanomaterials with enhanced selectivity, efficiency, and effectiveness for use in wastewater treatment. Nanotechnology for water treatment is the key to ensuring the safety and cleanliness of water supplies worldwide. Table 2 summarizes the nanotechnology applications which can be used to treat wastewater.

Nanotechnology-based remediation techniques are safer, more cost-effective, and more effective than conventional methods. Pollutant sensing and detection, cleaning,

Table 2 Applications of green nanotechnology in soil and water treatment [119]

Nanomaterials	Properties	Applications
Metal and metal oxides	Photocatalytic	Largely used for environmental remediation
	Nontoxic	Slurry reactors
	Green chemistry-based	Heavy metal, dyes, industrial effluent treatment
Adsorbents	Higher surface area	Removal of heavy metals
	Higher SVR	Dyes
	Higher adsorption rates	Pesticide degradation
	Easy to modify	Removal of organic pollutants, bacteria
Membrane and processes	Reliable	Treatment of water and wastewater
	Most trusted	Purification
	Widely used	Desalination
	Automated process	All fields of water and wastewater treatment

and pollution control are all potential applications for nanomaterials [115]. The nanomaterial's high SVR makes them ideal for water treatment and purification. Semiconductor nanomaterials are layered on top of conventional membrane treatments for purification and to create unique photocatalytic membranes [122]. Nanofiltration, photocatalytic processes, and adsorption are some of the methods used to solve wastewater treatment problems [13, 182].

Nanoparticles, nanomembranes, and other nanomaterials can be used for the detection and removal of a wide variety of chemical and biological pollutants [2, 9, 118, 120, 154]. Both filtration and photocatalysis can be accomplished with the use of membrane processes and nano-based materials [3, 141]. The use of environmentally friendly wastewater treatment solutions has become increasingly important due to sustainability concerns. Through the use of green chemistry to synthesize nanomaterials for environmental cleanup, hazardous waste generation can be reduced and toxic end products eliminated.

2.5 Green Nanotechnology in Renewable Energy Generation

The primary focus of this research is to develop green chemistry-based nano-enabled solar cells. Solar-absorbing polymers such as quantum dots, titanium dioxide, and cadmium telluride (CdTe) are among them [92]. Compared to existing solar cells, these nano-based solar cells are much more cost-effective [222]. The effectiveness of solar cells is being improved by a number of efforts in this area. For the design of environmentally friendly products in the future, other techniques such as the deposition of nano-crystals, the use of nanowires, and the development of a very durable lamination layer that covers solar cells are also being investigated [150]. Energy storage devices for renewable energy have also been developed using nanotechnology research. The performance and cost benefits of solar devices based on nanotechnology are significant [212].

2.6 Green Nanotechnology in Green Building Constructions

Nanotechnology is an important technology in the field of green manufacturing as it has the potential to contribute to environmental sustainability. The services provided by green building professionals, engineers, and architects are directly affected by the innovations [51, 52]. Due to advances in nanotechnology, suitable materials with unique properties are now available. In the past, designers had to rely on a limited number of standard materials. The design and construction of buildings will be directly affected by nanotechnology due to its impact on information technology, sustainability, and the development of novel materials and uses [129]. The value chain established by nanotechnology in building design and construction is depicted in Fig. 7. This value chain was developed using a comprehensive strategy and deep

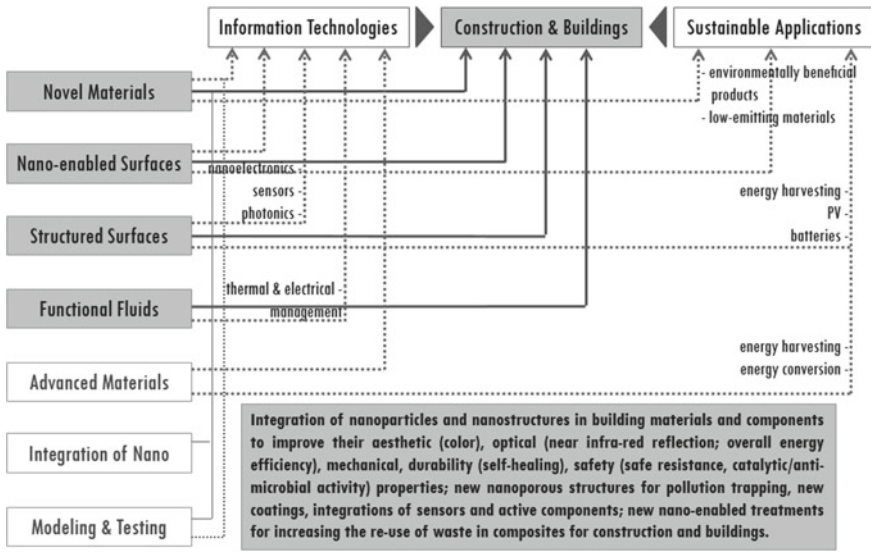


Fig. 7 Value chain created by nanotechnologies [51]

integration of state-of-the-art technologies via nanotechnology in green building design. Considerations of aesthetics, utility or functional performance, life-cycle cost, and sustainability from the user’s point of view are at the heart of the most realistic and practical applications of nanotechnology [53].

All aspects of the project, material or product, and service must be questioned in a green building project. Teams working on buildings are urged to employ life-cycle thinking when calculating the environmental implications of the structure as a whole, rather than just its components. “Life-cycle assessment (LCA) and life-cycle costing (LCC)” are two methods used to determine total cost of ownership (TCO). Fuel, installation, operation, maintenance, disposal, financing, and replacement are all parts of LCC, which is used to evaluate each proposed technology and method for the project’s environmental and economic viability [46].

As part of the green building lifecycle, it is essential to maximize the use of materials and energy. Green building design ideally has a fully closed-loop lifecycle. The objective is to minimize garbage leftover after a product has served its useful purpose. To ensure long-term viability, the material must be durable [54]. To last, a material must be structurally and aesthetically strong. There are various many advantages to designing for disassembly. It helps to increase the life of building components and systems, making them easier to repair or modernize. It also helps in recycling construction materials and rebuilding entire parts. Conventional energy sources such as “coal, oil and gas” have limited supplies and emit greenhouse gases into the atmosphere. “To improve our quality of life while preserving the planet’s ability to support us, we must transition to renewable energy and design for energy efficiency.” Reducing dependence on finite fossil fuel supplies and avoiding the

effects of air pollution and climate change are just two of the environmental and social benefits of renewable energy [54].

Eco-friendly buildings are more efficient than buildings that are not. Environmentally friendly management refers to an organization that aims to reduce costs and improve operational efficiency by implementing sustainable practices in its buildings. The total cost of the facility is explained as follows: Only 10% of the time is spent on the building; 90% of the time is spent on building operating and maintaining the facility. Clearly, a great way to reduce costs and increase revenue is to have tight control over facility operating costs. A large portion of the company's budget is paid for fuel and other necessities. The organization/company can only achieve sustainability if it provides a work environment free of harmful air, chemicals, and materials [225].

Nanotechnology has the potential to greatly improve sustainability in a variety of ways, including material and energy efficiency, process efficiency, and productivity. Titanium dioxide (TiO_2) nanoparticles are being tested, for instance, by scientists in Hong Kong and Japan as a means of reducing air pollution [54]. Up to 90% of nitrogen oxides were removed in the experiments, suggesting that dusty cities could face major health risks by embedding these nanoparticles in roads and structures. TiO_2 is also used by the Japanese company Toto as a coating for the manufacture of tiles. Indoor air quality can be improved with the use of certain nanomaterials. This is possible by coating the concrete with a thin layer of TiO_2 nanoparticles that consume pollution. This catalytic action degrades pollutants in contact with the surface [54].

Surface applications add new functionality to the texture of new materials, improving the quality of structures. Many companies are experimenting with nanotechnology to improve the properties of various materials. Currently, materials and coatings improve the health and safety of buildings and homes, as well as increase their energy efficiency by storing the sun's rays for later use. Nanomaterials are also used in air quality monitoring, air filtration, and energy-efficient air-conditioning systems [54].

2.7 Green Nanotechnology in Coating Industry Applications

Coating technology is widely used in many areas of our daily lives. Coating materials are manufactured for a variety of purposes, from food and pharmaceuticals to wearable and consumer goods, industry and machinery, and auto and construction components [84]. A film of coating material is often applied to the surface or bulk material of an object to protect, enhance, or provide additional capabilities and properties. This can be achieved by using coating technologies that help to protect surfaces from degradation caused by exposure to environmental factors such as moisture, UV rays, as well as preventing or reducing fouling and biofouling [241]. They can reduce chemical and structural degradation as well as wear and tear. Antimicrobial properties used for self-cleaning properties, such as super-hydrophobicity or super-hydrophilicity, are added to surfaces by coating methods [84]. Also, in food and

medicine, functional coatings can be used to mask taste and smell, protect and stabilize the physical environment, and release specific amounts into the body. As a result of the strong demand for functional coating materials and technologies resulting in economic value, more time and effort are devoted to research and development [241].

Functional coating technology mainly focuses on the development of coating materials and deposition processes for various applications. Inorganic nanoparticles and organic polymers can be used as functional coating materials based on their specific properties and functions [81]. There has been a meteoric rise in the creation of novel nanotechnology-based coatings in the last few years.

Nanotechnology has led to new advances in coated materials such as antifouling, anti-reflective, and fire-retardant coatings [101, 138, 227] (Fig. 8). Several silicone resin polymer foam composites have been used, including “silicone resin polymer foam composites [226], polydimethylsiloxane/graphene foam nanocomposites [35], water-based clay/graphene oxide nanoribbon networks [234] and composites of graphene oxide and melamine sponge” [36]. Tang’s team created several types of fire-proof coatings and alarm coatings based on the GO Network [37, 229]. However, Lejars et al. [128], Banerjee et al. [19], and Detty et al. [56] provide in-depth studies of the use of sol–gel technology to antifouling coatings, surface design, and alterations to thwart biofouling growth. Raut et al. [169] summarizes anti-reflective coatings made of silicon and TiO₂, functionalized polymers, and gallium as well as their production methods. Coating materials can benefit from the introduction of nanotechnology, which provides new features and functionalities that can be used to improve the performance of coating materials.

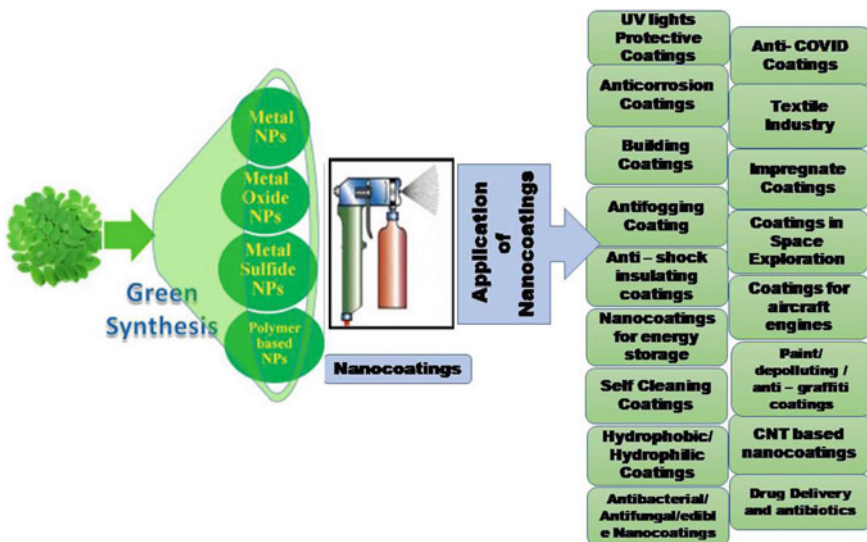


Fig. 8 Green nanotechnology in coating applications [84]

Generally, functional coating materials based on nano-composite chemistry are synthesized and then applied to surfaces [24, 151, 243]. Instead, deposition techniques are used to create or change the surface structures of coating materials at the nanometer level. There are several methods of coating application, including spraying and drop-casting, as well as dip coating and cast coating [15, 73, 93, 116].

