Chapter 2
Green Nanotechnology for the Environment and Sustainable Development

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Contents

Abstract With the increase in the global human population, the adequate supply of resources has become limited. The development of pollution-free technologies for environmental remediation and clean energy supplies for the sustainable growth of human society is the need of the hour. Nanotechnology can have a substantial impact on developing 'cleaner' and 'greener' technologies with significant health and environmental benefits. The applications of nanotechnology are being explored for their potential to provide solutions to manage, mitigate, and clean-up air, water, and land pollution, as well as to improve the performance of conventional technologies used in environmental clean-up. Green nanotechnology is the branch of nanotechnology that envisages sustainability through various applications.

The present chapter deals with the topics related to green nanotechnology for sustainable development. The applications of nanotechnology used to solve environmental issues by reducing the overall energy consumption during the synthesis and manufacturing process, the ability to recycle products after use, and to develop

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and use eco-friendly materials were summarized in this chapter. The sections have been divided according to the applications of green nanotechnology. The nanomanufacturing processes, green synthesis of nanomaterials, and the treatment of wastewater with reference to the principles of green chemistry have been discussed in detail. Currently, nanotechnology shows great promise to solve the sustainability issues, but it is impossible to overlook the adverse effects of nanomaterials on the environment and human health. In spite of the high performance and low cost of nano-remediation technology, advanced research is necessary to understand and prevent the potential adverse environmental impacts, i.e., ecosystem-wide impacts. The present chapter highlights the green chemistry principles influencing the life cycle of nano-products from design to disposal. The various applications and limitations of green nanotechnology have been discussed in the light of green chemistry principles for sustainability.

Keywords Green Nanotechnology · Photocatalysis · Remediation · Sustainable · Nanomaterials

2.1 Introduction

One of the biggest challenges of the present situation is to provide sustainable development for the coming generations utilizing the concepts and principles of green chemistry and green engineering to make nano-products and materials without noxious end products and to expend lifecycle thinking in all design and engineering phases (Galeazzo et al. 2014; Qu et al. 2013). Nanotechnology has the potential to use novel nanomaterials for groundwater, surface water, and wastewater remediation contaminated by heavy metal ions, organic–inorganic solutes, and a wide range of microorganisms (Kumar et al. 2017; Awual et al. 2015). At present, several nanomaterials are in the extensive research and development (R&D) stage for use in environmental clean-up and site remediation due to their unique activity toward nondegradable contaminants. Green manufacturing is the most efficient way to reduce and eliminate the release of toxic pollutants in soil, water, and air environments (Allen and Shonnard 2001). The use of nano-adsorbents can effectively remove organic pollutants, dyes, and dye effluents from contaminated water, such as clays, zeolites, metals, metal oxides, polymeric membranes, porous nanofibers, and zero-valent iron (West and Halas 2000; Seil and Webster 2012). Semiconductor-based photocatalysts are used in the advanced oxidation processes (AOP) for the degradation and mineralization under irradiation (natural & artificial) of toxic organic contaminants into environmentally friendly compounds (Tratnyek and Johnson 2006).

Nanoscience, considered as an emerging field, provides an informative framework to study the applications and implications of green chemistry in a broader and safer way. As compared to the previous remediation technologies, nano-remediation involves the overall reduction of contaminations (Bardos et al. 2015). Nano-based technologies can be used for the prevention, mitigation, and minimization of damage caused to human health and the environment (Hood 2004). The use of the green nano-manufacturing process involves the development of low-cost, nontoxic, and multifunctional efficient nano-products without generation of hazardous end products (Dornfeld et al. 2013). At present, nanotechnology is making substantial development in technologies for the protection of the environment, and it is being explored for its potential to provide new solutions to managing and eliminating air, water, and land pollution. It is also aims to improve the performance of conventional technologies used in clean-up efforts (Shapira and Youtie 2015).

The application of nanotechnology for in situ remediation provides a fast and cost-effective remediation technology solution (Diallo et al. 2013). Nano-based remediation technology has the potential not only to reduce the overall costs of remediation of contaminated sites but also to reduce clean-up time, eliminate the need for disposal and treatment of contaminated soil, and reduce the risk of contaminant to near zero (Gil-Díaz et al. 2016; Glavič and Lukman 2007). Owing to their unique activity toward recalcitrant contaminants, nanomaterials are being explored in advanced research and development for their use in environmental clean-up and on-site remediation (Zhang 2003; Smol and Stoermer 2010). Recently, many different nanomaterials have been evaluated for use in nano-remediation, such as nanoscale zeolites, metal–metal oxides, carbon nanotubes, dendrimers, noble metals, metal–polymer doped nanoparticles, etc. (Bardos et al. 2015; OECD 2011c). Nanotechnology has also contributed to reducing the presence of nonaqueous phase liquids (NAPL), in addition to the surface and groundwater remediation (Dreher 2004) by utilizing the nanomaterial oxide in situ to clean-up heating oil spills from the underground oil tanks (Fagan et al. 2013; Deif 2011; Rusinko 2007).

As compared to the previous remediation technologies, the nano-based approaches proved an efficient method for the reduction of overall contaminant levels (Sharma and Sanghi 2012). Green nanotechnology revolves around the use of nanotechnology applications for the development of eco-friendly products and processes (Dornfeld et al. 2013). The major objective of these technologies is the development of environmentally friendly designs that help to reduce the environmental and health implications by replacing the present applications (Maksimović and Omanović-Mikličanin 2017).

2.1.1 *Definition*

Nanotechnology is the major research area that involves the things working on the nanometer (nm) scale. It plays an important role in the expansion of innovative technologies for the design and development of new products, replacing the existing production equipment and formulating new chemicals and materials with enhanced performance (Leach et al. 2002; Dhingra et al. 2010).

The aim of the chapter is to highlight the concept of green nanotechnology under the light of green chemistry and sustainability. Green nano involves the principles of green chemistry, so it is very important to understand "*Green Chemistry*" and nanotechnology first. The purpose of green chemistry is to reinvent the use of chemicals to be safer and more efficient (Andraos 2005). At this point, the sustainability movement interferes in nanotechnology and the term sustainable and green chemistry are thoroughly used (Schulte et al. 2013). Table 2.1 provides the general definitions of the commonly referred to terms.

Green nanotechnology has two goals, *process and product*, which involve use of multifunctional nanomaterials for the renewable energy generation, nano-sensors for detecting and monitoring the pollution, green packaging, semiconductor photocatalysis for effective environmental remediation, and a novel membrane for more efficient treatment and purification of wastewater (Ran et al. 2008; Wei Guo 2011). The principles of green chemistry along with the sustainability help to recognize many opportunities for new research in this field (Anastas and Warner 2000). Green chemistry confirms that nanotechnologies lessen the unintentional hazards by providing the vision about the implications of the new technologies. When considering the implications and applications of recent technologies, green chemistry stands apart from other technological trends that focus entirely on products and processes (OECD 2011a).

Green nanotechnology is undoubtedly the most important branch of nanotechnology, utilizing the 12 principles of green chemistry for various potential applications. Being an emerging area, nanoscience offers promising opportunities to the principles of green chemistry to create sustainability and protect and promote occupational safety and health during the product manufacturing and process application (Matos et al. 2010; Anderson et al. 2010). After understanding the concept of green nano for sustainable development, the focus has been shifted toward the different application areas that are relevant to greener growth and sustainability (Lazaro et al. 2013; Mulvihill et al. 2011). Figure 2.1 presents the six application areas of green nanotechnology.

