REVIEW PAPER

Review on the amelioration of ZnO and its composites: synthesis and applications

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Abstract: Due to their enhanced biocompatibility and multifunctional capabilities, smart nanoparticles for various enhanced technological applications have attracted considerable attention. These materials are applied in the fields of solidstate physics, electronics, materials science, chemistry, biochemistry, medicine, in vivo imaging and modern drug delivery systems. ZnO nanoparticles have been used as anticancer agents in advanced physical therapies, bone tissue regeneration and nanoantibiotics due to their reduced size, large surface-to-volume ratio, photocatalytic and antibacterial activities and semiconducting capabilities. However, they may exhibit some instability in biological settings as well as unpredictable harmful effects. Doping appears to be a viable way to overcome the aforementioned constraints, allows for the tuning of optical characteristics and expands the usage of ZnO in nanomedicine. ZnO nanoparticles doped with transition metals and rare earth elements are typically prepared via sol–gel, hydrothermal, and combustion techniques. Biomedical uses, including improved antibacterial activities, contrast imaging capabilities, colloidal biocompatibility and stability in biological media, were shown for both dopant types. To serve as a preamble for young researchers in futuristic studies, this article aims to present comprehensive information on the present state of ZnO nanostructures and techniques. This review supports the idea that doping ZnO can improve its biomedical capabilities in comparison to those of its undoped counterparts. The current research also points toward the possibility of a novel use of ZnO nanoparticles in nanomedicine.

Keywords: Nanoparticles; Synthesis; Doping; Biomedical; Photocatalytic; Antibacterial

1. Introduction

Nanoparticles (NPs) are fundamental components of nanostructures, with sizes ranging from 1 to 100 nm [\[1](#page-18-0)]. In contrast to bulk materials, NPs have unique physical and chemical characteristics, such as higher surface-to-volume ratios, lower melting temperatures, specific optical properties, and improved thermal and electrical conductivities [\[2](#page-18-0)]. Bulk materials typically do not have the specific mechanical, magnetic, optical, electrical, or electronic properties that NPs possess [\[3](#page-18-0)]. Metal oxide nanoparticles have recently achieved great popularity due to their adaptable optical, catalytic, electrical, and magnetic potential [\[4](#page-18-0), [5](#page-18-0)]. Zinc oxide (ZnO) NPs have drawn attention due to their simple synthesis/production methods as

well as their distinctive properties, including a widened band gap (3.37 eV), high binding energy (60 meV), high electron mobility and photocatalytic ability in acidic, neutral, and basic media [\[6](#page-18-0)], sono-catalytic activity [\[4](#page-18-0), [7](#page-18-0), [8\]](#page-18-0), piezoelectricity [[9\]](#page-18-0), and pyroelectric behavior [\[10](#page-18-0)]. Solar cells, piezoelectric devices, acoustic devices, rubber products, photocatalysts, textiles, transistors, lightemitting diodes (LEDs), medications, food packaging, chemical biosensors, and antifungal and antibacterial agents are only a few of the products that use pure and doped ZnO NPs [[11\]](#page-18-0). However, doping increases the adaptability of ZnO nanostructures and strengthens their weak optical properties for use in various applications [\[12](#page-18-0), [13](#page-18-0)]. They have recently become more popular due to their enhanced surface area and improved quantum confinement, which result in exciting electrical and optical characteristics for a range of applications. By controlling the morphology at the nanoscale, the different *Corresponding author, E-mail: athakur1@ggn.amity.edu

characteristics of pristine and doped ZnO nanostructures (NSs) may be controlled. Our lives depend on energy in one way or another. Increasing population and development lead to increasing energy needs. Due to the depletion of fossil fuel reserves and the grave threat posed by climate change, there is an increasing demand for noncarbonaceous, green, and clean energy sources. Examples include the production of hydrogen through environmentally friendly benign processes, the cost-effective synthesis of fuel cells, and the use of unconventional energy sources [\[14](#page-18-0), [15](#page-18-0)]. More recently, research has been conducted on the photocatalytic evolution of hydrogen by doped ZnO NSs.

Although scientists primarily view ZnO as a semiconductor with possible applications in photonics, chemistry, optoelectronics, and electronics, it is instructive to mention that such uses have been dwarfed by the other typical applications of ZnO. Since 2000 BC, zinc has been used in ointments to cure skin diseases [[16\]](#page-18-0). ZnO has recently attracted much interest in nanomedicine. ZnO is widely acknowledged as a safe, inexpensive and abundant substance. It is also acceptable for many biomedical applications because of its approval from the Food and Drug Administration [[17\]](#page-18-0). A new area of study called nanomedicine aimed at the use of intelligent materials in healthcare is expeditiously evolving. Some real-world examples include enhanced drug delivery systems, contrast agents, tissue engineering, and in vivo imaging, as well as cuttingedge functional materials for physical therapy, such as photodynamics, sonodynamics, and hyperthermia. The amalgamation of nanomedical smart materials is difficult since there is a strict need for a matching size, which must be similar to that defining most biological systems. Nanomaterials are the most likely substitutes to fulfill these needs because their typical size is at the nanometer level. Additionally, because of their small size, nanomaterialbased medical solutions are supposed to be minimally invasive and potentially easily implantable in living systems.

2. Background

To achieve the controlled release of medicines, complex delivery mechanisms have been created, such as pH-activated release systems [\[18](#page-18-0)] or those that are activated externally using light or mechanical stimulation [[19,](#page-18-0) [20](#page-18-0)]. Due to their strong potential to combat antibiotic resistance [\[21](#page-18-0)] and promising antibacterial activity [[22\]](#page-18-0), nanoparticles have occasionally also been studied as nanoantibiotics. As next-generation nanodrugs for anticancer therapy, nanoparticles have recently begun to be researched independently [\[23](#page-18-0)]. In reality, chemotherapy-based conventional treatments have a number of drawbacks, such as the inability of chemotherapeutic drugs to be selective and soluble, which can lead to unfavorable side effects [[24\]](#page-18-0). On the other hand, the use of NPs to effectively treat cancer cells will be beneficial due to the following factors: (i) their smaller size (1–100 nm), with their reach and buildup in tumor locations lacking successful treatment; (ii) their large surface-to-volume ratio; and (iii) complex surface chemistry, allowing the anchoring of particular functional groups and increasing the selectivity of functionalized NPs for particular tumor cells [[25\]](#page-18-0). Recently, theranostic NPs have attracted much interest [[26\]](#page-18-0). Theranostics involves creating multifunctional platforms that can carry out both diagnostic and therapeutic procedures at the same time, also utilizing nanoparticles and nanotechnologies (nanotheranostics). As a result, the diagnostic and therapeutic actions of the same NPs are merged. Some materials are distinguished by the occurrence of particular chemical and physical features, such as catalytic, optical, or magnetic properties. Therefore, theoretically, it is possible to develop nanoscale materials that can be injected into a person's biological system, deliver the necessary therapeutic agent to the desired organ, and can be seen and observed at the targeted location.