In contrast, functional coatings play a crucial role in green construction. The most common type of coating is undoubtedly paint, which provides a variety of benefits including aesthetics and solar reflection [201, 209]. Other functional coatings such as self-cleaning, solar filtering, light and temperature control can be applied to external aspects of structures such as walls, ceilings, and windows [209].

Using nanotechnology for green building design and construction to improve properties and performance. Some examples are photocatalytic coatings, coatings that reduce surface solar radiation, and PCM coatings. These functional coatings are being developed by researchers around the world to reduce the carbon footprint of green building components. As a result of the self-cleaning and anti-icing capabilities of superhydrophobic coatings applied to building exteriors or civil engineering materials, additional resources and efforts are not required to successively clean, defrost, or repair worn or torn and cracked building components [228]. In addition, they contribute to the breathability of the wall, reduce thermal conductivity, and improve the resilience of the wall to biological agents such as bacteria [238]. As a result of the large surface area covered by water and the photocatalytic degradation of dirt and impurities under sunlight, the self-cleaning property reduces the effort and resources required for cleaning [159]. The anti-microbial [130] and moisture-controlling properties [61] of the hydrophilic coating have also been described. Solar reduction coatings, on the other hand, limit heat absorbed from the sun by using less energy to maintain a comfortable temperature inside the building [240]. Effectively reducing the temperature inside a building using phase change material coatings is a great way to save money on energy costs [111].

2.8 Green Nanotechnology in Cosmetic Applications

As defined by the Food and Drug Administration (FDA), cosmetic products are products designed “to enhance, promote, or alter the human body or any part thereof”. A cosmetic is any item used to enhance the skin’s natural beauty and cleanliness [83]. The worldwide demand for cosmetics has climbed by 4.5% each year in the twenty-first century, with yearly growth rates ranging from 3.0 to 5.5% [67, 181].

In the cosmetics industry, a product is considered to be “cosmetic” if it contains physiologically active substances that have a therapeutic impact on people [67, 136, 181]. Cosmetics possess bioactive components with quantifiable therapeutic properties that make them an excellent choice between pharmaceuticals and cosmetics. These ingredients are useful for treating a wide variety of issues, such as skin aging, hair loss, dryness, pigmentation, dark spots [114, 136] (Fig. 9).

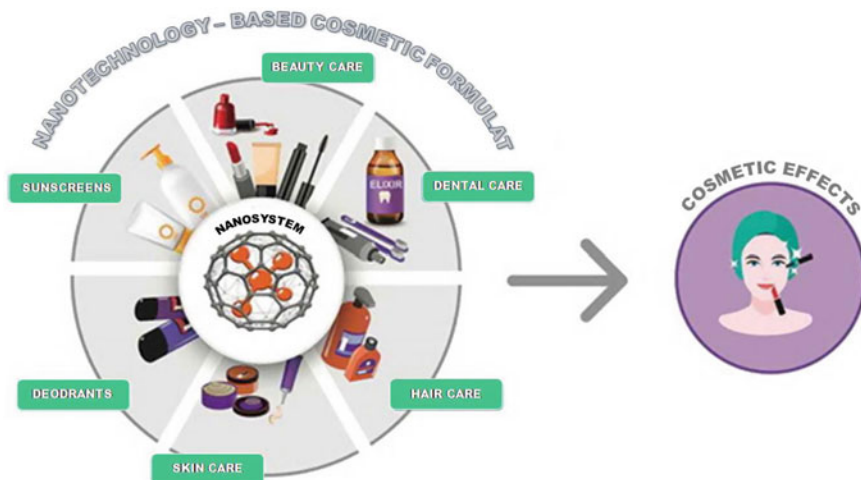


Fig. 9 Green nanotechnology in cosmetic applications [185]

As one of the most promising new technologies of the twenty-first century, nanotechnology is closely monitored by the cosmetics industry. It is possible to improve the delivery of bioactive chemicals with the use of nanotechnology in nanocosmeceutical formulations [100, 114]. Nanoparticles of cosmetic compounds can be prepared using this technology, which results in increased production efficiency and better skin damage repair due to the compounds' smaller size and higher absorption rate [197].

It has been shown that various types of nanoparticles can be used to enhance cosmetics, including “liposomes [206], niosomes [231], solid lipid nanoparticles [208], nanocapsules [178], micelles [235], dendrimers [147] and metal nanoparticles [137].” This process allows us to develop fragrances with extended longevity, cosmetics with enhanced UV protection, and effective anti-aging remedies (Fig. 9). The use of nanocarriers can reduce the size of bioactive ingredients in cosmetics, increasing their therapeutic potential [136].

The use of micellar nanoparticles in skin washing products is widely regarded as one of the most significant and cutting-edge breakthroughs in the field of cosmetics based on nanotechnology [40, 66, 79, 146]. Using nanotechnology, lipophilic bioactive ingredients can be incorporated into cosmetic formulations that possess a variety of physical and chemical properties. Nanoparticle size, encapsulation efficiency, and fabrication cost of micellar nanotechnology are superior to liposomes and niosomes [127, 207]. Many global and local cosmetics companies use micellar nanotechnology in their cleanser formulations to claim that their micellar nanotechnology-infused facial cleanser is the most effective on the market. With micellar nanotechnology, these brands have performed well. These cosmetics can benefit from using this process.

2.9 Green Nanotechnology in Textile Industry Applications

The textile industry is a leading user of nanotechnology, and numerous nanotextiles—including a wide range of consumer goods that employ nanoparticles—are currently on the market [1, 48, 68, 108, 113, 173, 187, 233]. Some of these high-tech textiles have built-in safety characteristics like being resistant to fire, dirt, water, and even ultraviolet light [4, 69, 70, 230]. The possibilities for textile applications are being broadened by the use of nanocoatings and nanofinishings [21, 74, 87, 107, 162]. High-performance textile coatings made from different nanomaterials can help a lot [23, 139, 172, 191, 196, 218]. Recent research on textile modification and characterization has focused on plasma and nano-pretreatment [200]. Fabrics created with nanotechnology are displayed in Fig. 10. Nanomaterials are able to offer greater functionality in textiles, despite their small size and large surface area. Commonly used carbon-based nanomaterials in textiles include “metal oxides, metal and nanoclay nanoparticles, core-shell nanoparticles, composite nanomaterials, hybrid nanomaterials, and polymeric nanomaterials such as graphene, carbon nanofibers, and carbon nanotubes.”

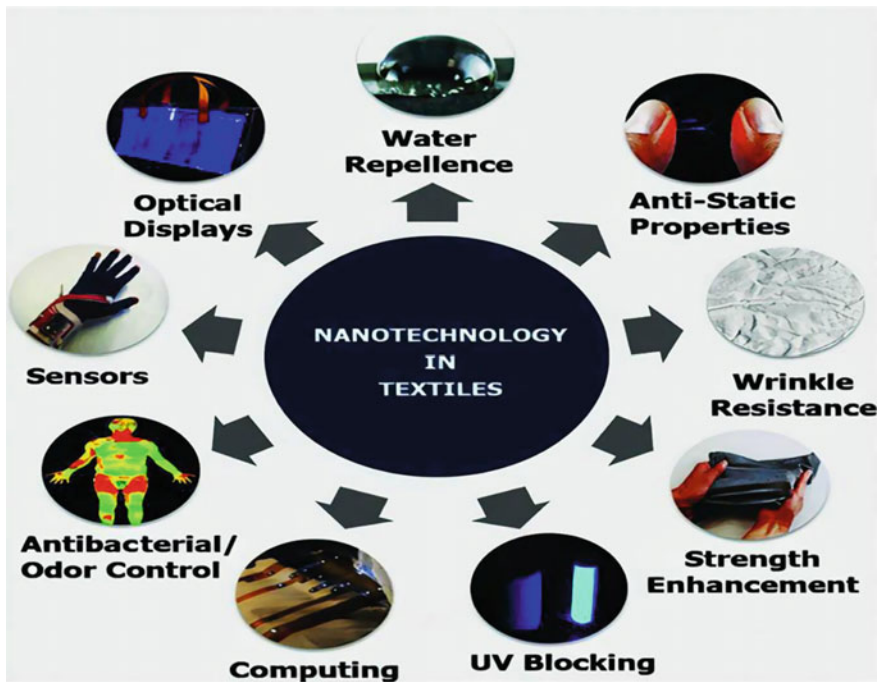


Fig. 10 Applications of nanotechnology in textiles [184]

3 Limitations of Green Nanotechnology

A new field of study, green nanotechnology, has its limits and limitations to overcome. The ACS Green Chemistry Institute (ACS GCI) reports on the main problems of green nanotechnology: Managing issues related to the toxicity of nanomaterials must also overcome economic and technical challenges. (1) Nanomanufacturing processes are subjected to regulatory procedures, (2) implementation of scale-up methods, (3) cycle of life aspects.

Green and sustainable development must take into account all of the above factors. Although green nanotechnology can reduce pollution and improve the environment, the expense and dangers of nano-based product manufacture are important limits. However, even if green nanotechnology has made progress, the level of sustainability has always been a challenge. However, upstream processing of green nanotechnology-based materials remains an important concern [44].

Green nanoproducts are now being investigated for their synthesis and application, although very few products have been developed in the commercial market so far [45]. The consensus is that the commercial potential of green nanotechnology is expected to be fully understood within a few years.

4 Conclusions

Using nanotechnology, we can solve the world's most serious issues. The term green nanotechnology refers to a technology that has a green advantage, as its name implies. Green chemistry is being thought about more and more in the context of nanotechnology because it provides a framework. Many benefits have been found through the studies, but some drawbacks and issues also need to be addressed. By using green nanotechnology, we can help solve the environmental crisis and promote sustainable development. For nanotechnology to be environmentally sustainable, life-cycle considerations must be included in the analysis of nanoproducts. New nanoproducts created through the nano-manufacturing process undergo life-cycle assessments before being released into commerce to fully assess their potential contribution to green development. However, there is always opportunity for development in bringing green chemistry ideas to nanotechnology.

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Carbon-Based Nanomaterials and Their Properties



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Abstract Carbon-based nanomaterials have attracted significant attention in recent years due to their unique electronic, mechanical, and thermal properties. This chapter provides an overview of the synthesis, characterization, and applications of carbon-based nanomaterials, including carbon nanotubes, graphene, and fullerenes. The chapter begins by discussing the properties and synthesis methods of these materials, including chemical vapor deposition, arc discharge, and laser ablation. The chapter also explores the various applications of carbon-based nanomaterials, including in electronics, energy storage, catalysis, and biomedical applications. Furthermore, we highlight the challenges associated with the large-scale production and commercialization of these materials, as well as the environmental and health impacts of their use. Finally, the chapter concludes with a summary of the current state of research and suggests possible directions for future work in this exciting field.

Keywords Carbon nanomaterials · Fullerenes · Nanotubes · Nanodiamonds · Quantum dots

1 Introduction

Carbon-based nanomaterials have been extensively researched for various applications due to their remarkable features. The exceptional properties of tunable carbon-based nanomaterials have garnered significant interest for their potential use in new technologies and addressing contemporary challenges. [1, 2] The carbon family comprises a range of distinct nanomaterials, including CNTs, fullerenes, graphene, carbon nanohorns, carbon-based quantum dots, and more. This section briefly outlines these nanomaterials, detailing their primary characteristics and significance.

