CHAPTER 12

Green Synthesis of Nanoparticles and Their Applications

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INTRODUCTION

Nanotechnology is an emerging technology that can revolutionize different scientific fields (Fakhari et al., 2019). The subject of nanotechnology was mentioned for the first time in 1959 at the annual meeting of the American Physical Society (APS) by Richard Feynman with his speech "There is Plenty of Room at the Bottom" and this speech became a source of inspiration for nanotechnology (Güven, 2022). Professor Norio Taniguchi of Tokyo University of Science has very well defined the term "nanotechnology" with the phrase "Nanotechnology deals with the processing of separation, assembly and deformation of materials by an atom or a molecule". In his words, nanotechnology deals with the branch of science of manipulating matter on an atomic or molecular scale.

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Nanotechnology allows the production and manipulation of minute objects that measure as little as one billionth of a meter (the nanometer). Nanotechnology got started in the early 1980s with the appearance of a new type of microscope (atomic force microscope), that allowed not only the observation of atomic and moleculer units, but also their physical manipulation and the relative scale of comparison as shown in Figure 1 (Brar et al., 2010). Nanomaterials are structures that are smaller than 100 nm, have a large surface area, and show various physical and chemical properties (Yakut and Karataş, 2021) and they have a remarkable difference in properties compared to the same material in bulk. These differences lie in the physical and structural properties of the element's atoms, molecules and bulk materials due to the difference in physicochemical properties and surface/volume ratio. With the advancement in nanotechnology, many nanomaterials with unique properties are emerging, opening up the range of applications and research opportunities (Srikar et al., 2016).

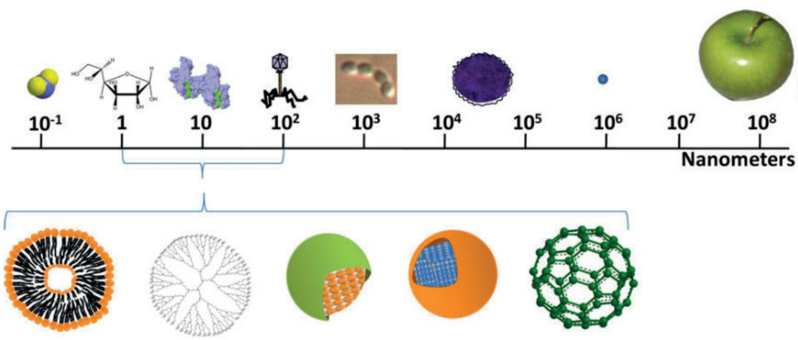

Figure 1. Comparison of nanoparticles with macroscale particles (Brar at al., 2010).

Nanotechnology is used in many fields such as optics, electronics, biomedical science, mechanics, drug-gene delivery, chemical industry, optoelectronic devices, nonlinear optical devices, catalysis, space industries, energy science and plays a critical role in many important technologies through nanoparticles (Jadoun et al., 2021). The field of nanotechnology is the most dynamic field of research in materials science and the synthesis of nanoparticles (NPs) is increasing significantly all over the world (Rafique et al., 2017).

NPs display completely new or improved properties, taking into account certain properties such as shape and structure (Rafique et al., 2017). Inorganic NPs; semiconductor NPs (such as ZnO, ZnS, CdS), metallic NPs (such as Au, Ag, Cu, Al) and magnetic NPs (such as Co, Fe, Ni), while organic NPs contain carbon NPs (such as fullerenes) (Rafique et al., 2017). With the development of nanotechnology, interest in the synthesis and characterization of metal nanoparticles has increased in recent years.

Two methods called "top-down" and "bottom-up" are used in the synthesis of NPs. The synthesis of nanomaterials via top-down and bottom-up approaches are given in Figure 2. The top-down method is based on the principle of reducing large-size materials to nano-size by chemical or mechanical interventions. In contrast to the physical top-down method, which is based on chemical reactions, in the bottom-up method, the process of growing atoms or molecules with a number of chemical reactions takes place (Şimşek, 2015).