In the above-mentioned areas, nano-based applications offer potential benefits, such as lower toxicity, lower cost, higher efficiency, reduced complexity, and reliability. It also offers the opportunity to overcome the adverse effects even before

Table 2.1 General definitions

Term	Definition
Nanotechnology	It is the branch of technology that deals with dimensions 1–100 nanometers, especially the manipulation of individual atoms and molecules
Green nanotechnology	The technology used to develop clean technologies in order to minimize health and potential environmental risks. It involves the use of nano-products and the nano-manufacturing process
Green chemistry	It is the design of *chemical* products and processes that diminish and eradicate the use and generation of toxic substances. It is applied throughout the life-cycle of a *chemical* product, including its design, manufacturing, use, and ultimate disposal (end-of-life)
Sustainability	*It is the development* that fulfills the needs of the present, without compromising the ability of future generations

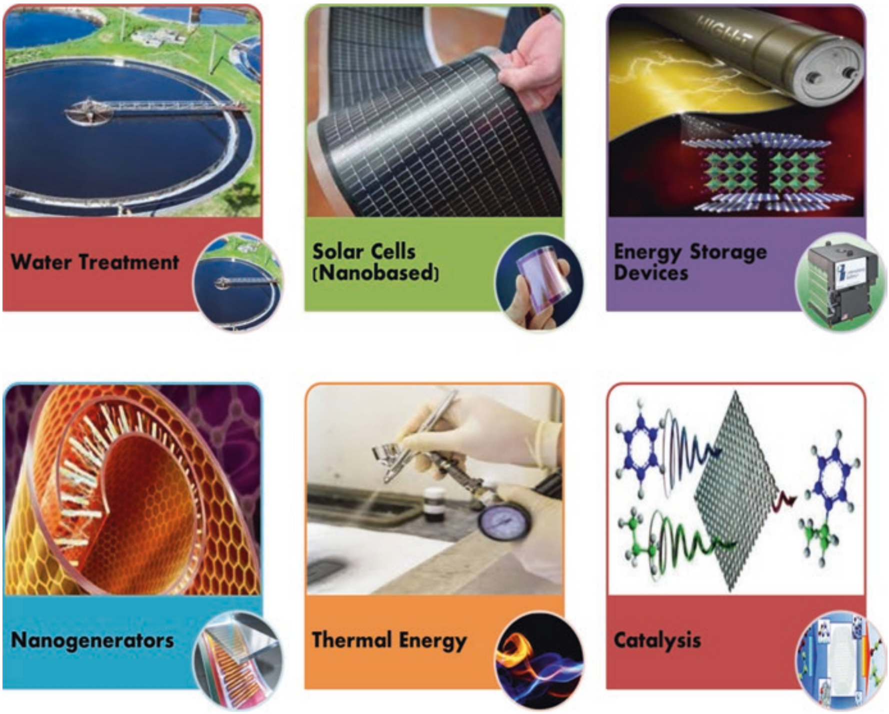


Fig. 2.1 Major research areas of green nanotechnology

they occur (Owen and Depledge 2005). Green nanotechnology can competently influence the design of nanomaterials and products by eliminating/minimizing pollution right from the synthesis, by life-cycle assessment, by estimating and mitigating where environmental impacts might occur in the product chain, and by designing nontoxic nanomaterials and utilizing them for the solution of the existing environmental problems (Som et al. 2010; Iavicoli et al. 2014). Apart from the obvious areas, using nanomaterials in the field of photocatalysis (Hashimoto et al. 2005), solar cells (Fujihara et al. 2007), fuel/bio-fuel cells (Ramsurn and Gupta 2013), and applications of green nanotechnology also involves cleaner production and processes, such as synthesis of nanoparticles using greener methods (biological synthesis). Further, recycling of industrial waste materials into nanomaterials by turning diesel soot into carbon nanomaterials, flyash into silica, alumina, and iron oxide nanomaterials is also included in the applications of green nano (Matos et al. 2010; Biju et al. 2008).

It is a general perception that nanotechnology will develop greener and cleaner technologies for the benefit of the environment and will involve diverse areas of waste. The very first idea about the concept of green nanotechnology was given by the ACS Green Chemistry Institute in partnership with the Oregon Nanoscience and Microtechnologies, addressing the challenge and opportunities involving green nanotechnology. Scientists and engineers assume that the safest future for the advancement in nanotechnology for sustainable development can be achieved by using the principles of green chemistry (Anastas and Kirchhoff 2002). There are 12 principles of green chemistry that green nanotechnology revolves around. The application of green chemistry involves the designing of processes and products that eliminate toxic substances from the beginning to the end of a chemical's life-cycle (Tang et al. 2005). Green nanotechnology revolves around the principles of green chemistry and green engineering and emphases them through unique effects that occur in nanoscale materials.

Before discussing green nanotechnology, it is of utmost importance to understand the basic *"Principles of Green Chemistry"* that were posted by the USEPA. Green chemistry, sometimes referred to as sustainable chemistry, involves the design, development, and production of chemical products and processes that can reduce the generation risk of toxic waste and hazardous end products during the manufacturing process (Naidu et al. 2008). It is noteworthy that the principles of green chemistry completely apply to green nanotechnology and nano-manufacturing processes. The 12 principles of green chemistry are given in Table 2.2.

The principles of green chemistry can be applied to produce cleaner, safer, and more sustainable nanomaterials and manufacturing processes. On the other hand, a principle of nanoscience along with green chemistry eases the syntheses of bulk and makes nanomaterials more environmentally friendly (Jahangirian et al. 2017; Anastas and Warner 1998a, b). Thus, green nanotechnology is closely interconnected with both the principles of green chemistry and green manufacturing.

In this chapter, the concepts of green engineering/green chemistry and green manufacturing are explored with a special reference to nanoscience. As the vast majority of the research in this area has been focused on the development of greener processes and approaches, this chapter will be mainly focused on the synthesis and applications of nanomaterials. Figure 2.2 demonstrates the pictorial representation of the principles of green chemistry involved in the green synthesis process.

Nanotechnology offers immense hope for the development of new technologies that are greener and more sustainable than the present technologies. Almost all the major sectors have a significant impact on the advancement of nanotechnology involving the incorporation of nanomaterials in the products and processes. The synthesis of nanomaterials for these very products uses many chemicals and chemical manufacturing processes. Owing to that, the synthesis process results in the production of toxic end products causing adverse health and environmental implications (Virkutyte and Varma 2013). The main aim behind green nano is the development of nonhazardous protocols for the products syntheses and other associated processes. The major goal is the minimization of the risks and hazards associated with the nanomaterial synthesis as the release of toxic nanomaterials give rise to the nanotoxicity issues (Fischer and Chan 2007). Thus, the green nanoproducts are those nanomaterials that are synthesized using the principles of green chemistry and directly and indirectly used for environmental applications, such as environmental remediation, treatment of wastewater, etc.