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2 Fullerenes

Fullerenes are a class of carbon-based nanomaterials that were first discovered in 1985 by Harold Kroto, Richard Smalley, and Robert Curl. They are also known as “buckyballs” due to their spherical shape, which resembles a soccer ball or a geodesic dome. Fullerenes are composed entirely of carbon atoms, arranged in a closed shell structure. They are composed entirely of carbon atoms arranged in a unique three-dimensional structure, resembling a hollow sphere, ellipsoid, or tube. Fullerenes can be thought of as molecules made of carbon atoms that are bonded together in a highly symmetrical pattern. The most commonly known fullerene is C₆₀, which consists of 60 carbon atoms arranged in a soccer ball-like structure composed of 20 hexagons and 12 pentagons. There are also other types of fullerenes with different numbers of carbon atoms, such as C₇₀, C₇₆, C₈₄, and so on as shown in Fig. 1 [3, 4].

The unique features of small size, spherical shape, and isotropy make fullerene (C₆₀) a highly desirable zero-dimensional material [6]. As the first symmetric material in the carbon-based nanomaterial family, fullerenes have played a crucial role in expanding our understanding of nanomaterials. This breakthrough has paved the way for the discovery of other carbon-based nanostructures, including carbon nanotubes

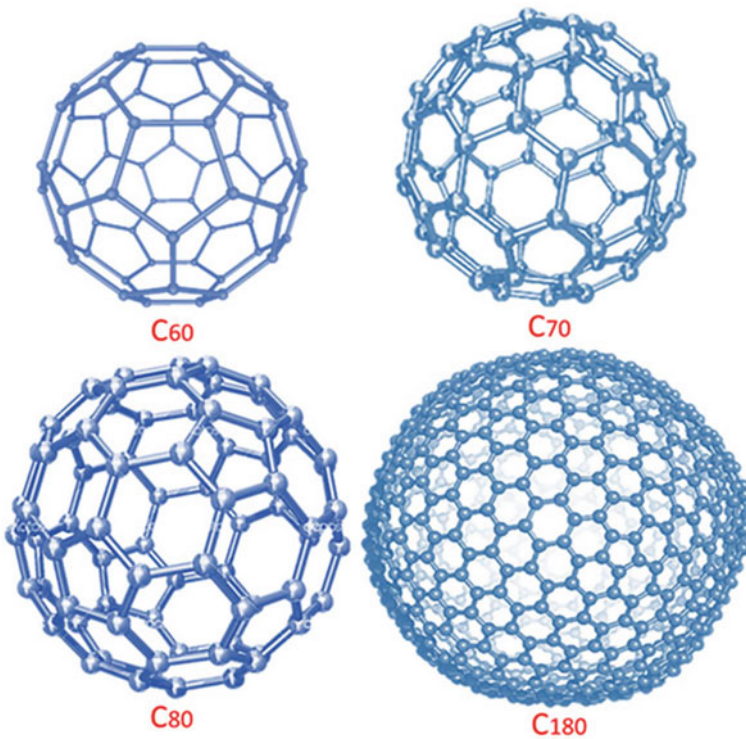


Fig. 1 Few of the fullerene analogues [5]

and graphene [7]. Furthermore, fullerenes have been found both in nature and in interstellar space [8]. Fullerenes possess unique physical and chemical properties that make them useful in a wide range of applications. They are highly stable and have high melting and boiling points. They are also good conductors of electricity and have high tensile strength, making them useful for strengthening materials [9–11]. Fullerenes also have a variety of potential medical applications. For example, they can be used as drug delivery systems, as they can encapsulate drugs and deliver them directly to target cells. The water-soluble cationic fullerene, tetra(piperazino) [12] fullerene epoxide (TPFE), has been employed to deliver DNA and siRNA specifically to the lungs, targeting diseases affecting this organ [13]. For effective treatment of lung or other organ diseases, active agents must be delivered to the precise location within the organ. However, the accumulation of carrier vehicles in the lungs, which can be in the micrometer size range, can cause embolization and inflammation, complicating lung-selective delivery. To overcome this challenge, size-controlled blood vessel carrier vehicles utilizing TPFE have been developed. In the bloodstream, TPFE and siRNA agglutinate with plasma proteins, forming micrometer-sized particles that clog lung capillaries and deliver siRNA to lung cells. After siRNA delivery, the micrometer-sized particles are swiftly cleared from the lungs [14]. They can also be used in photodynamic therapy, where they are activated by light to produce reactive oxygen species that can kill cancer cells. Another important application of fullerenes is in the field of electronics. They have been used to create thin films and coatings that can protect electronic devices from corrosion and oxidation. They can also be used as semiconductors in electronic devices such as transistors.

One of the most important properties of fullerenes is their ability to act as excellent electron acceptors and donors, allowing them to participate in a wide range of chemical reactions. They can form stable complexes with various molecules, including metals, organic compounds, and biological molecules. This makes fullerenes useful for applications such as drug delivery, catalysis, and electronic devices. Fullerenes also have interesting optical properties. They are highly fluorescent, meaning they emit light when excited by a light source. This property has been exploited for various applications, including biological imaging and photodynamic therapy. Fullerenes are a class of carbon-based nanomaterials that have unique physical, chemical, and optical properties. Their applications include drug delivery, catalysis, electronics, and biological imaging, among others. Fullerenes and their derivatives have diverse applications in the field of lubrication. They are utilized as modifiers for both greases and individual solid lubricants, leading to the development of advanced lubricants [15]. Additionally, fullerenes possess remarkable medicinal properties, including anticancer, antioxidant, anti-bacterial, and anti-viral activities, making them highly significant in the medical field [5].

3 CNTs

Carbon nanotubes (CNTs) are a class of carbon-based nanomaterials that were first discovered in 1991 by Sumio Iijima [16]. They are cylindrical in shape and consist of rolled-up sheets of graphene, a single layer of carbon atoms arranged in a hexagonal lattice [17]. Carbon nanotubes are cylindrical tubes composed of a single layer of sp^2 -hybridized carbon atoms that are rolled into a seamless structure. The surfaces of these tubes are made up of hexagonally arranged sp^2 -hybridized carbon atoms [18].

CNTs can be single walled (SWCNTs), consisting of a single sheet of graphene rolled up into a tube, or multi-walled (MWCNTs), consisting of multiple sheets of graphene rolled up into concentric tubes. They can range in diameter from less than a nanometer to several micrometers and in length from a few nanometers to several centimeters. CNTs can be single walled or multi-walled, with single-walled CNTs (SWCNTs) having a diameter of about 1–2 nm and multi-walled CNTs (MWCNTs) having a diameter of about 5–20 nm as shown in Fig. 2. CNTs can be hundreds of times stronger than steel, while being much lighter and more flexible [19–21]. There are several methods for synthesizing carbon nanotubes, including chemical vapor deposition [22], laser ablation [23], arc discharge [16], and gas-phase catalytic growth [24].

CNTs have several unique properties that make them attractive for various applications. They are incredibly strong and stiff, with a tensile strength that is orders of magnitude greater than steel, yet they are lightweight and flexible. They also

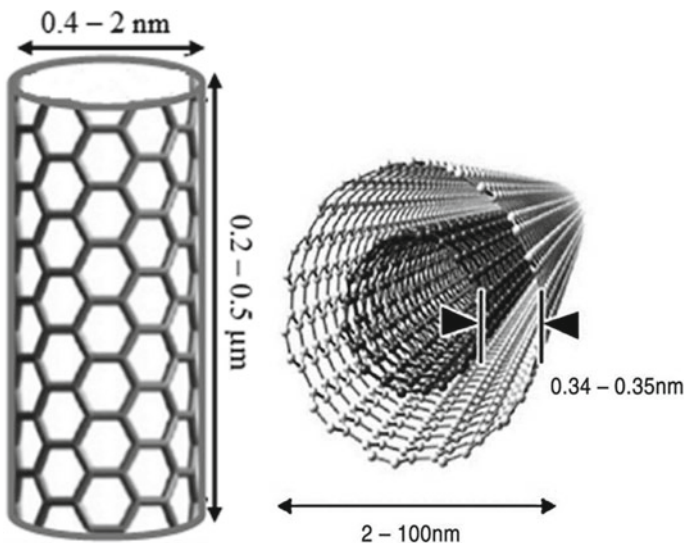


Fig. 2 Carbon nanotubes single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) [25]

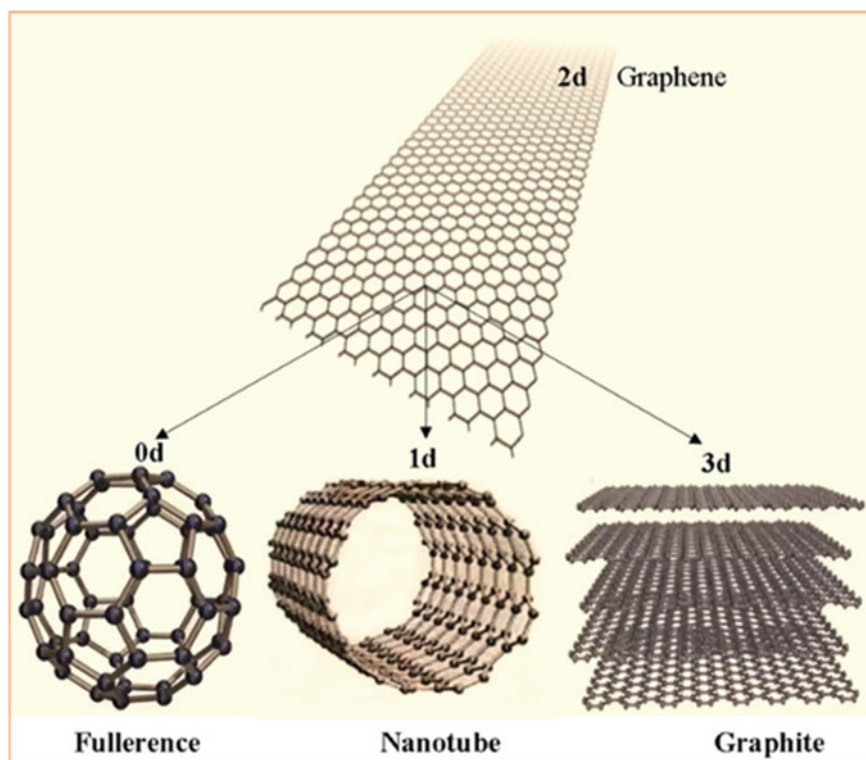


Fig. 3 Crystal structures of different allotropes of carbon: graphite (3D); graphene (2D); nanotubes (1D); and fullerene (buckyballs) (0D) [26]

have high thermal and electrical conductivity, making them useful in electronics and thermal management applications [27, 28]. CNTs have unique mechanical, electrical, and thermal properties making them useful for various applications such as reinforcing materials in composites, producing lightweight and strong materials, and building new types of nanoscale electronic devices.

One of the most significant challenges in working with CNTs is their tendency to form clumps or bundles, which can limit their usefulness in applications. However, various techniques, such as chemical functionalization, have been developed to disperse CNTs and improve their solubility in various solvents and polymers [29, 30].

CNTs have been explored for numerous applications, including electronics, energy storage, sensing, and drug delivery. They have been used to create flexible and transparent conductive films, high-performance transistors, and efficient energy storage devices. CNT-based sensors have been developed for detecting gases, biomolecules, and environmental pollutants, among other applications. CNTs also have excellent electrical conductivity, allowing them to be used as conductive elements in electronic devices such as transistors, sensors, and nanoelectronic

circuits. They also have excellent thermal conductivity, which makes them useful for applications such as heat dissipation in electronic devices [29].

CNTs have been explored for numerous applications, including biomedical applications, energy storage, and water purification. In biomedical applications, CNTs have been studied for drug delivery, imaging, and tissue engineering. They have also been used in energy storage devices such as batteries and supercapacitors due to their high surface area and excellent electrical conductivity. CNTs can also act as a catalyst in chemical reactions, which can be useful in a variety of industrial processes. Therefore, carbon nanotubes are a class of carbon-based nanomaterials with unique physical and chemical properties. Their applications include electronics, energy storage, sensing, and drug delivery, among others. Ongoing research and development in this field may unlock new opportunities for utilizing these remarkable materials in various technological and scientific applications.