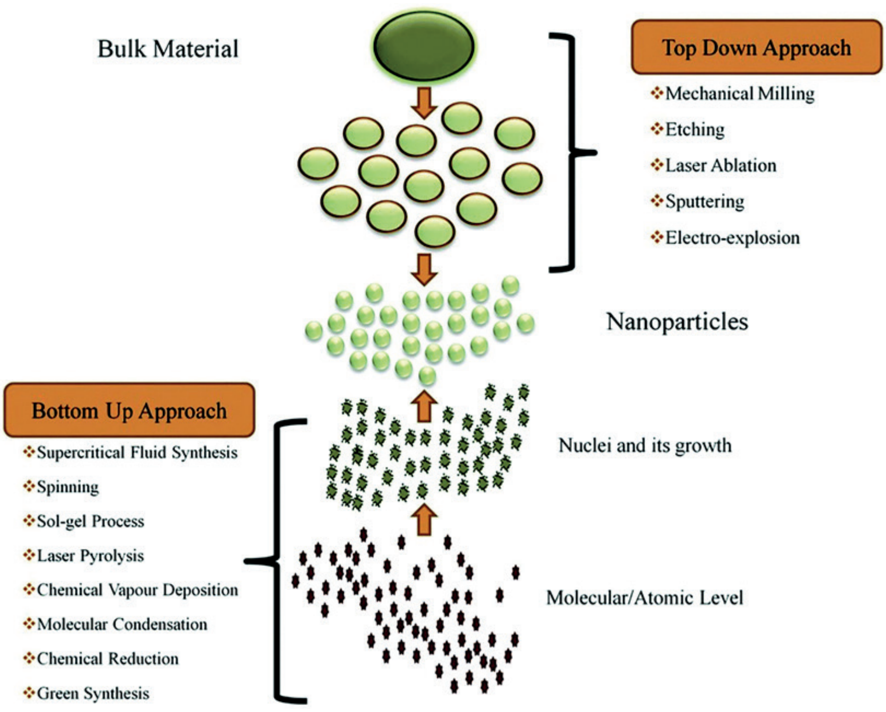

Figure 2. Approaches used in NPs production (Baig et al., 2021)

NPs can be produced by many methods such as chemical reduction, physicochemical reduction, photochemical reduction, electrochemical reduction, radiolysis and heat evaporation (Hatipoğlu, 2021). The use of NPs has increased in many areas with the increase of researches on NPs and obtaining efficient results. Especially in the field of engineering, the use of these materials is frequently encountered (Yakut and Karataş, 2021). Nowadays, it is more preferred to produce nanoparticles with low-cost "green synthesis" procedures that do not pollute the environment, do not use toxic solvents, instead of traditional methods. In this context, scientific studies have focused on synthesizing these nanoparticles from biomaterials such as plants, bacteria, fungi, algae and viruses (Hatipoğlu, 2021).

SYNTHESIS METHODS OF NANOPARTICLES AND ITS APPLICATIONS

The synthesis of NPs is carried out by three methods. These are chemical, physical and biological methods (Umaz and Koç, 2019). Most chemical methods use toxic chemicals and often produce non-polar organic solutions and non-environmentally friendly by-products. In addition, physical and chemical methods are not preferred much because of their excessive power consumption, high cost and requiring the use of various devices (Baykal, 2022). Synthesis of NPs by biological method is superior to physical and chemical methods due to its low cost, process simplicity, less chemical use, less energy requirement and environmentally friendly (Umaz and Koç, 2019).

Recently, many approaches have been developed with the biological synthesis method to synthesize different NPs (Umaz and Koç, 2019). The synthesis of NPs is generally carried out by two different synthesis methods, the bottom-up approach and the top-down approach (Gour and Jain, 2019). In the top-down approach, synthesis methods such as suitable bulk material, grinding, sputtering, thermal/laser ablation (Gour and Jain, 2019; Jadoun et al., 2021), mechanochemical synthesis method, and electron beam lithography (Baykal, 2022) are used (Gour and Jain, 2022). 2019; Jadoun et al., 2021). It is based on the principle that larger molecules decompose into smaller units and then these units are converted into suitable NPs by physical methods. Ag, Au, PbS and fullerene nanoparticles are synthesized using this technique. Mechanical grinding is associated with the synthesis of fine particles and powders by providing pressure and friction to bulk materials. Sputtering is used for nanostructured material synthesis of the surface atoms of the evaporated material. The laser ablation method is used to synthesize NPs with narrow size distribution with laser beam pulses. The mechanochemical method is based on the synthesis of NPs using a ball mill and a reducing agent at room temperature. Electron beam lithography is a method used for synthesizing nanometer scale patterns and synthesizing 3-D micro and nano structures. These methods are simple and have the advantage of bulk synthesis of NPs. However, the biggest disadvantages of these approaches are that they are a costly and slow technique and negatively affect the surface structure due to crystallographic damage (Baykal, 2022).