To aid in the restoration of damaged tissues and organs, nanomaterials have proven to be promising materials and have been used successfully in wound healing and tissue engineering (TE) [[27\]](#page-18-0). The benefit of utilizing NPs in TEs arises due to their decreased size. These characteristics enable simple surface functionalization of the particles with proteins, peptides, and ligands, facilitated cellular uptake, and simple diffusion across membranes. Several ZnO NPs have been effectively used in TEs [\[28](#page-18-0)]. ZnO nanowires (NWs) [\[29](#page-18-0)], nanorods (NRs) [[30\]](#page-18-0), and nanoflowers [[31\]](#page-18-0) have been shown to promote the adherence, division, and proliferation of different cell lines. Due to their small size, ZnO NPs can be easily absorbed by cells and are hence easily administered in the human body [\[32](#page-18-0)]. As a result, the promising osteogenic and angiogenic capabilities of ZnO NPs as well as their application as nanotherapeutic agents for treating bacterial infections have been proven to be significant [[33,](#page-18-0) [34\]](#page-18-0). As diagnostic agents [\[35](#page-18-0)], imaging agents [[36\]](#page-18-0), cell labeling agents [\[37](#page-18-0)], tumor targeting agents [[38\]](#page-18-0), nanodrugs to treat cancer cells [\[39](#page-18-0), [40](#page-19-0)], and ZnO NPs have also been utilized. As ZnO interacts with aqueous media, detrimental species are released, producing a therapeutic effect [[41–43\]](#page-19-0). In vitro testing verified the therapeutic effectiveness of the ZnO NPs against various cancer cell types. Moreover, NPs may exhibit greater biocompatibility in specific circumstances, and their size is comparable to that of the extracellular matrix of tissue components on the nanometric scale. Silica, metal oxides, and carbon-based nanomaterials have been utilized to create smart scaffolds with enhanced biological, mechanical, and electrical capabilities [\[44–46](#page-19-0)]. Metal/metal oxide NPs with antibacterial properties have also been proven to be useful for controlling bacterial infections in patients after surgery or organ/tissue replacement [[47\]](#page-19-0).

Crystal growth behavior, shape, particle size, and optical properties all had an impact on the antibacterial and catalytic activity of undoped and doped ZnO samples as a whole. Undoped and doped ZnO NSs are widely used to kill Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli) bacteria as well as for photocatalytic activity with different dyes [\[48](#page-19-0)]. Due to their potential antibacterial activities against gram-positive and gram-negative bacteria, ZnO NPs are considered future nanoantibiotics. By choosing the best ZnO morphology from the wide variety available, the aforementioned qualities can be combined and even strengthened. It is simple to produce thin films [\[49](#page-19-0), [50\]](#page-19-0), nanowires (NWs), nanorods (NRs), nanoparticles (NPs), nanobelts [[51\]](#page-19-0), nanorings, nanosprings, nanosaws, nanotubes, flowers, boxes, discs, stars [\[52](#page-19-0)], and flower-like structures [\[53](#page-19-0)] using wet and dry synthesis techniques. Figure [1](#page-3-0) shows morphologically different types of ZnO nanostructures.

Despite these positive outcomes, ZnO has not yet attained its full potential due to certain problems that need to be solved. ZnO NPs have some inherent limitations that prevent their use in nanomedicine, such as their limited stability in biological fluids and uncontrolled production of toxic Zn^{2+} species [\[55](#page-19-0), [56\]](#page-19-0). Thus, more work is needed to improve and establish the use of ZnO in biological systems. For this reason, doping ZnO acts as a potent method to provide new characteristics in place of enhancing existing characteristics. After doping ZnO with the correct elements, the optical [\[57](#page-19-0)], electrical [\[58](#page-19-0)], electromechanical [\[25](#page-18-0)], and catalytic [\[7](#page-18-0)] capabilities might be tailored, strengthened and adjusted. This review mainly focuses on various methods for synthesizing doped ZnO and their uses. It is impossible for one individual to study all the published work in depth; thus, it is very challenging to keep up with new advances in the field of pitch. The objective of this study is to provide a large amount of information on the performance and architectures of ZnO materials, with an emphasis on their intended uses. The general characteristics of ZnO are presented first, followed by a variety of techniques for creating ZnO structures, ZnO-based applications for every type of structure, such as nanostructures, nanoparticles, and epitaxial materials, and finally, a description of the principal issues still facing ZnO technology.

3. General properties of ZnO

ZnO is a semiconductor with a fairly broad band gap and a significant exciton binding energy of approximately 60 meV [[59\]](#page-19-0), facilitating effective excitonic emission at room temperature. It is transparent in the visible region and suitable for UV and blue spectrum opto-electronic applications. A low refractive index of approximately 2.5 makes it simpler to extract light. ZnO has a strong piezoelectric polarization because of its wurtzite crystalline structure, with lattice parameters of 3.2495 Å and 5.2062 Å [\[60](#page-19-0)], respectively, allowing for the fabrication of piezoelectric devices and 2D high-quality electron gas structures [[61\]](#page-19-0). In terms of chemistry, the lattice is composed of two interconnected hexagonal close-packed Zn and O lattices. ZnO has special optical and piezoelectric features in addition to complex electrical properties. Even when not purposefully doped, ZnO is typically said to have n-type conductivity in the region of 100 cm^2V^{-1} s⁻¹ with high carrier mobilities. Therefore, it is generally acknowledged that the intrinsic n-type conductivity of ZnO NSs is caused by impurities present throughout the development process. Nonetheless, researchers working with ZnO materials still do not seem to pay enough attention to the most recent developments in defect level identification.

ZnO is a substance that is far from inert because it is composed of ions that are extremely chemically active. First, it is well suited for wet chemical etching, which simplifies the processing of epitaxial devices down to the nanoscale. This chemical reactivity of ZnO is also advantageous for the fabrication of materials because ZnO readily precipitates in solution and can take on a wide range of morphologies depending on the reaction conditions. This is one of many factors contributing to the extensive use of ZnO nanoparticles in research. These structures are significantly important for particle absorption applications due to their surface reactivity and high surface-to-volume ratio, whether for solar cells [\[62](#page-19-0)], biomedical sensors [\[63](#page-19-0)], or gas sensors. Moreover, ZnO NSs and NPs are materials of interest to scientists in biological and environmental systems because of their low toxicity, biocompatibility, and biodegradability. High heat conductivity, high radiation hardness, and strong nonlinear optical behavior are three other less well-known characteristics of ZnO that make this material intriguing for use in space applications, thermoelectric generators, and nonlinear optical components, respectively.

Fig. 1 Morphology of different types of ZnO nanostructures: (a-i) tripod, tetrapod, nanosheets, nanoshells, multipods, nanorods, nanograins, and nanoniddle nanotubes [[54](#page-19-0)]. Copyright

4. Doping materials for ZnO nanoparticles

Doping is the process of adding an ion that was not initially present in the starting material into a crystal lattice. To build a multifunctional system, it may be more advantageous to incorporate new functionalities into ZnO in addition to the aforementioned ones than to enhance the ones that already exist. Doping is a useful method for adjusting certain ZnO properties for this purpose [\[64](#page-19-0)]. Modulating the energy band gap can be very helpful because it directly affects the photocatalytic capabilities of ZnO and the associated antibacterial activity. Additionally, the incorporation of specific elements into the ZnO lattice permits the development of weak ferromagnetic behavior

in the resultant doped particles [[65–67\]](#page-19-0), the control of aqueous environment degradation features [\[7](#page-18-0)], or even the regulation of the electromechanical response [\[68](#page-19-0), [69](#page-19-0)]. All of these elements, which are outlined in Fig. [2](#page-4-0), might be utilized for various applications in different fields [\[70](#page-19-0)]. The ultimate characteristics of the doped material are actually determined by a number of factors, including the size of the ions, their electronegativity, their coordination state, etc. [\[71](#page-19-0)]. Due to these factors, the anticipated new functionality must be taken into account when predicting the use of ad hoc dopants. Figure [2](#page-4-0) shows the different types of doping materials and their changes in properties due to doping, along with their applications. The most frequently employed ions mentioned in the literature are briefly

Fig. 2 Doping of ZnO by different materials, their change in properties and applications

Doping Materials Rare Earths/Transition Metals/Other Metals

discussed along with their impacts on the wurtzite ZnO crystal structure in the following sections.