4 Graphene

Graphene is a two-dimensional carbon-based nanomaterial that consists of a single layer of carbon atoms arranged in a hexagonal lattice structure. It was first isolated and studied in 2004 by Andre Geim and Konstantin Novoselov, who were awarded the Nobel Prize in Physics in 2010 for their work. Graphene is incredibly strong, flexible, and lightweight. It has a tensile strength of over 130 gigapascals, making it one of the strongest materials known. Graphene is also transparent, with a high electrical conductivity and excellent thermal conductivity [31–33]. Graphene is the thinnest and strongest material known to exist, with a thickness of only one atom and a tensile strength of over 130 gigapascals [34]. It is also highly conductive, with an electrical conductivity that is orders of magnitude higher than copper. Graphene's high surface area and ability to form strong chemical bonds make it useful for a wide range of applications [35]. Graphene has many unique properties that make it useful for various applications. Its high electrical conductivity and transparency make it an excellent material for use in touchscreens, flexible electronics, and solar cells. Its high thermal conductivity makes it useful for heat management in electronic devices. Graphene is also being explored for use in water filtration and desalination due to its ability to selectively filter out ions and other contaminants. Its strong mechanical properties make it useful for use in composite materials, such as those used in the construction of airplanes and automobiles [36].

In biomedical applications, graphene has shown potential as a drug delivery vehicle, biosensor, and tissue engineering scaffold. Graphene has also been studied for use in energy storage devices such as batteries and supercapacitors due to its high surface area and electrical conductivity [37, 38]. Graphene's unique properties have made it an attractive material for electronic devices such as transistors, sensors, and flexible electronics. It has also been explored for energy applications such as solar cells, batteries, and supercapacitors. Its high surface area and strong chemical bonds make it useful for catalysis and water purification. Graphene is also being studied

for biomedical applications such as drug delivery, biosensing, and tissue engineering [39, 40].

In addition to its exceptional properties, graphene can be easily produced in large quantities using a variety of methods such as chemical vapor deposition and exfoliation. However, challenges still exist in scaling up the production of high-quality graphene and integrating it into practical applications. In conclusion, graphene is a unique carbon-based nanomaterial with exceptional electronic, mechanical, and thermal properties. Its applications are diverse and include electronic devices, energy applications, catalysis, water purification, and biomedical applications. While challenges still exist in scaling up production and integrating it into practical applications, graphene holds great promise for the future of materials science and technology.

5 Nanodiamonds

Nanodiamonds are a type of carbon-based nanomaterial that are formed from diamond particles with sizes typically ranging from 2 to 10 nm. They can be synthesized from various sources, such as high-pressure and high-temperature treatment of graphite, detonation of explosives, or from diamond polishing waste. Nanodiamonds are a type of carbon-based material that possess a wide range of attractive properties for various applications. They were first discovered in the 1960s during explosives research in the USSR [41], but their potential was not fully recognized until the late 1990s [42]. Nanodiamonds are defined as monocrystalline diamonds with a particle size of less than 100 nm [43], and they consist of sp^3 -hybridized carbon nanoparticles as shown in Fig. 4. They have exceptional optical and mechanical properties, high specific surface areas, and rich surface structures. Nanodiamonds can be synthesized using various methods such as ion irradiation of graphite [44], high-energy ball milling [45], carbide chlorination [46], chemical vapor deposition [47], and laser ablation [48]. They possess a core-shell structure and have rich surface chemistry with numerous functional groups, such as amide, aldehyde, ketone, carboxylic acid, alkene, hydroperoxide, nitroso, carbonate ester, and alcohol groups, which allow for further functionalization for specific applications [49].

Nanodiamonds have unique properties that make them useful for a wide range of applications. They are extremely hard and wear resistant, with a high thermal conductivity and a low coefficient of friction. They are also biocompatible and non-toxic, which makes them useful for biomedical applications. One of the most promising applications of nanodiamonds is in biomedical imaging and drug delivery. Nanodiamonds can be functionalized with various biomolecules, such as antibodies, peptides, or nucleic acids, and used as targeted drug delivery vehicles. They can also act as fluorescent probes for biomedical imaging, as they have unique optical properties that make them easily detectable.

Nanodiamonds have also been studied for their mechanical properties, particularly as a reinforcement material for composites. Their high hardness and wear resistance make them useful in applications where abrasion and wear are a concern,

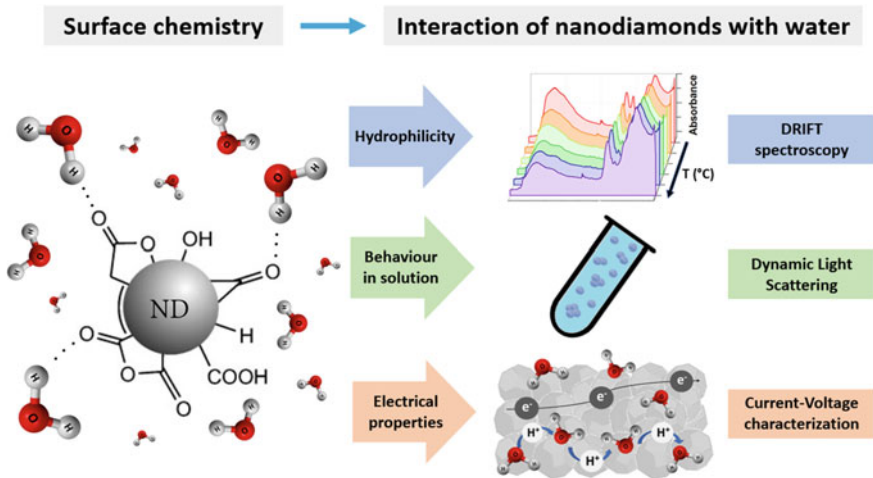


Fig. 4 NDs and their interaction with water [50]

such as cutting tools, polishing materials, and coatings. In addition, nanodiamonds can be used as a lubricant additive, as they have a low coefficient of friction and can reduce wear and tear on machinery. They can also be used in thermal management applications, due to their high thermal conductivity [51].

Nanodiamonds can also be functionalized with a variety of molecules, making them useful for applications such as biosensing and drug delivery. Their small size allows them to easily cross cell membranes and penetrate tissues, making them ideal for targeted drug delivery applications [52]. In addition, nanodiamonds have been explored for applications in electronics, photonics, and quantum computing. They have been used to create high-performance electronic devices and as a platform for single-photon sources and quantum sensors. Nanodiamonds are also being studied for their potential use in water purification, as they can adsorb a wide range of contaminants and heavy metals due to their high surface area and unique surface chemistry. In conclusion, nanodiamonds are a unique class of carbon-based nanomaterials with exceptional mechanical, thermal, and biocompatible properties. Their applications are diverse and include cutting tools, thermal management, biomedical applications, electronics, photonics, quantum computing, and water purification [53–56]. As research into nanodiamonds continues, they hold promise for a wide range of future applications.

6 Carbon-Based Quantum Dots

Carbon-based quantum dots (CQDs) are a type of carbon-based nanomaterials that are typically less than 10 nm in size. They are composed of graphene, carbon nanotubes, or other carbon-based materials and have unique optical and electronic properties that make them attractive for various applications. Carbon-based quantum dots (CQDs) are a class of carbon-based nanomaterials that have emerged as a promising alternative to traditional semiconductor-based quantum dots [57–59].

CQDs have a tunable bandgap, which allows them to absorb and emit light in a controllable manner. This makes them useful in optoelectronic applications such as solar cells, sensors, and light-emitting devices. They can also be used as fluorescent probes in biological imaging and drug delivery applications. CQDs can be synthesized using a variety of methods, including chemical vapor deposition, electrochemical synthesis, and laser ablation. They can be surface functionalized with different molecules, making them useful for applications such as biosensing and drug delivery. CQDs have also been studied for their potential use in quantum computing and information processing. They can be used as qubits, which are the basic building blocks of quantum computers [60–63]. Figure 5 shows the typical synthesis processes of these carbon quantum dots.

In addition, CQDs have been explored for energy storage applications such as supercapacitors and batteries. Their small size and high surface area make them ideal

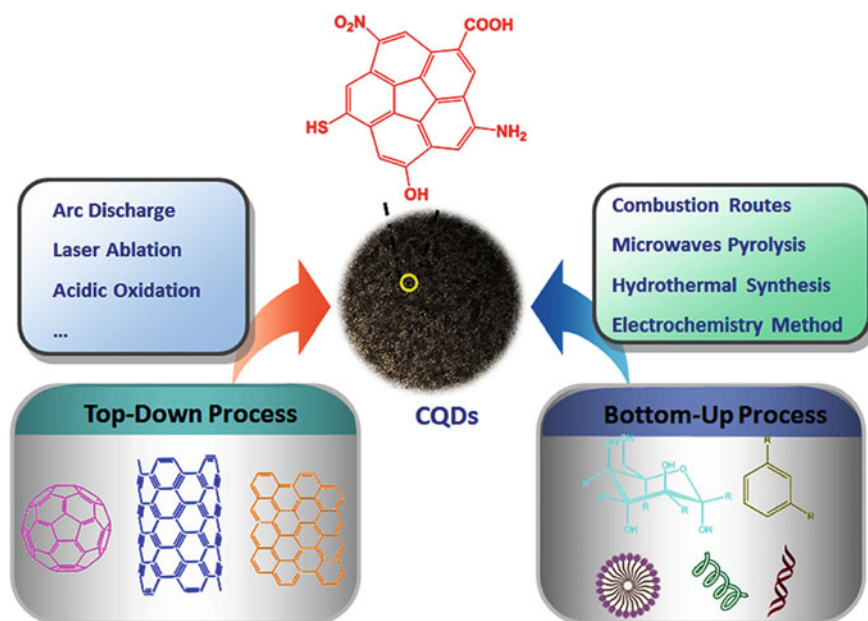


Fig. 5 Typical synthesis process of CQDs [64]

for energy storage and conversion applications. CQDs have also been investigated for their potential use in water purification and environmental remediation. They can be used as adsorbents for heavy metal ions and organic pollutants due to their unique surface chemistry and high surface area. CQDs have high surface area and high surface energy, which makes them suitable for applications such as catalysis, energy storage, and water purification. They have also been explored for biomedical applications such as drug delivery and bioimaging, due to their biocompatibility and low toxicity. CQDs can be synthesized using various methods, including chemical synthesis, microwave irradiation, and electrochemical synthesis. The properties of CQDs can be tuned by adjusting the synthesis conditions, such as the precursor materials and the reaction temperature. CQDs have several advantages over traditional semiconductor quantum dots, including their lower toxicity, biocompatibility, and lower cost. They are also environmentally friendly, as they can be synthesized from renewable resources such as biomass [59, 65, 66]. In conclusion, carbon-based quantum dots are a promising class of carbon-based nanomaterials with unique optical and electronic properties. Their applications are diverse and include sensing, imaging, lighting, catalysis, energy storage, water purification, and biomedical applications. As research into CQDs continues, they hold great potential for the development of new technologies in various fields.

7 Carbon Nanohorns/Nanocones

Carbon nanohorns (CNHs) and carbon nanocones (CNCs) are two related types of carbon-based nanomaterials that have a conical or horn-shaped structure. CNHs and CNCs are typically synthesized through a combination of arc discharge and laser ablation methods, which allow for the controlled synthesis of these complex structures. Carbon nanohorns are carbon-based nanostructures with lengths of approximately 40–50 nm and diameters ranging from 2 to 5 nm [67]. The assembly of thousands of single-walled carbon nanohorns (SWNHs) results in the formation of nanohorn aggregates with a diameter of around 80–100 nm [68]. Aggregation of carbon nanohorns can be observed [69]. Three types of carbon nanohorns have been identified, including dahlia-like CNHs, bud-like CNHs, and seed-like CNHs [70]. One significant advantage of carbon nanohorns over carbon nanotubes is that they can be synthesized without toxic metal catalysts and at room temperature, making large-scale production more feasible. In contrast, carbon nanotube synthesis requires metal particles, and harsh conditions, such as the use of strong acids, are necessary to remove metallic catalysts. CNHs and CNCs have been studied for various biomedical applications, including drug delivery, bioimaging, and tissue engineering. They have been shown to have low cytotoxicity and high biocompatibility, making them suitable for use in biomedical applications.