Table 2.2 General principles of green chemistry (Anastas and Warner 1998a, b)

S. No.	Principle	Description
1.	Prevention	Better to prevent waste than to treat or clean up waste after it has been created
2.	Atom economy	Synthesis methods should be designed to maximize the incorporation of all materials used in the process into the final product
3.	Less hazardous chemical syntheses	Wherever practicable, synthesis methods should be designed to use and generate substances that possess no toxicity to human health and the environment
4.	Designing safer chemicals	Chemical products should be designed to affect their desired function while minimizing their toxicity
5.	Safer solvents and auxiliaries	The use of auxiliary substances, such as solvents, separation agents, etc., should be made unnecessary wherever possible and innocuous when used
6.	Design for energy efficiency	Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthesis methods should be conducted at ambient temperature and pressure
7.	Use of renewable feedstocks	A raw material should be renewable rather than depleting whenever technically and economically practicable
8.	Reduce derivatives	Unnecessary use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes, etc., should be minimized and avoided if possible because such steps require additional reagents and can generate waste
9.	Catalysis	Catalytic reagents (as selective as possible) are superior to stoichiometric reagents
10.	Design for degradation	Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment
11.	Real-time analysis for pollution prevention	Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances
12.	Inherently safer chemistry for accident prevention	Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires

As we know, the processes and product applications of green nano comprise synthesizing nanomaterials using environmentally friendly methods and using the as-synthesized nanomaterials in environmental clean-up processes making the whole concept of green nano even more feasible and acceptable. The best example of synthesizing nanomaterials using a greener approach is by biological synthesis methods using plants, microbes, etc. (Ramya and Subapriya 2012). Also, during chemical synthesis, replacement of organic solvents with less toxic and harmful solvents reduces the toxicity manifolds. Additionally, in order to come under the green tag, the processes and products must be considered under the lifecycle framework.

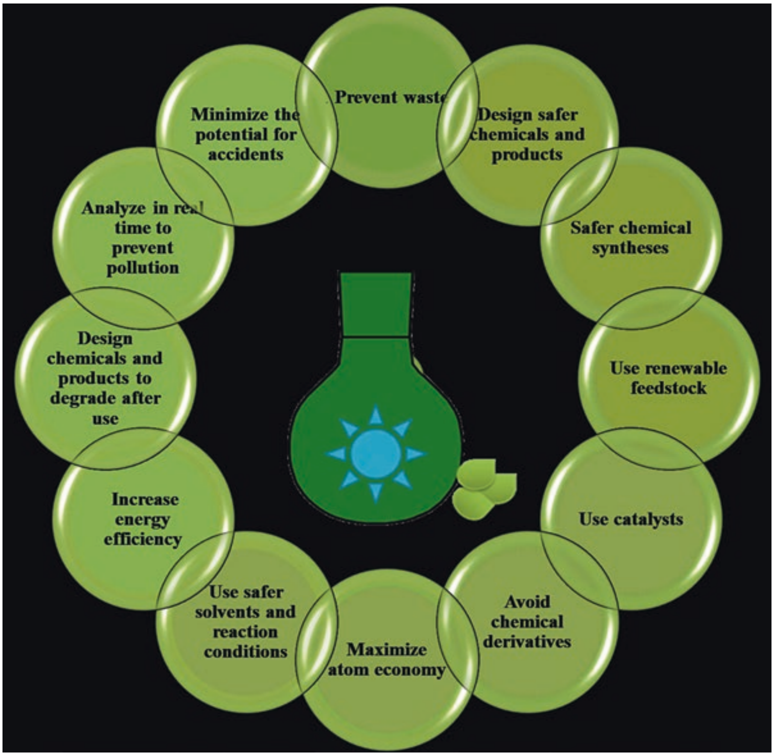


Fig. 2.2 Pictorial representation of the principles of green chemistry in green synthesis

A large number of outstanding reviews have already been published on the synthesis and functionalization of nanomaterials; hence, this chapter has focused on the aspects of products and processes relevant to green chemistry instead of focusing on the details of synthesis processes.

2.1.2 Green Nanotechnology

As the term green suggests there is something environmentally friendly here. Green nanotechnology involves the development and application of products in an environmentally friendly way, whereas green chemistry is defined as the “the utilization of the twelve principles that reduces and eliminates the use or generation of hazardous substances in the design, production, and application of chemical products and processes” (Karn and Bergeson 2009). The principles of green chemistry, defined by Anastas and Warner (1998a, b) and given in Table 2.1, are applied nowadays for the production of a wide range of chemicals with the aim of reducing hazards to health and the environment, minimizing wastes, and preventing pollution. The application of the 12 principles of green chemistry has decreased the consumption of toxic solvents and reagents manifold, enhanced the design of products for the end-of-life, and enhanced the material and energy efficiency of chemical procedures. The application of these principles of green chemistry to nanoscience will ease the synthesis and processing of safer and greener nanomaterials (Anastas and Eghbali 2010). Green nano involves the application of green chemistry to the design and development of nanomaterial production methods (small and large scale) and the application of nanomaterials in various areas (Albrecht et al. 2006). It also aims to provide knowledge about the properties of nanomaterials with reference to the toxicity issues and the design of multifunctional nanomaterials that can be used in high capacity products, which can pose a threat to human health and the environment (Tobiszewski et al. 2010). Most importantly, it attempts to develop the synthesis/methods that can eliminate the need for harmful chemicals while enhancing the efficiency of these existing synthesis methodologies (Varma 2014). It also provides the outlines for assuring that the as-synthesized nanoproducts are safer by accessing the ecological risks and hazards with reference to the design. Further, it seeks the application of nanotechnology that has a broader societal benefit by decreasing the adverse impact on health and the ecosystem. Thus, green nano starts with the development of materials, their processing, and application, throughout the life cycle, right from the beginning from the selection of raw material to the end of life (safer release to the environment) (Smith 2011). Figure 2.3 shows the benefits of green nanotechnology.

Fig. 2.3 Green nanotechnology

2.2 Application of Green Chemistry Principles to Nanoscience

Nanomaterials have a high surface to volume ratio and tunable properties make them efficient for a wide range of applications from healthcare to environmental remediation (Klabunde and Richards 2009). Nanomaterials are almost everywhere due to their multifunctionality and properties (Lue 2007). The applications of nanotechnology are growing day by day, promising environmental benefits, such as nanocatalysts for environmental remediation, thermo-electric materials for cooling-down without the use of refrigerants, efficient photovoltaic, lightweight nanocomposite materials for vehicles, mini devices to reduce the consumption of material, and nanosensors, which eliminate the need of wet chemical analysis. Nanosensors are fasters and their lower detection limits make on-site detection possible (Liang and Guo 2009). The new nanotechnologies are beneficial yet possess little harm to human health and the environment; therefore, it is necessary to design and develop the green nanomaterials and their synthesis methods (Schmidt 2007). First, the nano-manufacturing process has been discussed in the light of green chemistry, and later the application part has been discussed.