4.1. Rare earth elements

Lanthanides, often known as rare earth elements (REs), are frequently used to dope ZnO and suitably alter the related electrical band structure [[72,](#page-19-0) [73](#page-19-0)]. Cerrato et al. studied and established that ZnO quickly recombines photogenerated charge carriers when exposed to light [\[74](#page-19-0)]. As a result, when this system functions as a photocatalyst, its quantum efficiency is low. The use of lanthanides, because of their 4f configuration, may aid in extending the electron/hole pair recombination period in semiconductors [[75\]](#page-19-0), which will increase the efficiency of the photocatalytic process and have an impact on antimicrobial activity. It has been demonstrated, for instance, that cerium improves the photocatalytic abilities of ZnO nanorods [\[76](#page-19-0)], exceeding the performance of titanium dioxide $(TiO₂)$, which is usually used as a reference for these reasons. Because of the trapped states created by doping, which serve as radiative recombination sites, the optical characteristics of ZnO can be adjusted. These states influence the band gap of the system, along with other characteristics, such as the crystallite size. It is crucial to note that gadolinium, an RE, has been shown to successfully produce magnetic behavior in ZnO NPs, even though TM is the greatest option for inducing RT ferromagnetism in ZnO [\[77](#page-19-0)]. RE elements have received increased attention due to their potential to improve the electromechanical and optical properties as well as the photocatalytic activity of ZnO NPs.

4.2. Transition metal (TM) elements

Transition metals are a different family of materials that are used extensively as ZnO doping agents. ZnO has been successfully modified by the addition of elements such as chromium (Cr) $[78]$ $[78]$, copper (Cu) $[79]$ $[79]$, iron (Fe) $[80]$ $[80]$, and manganese (Mn) [\[81](#page-19-0)], which is intriguing from the perspective of nanomedicine. Because TM-doped ZnO can function as a dilute magnetic semiconductor (DMS), the study of this material has attracted much attention. Dilute magnetic semiconductors are semiconducting materials that also exhibit ferromagnetic behavior due to the presence of transition metal (TM) ions, which, like Mn and Fe, are ferromagnetic in their pure state. Similar to RE, doping with TMs influences the ferromagnetic behavior of ZnO as well as its optical [[82\]](#page-19-0) and electrical [[83\]](#page-19-0) properties, all of which are strongly influenced by factors such as ionic radius, electronegativity, oxidation state, and other dopant characteristics [\[71](#page-19-0)]. Iron is one of the most popular TM dopants. Fe²⁺ and Fe³⁺ are two distinct oxidation states in which this metal can exist. Because of the varying ionic radii and charges carried in the system, they both have a significant impact on the structural and electrical properties. The investigation of the corresponding magnetic characteristics is the main focus of studies on Fe-doped ZnO. However, other studies have also demonstrated that Fe doping is a successful strategy for enhancing the electromechanical responsiveness [\[84](#page-19-0)] or the chemical stability of ZnO NPs under aqueous conditions (Fig. [3\)](#page-5-0) [[85\]](#page-19-0).

Manganese has also been widely employed as a dopant. Mn has a variety of oxidation states that make it more challenging to regulate this parameter. Moreover, the

Fig. 3 (a) SEM image of a Co implanted nanowire, (b, c) elemental maps of Zn and Co, and (d, e) Zn K-edge XANES spectra oriented perpendicularly and parallelly, respectively [\[86\]](#page-19-0). copyright

optical, structural, and magnetic characteristics of the resultant ZnO are altered by the dopant agent [\[77](#page-19-0)]. The ferromagnetic behavior of Mn-doped ZnO depends on the quantity of doped material, but there was no linear relationship between the two variables [[87\]](#page-19-0).

Copper can be used as a TM dopant to improve the antibacterial properties of ZnO. Coatings of Cu-doped ZnO with improved antibacterial properties against E. coli were effective, as demonstrated by Hassan et al. [[79\]](#page-19-0). Cu doping was shown to release cytotoxic Zn^{2+} and Cu^{2+} ions, increasing reactive oxygen species (ROS) levels and improving performance [[88\]](#page-19-0). Other researchers have used cobalt (Co) and chromium (Cr) as doping agents [[73\]](#page-19-0).

Noble metals such as gold (Au) and silver (Ag) have also been utilized in a variety of ways [\[89](#page-19-0), [90](#page-19-0)]. Doping with Au and Ag has been researched for potential use as a ZnO antibacterial enhancer [\[91](#page-19-0)]. In this study, it was discovered that Ag and Au ions might be used to enhance the photocatalytic characteristics of ZnO. Ag-doped ZnO NPs demonstrated increased antifungal activity, whereas Au was unable to significantly boost the antibacterial activity of ZnO. Another study produced Ag-doped ZnO nanoflowers using a green combustion technique and assessed their antibacterial activity. The findings demonstrated good antibacterial activity as well as antifungal efficiency [[92\]](#page-19-0). Doping ZnO with transition metals could be a useful method for the development of novel multifunctional ZnO nanomaterials with recently discovered bioimaging properties, such as MRI.

4.3. Other elements

Several elements, in addition to rare earth and transition metal elements, have also been utilized as dopants. For instance, flexible detectors have primarily been made of aluminum. By permitting Al ion passage in a grid of vertically aligned ZnO nanorods, for instance, a stretchy $NO₂$ gas sensor was created [\[93](#page-19-0)]. Another popular option for doping ZnO is magnesium, which was primarily employed to enhance the optical and electromechanical capabilities of pure ZnO. Mg doping increased the photoluminescence (PL) capabilities of ZnO in the visible range, similar to what was observed for gold [[93](#page-19-0)].

The choice of dopant is very broad, and many researchers have reported the use of different elements, such as antimony, chlorine, fluorine, and lithium, which change the particular properties of pristine ZnO for specific applications [\[67](#page-19-0), [94–97](#page-19-0)].