In addition, CNHs and CNCs have been explored for energy storage and conversion applications. They have high surface area and high electrical conductivity, making them useful for energy storage applications such as supercapacitors and

batteries. They have also been studied for use in solar cells and fuel cells, due to their unique electrical and mechanical properties. CNHs and CNCs are also being investigated for their potential use in water purification and environmental remediation. Their high surface area and unique surface chemistry make them effective at adsorbing and removing various contaminants from water and soil. In nutshell, carbon nanohorns and nanocones are a unique class of carbon-based nanomaterials with exceptional mechanical, electrical, and surface properties. Their applications are diverse and include drug delivery, sensing, catalysis, energy storage and conversion, water purification, and environmental remediation. As research into CNHs and CNCs continues, they hold great promise for the development of new technologies in various fields [70–73].

8 Conclusions

Carbon-based nanomaterials are a diverse and promising class of materials that have attracted significant attention in recent years due to their unique properties and potential applications. These materials, which include fullerenes, carbon nanotubes, graphene, nanodiamonds, carbon-based quantum dots, carbon nanohorns, and carbon nanocones, offer exceptional mechanical, thermal, electrical, and optical properties, making them suitable for a wide range of applications in fields such as electronics, energy, biomedicine, and environmental remediation. Carbon-based nanomaterials are highly customizable, with their properties being highly tunable through synthesis, functionalization, and structural manipulation. This makes them highly attractive for various applications. For example, carbon nanotubes are highly conductive and strong, making them useful for electrical and mechanical applications, while graphene's unique electronic and optical properties make it an ideal candidate for applications such as sensors and optoelectronics. Despite the significant potential of carbon-based nanomaterials, there are also concerns regarding their safety and environmental impact. As with any emerging technology, it is important to carefully assess the potential risks and benefits of carbon-based nanomaterials before widespread deployment. Overall, carbon-based nanomaterials hold great promise for the development of new technologies and the advancement of various fields. Ongoing research and development efforts in this area are expected to continue to drive innovation and progress in the years to come.

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Two-Dimensional Nanomaterials as Technology Marvels



Eddie Yin Kwee Ng, Balbir Singh, and Kamarul Arifin Ahmad

Abstract Two-dimensional (2D) nanomaterials have emerged as a new class of materials with unique properties and potential applications in various fields, such as electronics, energy, and medicine. This chapter provides precisely an overview of the synthesis, properties, and applications of 2D nanomaterials, including graphene, transition metal dichalcogenides, and black phosphorus. We begin by discussing the each of these 2D materials, their methods to synthesize, such as mechanical exfoliation, chemical vapor deposition, and liquid-phase exfoliation etc. Next, we describe their remarkable properties, such as high electrical conductivity, large surface area, and tunable bandgap that make them suitable for diverse applications. We then explore their various applications, including in flexible electronics, energy storage and conversion, sensing, and biomedicine inside each material description. Moreover, we highlight some of the challenges and limitations that need to be addressed for their commercialization and large-scale production. Finally, the chapter concludes with a summary of the current state of research and suggests possible directions for future work in this exciting field.

Keywords 2D materials · MXenes · Graphene · Metal–organic framework · Nanosheets · Nanoparticles

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1 Introduction

Two-dimensional (2D) nanomaterials are a class of materials that have a thickness of only a few atomic or molecular layers, while their other two dimensions extend to macroscopic scales. These materials are also known as 2D materials, ultrathin materials, or nanosheets. Two-dimensional (2D) nanomaterials are a class of materials that are characterized by their ultrathin and flat nature, with thicknesses typically measured in the nanometer scale [1, 2]. They possess unique physical, chemical, and mechanical properties that differ from their bulk counterparts, making them highly attractive for a wide range of applications in various fields such as electronics, optoelectronics, catalysis, energy, and biomedicine [3]. Graphene, a single layer of carbon atoms arranged in a honeycomb lattice, is the most well-known 2D material [3, 4]. However, there are many other 2D materials, including transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS_2), boron nitride (BN), and black phosphorus (BP), among others. 2D materials have unique physical and chemical properties compared to their bulk counterparts. Due to their large surface area to volume ratio, they exhibit enhanced surface reactivity and catalytic activity. In addition, they have high mechanical strength and flexibility, which makes them attractive for use in electronic and optoelectronic devices, as well as in nanocomposites and energy storage applications [5].

One of the most promising applications of 2D materials is in electronics, where they can be used to create faster, more efficient, and more compact devices. For example, graphene is an excellent conductor of electricity and has been used to make high-speed transistors and flexible, transparent conductive films. TMDs, on the other hand, have a bandgap, which allows them to be used in optoelectronic devices such as photodetectors and solar cells. Graphene, a single layer of carbon atoms arranged in a hexagonal lattice, is the most well-known 2D nanomaterial. However, over the past decade, there has been a rapid development of new 2D materials, including transition metal dichalcogenides (TMDs), boron nitride (BN), black phosphorus (BP), and many others as shown in Fig. 1a and b.

TMDs, such as MoS_2 and WSe_2 , are composed of a transition metal layer sandwiched between two chalcogenide layers. They exhibit excellent electronic and optical properties, making them promising for applications in transistors, photodetectors, and solar cells. BN, which has a similar structure to graphene, consists of boron and nitrogen atoms arranged in a hexagonal lattice. It possesses high thermal and chemical stability, making it an ideal insulator for electronics and photonics applications. BP, which consists of a single layer of phosphorus atoms arranged in a puckered honeycomb lattice, has attracted much attention due to its excellent electronic and optoelectronic properties. It has been explored for applications in solar cells, sensors, and transistors. Other 2D materials that have been extensively studied include transition metal carbides and nitrides (MXenes), metal–organic frameworks (MOFs), and perovskites. Overall, 2D nanomaterials offer tremendous potential for a variety of applications due to their unique properties, and their further development and exploration is an active area of research in materials science and engineering.

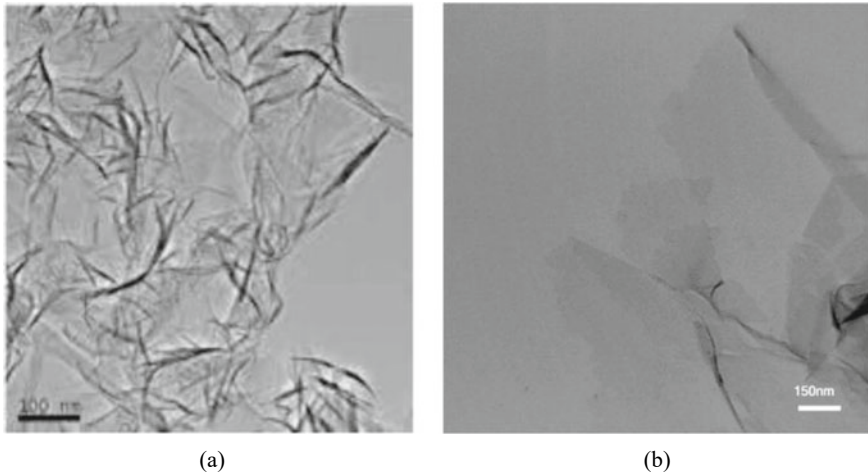


Fig. 1 Transmission electron microscopic images of **a** crumpled grapheme and **b** two relatively large centrally overlapped BNNSs [6]

2 Silicene

Silicene is a 2D material that consists of a single layer of silicon atoms arranged in a honeycomb lattice, similar to graphene. It was first proposed theoretically in 1994, but it was not until 2010 that researchers were able to synthesize it for the first time, using a silver substrate to stabilize the silicon atoms. Silicene is a 2D allotrope of silicon, which is composed of a single layer of silicon atoms arranged in a honeycomb lattice. It is analogous to graphene, which is composed of a single layer of carbon atoms arranged in a similar lattice. Silicene was first predicted to exist in 1994 by Takeda and Shiraishi, but it was not until 2010 that it was successfully synthesized by researchers in Germany [7, 8].

Silicene has a number of unique properties that make it highly attractive for potential applications. Like graphene, it is highly flexible, strong, and lightweight, and it exhibits excellent electrical conductivity. However, unlike graphene, silicene is a semiconductor, with a bandgap that can be tuned by controlling the size and shape of the lattice. Silicene has a number of unique physical and electronic properties, including high electron mobility, a tunable bandgap, and strong spin-orbit coupling. These properties make it a promising candidate for use in electronics and optoelectronics applications. Unlike graphene, silicene has a buckled structure, which gives it a distinct electronic structure with two different types of silicon atoms [9].

Figure 2 reveals the energy-crystal wave vector ($E-k$) dispersion of silicene. Silicene can be synthesized by a number of methods, including molecular beam epitaxy (MBE) and chemical vapor deposition (CVD). In MBE, silicon atoms are deposited onto a substrate in a high vacuum environment, where they arrange themselves into a silicene lattice. In CVD, silicon-containing gases are passed over a

substrate at high temperatures, where they react to form a silicene layer. Silicene has been proposed for a range of potential applications, including in electronics, optoelectronics, and energy storage. For example, silicene-based transistors could potentially offer better performance than traditional silicon-based transistors due to their superior electron mobility. Additionally, silicene could be used as a catalyst for various chemical reactions due to its high surface area and reactivity. Silicene has potential applications in a variety of fields, including electronics, optoelectronics, and energy storage. It could be used to create more efficient transistors and sensors, as well as to create new types of solar cells and batteries. Its unique properties also make it a promising candidate for use in quantum computing.

However, there are also several challenges that need to be addressed before silicene can be widely used in practical applications. One major issue is the difficulty of synthesizing and stabilizing silicene in a controlled manner, since it is highly reactive and tends to form clusters or even revert back to bulk silicon. Another challenge is the lack of large-area, high-quality silicene samples, which limits the ability to study its properties and develop practical devices. One of the main challenges in the use of silicene is its stability. Unlike graphene, which is stable under normal conditions, silicene is highly reactive and can easily oxidize in air. This limits its potential use in practical applications, and researchers are working to develop methods to stabilize it. In addition, the synthesis of silicene is still a challenging process, and further research is needed to develop more efficient and scalable methods of synthesis. In conclusion, silicene is a promising 2D material with unique electronic and physical properties that make it attractive for a range of applications. While there are still challenges to be addressed in its synthesis and stability, ongoing research is expected to yield new insights into its properties and potential uses [7–9, 11–31].

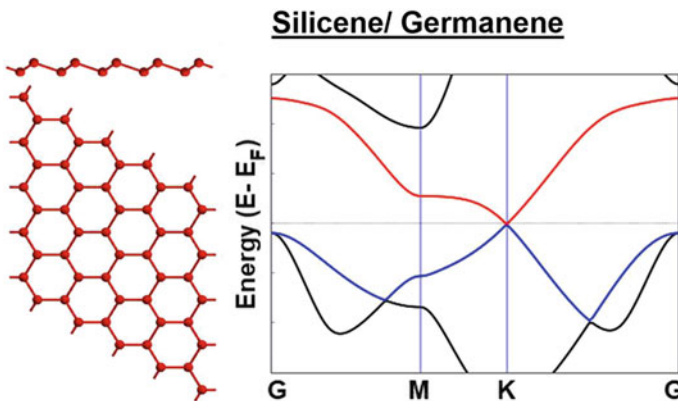


Fig. 2 ($5 \times 5 \times 1$ Supercell) of the monolayer silicene/germanene and its energy-crystal wave vector (E - k) dispersion [10]

3 MXenes

MXenes are a family of two-dimensional materials that are composed of transition metal carbides, nitrides, and carbonitrides. MXenes were first discovered in 2011 by researchers at Drexel University in Philadelphia, who were studying the synthesis of MAX phases. MAX phases are ternary compounds that are composed of a transition metal, a group A element, and carbon or nitrogen. MXenes are produced by selectively etching the A element layer from the MAX phase, leaving behind a layered two-dimensional structure. MXenes are a relatively new class of 2D materials that have attracted a lot of attention due to their unique properties and potential applications in a variety of fields. MXenes are transition metal carbides or nitrides that are produced by selectively etching the A layers of MAX phases, which are layered materials composed of a transition metal (M), a Group IIIA or IVA element (A), and carbon and/or nitrogen (X) arranged in a layered structure. MXenes have a number of unique properties that make them attractive for various applications. For example, they have high electrical conductivity, high surface area, and excellent mechanical properties.