It is a known fact that nanomaterials have rich structural diversity, providing a wide opportunity to tune the physical, chemical, optical, and toxicological properties. During experimental design and analysis, extreme care should be taken as the complexity and diversity of nanoparticles can alter the toxicity related issues (Maynard 2006). Significantly, the use of different synthesis methods for the production of similar products means the difference in the methodology and reaction routes leads to a difference in product purity, quantity, intermediate, and end product. Also, the synthesized nanomaterials should be characterized in detail by known particle size, shape, size distribution, surface area, morphology, solubility, crystallinity, physical, chemical, optical, and electronic properties (Rawle 2017; Montone et al. 2015). The utilization of these well-characterized nanomaterials allows accurate biological and ecological impact assessment (Ikhmayies 2014). The principles also focused on the impact of nanomaterials that may be released to the environment after the application. Thus, the design of material should also focus on the very aspect that it should reduce harm to the environment by using environmentally friendly materials (Hutchison 2008). It also aims to design such materials that are safer and radially degrade into the environment without generating toxic intermediates and hazardous end products (Colvin 2003). To implement the principles, the fate and life cycle assessment of the nanomaterial is needed. Various short-term and long-term effects of the nanomaterials in the water, soil, and air should also be considered in view of human health (Milburn 2012) as the prolonged persistence of nanomaterial in the environment gives rise to nanotoxicity related issues. Nanotoxicology is intended to describe the toxicological properties of an engineered nanomaterial to decide whether and to what extent nanomaterials pose a threat to the environment and human health (Hoet et al. 2004). In terms of their fate in the human body and in the environment, the size of nanoparticles and lack of detection method presents a huge drawback in the context of identification and remediation (Linkov et al. 2011; Maynard et al. 2006). It is noteworthy that not all the nanoparticles are toxic to the environment; it depends on their concentration, dosage, and exposure rate (Martin et al. 2008; Krishnaswamy and Orsat 2017). Over the past decades, the fate, transport, and toxicity of engineered nanomaterials have been a major focus of environmental health and safety research throughout the globe. The basic and fundamental properties concerning the fate of nanomaterials are not well understood due to the lack of research studies (Klaine et al. 2008). The rapid consumption, usage, and production of nanomaterials ultimately lead to environmental exposure (Khan et al. 2015; Dhawan et al. 2009). Also, less is known about the eco-toxicological concerns and chronic effects of nanomaterials to date. Green nanotechnology focuses on various processes as summarized in Fig. 2.4:

The major application of Green Nanotechnology involves:

Fig. 2.4 The main focus area of green nanotechnology

2.2.1 Nanomanufacturing

The application of the principles of green chemistry in the nanomanufacturing/nano synthesis process is an emerging area aimed at sustainable development. It has gained worldwide attention in recent years due to its potential for designing multifunctional, energy efficient, and nontoxic synthesis routes (Şengül et al. 2008). It is associated with the chemicals, reagents, and solvents used during the preparation and synthesis methods. This section will focus on the synthesis routes of nanomaterials and nanoproducts with special attention to the significant environmental impacts (Chen and Schluesener 2008). All the nano-products must proceed via the various development stages to produce the particles, materials, and devices in the nanoscale dimension. A life-cycle assessment analysis checks the manufacturing of a nanomaterial and also its fate after the release in the environment up to its end-of-life (Steinfeldt 2014). The newly developed materials are expected to (a) possess high surface functionality, (b) exhibit size-dependent properties, and (c) incorporate a wide range of material and elemental compositions (Dahl et al. 2007). The assessment of these materials, before their acceptance in the commercial front, presents an opportunity for reducing the negative impact of the material, which is a must. The production of a highly precise, low waste generating method for the nanomanufacturing process will be essential for the commercialization of these products.

Green chemistry also provides the platform to increase the public perception of nanotechnology, as the present approach is comparatively easy to understand and useful to convey the responsible attitude toward the expansion of green nanotechnology (Fleischer and Grunwald 2008). That is the reason green chemistry can play the pivotal role in the growth of nanotechnology with the aim of providing the maximum benefit of these products to society (Eckelman et al. 2008). The advantages of green nanomanufacturing are as follows:

1. Production of relatively safer and greener nanoproducts
2. Eliminates the necessity of hazardous chemicals and solvents for the purpose of synthesis
3. Comparatively cheaper and environmentally friendly
4. No toxic end product
5. Requires fewer manufacturing and safety controls for the production.

Nanomanufacturing processes are widely associated with human health and environmental impacts (Asmatulu et al. 2012). It is important to evaluate nano-products for their green approaches, incorporating risk analysis and life-cycle assessment using the sustainable manufacturing approaches and employing green chemistry alternatives are the possible solution (Hutchison 2016, USEPA). Basically, for nanomaterial manufacturing, the widely used approaches are bottom-up and top-down techniques (Cao 2004; Chen and Mao 2007).

(a) ***Top-down approach:*** Reducing the material from bulk to the nanoscale. It is preferred to synthesize nanomaterials by templating.

(b) ***Bottom-up approach:*** Synthesis of organic/inorganic materials into nanostructures starting from the atom level to the nanoscale by self-assembly.

The top-down process involves the physical methods of nanomaterial syntheses, such as lithography, milling, and etching (Yadav et al. 2012). The top-down approaches start with micro-systems and miniaturizes them to the nanoscale; through grinding, it cut downs the larger material until it reaches the nanoscale dimensions (Rao et al. 2006). On the other hand, bottom-up approaches assemble the matter at the atomic scale via growth and nucleation using a precursor by means of chemical reactions, such as sol-gel, self-assembly, etc. (Biswas et al. 2012). Top-down approaches are more common compared to bottom-up for the synthesis of nanomaterials due to the ease and accessibility of use (Varma 2014). However, at the same time, it is also supposed that top-down techniques are more waste-generating compared to the bottom-up techniques. Thus, the bottom-up techniques are the ultimate tools for sustainable production as they offer the customized design of reaction, methodology, and size- and shape-controlled synthesis at the molecular level by reducing unintended waste (Bergeson and Auerbach 2004). Table 2.3 summarizes the general methods of nanomanufacturing with examples.

The nanomaterials synthesized using the above-mentioned methods are commonly referred to as engineered nanoparticles (ENPs). Nanomaterials can be classified as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) (Amin et al. 2014; Nakagawa et al. 2013). Many of the nanomanufacturing processes have low product yield causing low material efficiency leading to the generation of excessive waste. Also, some of the synthesis methods have the potential to cause unwanted human health effects (acute and chronic) due to the accidental release of nanomaterials in the environment. The examples of nanomaterials are summarized in Fig. 2.5.

The nature of these ENPs and their use gives convincing reasons for utilizing the principles of green chemistry for the development of new nanomaterials and their applications (Savolainen et al. 2010). The production of any nanoproduct requires high energy consumption, hazardous chemicals, low material conversion, and wasteful and repetitive purification; thus, there are several other ways to develop greener processes for the synthesis of nanomaterials (Gladysz 2001). The greener synthesis of nanomaterial attracts attention worldwide. There are several benefits to the green synthesis of nanomaterial over the chemical based synthesis. Through green synthesis, highly efficient, multifunctional, and less hazardous synthesis of nanomaterials can be achieved producing a higher number of particles in less time under mild reaction conditions (Schwarz 2009). Nanotechnology research can overcome the need for hazardous chemicals during the nano synthesis process through the following suggested ways:

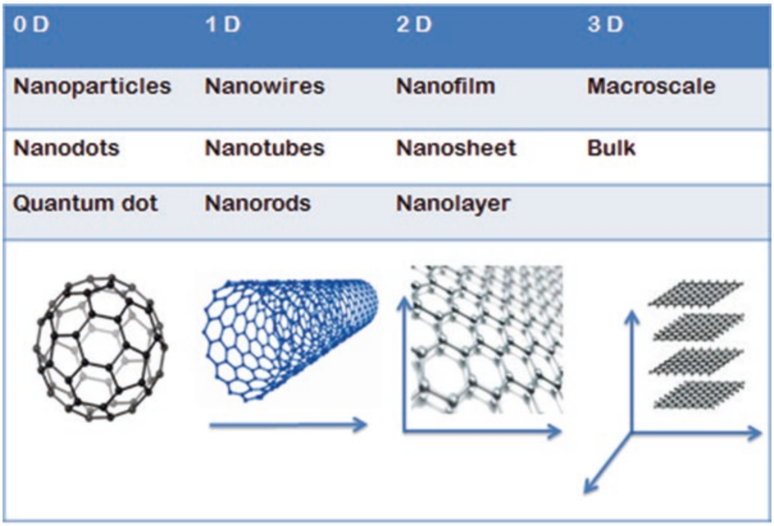
(a) Bottom-up synthesis of novel nanocatalyst (at atomic or molecular level),
(b) Molecular self-assembly as the basis of new materials,
(c) Adding information to molecules for developing new molecules,
(d) Developing nanomaterials in the micro-reactors.