In the bottom-up approach, atoms or molecules are synthesized into nanoscales by self-assembly using chemical and biological methods (Gour and Jain, 2019; Jadoun et al., 2021). Chemical and biological synthesis methods such as sol gel, green synthesis, chemical reduction and laser pyrolysis are considered bottom-up synthesis of NPs. The laser pyrolysis method is based on the synthesis of small sized nanoparticles with rapid heating and cooling using a powerful laser beam in some noble gas environment. The physical vapor deposition method focuses on synthesizing gas phase nanostructures by heating the main bulk material using an electron beam. The chemical vapor deposition method is used for the synthesis of highly pure nanostructural thin films with high performance at high temperatures, while the sol-gel method is used for the synthesis of nanomaterials with magnetic or optical properties. Synthesis by chemical reduction is an oxidation-reduction reaction. The microemulsion method is based on the use of oil-water and water-oil inorganic phases in the homogeneous and size-controlled synthesis of metal NPs. The biggest advantages of these methods are the synthesis of large amounts of homogeneous NPs in a short time and the controllable particle size and morphology. Low synthesis rate, high energy consumption, use of toxic materials and being expensive are the disadvantages of these synthesis methods (Baykal, 2022).

NPs are used in a wide variety of applications due to their physicochemical properties. These applications include medical, biomedical, environmental, agriculture, catalysis, textile, electronics, transportation and other fields. Nano-sized inorganic NPs are frequently used in the development of new nanodevices that can be used in biomedical and pharmaceutical applications thanks to their physical and chemical properties. With the help of nanomaterials, early diagnosis, prevention and appropriate treatment of diseases is possible. Carbon nanotubes (CNT) have been developed as biosensors in the medical field, in the diagnosis of cancer disease, lipid and polymer-based NPs in drug delivery systems, ironoxide NPs in applications such as magnetic resonance imaging (MRI) and drug delivery, AgNPs are used in wound healing due to their antimicrobial activities. It is increasingly used in dressings, catheters, various household products. NPs is widely used in energy production and storage, photocatalytic applications due to its large surface areas, optical behavior and catalytic structures. Carbon nanotube fuel cells are used in electric cars, semiconductor nanomaterials in the form of miniature chips in the electronics industry, nano-structured fillers are used as electrical insulators in high voltage lines, and in thermoelectricity using nano-structured layer systems. The applications of nanotechnology in the field of environment, by addressing issues such as water and soil treatment processes, energy storage; It includes sustainable products that do not harm the environment, remediation of materials contaminated with hazardous substances, and the development of sensors for the detection of environmental pollutants. Nanotechnological devices and tools such as nanocapsules, nanoparticles and viral capsids are used in water treatment processes, CNTs, iron oxide and titanium dioxide nanomaterials are used in the removal of many pollutants from water such as heavy metals, organic compounds, pharmaceuticals, personal care products due to their high surface areas. As adsorbent material, titanium dioxide nanoparticles are used as nano membranes to prevent air pollution. Noble metal nanoparticles, magnetic nanoparticles and CNTs are also used in the detection of pollutants, thanks to their wide absorption spectra (Baykal, 2022).

With the help of smart sensors developed with biotechnology, the productivity in this process can be increased by destroying viruses and pathogens that negatively affect the growth and development of plants in agricultural studies. Nanotechnology is used in many fields as well as in the field of food. Studies in this field provide benefits in many areas such as developing and producing food products, increasing nutritional values, detecting microorganisms, measuring food quality. As a field of application, when smart packaging is observed rather than traditional methods in the packaging of food products, it can provide convenience in many criteria such as food safety, shelf life, signs of deterioration. One of the other disciplines that nanotechnology is interested in is veterinary medicine. Making animal feed more efficient, increasing its positive effects on herd health and reproduction are among the studies carried out. While nanotechnology increases the performance of products that can be used in the military field, it reduces their size and enables the production of lighter, longer-lasting and high-strength materials. With its video camera options (unmanned aerial vehicles, etc.), it provides surveillance superiority and at the same time, it can provide superiority in the field of defense by facilitating the detection of harmful and radioactive gases by nano-detectors. Developed to protect from the harmful rays of the sun, sunscreens are an indispensable cosmetic product with their zinc oxide nanoparticles up to 20 nm in size, while preventing the damage of ultraviolet rays and reflecting all other colors. Nanocapsules, which can be produced due to their nano properties, are used in the production of anti-wrinkle creams, allowing them to reach the depths of the skin, and this feature can increase the preferability of zinc oxide nanoparticles. Nanomaterials, which have a wide use in textile products, serve the field of materials that provide longer- lasting use by adding or developing new features to the products (Gençay, 2022).