MXenes are also hydrophilic, meaning they can be dispersed in water, making them easy to process. MXenes have a number of unique properties that make them promising candidates for a wide range of applications, including high electrical conductivity, high mechanical strength, and excellent thermal stability. They also exhibit tunable surface chemistry, which can be modified by changing the nature of the A element or by functionalizing the surface with organic or inorganic molecules. MXenes can be synthesized by a two-step process that involves etching the A layers of a MAX phase using a strong acid, followed by washing and delaminating the resulting material to produce MXene sheets. There are many different types of MXenes, each with unique properties, depending on the transition metal, the A layer element, and the etching conditions used in the synthesis. MXenes can be synthesized using a variety of methods, including chemical etching, electrochemical etching, and hydrothermal synthesis shown in Fig. 3. The most common method is chemical etching, which involves the use of strong acids such as hydrofluoric acid (HF) or hydrochloric acid (HCl) to selectively remove the A element layer from the MAX phase. Electrochemical etching involves using an electrical current to selectively etch the A element layer, while hydrothermal synthesis involves the use of high temperatures and pressures to synthesize MXenes from precursors.

MXenes have potential applications in a wide range of fields, including energy storage, catalysis, and sensors. In energy storage, MXenes have been explored as anode materials for lithium-ion batteries, as well as for supercapacitors, due to their high conductivity and high surface area. In catalysis, MXenes have been shown to have excellent activity for a variety of reactions, including hydrogen evolution and oxygen reduction. In sensors, MXenes have been used for gas sensing and biosensing applications, due to their high surface area and ease of functionalization. MXenes

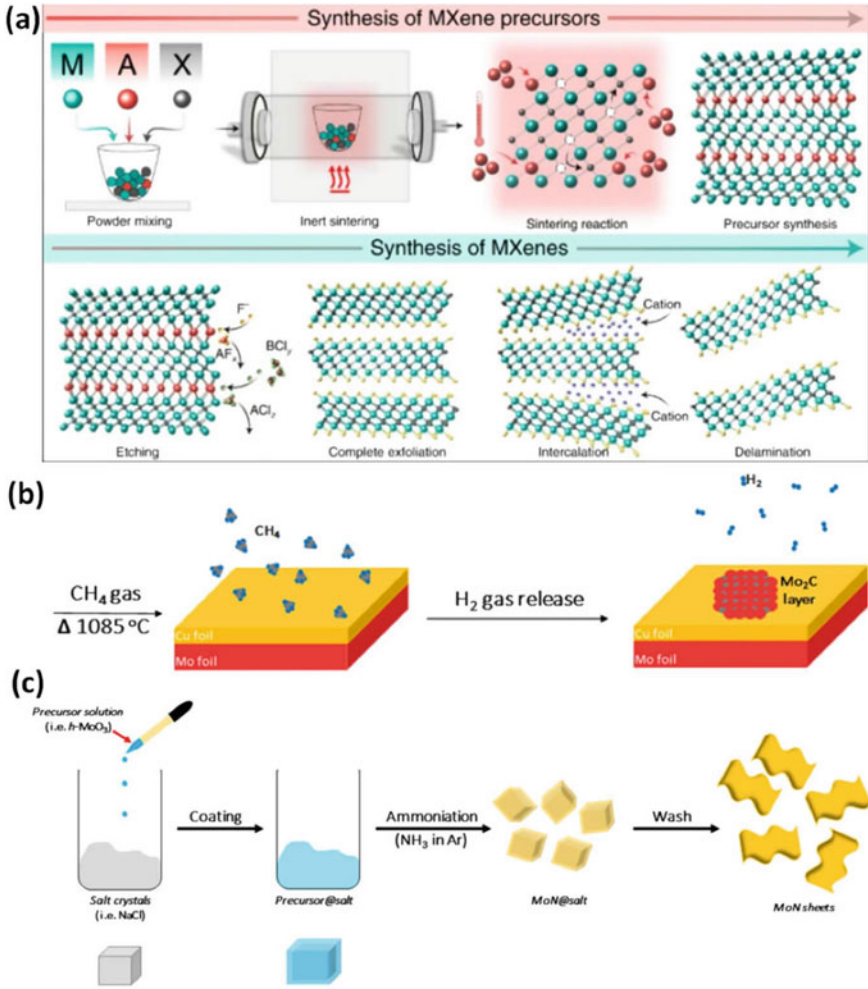


Fig. 3 Steps in the synthesis of MXene nanomaterials by top-down method from precursor to etching; bottom-up techniques are shown schematically in **b** [32]

have potential applications in a wide range of fields, including energy storage, catalysis, sensors, and electronics. They have been studied as electrode materials for supercapacitors and batteries due to their high electrical conductivity and large surface area. MXenes have also been explored as catalysts for hydrogen evolution reactions and as sensors for the detection of gases and biomolecules. Their high mechanical strength and thermal stability make them promising candidates for use in electronic devices such as flexible displays and touch screens.

One of the main challenges in the use of MXenes is their tendency to oxidize in air, which can affect their properties and limit their stability. Researchers are working to

develop methods to stabilize MXenes and improve their performance under ambient conditions. In addition, the synthesis of MXenes can be a complex process, and there is a need for further research to develop more efficient and scalable methods of synthesis. One of the main challenges in the use of MXenes is their stability. MXenes are highly reactive and can easily oxidize in air, which can limit their potential use in practical applications. Researchers are working to develop methods to stabilize MXenes, such as by using protective coatings or by functionalizing the surface with molecules that can inhibit oxidation. In addition, the synthesis of MXenes is still a challenging process, and further research is needed to develop more efficient and scalable methods of synthesis. In conclusion, MXenes are a promising class of 2D materials with unique properties and potential applications in a wide range of fields. While there are still challenges to be addressed in their synthesis and stability, ongoing research is expected to yield new insights into their properties and potential uses. In conclusion, MXenes are a promising class of 2D materials that offer a wide range of properties and potential applications. While there are still challenges to be addressed in their synthesis and stability, ongoing research is expected to yield new insights into their properties and potential uses [33–51].

4 2D Metal–Organic Framework Nanosheets (2D MOFs)

Two-dimensional metal–organic framework (MOF) nanosheets are a class of crystalline materials composed of metal ions or clusters coordinated to organic ligands. They have a layered structure, with a thickness of only a few nanometers, and can be synthesized through a variety of methods. Two-dimensional (2D) metal–organic framework (MOF) nanosheets are a type of 2D nanomaterial composed of metal ions or clusters linked by organic ligands. MOFs are typically three-dimensional materials, but the use of specific ligands and metal ions can result in the formation of 2D MOF nanosheets.

2D MOF nanosheets have a number of unique properties, including high surface area, tunable porosity, and catalytic activity. They can be functionalized with a variety of functional groups, making them versatile materials for a range of applications. The porosity of MOFs allows for the incorporation of guest molecules within the structure, making them ideal for gas separation, storage, and sensing applications. 2D MOF nanosheets have a number of unique properties, including a high surface area, porosity, and tunable chemical and electronic properties. The porosity of these materials makes them attractive for applications such as gas storage and separation, catalysis, and sensing. Their tunable properties make them attractive for applications such as electronic and optical devices.

2D MOF nanosheets can be synthesized through a variety of methods, including solvent-assisted exfoliation, surfactant-assisted exfoliation, and liquid-phase exfoliation as shown in Fig. 4a–d. In solvent-assisted exfoliation, MOFs are dispersed in a solvent, and sonication is used to exfoliate the material into nanosheets. Surfactant-assisted exfoliation involves the use of surfactants to stabilize the nanosheets in

a solvent. Liquid-phase exfoliation is a more recent method that involves the use of high-pressure homogenization to exfoliate the MOFs in a liquid medium. 2D MOF nanosheets can be synthesized using a variety of methods, including solvothermal synthesis, liquid-phase exfoliation, and chemical vapor deposition (CVD). In solvothermal synthesis, metal ions or clusters and organic ligands are combined in a solvent and heated under high pressure to form 2D MOF nanosheets. In liquid-phase exfoliation, bulk MOF crystals are dispersed in a solvent and sonicated to produce 2D nanosheets. CVD involves the deposition of metal and organic precursors onto a substrate, followed by thermal treatment to form a 2D MOF nanosheet.

2D MOF nanosheets have a wide range of applications in areas such as gas storage, catalysis, and sensing. Due to their high surface area and tunable porosity, they can be used as efficient adsorbents for the separation and storage of gases such as CO_2 and H_2 . They have also been studied as catalysts for various chemical reactions, including the reduction of CO_2 to produce valuable chemicals such as methanol. In addition, their unique properties make them promising candidates for use in electronic and photonic devices. 2D MOF nanosheets have potential applications in a wide range of fields, including gas storage and separation, catalysis, sensing, and electronics. Their high surface area and porosity make them attractive for use in gas storage and separation applications, such as carbon capture and storage. They also have potential as catalysts for chemical reactions, due to their tunable chemical properties. 2D MOF nanosheets have also been explored as sensors for the detection of gases and biomolecules, and as electronic devices such as field-effect transistors.

One of the main challenges in the use of 2D MOF nanosheets is their stability. MOFs are sensitive to moisture and can degrade over time, which can limit their

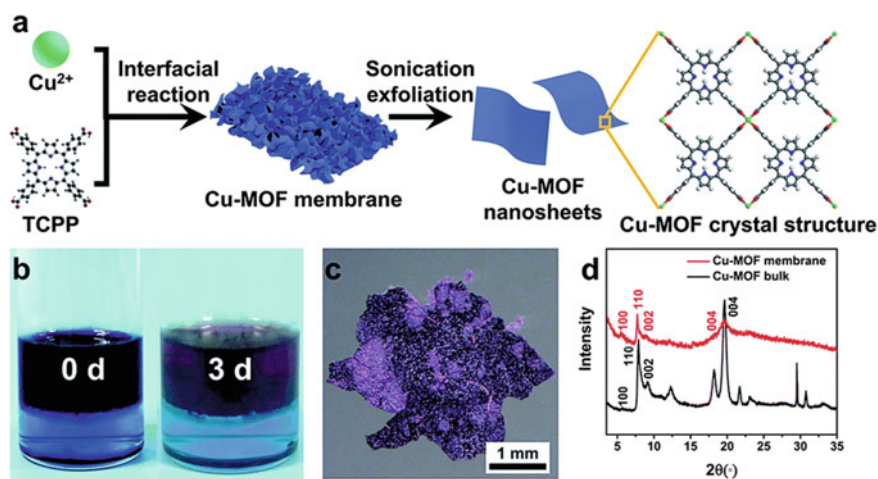


Fig. 4 **a** Synthetic procedure and crystal structure of Cu-MOF nanosheets (schematic). **b** Photographs of the color changes of two immiscible phases before and after the reaction. **c** Optical image of a Cu-MOF membrane. **d** PXRD spectra of a Cu-MOF membrane and Cu-MOF bulk counterparts [52]

potential use in practical applications. Researchers are working to develop methods to stabilize MOFs, such as by using protective coatings or by modifying the structure of the material. In addition, the synthesis of MOF nanosheets is still a challenging process, and further research is needed to develop more efficient and scalable methods of synthesis. One of the main challenges in the use of 2D MOF nanosheets is their stability. Like other 2D materials, they can be prone to oxidation and degradation in air and water. Researchers are working to develop methods to stabilize 2D MOF nanosheets, such as by using protective coatings or by functionalizing the surface with molecules that can inhibit degradation. In addition, the synthesis of 2D MOF nanosheets is still a challenging process, and further research is needed to develop more efficient and scalable methods of synthesis. 2D MOF nanosheets are a promising class of materials with a wide range of properties and potential applications. While there are still challenges to be addressed in their stability and synthesis, ongoing research is expected to yield new insights into their properties and potential uses. In conclusion, 2D MOF nanosheets are a promising class of 2D materials with unique properties and potential applications in a wide range of fields. While there are still challenges to be addressed in their stability and synthesis, ongoing research is expected to yield new insights into their properties and potential uses [53–57].