Table 2.3 Common nanomanufacturing techniques

Bottom-up	Top-Down
Self-assembly	***Physical milling***
Langmuir–Blodgett self-assembly	Ball milling
Electrostatic self A	Mechanical milling
SA monolayers (SAMs)	Cryomilling
	Mechanochemical
Vapor-phase deposition techniques	
Molecular beam epitaxy (MBE)	***Electrospinning***
Plasma-enhanced chemical vapor deposition	
Atomic laser deposition	***Etching***
Pulsed laser deposition	Dry etching
Evaporation	Plasma etching
Sputtering	Reactive ion etching
Vapor phase epitaxy	Wet etching
Nanostructured material synthesis techniques	***Lithography***
Flame synthesis	Photolithography
Arc deposition	E-beam lithography
Laser ablation	Immersion lithography
Evaporation	X-ray lithography
	Extreme UV lithography
Liquid phase synthesis techniques	Focused ion beam lithography
Sol-gel method	Nanoimprint lithography
Sonochemical synthesis	Soft lithography
Solvothermal synthesis	
Microwave-assisted synthesis	
Chemical precipitation	
Electrodeposition	
Reverse micellar synthesis	
Biological synthesis	
Plants	
Bacteria	
Fungus	
Plant wastes	

2.2.2 Green Synthesis of Nanomaterials

Green synthesis, using the principles of green chemistry, is a new platform to design novel nanomaterials that are nonhazardous to human and environmental health and has the extensive potential to revolutionize large-scale nanomanufacturing processes (Duan et al. 2015; Wang et al. 2012). These greener nanomaterials have wide possibilities in the field of nanomedicine as novel drug carriers, etc., in the near future (Nath and Banerjee 2013). Greener synthesis of nanomaterials sets the



0 D	1 D	2 D	3 D
Nanoparticles	Nanowires	Nanofilm	Macroscale
Nanodots	Nanotubes	Nanosheet	Bulk
Quantum dot	Nanorods	Nanolayer	

Fig. 2.5 Examples of 0, 1, 2, and 3D nanomaterials

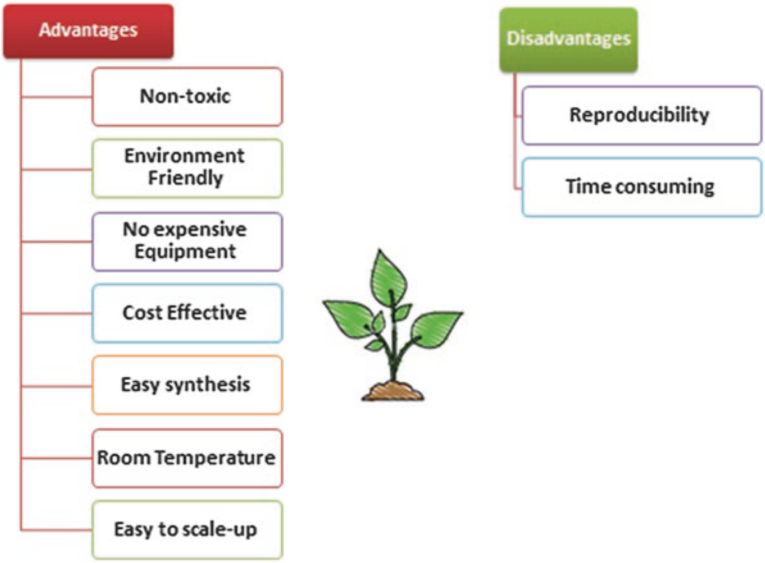


Fig. 2.6 Advantages and disadvantages of green synthesis

benchmark for the development of cleaner, safer, and sustainable nanoproducts and nanomaterials (Gawande et al. 2013). Figure 2.6 presents the advantages and disadvantages of using green synthesis processes.

The basic principles of green chemistry are the utilization of nontoxic, biodegradable, cost-effective resources and energy efficient reactions. The nanomaterials synthesized using plants, microbes, and other natural resources are commonly termed green synthesized nanomaterials. Some chemical methods also qualify for the green chemistry based synthesis methods; however, utilization of all natural products for the synthesis of nanomaterials has gained widespread attention in the nanomanufacturing area (Albrecht et al. 2006). It has been reported in the various literature that the nanomaterials synthesized using green synthesis methods are similar to their chemical counterparts and have similar efficiency. The green syntheses approaches of nanoparticles are easier, cheaper, more efficient, and eco-friendly compared to chemical or microbe-mediated synthesis. The chemical synthesis method involves the use of toxic solvents, high pressure, energy, and high-temperature conversion. On the other hand, microbe mediated syntheses are not feasible at large scale due to their lab maintenance. It is also possible to alter the properties of nanomaterials by controlling the reaction conditions, such as temperature, pH concentration, etc., in a similar way to the chemical synthesis (Vigneshwaran et al. 2006). The major applications of these greener nanomaterials lie in nanosensing, nanomedicine, nano-therapeutics, energy storage, and so on. Most importantly, greener synthesis approaches paved the way for safe and sustainable nanotechnology (Yoshida et al. 2011). Many challenges and issues are associated with green nanotechnology but that does not reduce the potential of the green and sustainable approach. Figure 2.7 shows the general methodology of green synthesis of nanomaterials.

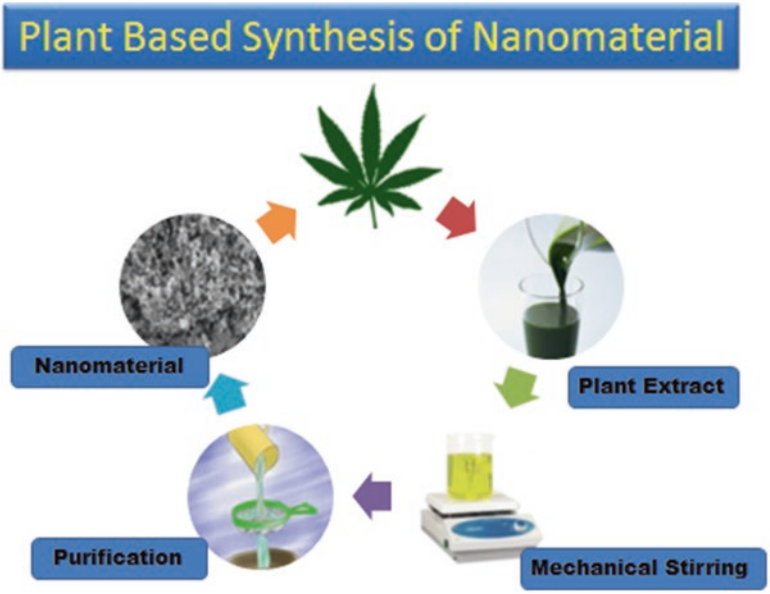


Fig. 2.7 General methodology of green synthesis

A variety of multifunctional green nanomaterials with definite composition, size, morphology, and crystallinity have been synthesized by different methods, and their potential applications have been explored. Green synthesis of nanomaterials using plants is actually a type of bottom-up approach involving oxidation and reduction as the main reaction (Sangeetha et al. 2011; Raveendran et al. 2003). The extract of the plant contains several primary and secondary metabolites, i.e., alkaloids, flavonoids, phenolic acid, and terpenoids. These compounds are responsible for the reduction/conversion of bulk into nanoparticles (Vijayakumar 2013; Makarov et al. 2014). These metabolites are mainly responsible for the redox reaction for the synthesis of eco-friendly green nanomaterials. After reviewing the literature, it was found that the synthesis phase is the major contributor to the life cycle impact of the nanomaterials as at this stage toxic waste is more prone to generate (Nune et al. 2009). Less transparency, large inconsistencies in data collection, and different methodologies were also stated by many researchers. Table 2.4 summarizes the plants used for the synthesis of different nanoparticles.