GREEN SYNTHESIS AND APPLICATIONS

Conventional methods for the production of nanoparticles are not expensive, toxic and environmentally friendly. To overcome these problems, researchers have found naturally occurring sources and their products that can be used for green synthesis, that is, the synthesis of NPs (Rafique et al., 2017). The presented biological method as an alternative to chemical and physical methods provides an environmentally friendly way to synthesize NPs. Moreover, this method does not require expensive, harmful and toxic chemicals. Thanks to green synthesis, which has been actively used in recent years, metallic nanoparticles with various shapes, sizes, contents and physicochemical properties can be synthesized. Green synthesis can be done in one step using biological organisms (Nadaroğlu et al., 2017). Green synthesis of NPs is carried out using different biomaterials such as bacteria, fungi, yeast, algae, plant and virus DNA (Rafique et al., 2017). Molecules such as proteins, enzymes, phenolic compounds, amines, alkaloids and pigments found in plants and microorganisms are reduced and synthesize nanoparticles (Nadaroğlu et al., 2017).

The three most important conditions for the synthesis of NPs are the choice of a green or environmentally friendly solvent, a good reducing agent, and a harmless material for stabilization (Jadoun et al., 2021). In traditional chemical and physical methods; Reducing agents involved in the reduction of metal ions and stabilizing agents used to prevent unwanted aggregation of the produced nanoparticles carry a risk of toxicity for the environment and the cell. In addition, the contents of the produced nanoparticles are thought to be toxic in terms of shape, size and surface chemistry. In the green synthesis method, where biocompatible nanoparticles are produced, these substances are naturally present in the biological organisms used (Nadaroğlu et al., 2017). Copper (Cu) and copper oxide (CuO), zinc oxide (ZnO), cerium oxide (CeO2), cadmium sulfide (CdS), silver (Ag) and gold (Au), iron (Fe) and their oxides synthesized by green synthesis, cadmium sulfide (CdS), palladium (Pd), lead sulfide (PbS), ruthenium (Ru), and titanium dioxide TiO_2 NPs have important roles in human well-being (Gour and Jain, 2019).

Green synthesis offers areas with effective applications from traditional chemical techniques to medical and environmental technologies (Ahmad et al., 2019). The use of metal NPs in fields such as biomedical, pharmaceutical, medicine, agriculture, environment and energy is increasing day by day (Çiftçi et al., 2021). Green synthesized NPs play important roles in drugs, clinical applications, and in vitro diagnostic applications. NPs synthesized by green methods show excellent antibacterial, antifungal and antiparasitic effects (Figure 3). NPs in the 1-100 nm size range readily bind with HIV-1 virus on gp120 glycoprotein knobs. This particular interaction of NPs prevents the virus from binding to host cells, thus helping to prevent and control HIV infection. NPs can cause cell wall damage, membrane damage, or generate free radicals, causing oxidative, DNA or electron transport chain damage, ultimately leading to bacterial death (Hussain et al., 2016).

Au-NPs have been applied for the specific release of drugs such as paclitaxel, methotrexate, and doxorubicin. Au-NPs have also been used in tumor detection, angiogenesis, genetic disease and genetic disorder diagnosis, photoimaging, and photothermal therapies. Iron oxide NPs are applied in cancer therapy, hyperthermia, drug delivery, tissue repair, cell labeling, targeting and immunological testing, detoxification of biological fluids, magnetic resonance imaging, and magnetically sensitive drug delivery.