5 Metal Nanostructured Materials

Metal-based nanomaterials have gained attention for various applications due to their promising properties [58, 59]. One important area of research is the development of nanoscale catalysts, which exhibit exceptional catalytic activity and offer more efficient and effective reactions. At the nanoscale level, these materials have a large surface area, numerous binding sites, and favorable thermodynamics and kinetics for heterogeneous reactions [60], making them highly desirable for catalysis. They are also being explored for creating artificial enzymes [61]. Researchers are now focusing on designing specific nano-architectures to improve their performance. There are several synthesis methods available for creating these materials, including hydrothermal, solvothermal, sol–gel, electroless, electrochemical, and physical methods.

Due to the growing demand for alternative, clean, and renewable energy sources, metal-based nanostructured materials are being extensively studied for the production of robust electrodes that can be used in water splitting, batteries, and solar cells [60]. Researchers are striving to improve the performance of existing lithium-ion batteries by improving their safety, lifetime, and size [62]. Nanostructured metal-oxide-based materials show promise as electrode materials for high-performance charge storage devices, and metal-based nanostructured electrodes are being evaluated for use as both anodes and cathodes to overcome the challenges of conventional electrodes [63].

6 Nanoparticles with Core–shell

Nanoparticles can be classified into three categories based on their composition: simple, composite, or core–shell. Simple nanoparticles are made up of a single material, while composite and core–shell nanoparticles consist of two or more materials. Core–shell nanoparticles consist of an inner material (the core) and an outer material (the shell). Different combinations of materials can be used to create core–shell nanoparticles, including organic/organic, inorganic/organic, inorganic/inorganic, and organic/inorganic materials [64].

Spherical core–shell nanoparticles are a practical way to introduce multiple functionalities on a nanoscopic scale [65]. The properties of the core and shell can be controlled by adjusting the ratio of the constituent materials, and their shape, size, and composition are critical factors in determining their properties. The shell material can improve the chemical and thermal stabilities of the core material, making it more durable [66]. The core–shell design is particularly useful when an inexpensive material is unstable or easily oxidizable. For example, magnetic nanoparticles are sensitive to air, acids, and bases, but coating them with organic or inorganic shells can protect them from degradation [67].

7 Conclusions

In conclusion, 2D nanomaterials have emerged as a fascinating area of research in nanoscience and nanotechnology due to their unique and extraordinary properties. Graphene, the first 2D material discovered, has opened up new possibilities for a wide range of applications in electronics, energy storage, and biomedicine. Other 2D materials such as transition metal dichalcogenides, black phosphorus, and boron nitride have also shown promise for various applications. The synthesis and functionalization of 2D nanomaterials have advanced significantly in recent years, enabling the development of new devices with improved performance. Although challenges such as scalability and commercial viability still exist, 2D nanomaterials hold tremendous potential for future technological advancements.

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Future Enabled by Nanomaterials: Editor Summary



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Abstract This chapter presents a summary of the exciting potential and challenges of nanomaterials, as discussed in the various contributions to the book. The chapter begins with an overview of the unique properties of nanomaterials, which arise from their small size and large surface area. The authors then discuss the various applications of nanomaterials in fields such as medicine, energy, and electronics, as well as their potential for environmental remediation. The chapter highlights some of the key themes that emerged from the book, such as the need for interdisciplinary collaboration to drive innovation, the importance of responsible development and deployment of nanomaterials, and the potential risks and uncertainties associated with their use. The authors also discuss some of the challenges facing the field, such as the need for standardized characterization and safety testing of nanomaterials, as well as the high-end equipment and software used for the characterization of these materials. The chapter concludes by emphasizing the importance of continued research and development in the field of nanomaterials to ensure their safe and sustainable use, as well as their potential to revolutionize various industries and benefit society as a whole. Overall, this chapter provides a concise summary of the

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various contributions to the book, highlighting the exciting potential and challenges of nanomaterials and their future.

Keywords Green nanotechnology · Soft nanomaterials · Nanocomposites · Bio-nanomaterials · Carbon-based nanomaterials · 2D nanomaterials

1 Editor Note or Summary

Nanomaterials have the potential to revolutionize a wide range of industries and fields in the future, thanks to their unique properties and applications. Here are some ways in which nanomaterials could enable a more advanced future: It is difficult to predict the exact advancements that will be made with nanomaterials by 2050, but it is likely that there will be significant progress and breakthroughs in this field. Here are some possible developments.

Nanomaterials could be used to create personalized medicine, where drugs are tailored to an individual's specific genetic makeup. This could improve the effectiveness of treatments and reduce side effects. Nanomaterials could also be used to create more advanced prosthetics and implants that are more biocompatible and durable. Nanomaterials have revolutionized the field of health care with their unique properties such as high surface area to volume ratio, small size, and tunable physical and chemical properties. These properties make them ideal for various applications such as drug delivery, imaging, diagnosis, and therapy. In drug delivery, nanomaterials have been used to enhance the bioavailability and efficacy of drugs. They can target specific tissues and cells, release drugs in a controlled manner, and reduce the toxicity of drugs. Nanoparticles such as liposomes, dendrimers, and polymeric nanoparticles have been used in pre-clinical and clinical trials for drug delivery. In imaging, nanomaterials have been used as contrast agents for various imaging modalities such as magnetic resonance imaging (MRI), computed tomography (CT), and ultrasound. These contrast agents enhance the sensitivity and specificity of imaging, leading to better diagnosis and treatment. In diagnosis, nanomaterials have been used as biosensors for the detection of various biomolecules such as proteins, DNA, and RNA. They can detect these biomolecules with high sensitivity and specificity, leading to early diagnosis of diseases. In therapy, nanomaterials have been used for targeted therapy such as photodynamic therapy, gene therapy, and immunotherapy. These therapies can target specific cells and tissues, leading to better outcomes with reduced toxicity. The future of nanomaterials in health care is promising, with ongoing research focused on developing new nanomaterials and applications. Some of the areas of research include nano-enabled tissue engineering: Nanomaterials can be used to create scaffolds for tissue engineering, leading to the development of functional tissues and organs. Nanorobotics: Nanomaterials can be used to develop nanorobots that can perform targeted drug delivery, imaging, and diagnosis. Personalized medicine: Nanomaterials can be used to develop personalized medicine, where

drugs are tailored to individual patients based on their genetic makeup. Nanomaterials can be used in nanopore sequencing, a new sequencing technology that can sequence DNA in real time. In conclusion, nanomaterials have the potential to transform health care with their unique properties and applications. Ongoing research in this area is likely to lead to new and innovative nanomaterials and applications that will improve the diagnosis and treatment of diseases.

2 Applications of Nanomaterials

2.1 Health Care

Nanomaterials such as liposomes, dendrimers, and nanoparticles can be used as carriers for drugs to improve their bioavailability, stability, and targeted delivery to specific cells or tissues. Nanomaterials such as quantum dots, carbon nanotubes, and gold nanoparticles can be used as contrast agents for various imaging techniques such as magnetic resonance imaging (MRI), computed tomography (CT), and fluorescence imaging. Nanomaterials such as biosensors and nanochips can be used for the detection of disease biomarkers and other analytes in biological samples with high sensitivity and specificity. Nanomaterials such as nanofibers and hydrogels can be used as scaffolds for tissue engineering and regenerative medicine applications. The future of nanomaterials in health care is promising, with ongoing research focused on developing new nanomaterials and applications. Some of the areas of research nanomaterials can be used in the development of personalized medicine approaches that take into account the individual variability in disease susceptibility and drug response. Nanomaterials can be used in the development of targeted cancer therapies that selectively deliver drugs or other therapeutic agents to tumor cells while minimizing toxicity to normal cells.

Nanomaterials can be used in the development of gene therapy approaches for the treatment of genetic diseases and other disorders. Nanomaterials can be used in the development of immunotherapy approaches that enhance the immune response to cancer and other diseases.

So, nanomaterials have the potential to revolutionize health care by enabling the development of new diagnostic and therapeutic technologies with improved sensitivity, specificity, and targeted delivery. Ongoing research in this area is likely to lead to new and innovative nanomaterials and applications that will address some of the major challenges faced by health care such as personalized medicine, cancer therapy, gene therapy, and immunotherapy. However, it is important to consider the potential risks and ethical implications associated with the use of nanomaterials in health care.

2.2 *Applications of Nanomaterials in Energy Sector*

Nanomaterials could enable the development of more efficient and cost-effective solar cells and batteries. This could lead to widespread adoption of renewable energy sources and a significant reduction in greenhouse gas emissions. Nanomaterials have the potential to revolutionize the energy sector by improving the efficiency of energy production, storage, and usage. The unique properties of nanomaterials such as high surface area to volume ratio, tunable physical and chemical properties, and quantum confinement effect have made them ideal for various applications in the energy sector.

Some of the applications of nanomaterials in the energy sector include nanomaterials such as quantum dots, nanowires, and nanotubes that can be used to improve the efficiency of solar cells by enhancing light absorption and charge separation. Nanomaterials such as nanowires, nanotubes, and nanoparticles can be used to increase the energy density and cycle life of batteries by improving the electrode materials. Nanomaterials can be used as catalysts in fuel cells to improve their efficiency and reduce the cost. Nanomaterials can be used as supercapacitors and nanocapacitors for energy storage due to their high surface area and high capacitance.

Nanomaterials such as thermoelectric materials can be used to convert waste heat into electrical energy. The future of nanomaterials in the energy sector is promising, with ongoing research focused on developing new nanomaterials and applications. Some of the areas of research include nanomaterials that can be used to develop nanogenerators that can harvest energy from the environment such as mechanical energy, thermal energy, and solar energy. Nanomaterials such as nanocrystals can be used in smart windows that can selectively reflect or absorb sunlight to regulate the temperature of buildings. Nanomaterials can be used in nanosensors for monitoring energy usage and efficiency in buildings and transportation. Nanomaterials such as quantum dots can be used in energy-efficient lighting such as LED lights. Nanomaterials can be used in the development of artificial photosynthesis systems that can mimic the process of natural photosynthesis to convert sunlight into fuels such as hydrogen. Nanomaterials can be used in the development of advanced energy storage devices such as supercapacitors and flow batteries. Nanomaterials such as metal-organic frameworks (MOFs) and carbon nanotubes can be used in the development of carbon capture and storage (CCS) systems for reducing greenhouse gas emissions. Nanomaterials can be used in the development of sensors and other devices for smart grid applications such as real-time monitoring and control of energy production and consumption. They have the potential to improve the efficiency and sustainability of energy production, storage, and usage. Ongoing research in this area is likely to lead to new and innovative nanomaterials and applications that will revolutionize the energy sector.