Table 2.4 Plants used for the synthesis of different nanoparticles

Plant	Nanoparticle	Size (nm)	Shape	Plant part	References
Alovera	In_2O_3	5–50	Spherical	Leaf	Maensiri et al. (2008)
Acalypha indica	Ag, Au	10–30	Spherical	Leaves	Krishnaraj et al. (2010)
Alternanthera sessilis	Ag	40–50	Spherical	Whole	Niraimathi (2012)
A. *maxicana*	Ag	20–50	Spherical	Leaves	Singh et al. (2010)
Artemesia *nilagirica*	Ag	70–90	Spherical	Leaves	Song and Kim (2009)
Andrographis paniculata	Ag	65–90	Spherical	Leaves	Suriyakalaa (2013)
Azadiricta *indica*	Ag	10–30	Spherical	Leaves	Tripathy (2010)
Boswellia serrata	Ag	7–10	Spherical	Gum	Kora et al. (2012)
Cassia fistula	Au	55	Spherical	Stem	Daisy and Saipriya (2012)
Caria *papaya*	Ag	15	Spherical	Fruit	Jain (2009)
Citrus sinensis	Ag	35	Spherical	Peel	Kaviya (2011)
Citrullus colocynthis	Ag	5–80	Triangle	Callus	Satyavani (2011)
Cinnamon *zeylanicum*	Ag	45	Spherical	Leaves	Sathishkumar (2009)
Dillinia *indica*	Ag	11–25	Spherical	Fruit	Singh et al. (2013)
Euphorbia prostrata	Ag	52–55	Rod	Leaves	Zahir and Rahuman (2012)
Mentha *piperita*	Au	90–150	Spherical	Leaves	MubarakAli (2011)
Mirabilis jalapa	Au	100	Spherical	Flowers	Vankar and Bajpai (2010)
Tinospora *cordifolia*	Ag	35	Spherical	Leaves	Jayaseelan (2011)
Withania somnifera	Ag	5–40	Irregular	Leaves	Nagati et al. (2012)
Melia azedarach	Ag	80	Irregular	Leaves	Sukirtha (2012)

There is a day by day increase in the demand of these nanoproducts, according to an estimate by The Royal Society the total production of nanomaterials annually may exceed 100,000 metric tons worldwide by the end of 2020. Thus, the development of sustainable alternatives for the novel synthesis and production methodologies is the urgent need of the hour to overcome the associated risks (Iravani 2011). It is a fact that every country that is associated with the synthesis and use of nanomaterials are very much aware of their potential risks and toxicity, though no specific regulations have been implemented regarding the use of nanomaterials so far (Science Policy Council 2005; Davis 2007; Nel et al. 2006). However, the US-EPA permits a limited production of new nanoscale material under the Toxic Substance Control Act. There is an urgent need for the pioneering countries, such as Japan, the USA, and European Union, to implement regulations on toxic synthesis approaches and the hazardous products. The nanomanufacturing processes associated with negative human and environmental impacts should be thoroughly accessed while evaluating nanomaterials for their *greenness* for sustainable development (Lu and Ozcan 2015). Figure 2.8 shows the plant-mediated nanoparticles and their applications.

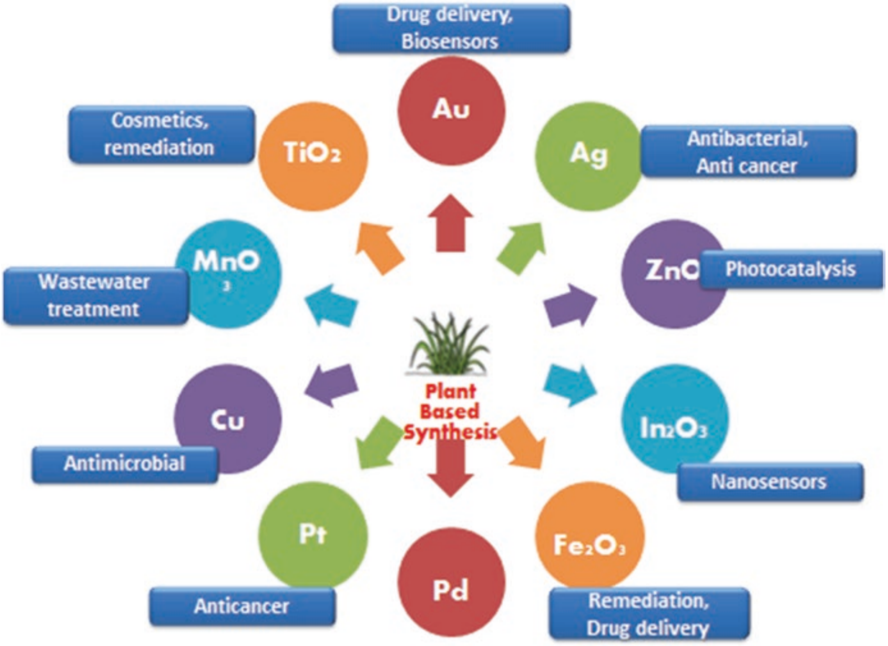


Fig. 2.8 Green synthesized nanomaterials and their applications

2.2.3 *Wastewater Treatment Using Nanomaterials*

The availability of clean and safe drinking water is a global challenge. Water and wastewater treatment methods are chemically intensive as well as costly and harmful to the environment to a certain extent (Naushad et al. 2016). The conventional treatment technologies require high capital input, a large area, and high maintenance costs, and they just transfer the pollutants from one phase to another, rather than completely degrading them into an environmentally friendly end product (Naushad et al. 2013; De Kwaadsteniet et al. 2011). This necessitates an alternative technology for the treatment of wastewater in a greener and more sustainable way. At present, many physicochemical methods, such as carbon adsorption, distillation, ion-exchange, reverse osmosis, and nanofiltration, are used for the purification of wastewater (Göbel et al. 2007; Clara et al. 2005). Major drawbacks associated with these methods include membrane deformation, high cost, handling, sludge formation, and disposable problems. On the other hand, non-biodegradable pollutants pose a serious threat as the majority of these pollutants require a high priority treatment (Khulbe et al. 2012). This necessitates an advanced, greener, more cost-effective method for wastewater treatment. Figure 2.9 shows the conventional and advanced wastewater treatment technologies.