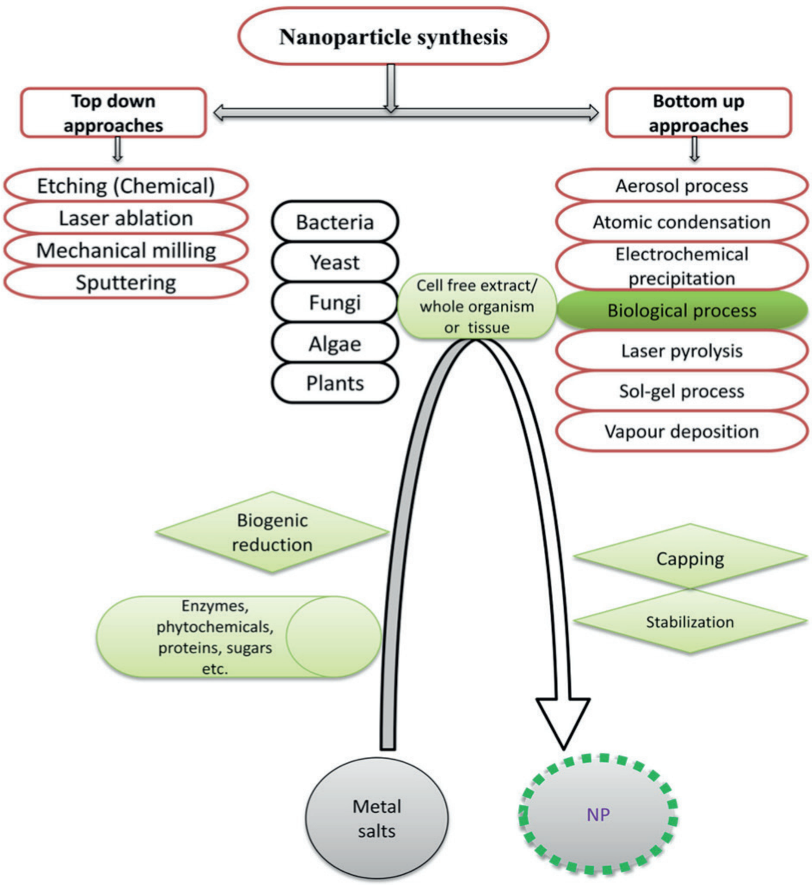

Figure 3. The flow chart of various physico– chemical approaches of nanoparticles synthesis with highlighting of biological synthesis (Hussain et al., 2016)

Ag-NPs are used for many antimicrobial purposes, as well as in anticancer, anti-inflammatory and wound treatment applications. In addition, Ag-NPs are among the most attractive nanomaterials. Ag-NPs, diagnosis, treatment, drug delivery, medical device coating, personal health care (Çiftçi et al., 2021) cardiovascular implants, wound dressings, catheters, orthopedic implants, dental composites, nano-bio-sensing and agricultural engineering (Rafique et al., 2017) have emerged with leading contributions in nanomedicine, chemical sensing, data storage, cell biology, textile, food industry. It has a great function as a disinfectant and antimicrobial agent (Ahmad et al., 2019).

Ag-NPs can increase the durability and service life of fabrics. Ag-NPs are used in self-cleaning fabrics, towels, furniture items, kitchen fabrics, bed linens or reusable surgical gloves, veils, patient gowns and antibacterial injury dressings, protective face covers, biohazard clothing, sportswear and water-repellent materials. There are potential application areas in production (Rafique et al., 2017). Thanks to nano textile applications, textile products with properties such as waterproof, dirt-proof, non-wrinkling of the fabric, antimicrobial effect, flammability or non-flammability, air permeability and holding the applied paint can be produced. While increasing the performance of products that can be used in the military field, it reduces the dimensions and enables the production of lighter, long-lasting and high-strength materials. With its video camera options (unmanned aerial vehicles, etc.), it provides surveillance superiority and at the same time, it can provide superiority in the field of defense by facilitating the detection of harmful and radioactive gases by nano-detectors (Güven, 2022).

Excellent delivery system for nanofertilizers, nanopesticides containing nanoherbicides, nanocoating and plant nutrients are widely used as part of agribusiness with numerous manufacturing industries containing 100–250 nm Ag-NPs that are more water soluble, thereby increasing their activity. Nanofertilizers have the capacity to synchronize nutrient release with the uptake of plants, avoiding nutrient losses and reducing the risks of groundwater contamination. Ag-NPs are also used in the field of expanded nanotechnology, in various consumer by-products such as water filters and sanitation system, deodorants, soaps, socks, food preservation and air fresheners, expanding the commercial sector of Ag-NPs and their composites have greater catalytic activities in dye reduction and removal (Rafique et al., 2017).