5. Methods of synthesis

There are many different ways to obtain nanostructures with different morphologies, as demonstrated in Fig. [4](#page-6-0). All kinds of nanoscale structures, including nanotubes [\[98](#page-19-0)], nanorods [\[99](#page-19-0)], nanospheres [[100\]](#page-19-0), nanoplates [\[101](#page-19-0)], nanoneedles [[102\]](#page-19-0), nanoribbons [[103\]](#page-19-0), nanodendrites [\[104](#page-19-0)], nanopyramids $[105]$ $[105]$, belts $[106]$ $[106]$, sheets $[107]$ $[107]$, trees [\[108](#page-19-0)], flowers [\[109](#page-19-0)], shells [\[110](#page-19-0)], corals [[111\]](#page-19-0), volcanoes

Fig. 4 (a) SEM images of pristine ZnO (b) Mn:ZnO (0.5 mol%) (c) Mn:ZnO (1.0 mol%) (d) Mn:ZnO (1.5 mol%) (e) J-V curves (f) IPCE spectra (g) current density stabilities (h) on/off operation of Mn:ZnO DSSCs [\[128](#page-20-0)]. copyright

[\[112](#page-20-0)], columns [[113](#page-20-0)], towers [\[114](#page-20-0)], combs [[115\]](#page-20-0), and rings [\[116](#page-20-0)], can be synthesized using various techniques. Thus, it is challenging to create a thorough summary of all the options that are already available. For instance, Wang explained the process of synthesizing nanowires, nanocombs, nanotubes, nanosprings, nanohelixes, nanobelts, nanopropellers, nanoshells, and nanorings using sublimation and deposition of ZnO powder [\[117\]](#page-20-0). Ko et al. used a hydrothermal method for the creation of an ordered ZnO nanoforest [[118](#page-20-0)]. Furthermore, dynamic template-assisted electrodeposition [\[119](#page-20-0)] and nanotube membranes [[120\]](#page-20-0) have been used to create porous ZnO. This review focuses on efficient, economical, and high-yield techniques for the synthesis and production of doped ZnO NPs. Chemical procedures are first discussed in the paragraphs that follow. This category is perhaps the most ambiguous since it offers a great balance between high material quality, adaptability, and low instrumentation requirements, especially when doping ZnO with rare earth elements. Subsequently, various physical, biological, and chemical techniques that are extensively utilized for producing both doped ZnO films and nanoparticles have been described, including flame spray pyrolysis [[85\]](#page-19-0), laser ablation, arc discharge, hydrothermal, precipitation, sol–gel, biological reduction and chemical vapor deposition techniques [\[121–124](#page-20-0)], sputtering [[125\]](#page-20-0), and pulsed laser deposition [\[126](#page-20-0)]. By carefully adjusting the relevant parameters, one can synthesize nanostructures with distinct sizes and shapes. When removed as precipitates, nanostructures have larger dimensions as a result of aggregation, which causes the loss of distinctive features. Aggregation is prevented by using different organic molecules, such as stabilizing ligands and surfactants [[127\]](#page-20-0). These substances regulate the growth

process, so it is possible to customize their size and shape by using different stabilizers. Moreover, epitaxial structures, nanostructures, thin and thick film structures, nanoparticles, and large-scale single crystals can all be created from ZnO throughout its growth process. The approaches are typically selected in accordance with their normal benefits and limitations (Fig. [5\)](#page-7-0).

5.1. Chemical methods

One of the most promising approaches used for creating nanostructured materials is wet chemistry. The key benefits include the use of nontoxic solvents, moderate synthesis temperatures, and straightforward instruments. Chemical methods seem to be a good option for the synthesis of doped ZnO NPs because of the relatively high purity and subsequent stoichiometry of the material [[129\]](#page-20-0). Combustion-based synthesis techniques for the synthesis of doped ZnO nanoparticles have been researched as alternatives to wet chemical processes. In solution combustion methods, the precursors of the required material, such as zinc and dopant precursors, are first dissolved in a fuel. A muffle boiler preheated to a temperature higher than the ignition temperature of the fuel is then filled with the solution. A potent exothermic interaction between the fuels and the oxidizing agents in the solution results in the production of the target oxide and gaseous species during the combustion of the fuel [\[130](#page-20-0)]. The solid phase expands in volume and rapidly cools as a result of gas generation, giving rise to ultrafine and uniformly dispersed powders. The biomedical industry must consider this final factor since cluster formation must be reduced to avoid affecting the cellular uptake of nanoparticles. This flexible synthesis technique

Fig. 5 Various methods of ZnO nanostructure synthesis

- **Pulsed laser deposition**
- **Physical vapor deposition**
- Arc discharge method
- Magnetron sputtering
- **Electrospinning**

was used to create a variety of ZnO nanomaterials with diverse morphologies, including nanodisks, nanoparticles, and pyramid-shaped particles, by adjusting the amount of fuel in the solution [\[131](#page-20-0)]. Several ions have been successfully incorporated into ZnO for the doping of nanomaterials. Noble metals such as gold and silver serve as examples.

5.1.1. Hydrothermal methods

An efficient chemical method for producing NPs with significant surface defects that have an impact on deeplevel emissions is hydrothermal methods [\[132](#page-20-0)]. Thin films were made by combining reagent-grade chemicals with the thermal breakdown of metallic compounds in an enclosed autoclave. In the hydrothermal process, crystal formation occurs in an aqueous solution with a high pressure and temperature gradient. The crystal starting ingredients must dissolve under high pressure (15–150 MPa) at a lower temperature than they would under ambient pressure. The ingredients are delivered to the lower temperature area of the autoclave where growth occurs on a beginning seed crystal under heightened pressure in a higher temperature area. This technique has been successfully applied in industry. By doping crystals during the growth of mineralizers containing Li or N acceptors, the crystals can be rendered semi-insulating while still having electron conductivity [\[118](#page-20-0)]. These crystals are excellent substrates for both ZnO-based structures with homoepitaxy and GaNbased structures. Investigations into hydrothermal methods for bulk ZnO nanostructures are now focused on surface characteristics, studies of dopant diffusion, and defectrelated luminescence. The following reactions serve as the foundation for a hydrothermal approach for creating ZnObased products [\[53](#page-19-0)].

$$
Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \tag{1}
$$

$$
Zn(OH)_2 + 2OH^- \to Zn(OH)_4^{2-}
$$
 (2)

$$
Zn(OH)42- \to ZnO + 2H2O + 2OH-
$$
 (3)

Typically, a mineralizing agent helps provide the OHgroups needed for adjusting the pH of the solution, preventing the precipitation of $Zn(OH)_2$ and encouraging the production of ZnO. Commonly used mineralizing agents are KOH [[53\]](#page-19-0), NaOH [\[133](#page-20-0)], and, less frequently, NH4OH [\[134](#page-20-0)]. The most common zinc precursors utilized in this type of reaction are zinc nitrate $[135, 136]$ $[135, 136]$ $[135, 136]$ $[135, 136]$ zinc acetate $[137, 138]$ $[137, 138]$ $[137, 138]$, and zinc chloride $[139, 140]$ $[139, 140]$ $[139, 140]$ $[139, 140]$ $[139, 140]$, all of which are easily soluble in the majority of solvents, such as water [[141,](#page-20-0) [142](#page-20-0)], ethanol [[143\]](#page-20-0) and methanol [[144\]](#page-20-0). The most common options and popular choices for dopant precursors are nitrates, chlorides and acetates [\[145–148](#page-20-0)]. Then, before mixing with the base and combining the dopant with the precursor, the inclusion of the dopant can be achieved in a comparatively simple manner. The creation of particles with the correct morphology is another difficult task. Through the use of surfactants such as cetyl-tri-methyl-ammonium bromide [\[149](#page-20-0)] or sodium dodecyl sulfate [\[150](#page-20-0)], it is possible to control nanostructures shape and size. Moreover, it has been observed that using various surfactants at varying concentrations radically alters the ultimate morphology of the particles, resulting in highly odd structures [[151\]](#page-20-0).