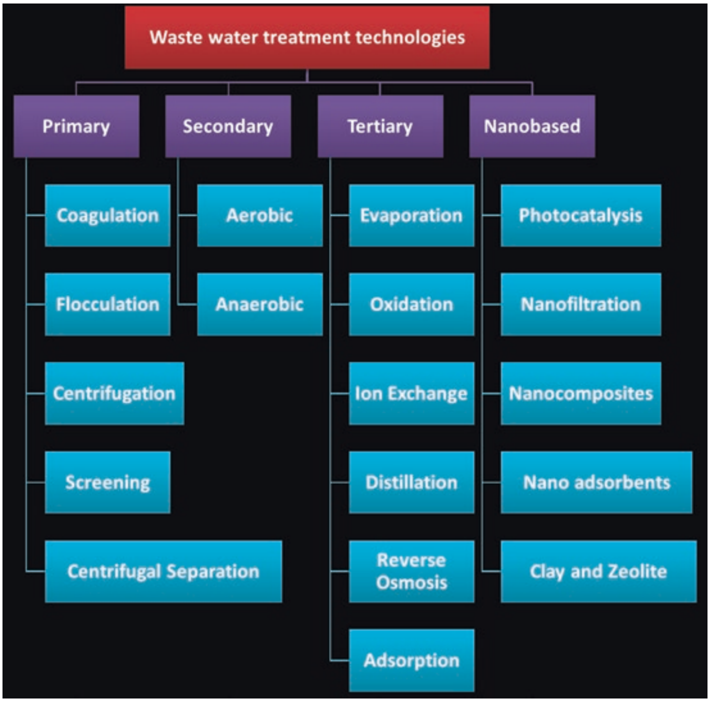


Fig. 2.9 Conventional wastewater treatment technologies

Nanotechnology provides the solution to the existing problem. Nano-based catalysts, adsorbents, and membranes can create eco-friendly solutions to wastewater treatment (Tiwari et al. 2008). Nanomaterials have gained widespread attention in the field of environmental clean-up and remediation due to their higher surface-to-volume ratio (Diallo and Brinker 2011). The other specific changes in their physical, chemical, and biological properties developed owing to their size are also an added advantage (Theron et al. 2008). Research is underway for the development of novel nanomaterials with increased efficiency, selectivity, and capacity for the treatment of wastewater. There are several benefits of using nanomaterials due to their higher surface reactivity and surface-to-volume ratio (Brame et al. 2011). Nanotechnology for water purification plays an important role in providing global water purity and security. The application of nanotechnology for the treatment of wastewater could be summarized under the following points:

(i) By nanoscale filtration techniques, such as nanofiltration using membranes,
(ii) By nano-adsorbent materials, such as sorbents, nanoclays, zeolites,
(iii) Nanophotocatalysis using nano-sized semiconductor material for environmental remediation,
(iv) Nanocomposites, such as metal–polymer nanocomposites for various applications,
(v) Nanomaterials for heavy metal remediation,
(vi) Metal and metal oxides for the removal of deadly microbes from the water.

Many research studies indicate that nano-based remediation technologies will be safer, more economical, and more efficient than the conventional techniques. Nanomaterials can be used for the sensing and detection of pollutants, remediation, and prevention of pollution (Kaur et al. 2017). Additionally, nanomaterials can also be used for the improvement of membrane separation processes resulting in higher selectivity and lower cost (Gehrke et al. 2015). Nanomaterials have several advantages, such as unique size-dependent properties emerge owing to the quantum confinement effect. The specific characteristics allow the development of high-performance nanomaterials for efficient wastewater remediation (Horizon 2020). The most promising applications of nanomaterials for wastewater remediation are highlighted in Table 2.5.

Nanotechnology offers great potential in the area of water treatment and purification due to the large surface-to-volume ratios (SVR) of the nanomaterials. The preparation of novel photocatalytic membranes by implanting semiconducting nanomaterials over the conventional membranes is used for the purification and treatment process (Krishnan et al. 2008). Various approaches, such as photocatalysis, nanofiltration, and adsorption, using titanium dioxide (TiO_2), zinc oxide (ZnO), polymer membranes, ceramic membranes, carbon nanotubes, nanowire membranes, and magnetic nanoparticles (nZVI), are used to resolve problems involving treatment of wastewater (Bhattacharya et al. 2013; Andreescu et al. 2009). Novel metal/metal oxide nanoparticles, nanomembranes, and other nanomaterials are used for detection and removal of chemical and biological contaminants, including heavy metals, pharmaceutical wastes, pesticides and their intermediates, cyanide, algae,

Table 2.5 Application of nanomaterials in wastewater treatment

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
	Reusable	
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

viruses, bacteria, parasites, organics, antibiotics, etc., from wastewater (Alqadami et al. 2016; Khan et al. 2018; Adeleye et al. 2016; Naushad et al. 2015; Khin et al. 2012). Membrane processes, nano-based materials, and the combination of both offer wide possibilities for water treatment by filtration and photocatalysis at the same time (Martin 1994; Adriano et al. 2004). With the sustainability issues, the focus has been shifted toward the use of greener methods for the treatment of wastewater for environmental applications. Thus, the nanomaterials synthesized using green chemistry-based approaches used for the environmental clean-up will reduce the risk of hazardous waste generation and eliminate the risk of toxic end products.

2.2.4 Photocatalysis or Nanocatalysis

The inability of conventional technologies toward environment sustainability has led to the research in the field of “Advanced Oxidation Processes (AOPs)”, including the nano-based wastewater treatment technologies (Swaminathan et al. 2013). The main aim of these AOPs is the generation of highly reactive species (in situ) or generation of free radical charged particles for rapid degradation and mineralization of unmanageable organic compounds and pollutants, water pathogens, toxicants, pesticides, and disinfection by-products (Oturan and Aaron 2014; Sheldon et al. 2007).

Over the past few years, nano-based photocatalysis has shown great potential as a green chemistry-based remediation technology. Among the several green earth projects underway, nano-photocatalysis has emerged as the most promising treatment technology; it utilizes the energy of natural sunlight or artificial illumination that is available in abundance (Polshettiwar and Varma 2010). In recent years, photocatalytic processes have been successfully utilized for the elimination of these contaminants from wastewater. Photocatalytic oxidation has already proven its potential for the degradation of various compounds, such as dyes, pharmaceuticals, endocrine disrupting compounds, phenols, and pesticides, from wastewater (Oller et al. 2011). The photocatalytic processes have proven successful in the degradation and mineralization of organic bio-recalcitrant compounds and emerged as the most effective treatment technique (Sheldon 2008). The increasing public concern about several environmental pollutants has provoked the need to develop advanced treatment technologies, where advanced oxidation, i.e., photocatalysis, is gaining a lot of attention in the field of environmental remediation. There are several advantages to using nanocatalysts; they are:

(i) Nontoxic,
(ii) Low cost,
(iii) Highly efficient,
(iv) Reusable,
(v) No toxic and hazardous end product,
(vi) Efficiently work on a wide range of pollutants,
(vii) Highly reactive.

Also, the major advantage of the photocatalytic process over the existing technologies is that there is no requirement for further treatment, thus eliminating the need for secondary disposal methods. Compared to other advanced oxidation processes, especially those involving the use of oxidants, such as hydrogen peroxide and ozone, here expensive oxidizing agents are not required because atmospheric oxygen acts as the oxidant, which is the added advantage of nano photocatalysis (Kalidindi and Jagirdar 2012). As the selectivity and efficiency of nanocatalysts largely depend on the shape, size, and surface structures, synthesis of nanocatalysts having the desired physicochemical properties is a must to achieve the goal of green nanotechnology (Stasinakis 2008; Xu et al. 2012). The design and production of nanocatalysts is the basis of achieving the complete degradation of pollutants into environment-friendly end products (Anastas et al. 2001). It is among this area where nanotechnology enables green chemistry to offer a way to green nanotechnology toward sustainable remediation. It is a known fact that most of the organic and inorganic pollutants can be easily degraded by heterogeneous photocatalysis (Campelo et al. 2009). Photocatalysis is a process of degradation of pollutant by accelerating the rate of chemical reaction in the presence of a semiconductor catalyst without itself being consumed. The process principally depends on the generation of hydroxyl radicals (OH) that are capable of converting various toxicants/nonbiodegradable pollutants into nontoxic end products, such as CO_2, H_2O, and other environmentally friendly compounds (Min and Friend 2007). Nano-photocatalysis is a technology used for the removal as well as the mineralization of contaminants from the waste in order to environmentally clean-up in a sustainable manner (Mishra and Khushalani 2013). Figure 2.10 shows the photocatalytic process over the surface of a nanocatalyst.