Nanoparticles can provide versatile benefits, especially in food packaging materials. They can create a gas barrier, suppress the growth of microorganisms, and improve the temperature and humidity resistance of the packaging. Thus, food safety and shelf life can be increased (Hatipoğlu, 2022). In addition, there are applications to ensure the creation of new functional products by adding nanoparticles with different colors, flavors and nutritional content (Güven, 2022).

Zinc and titanium NPs with biocompatible, non-toxic, self-cleaning, skin compatible, antimicrobial and dermatological properties are used in biomedical, cosmetic, ultraviolet blocking agents. Dose optimization is necessary for drugs to reach the level of bioavailability, and the drug taken must have a specific target. That is, theoretically high doses of the drug should be taken to achieve proper bioavailability, but this will cause more side effects. With NPs, it is possible to distribute drugs specific to the region. Thanks to this approach, appropriate drug dosage will be used and side effects will be significantly reduced. The use of small amounts of drugs for specific targets both reduces drug costs and increases patient comfort (Çiftçi et al., 2021).

In recent years, researchers have been working on the delivery of chemotherapy drugs with nanoparticles, especially in anticancer applications. Passive and active targeting methods can be done with dendrimer, liposomes, metal nanoparticles and polymer micelles. The drug delivery system has the best distribution of therapeutic agents for cancer treatment. Especially Au and Ag NPs have enabled important studies on this subject. Nanoparticle forms of metals such as copper, iron and zinc are also used as drug delivery systems in biomedical applications (Kütük and Çetinkaya, 2019).

NPs or their products are useful in environmental remediation. On these greener routes, organisms or their products, or NPs, clean up hazardous waste sites and treat pollutants. Green NPs have a wide scope in the treatment of surface water, groundwater and wastewater contaminated with toxic metal ions, organic and inorganic solutes and microorganisms. Self-cleaning nanoscale surface coatings can eliminate many cleaning chemicals used in regular maintenance routines. NPs are used in domestic water treatment systems to remove viruses from drinking water. Fe-NPs are of great interest due to their rapidly developing applications for disinfection of water and recovery of heavy metals from soil. The use of nanoparticles, as an alternative to expensive methods such as excavation, soil washing and thermal desorption for soil pollution removal, gives successful results in the treatment of contaminated soils, removal of heavy metals, polycyclic aromatic hydrocarbons and pesticides (Wang et al., 2019). NPs are an alternative to pesticides in the control and management of plant diseases and also act as effective fertilizers that are environmentally friendly and increase crop production. The use of green nanoparticles has increased in recent years in the removal of PAHs from air pollutants, gases such as carbon monoxide and sulfur dioxide, and in the detection of some gases (Ghandhi et al., 2014). Magnetite (Fe_3O_4)/gregite (Fe_3S_4) and siliceous materials produced using bacteria and diatoms are successfully used in optical coatings for solar energy applications and as ion placement materials for electric cell applications. Nanoscale catalysts perform chemical reactions more efficiently (Hussain et al., 2016).

NPs are popular due to their excellent catalysis and good sensor properties, large NPs surface area and high reactivity, and can be used as adsorbent. The densities of small and spherical NPs increase exponentially as their diameter gets smaller. In addition, the nanoparticle dexterity (agility) in the solution is greater and can scan the entire solution due to its small size and large surface area. NPs with these unique properties can be used to remove pollutants from water. Organic wastes are absorbed on the surface of the NPs and can then be removed by gravity or magnetic forces. For this reason, the size, shape and morphology of NPs are very important (Kütük and Çetinkaya, 2019).

CONCLUSION

Compared to traditional physical and chemical methods, green synthesis is a sustainable, safe, low-cost, easily available, environmentally friendly, easy-to-apply, low-energy biological method that does not require harsh or toxic chemicals in its synthesis. Moreover, NPs synthesized by green synthesis are more stable and effective compared to those produced by physical and chemical methods. In this method, NPs can be synthesized in one step. Waste products are non-toxic and easy to dispose of. NPs synthesized by green synthesis have applications in almost every field such as medicine, agriculture, biotechnology, imaging, optics, environment and energy. The many advantages of the green synthesis method will enable this method to be widely used in the future, and research on its potential applications will accelerate, and the field of sustainable, environmentally friendly applications will expand.

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