Fig. 6 Schematic of the (a) hydrothermal method [[152\]](#page-20-0) and (b) sol–gel method [\[153\]](#page-20-0). copyright

5.1.2. Sol–gel method

With its capacity to adjust optical and structural features, it is an effective and affordable approach for producing NPs. When doping ZnO with rare earth elements is desired, the sol–gel method is frequently used. By using wet chemical synthesis, other metals, such as lithium, magnesium, and aluminum, are doped in ZnO. Wet chemical techniques are most frequently employed for the production of doped ZnO NPs. The key benefits of these methods are their ease of use and large range of available morphologies. As shown in Fig. 6b, the procedure entails creating nanostructures by using either a sol or a gel as an intermediate product.

5.1.3. Emulsion technique

For a higher rate of nanostructure production, the emulsion technique has also been applied [\[154](#page-20-0)]. In the process, metal precursors are extracted from the initiator and secondary emulsions, which are then detonated at higher pressure to produce a gaseous plasma that contains the implicated components in the gaseous phase. The ablated materials create nanostructures under high supersaturation conditions by condensing at a higher pressure [[155\]](#page-20-0). By adjusting the quenching rate, the size of the NPs may be customized.

5.1.4. Chemical vapor deposition (CVD)

CVD is frequently used for producing thin films [\[156](#page-20-0)]. The MOCVD process [[157\]](#page-20-0) operates under ultrapure gas flow and moderate pressure (10–1000 Torr), leveraging surface chemical interactions between elemental precursors to regulate monolayer formation. Organometallic Zn compounds such as diethylzinc (DZO) and pure water or oxygen are utilized as precursors for the formation of ZnO. The partial pressure and substrate temperature have a significant impact on the characteristics of the resultant products. This technique produces the finest epitaxial structures with precisely regulated composition, thickness, dopant, and impurity levels using expensive and complex equipment operating at a very high temperature (approximately and above 550 $^{\circ}$ C) for ZnO. These methods can also be used to create quantum structures and band-engineered films (Fig. [7\)](#page-9-0).

Zn nanostructures are most easily formed when zinc metal is oxidized. Even regulated oxidation of properly placed zinc templates may produce crystalline ZnO whiskers or nanowires with high aspect ratios [\[159](#page-20-0)]. The vapor transport technique, in which Zn powder is vaporized at approximately 500 \degree C in an evacuated quartz tube and Zn vapors are transported to a lower temperature region by carrier gas where growth actually occurs on substrates by condensation in the presence of oxygen, is another straightforward method that has had a significant amount of success in fabricating ZnO nanostructures, particularly nanowires. The synthesis is governed by the tube pressure, flow rate, and condensation zone temperature. A straightforward and somewhat quick method, however, is constrained by the interior diameter of the tube and inside radial temperature gradients. However, the issue regarding the size of the substrate can be resolved by using adaptable condensation substrates. Thermally evaporated solid ZnO powders can also be used to create ZnO nanostructures [\[160](#page-20-0), [161\]](#page-20-0). This method uses a quartz tube reactor

and is comparable to the vapor transfer strategy. The tube temperature must be significantly high (approx. 1100° C) because the starting material is ZnO. Nevertheless, neither a base hoover nor a carrier gas is needed. Since the reactor walls are covered with the source material or substrates that are inserted, the method has the same scaling-up issues as the vapor transport technique and raises questions about the thermal stability of the substrates that are being utilized.

5.1.5. Sonochemical technique

Recently, this technique has also gained increased attention [\[162](#page-20-0)]. The process used to create the doped ZnO nanoparticles involved sonicating distilled water with a combination of ZnO NPs and ammonium ceric nitrate, followed by drying the precipitates. The remarkable adaptability of this technique has been demonstrated by its effective use in modifying ZnO by adding both typical and unusual doping substances, such as dysprosium [[163\]](#page-20-0) and praseodymium [\[164](#page-20-0)]. In a process known as microwave solvothermal (hydrothermal) synthesis, additional modifications can be made by switching from thermal heating to microwave heating. The key benefit of this method is that it uses microwaves to heat more effectively than traditional methods such as convection and conduction while maintaining more homogeneity with faster reaction times [\[165](#page-20-0)]. An additional solvothermal variant approach for creating ZnO nanostructures is called sonochemical synthesis, which uses ultrasound to mix the components by cavitation and bubble production in a standard solvothermal solution [\[166](#page-20-0)]. A nanostructured film is created when the nanoparticles are driven by the jet to a substrate at the bottom [\[167](#page-20-0)].

5.1.6. Electrochemical deposition

Compared to other gas-phase processes, this technique is relatively simple and affordable. This method involves depositing metallic oxide thin films by using appropriate metals and progressively employing O_2 or H_2O_2 gas. Only conducting substrates such as indium tin oxide-coated glass may be coated with this material, which is a typical research substrate. The working electrode substrate is submerged in a solution prepared by mixing zinc salt (often zinc acetate or zinc nitrate) in a heated $(50 °C)$ solvent such as water. The reference electrode serves as a potential reference and counter electrode to complete the circuit, and an electric current is applied between the anode and cathode via the solution. This causes the transfer of Zn^{2+} ions and the evolution of OH⁻ ions from the solution at the working electrode, resulting in the formation of zinc hydroxide at the surface of the electrode. The final reaction involving the production of ZnO and $H₂O$ requires a high temperature of the solution. This method is quick and enables coating of intricate geometries on substantial substrates, which is advantageous in applications such as photocatalysis [\[168](#page-20-0)].

5.1.7. Spray pyrolysis

Spray pyrolysis [\[169](#page-20-0)] is another method of thin ZnO film deposition that has gained some popularity. This method involves spraying a precursor solution resembling the sol– gel in a heated substrate direction while using a carrier gas. Zn acetate or nitrate is employed to produce ZnO at 400° C by using H_2O and an alcoholic solvent. The spray pyrolysis method is used to create doped nanoparticles. By atomizing the precursor and delivering methane and oxygen simultaneously, the solutions are sprayed, enabling combustion. The doped particles produced as a result are smaller than their pure counterparts, and the typical wurtzite phase peaks in the XRD patterns are the only peaks visible. In contrast to the previously stated process of normal solution combustion, the precursor solution is sprayed before being ignited. Similar to the solution combustion process, fuel is required to enable the flame to sustain itself [[170\]](#page-20-0). However, the solution precursor is often nebulized using a nozzle tip. Researchers have used this technique for Fe doping in ZnO nanoparticles by using flame spray pyrolysis. To create Fe-doped ZnO nanoparticles with better