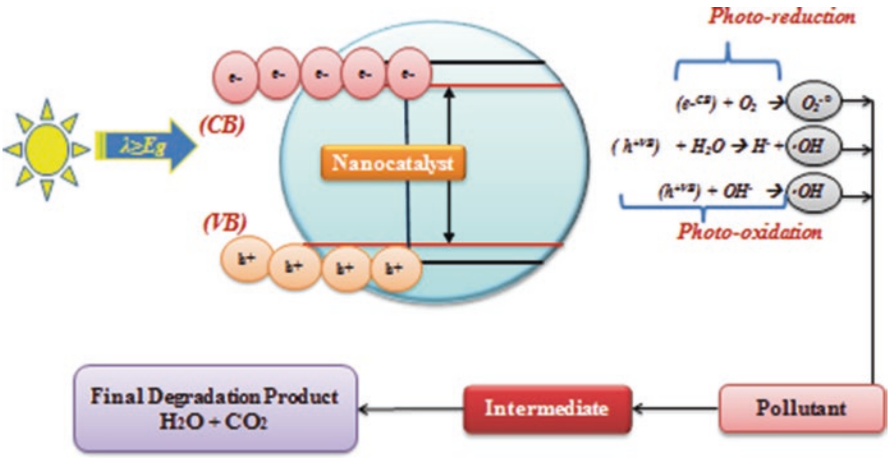


Fig. 2.10 Photocatalytic process over the surface of nanomaterial

Nano-based photocatalyst has shown potential as a low-cost, green chemistry-based, sustainable treatment technology (Ahmed et al. 2011). Most commonly used heterogeneous catalysts are semiconductors (Fenoll et al. 2011) having wide band gaps. Several types of nanomaterials, such as metal and metal oxide nanoparticles, doped nanoparticles, nanocomposites, nanotubes, and bimetallic nanoparticles, have been used for the treatment of a wide range of environmental pollutants (Berekaa 2016; Khin et al. 2012). The development of efficient semiconductor-based photocatalysts, which can work in solar, visible, and UV light, is a challenge despite substantial research in the area.

2.2.5 Water Filtration Using Nanofiltration

Membrane filtration, frequently referred to as the *"technology of choice"*, is a widely accepted and superior technology treatment of wastewater implemented by providing a barrier (physical) that effectively removes the unwanted molecules (Baker et al. 2007). For over three decades, membrane technology has been recognized worldwide for the successful separation of a wide range of contaminants from water and wastewater (Baruah et al. 2017). A membrane is a thin layer of a semipermeable material that separates substances when a driving force is applied across the membrane (Scott and Hughes 2012). Membranes provide the physical barrier that allows only certain components to pass through on the basis of their chemical and physical properties. Among all the other conventional technologies used for the treatment of water, membrane filtration emerges as the most trusted because it is very simple, highly effective, does not involve the use of chemicals and additives, is easy to scale-up, fast, and, importantly, because of its flexibility to combine with other advanced treatment technologies (Ersahin et al. 2012). The pressure driven filtration technology is classified as low pressure (MF & UF) and high pressure (NF & RO) on the basis of the molecular weight cut-off values (MWCO) of the particular membrane and trans-membrane pressure (Yangali-Quintanilla et al. 2011; Riungu et al. 2012). These four membrane filtration processes are best understood together in terms of the size of particles that can be removed from a mixture. Out of these, nanofiltration emerges as the sustainable alternative for the remediation of several contaminants.

NF is a high pressure driven technology, used to remove organic contaminants, bacteria, viruses, dairy, natural organic matter, and salts. It is also used for softening of hard water by removing multivalent and divalent ions. The pore size of the NF membrane is around 0.001 microns, typically under the range of 1–100 nm. Up to 99.9% removal of molecules in the range of 1–100 nm was achieved in the cases of different pesticides using NF membranes (Strathmann et al. 2011). NF is excellent for the removal of low molecular weight compounds, as low as 100–200 Da, and therefore selected for the removal of pesticides (Shon et al. 2005; Kim et al. 2011). Higher energy is required for NF than MF and UF. NF is the process between RO and UF, and is also referred to as loose RO. To date, NF is the only filtration technology known to remove organic contaminants and pesticides (Karimi et al. 2016).

2.2.6 Renewable Energy Generation

The major research area in this field is the design of nano-enabled solar cells utilizing the principles of green chemistry. The novel nanomaterials used for solar cells include titanium dioxide, quantum dots, cadmium telluride, and silver with a polymer that can absorb a large fraction of solar energy (Guo 2012). The cost of these nano-based solar cells will be much lower compared to those of commercially available solar cells (Wang et al. 2008). Intensive research is going on in this field to increase the efficiency of these solar cells. Other methods, such as the deposition of nano-crystals, suspended nanoparticles in quantum dots, nanowires, and the production of the highly stable laminate layer for the protection of solar cells, are also considered for sustainable product development (Musee 2011). Nanotechnology research is also happening in the field of energy storage by developing high-capacity energy storage devices for application in the area of renewable energy. Nano-based photovoltaic devices have considerable potential for high performance and cost reduction (Tennakone et al. 1995).

2.3 Limitations of Green Nanotechnology

Green nanotechnology is an emerging area, and it has its own limitations and challenges to address. According to the report of the ACS Green Chemistry Institute, the key challenges linked with green nanotechnologies are:

(i) Handling of toxicity related issues of nanomaterial
(ii) Technical and economic barriers
(iii) Regulatory policies for nanomanufacturing processes
(iv) Deployment of scale-up procedures
(v) Life cycle analysis

The above-mentioned points should be extensively considered for green and sustainable development. Green nanotechnology brings products that reduce pollutants and are eco-friendly but the major limitations are the costs and risks associated with the production of nano-based products. Though advances have been made in the development of green nanotechnology, the level of sustainability for greener applications of nanotechnology is always a concern. The products synthesized using green nanotechnologies are efficient, but the main worry lies with the upstream processing of the products (Clark 1999).

Research is under-way for the synthesis and application of greener nanoproducts, but when talking about the commercial front, there are very few products commercialized to date (Constable et al. 2002). It is a general conception that it will take a few years to fully understand the market potential of green nanotechnology.

2.4 Conclusions

Nanotechnology offers the opportunity to find the solution to global problems that significantly affect society. As the name implies, green nanotechnology has a certain green purpose. After reviewing the advances and applications of the field, the focus has been shifted to nano-based applications, as nanotechnology provides the framework to consider the application of green chemistry. Through research, it has been revealed that even after various advantages it has certain limitations and challenges to address. Green nanotechnology has the significant potential to make a contribution to addressing the green challenge along with sustainable development. The sustainable development of nanotechnology will require the incorporation of life cycle thinking to analyze the environmental impacts of the nanoproducts. Also, certain points such as possible life cycle assessment of the newly synthesized nanoproducts through nanomanufacturing before release to the commercial front must be taken seriously in accessing the contribution to the green growth. Application of the principles of green chemistry to nanotechnology helps to identify better products and processes but there is always hope for improvement.

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