2.3 Applications in Electronics

Nanomaterials could be used to develop even more advanced electronics, such as quantum computers and high-performance sensors. This could lead to significant improvements in fields such as communication, transportation, and medicine. Nanomaterials have the potential to revolutionize the electronics industry by enabling the development of new devices with improved performance, functionality, and miniaturization. The unique properties of nanomaterials such as high surface area to volume ratio, tunable physical and chemical properties, and quantum confinement effect have made them ideal for various applications in electronics. Some of the applications of nanomaterials in electronics include nanomaterials such as carbon nanotubes and graphene that can be used to develop high-performance transistors that are faster and more energy efficient than traditional transistors. Nanomaterials such as nanowires, nanoparticles, and quantum dots can be used to develop highly sensitive and selective sensors for various applications such as chemical and biological sensing.

Nanomaterials such as quantum dots and nanowires can be used in displays to improve color accuracy, contrast, and energy efficiency. Nanomaterials such as phase-change materials and magnetic nanoparticles can be used in memory devices to improve data storage density and speed. The future of nanomaterials in electronics is promising, with ongoing research focused on developing new nanomaterials and applications. Some of the areas of research include nanomaterials that can be used to develop nanophotonic devices such as optical switches, modulators, and detectors that can enable high-speed data transmission and processing. Nanomaterials such as memristors can be used in neuromorphic computing to develop artificial intelligence systems that can mimic the human brain. Flexible and wearable electronics: Nanomaterials such as nanowires and graphene can be used in flexible and wearable electronics that can conform to the shape of the body and enable new applications such as health monitoring and human-machine interfaces. Nanomaterials could be used to develop new materials and processes for pollution control and environmental remediation. This could help address some of the most pressing environmental challenges, such as air and water pollution, and climate change. Nanomaterials have the potential to address some of the major environmental challenges faced by humanity, including pollution, water scarcity, and climate change. The unique properties of nanomaterials such as high surface area to volume ratio, tunable physical and chemical properties, and reactive surface chemistry have made them ideal for various applications in environmental remediation.

2.4 Applications in Environment

Nanomaterials such as graphene oxide, nanocellulose, and carbon nanotubes can be used to remove contaminants from water such as heavy metals, bacteria, and organic compounds. Nanomaterials such as titanium dioxide and zinc oxide can be

used to remove pollutants from the air such as volatile organic compounds, nitrogen oxides, and particulate matter. Nanomaterials such as zero-valent iron and iron oxide nanoparticles can be used to remediate contaminated soil by degrading pollutants such as pesticides and hydrocarbons. Nanomaterials can be used in desalination processes to improve energy efficiency and reduce costs. The future of nanomaterials in the environment is promising, with ongoing research focused on developing new nanomaterials and applications. Some of the areas of research include nanosensors for environmental monitoring such as detecting pollutants in air, water, and soil. Nanomaterials such as metal–organic frameworks and carbon nanotubes can be used to capture carbon dioxide from industrial processes and power plants.

Nanomaterials can be used in agriculture to improve soil quality, increase crop yield, and reduce the use of fertilizers and pesticides. Nanomaterials can be used to enhance the effectiveness of bioremediation processes for environmental remediation.

Nanomaterials have the potential to revolutionize the environmental industry by enabling the development of new technologies for pollution control, environmental remediation, and sustainable energy generation. The unique properties of nanomaterials such as high surface area to volume ratio, tunable physical and chemical properties, and quantum confinement effect have made them ideal for various applications in the environmental sector. The future of nanomaterials in the environment is promising, with ongoing research focused on developing new nanomaterials and applications. Some of the areas of research include nanomaterials that can be used in the development of nanobiosensors for real-time monitoring of environmental pollutants. Nanomaterials can be used in the development of nanorobots that can perform tasks such as environmental monitoring and pollutant removal. Nanomaterials such as carbon nanotubes and graphene can be used as high-capacity adsorbents for the removal of pollutants from water and air. Nanomaterials such as metal nanoparticles can be used as efficient catalysts for the degradation of pollutants.

2.5 Applications in Materials Science

Nanomaterials could enable the development of new materials with unprecedented properties, such as super-strength, self-healing, and shape-shifting. These materials could be used in a wide range of applications, from aerospace and defense to consumer products and architecture. Nanomaterials have the potential to revolutionize material science by enabling the development of new materials with improved properties such as mechanical strength, electrical conductivity, and thermal stability. The unique properties of nanomaterials such as high surface area to volume ratio, quantum confinement effect, and tunable physical and chemical properties have made them ideal for various applications in material science. Some of the applications of nanomaterials in material science are nanomaterials such as nanocomposites, nanoceramics, and nanometals that can be used to develop materials with improved mechanical strength, toughness, and wear resistance. Nanomaterials such

as nanowires, nanoparticles, and nanotubes can be used in energy storage and conversion devices such as batteries, supercapacitors, and fuel cells. Nanomaterials can be used to develop coatings and surfaces with improved properties such as anti-corrosion, antifouling, and self-cleaning. Nanomaterials can be used as catalysts for various chemical reactions with improved efficiency, selectivity, and durability. The future of nanomaterials in material science is promising, with ongoing research focused on developing new nanomaterials and applications. Nanomaterials can be used to develop smart materials that can respond to changes in temperature, pressure, and other environmental stimuli. Nanomaterials can be used in the development of biomaterials such as tissue scaffolds, drug delivery systems, and biosensors. Nanomaterials can be used in the development of nanorobots that can perform various tasks such as drug delivery, sensing, and actuation. Nanomaterials can be used in the development of sustainable materials such as biodegradable plastics and recyclable composites. Nanomaterials can be used in 3D printing to develop new materials with improved properties and functionality. Nanomaterials can be used in the development of self-healing materials that can repair damage and extend the lifespan of materials. Nanomaterials can be used in the development of new electronic materials and devices with improved performance and functionality. Nanomaterials can be used to develop materials that mimic the properties and functionality of biological materials such as bone, skin, and muscle.

2.6 Applications in Construction Industry

Nanomaterials can be used to develop stronger, more durable, and lighter construction materials, such as concrete and steel. They can also be used to create self-healing materials that can repair cracks and other damage on their own. Nanomaterials have the potential to transform the construction industry by enabling the development of new materials with improved properties and performance. The unique properties of nanomaterials such as high surface area to volume ratio, tunable physical and chemical properties, and improved mechanical and thermal stability have made them ideal for various applications in construction. Some of the applications of nanomaterials in construction are: Nanomaterials such as carbon nanotubes and nanoparticles can be used to enhance the mechanical properties of concrete, increase its durability, and reduce its environmental impact. Nanomaterials such as aerogels can be used as insulation materials due to their low thermal conductivity and high surface area. Nanomaterials can be used in coatings to improve the durability, water resistance, and UV stability of building materials such as glass and metals. Nanomaterials such as titanium dioxide nanoparticles can be used to develop self-cleaning surfaces that can break down organic matter and prevent the growth of microorganisms.

The future of nanomaterials in construction is promising, with ongoing research focused on developing new nanomaterials and applications. Some of the areas of research include nanomaterials can be used in the development of smart materials that can sense and respond to environmental stimuli such as temperature, humidity,

and light. Nanomaterials can be used to develop advanced coatings that can reduce the need for cleaning and maintenance, improve energy efficiency, and provide additional protection against environmental factors. Nanomaterials can be used to develop new types of cement with improved strength, durability, and sustainability. Nanomaterials can be used in the development of sensors that can monitor the structural integrity of buildings and detect changes in temperature, humidity, and other environmental factors.

In conclusion, nanomaterials have the potential to revolutionize the construction industry by enabling the development of new materials with improved properties and performance. Ongoing research in this area is likely to lead to new and innovative nanomaterials and applications that will improve the efficiency, sustainability, and safety of buildings and infrastructure. However, it is important to consider the potential risks and ethical implications associated with the use of nanomaterials in construction. Nanomaterials have the potential to revolutionize the construction industry by enabling the development of new materials with improved properties and functionality. The unique properties of nanomaterials such as high surface area to volume ratio, tunable physical and chemical properties, and quantum confinement effect have made them ideal for various applications in construction.

3 High-End Equipment and Software Used for Characterization

Of course, with any new technology, there will also be potential risks and challenges associated with the widespread use of nanomaterials. It will be important to carefully evaluate and mitigate any potential risks to ensure their safe and responsible use in the future. The synthesis and fabrication of nanomaterials require advanced scientific equipment and software. Here are some examples of high-end equipment and software commonly used in this field.

Transmission electron microscopy (TEM): TEM is a powerful imaging technique that allows scientists to visualize the structure and morphology of nanomaterials at the atomic level. This information is crucial for understanding the properties and behavior of nanomaterials and for optimizing their synthesis and fabrication processes.

Scanning electron microscopy (SEM): SEM is another imaging technique that is commonly used to visualize the surface morphology of nanomaterials. It can also be used for elemental analysis and mapping, which provides information about the chemical composition of nanomaterials.

X-ray diffraction (XRD): XRD is a technique that is used to analyze the crystal structure of nanomaterials. It provides information about the lattice structure and orientation of nanomaterials, which is important for understanding their electronic and mechanical properties.

Atomic force microscopy (AFM): AFM is a high-resolution imaging technique that can be used to visualize the surface topography of nanomaterials. It is particularly

useful for studying the mechanical properties of nanomaterials, such as their stiffness and elasticity.

Chemical vapor deposition (CVD) systems: CVD systems are commonly used for the synthesis of nanomaterials, particularly for the fabrication of thin films and coatings. These systems use a gas-phase reaction to deposit atoms or molecules onto a substrate, resulting in the formation of a nanomaterial layer.

Molecular modeling software: Molecular modeling software, such as density functional theory (DFT) software, is used to simulate and predict the properties and behavior of nanomaterials at the atomic level. These simulations are crucial for designing and optimizing nanomaterials for specific applications.

Laser systems: Laser systems are often used in the fabrication of nanomaterials, such as in the process of laser ablation or lithography. They can also be used to study the optical properties of nanomaterials.

Overall, the synthesis and fabrication of nanomaterials require a multidisciplinary approach that integrates advanced scientific equipment and software from various fields, including physics, chemistry, and materials science.

4 Editor Outlook

As we continue to advance in the field of nanotechnology, the potential of nanomaterials to revolutionize various industries and benefit society as a whole becomes increasingly evident. However, it is crucial to ensure the safe and sustainable use of nanomaterials by continuing to invest in research and development. Nanomaterials have unique properties that make them highly attractive for a range of applications, from medicine to energy production. However, due to their small size, they can pose risks to human health and the environment if not properly controlled. To ensure their safe and sustainable use, it is crucial to invest in ongoing research and development that can provide insights into the risks and benefits of nanomaterials and guide the development of regulations and guidelines for their use.

Furthermore, continued research and development in the field of nanomaterials can lead to the discovery of new and innovative applications that can benefit society as a whole. For example, nanomaterials can be used to create more efficient and cost-effective solar panels, improve the efficiency of energy storage devices, and enhance the performance of medical implants. In conclusion, investing in ongoing research and development in the field of nanomaterials is critical to ensure their safe and sustainable use and to unlock their full potential to revolutionize various industries and benefit society as a whole. Let us continue to work toward a future where nanomaterials can be used to their fullest potential, while ensuring the safety and well-being of our planet and its inhabitants. The book provides a comprehensive overview of the exciting potential and challenges of nanomaterials ranging from soft to biological to green and so on. The various contributions cover a wide range of topics, from the synthesis and characterization of nanomaterials to their applications in medicine, energy production, and electronics. The book emphasizes the need for continued

research and development to ensure the safe and sustainable use of nanomaterials, while also highlighting their potential to revolutionize various industries and benefit society as a whole. Overall, the book presents a hopeful outlook for the future of nanomaterials, while acknowledging the challenges like potential environmental and health risks, cost and scalability of production, and regulatory challenges associated with the use that must be overcome to realize their full potential. The field of nanomaterials offers immense potential and requires further investigation. One fascinating area to explore is 2D materials and their diverse applications in fields such as wearables and energy. We encourage readers to delve into the upcoming three-volume book series, authored by the same group, which extensively covers the topics of 2D materials, metal, and covalent organic frameworks and their applications.