Method/ technique	Precursors	Characteristics	Refs
Precipitation method	$Zn(CH_3COO)$ ₂ and $(NH_4)_2CO_3/$ KOH/NaOH/NH ₃	Spherical shape having a diameter of 30 nm or less	$[174 - 176]$
		Hexagonal structure having flower shape	
		Particles having 200 nm diameter and 150 nm length	
	$\text{Zn}(\text{NO}_3)$ ₂ and NaOH	Sphere-shaped particles approximately 40 nm in size	$[177]$
	$ZnSO4$, NH ₄ HCO ₃ , and ethanol/ NH ₄ OH	Wurtzite structure with a particle diameter of 12 nm and a crystal size range of 9–20 nm,	[178, 179]
		Particles 0.1 to 1 m in diameter and 60 nm in length	
Sol-gel	$Zn(CH_3COO)_2$.2H ₂ O, C ₂ H ₂ O ₄ , C_2H_5OH , and CH_3OH	Particles having approx. 100 nm diameter and approx. 500 nm length that resemble rods	[180]
	$Zn(CH_3COO)$, .2H ₂ O, $HN(CH_2CH_2OH)_{2}$, and C_2H_2OH	Particles having approx. 70 nm diameter resembling nanotubes	$[181]$
Hydrothermal	$ZnCl2 + NaOH$	$100-200$ nm rodlike shape, 50-200 nm sheet morphology, 200-400 nm polyhedron	$[182]$
	$Zn(CH_3COO)_2 + NaOH$	55—110 nm diameter with spherical shape	$[183]$
Emulsion and microemulsion	$\text{Zn}(\text{NO}_3)_{2}$ with surfactants	Surfactants that are anionic are 20 nm or smaller, nonionic are 20–50 nm, and cationic are 40–50 nm in size	$[184]$
	$Zn(C_{17}H_{33}COO)_{2}$, NaOH, C ₁₀ H ₂₂ , H_2O , and C_2H_6O	Needle-shaped, almost spherical, and hexagonal particle aggregates, as well as spherical and pseudospherical aggregates	[185]
	$Zn(CH_3COO)_2$, NaOH, KOH along C_6H_{12} , and nonionic surfactants	Particles with a hexagonal structure display morphologies like solids, ellipsoids, rods, flakes, and more	[186]
	$Zn(NO_3)_2$, NaOH, C ₇ H ₁₆ , C ₆ H ₁₄ O, and Triton X-100	Hexagonal wurtzite structure with nanocolumns and needle-shaped particles with sizes between 80 and 100 nm and 50 and 80 nm, respectively	$[187]$
Additional methods	$Zn(CH_3COO)_2$ with thermal decomposition	\sim 20–30 nm sized uniform particles	$[188]$
	$Zn(NO3)2$ with ultrasonic irradiation	Nanorods and nanowires with hexagonal wurtzite structure	[189]

Table 1 Different methods used for the synthesis of ZnO nanostructures

biostability under aqueous conditions, many researchers have preferred this technique over sol–gel techniques [\[171–173](#page-20-0)]. The quicker synthesis process used here produced nanoparticles with better surface chemistry properties, which contributed to their enhanced stability (Table 1).

5.2. Physical methods

Pulsed laser deposition, magnetron sputtering, electrodeposition, and electron beam evaporation are examples of physical processes. The advantage of congruent evaporation provided by brief laser pulses enables pulsed laser deposition to maintain stoichiometry. The disadvantages of this method include the existence of particles in the size range of microns and restricted forward angular distribution, making large-area scale-up a highly challenging undertaking. Low temperature, congruence, and the presence of ionized species are benefits of physical methods.

5.2.1. Pulsed laser deposition (PLD)

PLD is the most common method for creating thin ZnO films with polycrystalline morphologies, which range in thickness from a few nanometers to a few microns. The target material is focused by a pulsed high-power laser beam, which results in instantaneous local heating, ablation, and evaporation, causing deposition on the substrate. This process is known as pulsed laser deposition [\[190](#page-21-0)]. Oxygen is supplied to the growth site to oxidize the growing film in the case of ZnO. However, PLD can provide step flow and epitaxial growth with heating of the substrate (usually 350° C). The comparatively quick processing time of this method has certain benefits, but the throughput suffers because of the small practical target and substrate regions.

5.2.2. Arc discharge technique

A flexible unconventional method for producing nanostructures in both gaseous and liquid media is the arc

discharge technique [\[191](#page-21-0)]. An arc is created among electrodes in a dielectric medium during operation, resulting in surface layer melting, which is followed by rapid condensation in gaseous or liquid media, producing nanostructures. This process has a number of benefits over alternative processes, including uniform nucleation, customizable nanostructure shapes, higher generation rates, lower costs, and simplicity.

5.2.3. Laser ablation

A common and flexible approach for depositing thin coatings of nanoparticles is laser ablation. Laser beam irradiation causes the target surface to vaporize in a gaseous or liquid medium inside the vacuum chamber [[123\]](#page-20-0). A thin layer with a greater level of crystallinity made of ablated material is then placed [\[192](#page-21-0)]. Pure metallic oxides and carbide nanoparticles can be created under ambient conditions using arc discharge and laser ablation procedures [\[193](#page-21-0)].

5.2.4. Magnetron sputtering

Magnetron sputtering is a method renowned for its simplicity for the deposition of various materials at a high rate for scaled-up synthesis [[194\]](#page-21-0). The source material utilized for ZnO is either Zn or ZnO, and the deposited material is used as the target material. The sputtering procedure was carried out in a Hoover chamber that was first evacuated by injecting Ar gas with a reactive gas such as O_2 , if necessary. The target and substrate are connected by a voltage of approximately 100 V, which causes cascade gas ionization (plasma), which bombards the target and ejects or sputters the target material over the substrate. ZnO thin films are typically produced on unshielded substrates; however, substrate heating between 300 and 550 \degree C can be used to produce films of greater quality [[195\]](#page-21-0). The large-scale homogeneity, good microstructure, reproducibility, and thickness control of the resultant films are all benefits of sputtering. Moreover, when the deposition is carried out at RT, this method can be immediately employed with lift-off photolithography patterning, greatly simplifying device processing using the deposited films. This approach is a well-established, highly stable, relatively sophisticated technique that requires specialized, frequently expensive equipment. Its advantage is in the synthesis of highly pure materials crucial for various electronic applications.

5.2.5. Electrospinning

A ZnO precursor along with a polymer solution mixed in a solvent is used as the initial material. When the prepared solution is injected using a needle, a charged thread appears from the needle's meniscus when an electric field is introduced. The aspect ratio of the material is very high, and the material needs to be calcined at $300-600$ °C to produce polycrystalline ZnO fibers [[196\]](#page-21-0).

5.3. Biological methods

Recently, scientists have focused their attention on more straightforward and environmentally friendly synthesis techniques. The manufacture of nanosized materials using the highly structured biosynthetic activity of microbial cells has opened up new avenues in the field of nanoscience. Numerous bacteria have been found to manufacture metallic nanoparticles and nanostructured mineral crystals with qualities that are comparable to or better than those of chemically synthesized materials while maintaining strict control over the particle size, shape, and makeup. Numerous instances of the synthesis of inorganic nanoparticles employing different biological systems, particularly bacterial cells, have been documented. However, the precise mechanism of production is still unknown and can be related to numerous enzymatic or proteolytic processes occurring within cells. Additionally, some biological systems have served as models for the production of highly crystalline, uniformly distributed nanosized particles [\[197](#page-21-0)].

Green synthesis or biological reduction green synthesis for the production of pure and doped nanostructures has recently been developed and is becoming increasingly popular because of its unique advantages, such as plentiful material sources, different morphologies, and simple reaction conditions (Fig. [8](#page-12-0)) [\[198](#page-21-0)].

It may be concluded that, in contrast to wet chemical approaches, combustion methods are less effective at incorporating the doping agent into the ZnO crystalline structure. This could be the reason why sol–gel or hydrothermal techniques are more frequently used to produce doped ZnO nanostructures than solution combustion methods. They offer a wide range of precursors and parameter options that greatly customize the final product. Other methods, such as combustion methods, have been shown to be significant because of their fast reaction time. Nevertheless, it is important to note that iron-doped ZnO nanoparticles produced by flame spray pyrolysis exhibited improved durability in biological media. Additionally, it is clear from the analysis of fabrication techniques that there is a broad separation of many physical and chemical methods. The former are primarily distinguished by greater complexity, having high dopant control and purity. The initial components for production are oxygen, elemental Zn, and zinc oxide. Both washing, coating on any substrate, drying, and annealing are used to produce the finished

Fig. 8 (a) Diagramatic representation of green synthesis of ZnO NPs. (b) Mechanism of nanostructure formation. (c) X-ray diffraction pattern. (d) FTIR spectroscopy and (e) TGA spectra of the prepared nanoparticles [[199](#page-21-0)]. copyright

product. Additionally, the development of biological methods for ZnO nanostructure synthesis is continually increasing because of the numerous synthesis possibilities and the extremely intriguing applications in the vicinity of biological and biochemical devices.

6. Applications of ZnO nanostructures

After reviewing the synthesis methods and techniques for various ZnO structures, this section will discuss the various real-world and hypothetical uses for nanostructured materials to provide an exhaustive picture of their potential. Figure [9](#page-12-0) explains various applications of ZnO nanostructures.

6.1. Photocatalysis.

Ashkarran et al. produced Ag:ZnO hybrid nanostructures and demonstrated that contrary to pure NPs and 3 mM Ag, doped NPs demonstrated photocatalysis when exposed to visible light (the destruction of rhodamine B) [\[200](#page-21-0)]. Additionally, an investigation of the mechanism of photocatalysis was performed, and it was discovered that the favorable value of the zeta potential aided in the formation of hybrid nanostructures. They also discovered that doped nanostructures exhibit catalysis in the presence of visible light, as doping reduced the band gap and the likelihood of ionic recombination. They discovered that when the Ag concentration increases, more electrons are captured, enhancing catalysis, but at a certain point, the photocatalytic effectiveness decreases because of decreased absorption by ZnO due to the presence of Ag^{++} ions in the surrounding environment. For various irradiation times, variations in the absorption spectra of undoped and doped ZnO NPs are displayed in Fig. 10. In doped nanostructures, photocatalysis events followed first-order kinetics.

Pure and Al-doped ZnO nanoparticles were prepared by Ahmad et al., and methyl orange degradation was used to gauge the photocatalytic effectiveness of the samples under solar and visible light illumination [\[202](#page-21-0)]. They discovered that 4% was the ideal doping concentration for effective photocatalysis. Hosseini et al. produced pure and Ag-doped ZnO NPs to perform photocatalytic activity on methyl violet and discovered that doping increased the photocatalytic effectiveness, with an ideal silver concentration of 2% [[203\]](#page-21-0). As photocatalysis starts by an interaction between oxygen and conduction band electrons, they discovered that Zn vacancies and analogous $O₂$ vacancies were the cause of the improved performance. Shahpal et al. studied the degradation of dyes, including alizarin red, by pure and Cu-doped ZnO NPs. S, Methylene Red, Methylene Blue, and Thymol Blue in hydrogen peroxide solution [\[204](#page-21-0)]. When the concentration of Cu increased, the doped nanostructures showed improved catalysis and were extremely sensitive to MB.

6.2. Electrocatalysis

Sun et al. created hybrid nanostructures of undoped and cobalt-doped ZnO and investigated their electrocatalytic activity for O_2 reduction reactions. They discovered that the doped nanostructures were more stable, tolerable to methanol, and had better electrocatalytic behavior than Pt. The electrocatalytic performance was assessed via CV. The results showed that doped nanostructures can be used to create a fuel cell that is both efficient and affordable [\[205](#page-21-0)].

Fig. 10 (a–d) Photocatalytic dye degradation of MB dye in the presence of ZnO nanoparticles, (e, f) $C/C₀$, photodegradation with time, degradation efficiency $(\%)$, and first-order kinetics using ZnO nanoparticles [[201](#page-21-0)]. copyright

Fig. 11 (a) Fabrication of the ZnO UV/gas sensor (b) camera image of the device (c) UV response (d) NO₂ gas response w.r.t. time [[208](#page-21-0)]. copyright

Dom et al. synthesized iron-doped ZnO NPs for the photoelectrochemical creation of hydrogen through water splitting. Doped ZnO particles with an iron concentration of $10^{-3}\%$ produced the highest photocurrent and, as a result, the highest H_2 evolution rate (306 mol/h), as shown in Fig. [12](#page-15-0) [[206\]](#page-21-0).

6.3. Gas sensing

Tan et al. prepared pure and In-doped ZnO nanoparticles with nanorod-like shapes [\[207](#page-21-0)]. With an ideal indium concentration of 4%, the responsiveness of the synthesized particles for CO sensing was nine times greater than that of existing devices. Figure 11a displays the fabrication of ZnO nanostructures for UV and $NO₂$ gas detection, whereas Fig. 11c, d shows the UV and $NO₂$ gas responses of the samples with respect to time.

6.4. Ferromagnetism

Singh et al. synthesized $NiFe₂O₄–Ag–ZnO$ and $ZnO–Cu/$ $NiFe₂O₄$ nanocomposites and showed that superparamagnetic properties appeared in the nanocomposites as a result of the interaction of diamagnetic ZnO and ferromagnetic $NiFe₂O₄$ [\[209](#page-21-0), [210\]](#page-21-0). The doped samples showed ferromagnetism above room temperature. At a Curie temperature of 423 K, a 3% doping concentration was ideal based on magnetization. Doped ZnO nanostructures are hence useful in spintronics. Iron doping of ZnO NPs has also increased their Curie temperature [[211\]](#page-21-0). With Co doped graphene-like zinc oxide, a chemically stable layered material in air, Chen et al. showed room-temperature ferromagnetism down to a single-atom thickness. Definite signs of spontaneous magnetization in such unusual material systems were detected at room temperature and above using the magneto-optic Kerr effect and X-ray magnetic circular dichroism studies. Figure [12a](#page-15-0) diagrammatically depicts Co doped monolayer gZnO, whereas Fig. [12](#page-15-0)b-c shows SEM and AFM, respectively; Fig. [12](#page-15-0)d shows longitudinal MOKE displaying typical ferromagnetic hysteresis loops; Fig. [12e](#page-15-0) shows alternately stacked rGO and gZCO heterostructures; Fig. [12](#page-15-0)f shows hysteretic M-H loops with solid ferromagnetic long-range order; Fig. [12](#page-15-0)g shows longitudinal MOKE at 300 K; and Fig. [12](#page-15-0)h, i shows alternatively stacked 2D gZCO/rGO heterostructures' temperature-dependent XMCD spectra for 11.9% and 12.1% doping concentrations, respectively.

Fig. 12 (a) Co-doped monolayer gZnO (b) SEM (c) AFM (d) longitudinal MOKE displaying typical ferromagnetic hysteresis loops (e) alternately stacked rGO and gZCO heterostructure (f) Hysteretic M-H loops showing solid ferromagnetic long-range order

(g) longitudinal MOKE at 300 K h, (i) alternatively stacked 2D gZCO/rGO heterostructures' temperature-dependent XMCD spectra for 11.9% and 12.1% doping concentrations, respectively [[212](#page-21-0)]. copyright

6.5. Photoluminescence

Singh et al. studied the photoluminescence of Ag-doped ZnO [[213\]](#page-21-0), and Mg-doped ZnO nanostructures were prepared by Arshad et al. They demonstrated enhanced photoluminescence and optical band gap, making them effective for creating fire safety markings, exit path markings, and escape route signs [[214\]](#page-21-0). Strong visible emission in the PL spectrum of synthesized QDs has been observed by several researchers. Due to the increased diameter of the QDs produced at 40 and 60 \degree C, both UV and visible emissions were observed for the QDs, as shown in Fig. [13](#page-16-0).

6.6. Solar cells

Cielak et al. synthesized carboxylate oligoethylene glycol (OEG)-doped ZnO NPs. The longer ionic separation times of the particles made them more stable and soluble in water, increasing their suitability for use in photocatalysis and solar cells (Fig. [14\)](#page-16-0) [[216\]](#page-21-0).

6.7. Antibacterial

The available literature amply demonstrates the antimicrobial activity of ZnO nanoparticles against a wide range of pathogenic bacteria, including E. coli, P. mirabilis, S.

Fig. 13 (a) Photoluminescence spectra (b) absorption spectra of ZnO QDs (c) 3D visualization of ML models superimposed on data samples [[215\]](#page-21-0). copyright

Fig. 14 (a) Photoinduced electron transfer (PET) spectra of the photoanodes (b) Voc voltage decay curves as a function of time c Electrochemical impedance (EIS) spectra of the devices [[128\]](#page-20-0). copyright

aureus, P. aeruginosa, K. aerogenes, S. pyogenes, B. subtilis, and M. tuberculosis. NPs have excellent antibacterial properties, but one important downside is their toxicity. The biocompatibility and antibacterial properties of nanoparticles can be improved by coating. Agarwal et al.

studied the antibacterial activities of ZnO synthesized by a biological route and explained the mechanism followed by the use of ZnO nanoparticles, as explained in Fig. [15](#page-17-0). Jan et al. synthesized undoped and Sn-doped ZnO NPs with various morphologies, such as nanorods and nanospheres.

Fig. 15 (a) Interaction of ZnO nanoparticles with gram $+$ and gram $-$ cell (b) Illustration of the mechanism followed by ZnO for antibacterial activity [\[218\]](#page-21-0). copyright

Testing samples against various bacterial strains allowed researchers to assess their antibacterial properties (S. aureus, P. aeruginosa, and E. coli) [\[217](#page-21-0)]. The inhibitory zone was reduced from 37 to 4%, and the maximal efficacy for skin bacteria (S. aureus) was shown by the doped nanostructures. Hence, it is possible to incorporate ZnO nanostructures in skin lotions, UV protection, and medical implants.

6.8. Other biomedical applications

The biocompatibility of ZnO has sparked interest in numerous applications across a range of healthcare-related fields [\[219](#page-21-0)]. Because of their antibacterial activity and biocompatibility, ZnO nanoparticles are used as coverings for bone implants to prevent them from becoming infected [\[220](#page-21-0)]. When doped with the proper ions for selective luminescence, nanoparticles, the building blocks of ZnO implant coatings, have also been explored as biomarkers [\[221](#page-21-0)]. They have been investigated as anticancer drugs because of their cell-specific antibacterial action, which is strong for fast-growing cells and significantly weaker for quiescent cells [\[222](#page-21-0)]. ZnO NP-based targeted medication delivery has been investigated [\[223\]](#page-21-0) and has shown encouraging results in oncological in vitro experiments [\[224](#page-21-0)] coupled with anticancer action. ZnO NP research is moving in a new direction for biomedicine due to its role in controlling Zn sources. The role of ZnO as a ZnO source for regulating insulin integrity in diabetic patients is a new direction for the use of ZnO nanoparticles in biomedicine. Animals treated with ZnO nanoparticles in vivo showed promising outcomes, with blood sugar levels decreasing and insulin levels increasing [[225\]](#page-21-0). ZnO nanostructures on woven fabrics in the shape of springs, rods, etc., were used to develop an entire field of piezotronics. Piezo/nanogenerators are used in these situations to harvest mechanical energy from environments that are usually wasted or underutilized, such as footsteps in hallways, automobile tyres on roads, or even ocean waves [\[226](#page-21-0)]. By way of wearable woven high capacitance supercapacitors, the same substances were demonstrated to be propitious for energy storage [\[227](#page-21-0)], and nanostructured ZnO was also described as the building block for totally transparent stisupercapacitors [\[228](#page-21-0)].

7. Constrains

Two of the biggest issues in ZnO technology are the inability to generate p-type conducting materials that are strongly conducting, stable over time, reproducible, and clearly discernible. Another issue is the wide range of synthesis conditions that lead to an overwhelming variety of different nanostructures with differing properties. However, caution must be exercised when using ZnO NSs under aqueous conditions because water dissolves ZnO at low concentrations, and the concentration threshold limit for dissolution increases sharply with decreasing pH, potentially creating a host of issues for practical, longlasting applications in fields such as biomedicine, biomedicine, biomedicine or photocatalysis. An appropriate morphological design and structure under these circumstances, occasionally in combination with the application of ultrathin surface passivation layers, may be an efficient

remedy. Chemical approaches, while generally affordable and simple to use, may encounter difficulties when applied as thick films or mg-sized doses rather than as kg-sized granules due to issues with consistency and repeatability. This is true despite years of diligent investigation by the scientific community using a variety of innovative experimental growth and characterization techniques, as well as computer studies discovering appropriate dopants and sophisticated doping schemes for parameter optimization. Additionally, the supersaturation of comparable studies on ZnO nanostructures in the literature makes it difficult to follow the field properly, decreasing the impact and reproducibility of the results and decreasing the likelihood that fresh, useful reports will be published.

8. Conclusion

The scientific community has clearly recognized the presence of zinc oxide as a crucial metal oxide. The large range of synthetic techniques it supports and the wide range of possible nanostructure morphologies that can be used in numerous devices, however, have led to a substantial increase in attention in the chemical community. Recent studies on ZnO NP doping by researchers have been reported in the current publication. The properties of pure ZnO NPs can be tailored by doping and adjusting the synthesis conditions, making them suitable for a variety of applications. Doping plays a critical role in modifying the characteristics of ZnO materials, which are multifunctional materials that can address the energy crisis and environmental problems, can detect harmful gases, can aid in the growth of affordable and effective solar cells and fuels, and can play a significant role in science and technology. The topic 'nanostructured ZnO', however, appears to be oversaturated with findings, and different shapes are frequently viewed as ''yet another'' research that accomplishes little to close the knowledge gap. To advance the commercial presence of this material, it is presumably the responsibility of each researcher to proceed from the synthesis stage to the actual product/device development stage using ZnO nanostructures.

In conclusion, doped ZnO nanostructures are currently in a stage in which largely thorough investigations are required to encourage the material to achieve its promising capabilities.

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