Chapter 4

Top-down and Bottom-up Approaches for Synthesis of Nanoparticles

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Abstract

There are numerous potential uses as nanoparticles produced from green methods in the medicinal and environmental sciences with a reduction of harmful chemicals and solvents. To synthesize nanoparticles use of safe organic resources like plants, and microorganisms producing nanoparticles for numerous applications such as catalysis, sensing, electronics, photonics and medicine. Aiming to minimize or prevent waste generated from reactions while maintaining efficacy. In this chapter, as well as the production of plant-mediated nanoparticles and some current uses of these materials, such as gold, silver, copper, palladium, platinum, zinc oxide, and titanium dioxide, the fundamentals of green chemistry have been discussed.

Keywords

Nanoparticles, Green Synthesis, Carbon-Based Nanomaterials, Metal-Based Nanomaterials

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1. Introduction

Nanotechnology is a branch of material science that deals with the synthesis and study of its physical and chemical properties with an average particle size of 1-100nm. These materials have wide applications and are used in various fields of science and technology due to their properties. The concern for the environment and the surrounding safety increased rapidly during the late 90s. As a result, certain environmentally conscious terms were introduced in the field of chemistry, such as clean, environmental, green, sustainable, and benign chemistry. These newly introduced terms became the topic of interest for the researchers and chemists to define the meaning and complete understanding of the concept involved. Considering the importance amongst all aspects, the present chapter deals with green chemistry, which covers the meaning of green chemistry, the twelve principles of green chemistry, green synthesis of nanomaterials, the application of green synthesis with challenges, and future perspectives [1].

Cathcart (1990) was probably the first chemist to use the term green chemistry, wherein he discussed the merits and demerits of the significant growth of the Irish chemical industry. The turning point came in 1996 when Anastas and Williamson (1996 a,b) published a matter entitled Green Chemistry: An overview in green chemistry: Designing Chemistry for the environment [2]. European Association for Chemical and Molecular Sciences members held a meeting on 28th February 2008 in Tundo about Green and Sustainable Chemistry where they commented: “no consensus in the scientific community,” which was further modified by Winterton in 2001 that “chemistry that calls itself green is necessarily going to lead to pollution prevention” [3]. Sustainable development aims to reduce the effect caused due to the substances used and produced. It also aims at judicial use of resources monitoring energy usage and production. As it takes years and years to form non-renewable resources like fossil fuels and petroleum products and due to excessive use of these, the rate of ozone depletion has increased and to avoid depletion rate, the transition or shift from non-renewable to renewable sources should be accelerated by considering the demand to fulfill the human requirements, limited access and rising cost [4]. Chemistry plays a vital role in ensuring the use of chemicals, materials, and energy used by future generations to be more sustainable than the current due to the increasing worldwide demand for environmentally friendly processes for developing novel and cost-effective approaches to prevent pollution. To achieve this sustainability, green chemistry was introduced, which involved utilizing principles to either reduce or eliminate the production or use of toxic materials by designing, manufacturing, or applying chemical products. Although certain principles are similar and seem to be common sense, it forms a designed framework to modify the process concerning the need. There is rapid growth in the field of green chemistry by focusing on methods to design environmentally friendly products and processes, which will be economical in the long term [4]. Sustainable development stresses providing goods and services for the growing population without sacrificing the needs of future generations and environmental quality. It is expected that by 2050, the world's population will reach 10.7 billion, which is nearly double, so the demand for goods will also be set double, thereby promoting the growth of chemical industries
coincident with the rising population. Due to population growth, there is an impact on the global environment tied to chemical processes or products, such as

- Loss of biological species from their habitat
- Water pollution
- Ozone layer depletion
- Climate change
- The rise in sea level
- Pollutants in ecosystem

Green chemistry promotes the elimination of hazardous organic solvents wherever possible or the replacement of hazardous solvents with the potential use of safer solvents (water, fluorous and ionic liquids, supercritical media). Catalysis also plays a vital role in green chemistry, which is energy efficient, selective, and economical by providing solutions to important problems, mainly in industries. The emerging area of green chemistry is not only demonstrates the growth in positive aspects of chemistry but also the success in terms of quantitative benefit to human health and the environment is paramount as well, merely a drop in the ocean as compared to the potential. To reach full potential, by creating awareness and by adapting to the methodologies and techniques, the development of green chemistry is necessary and is promoted. [5] Nanomaterials and their synthesis have great attention due to their tiny size, while the excellent ratio of surface to volume, which shows peculiar differences in their physical and chemical properties (catalytic activity, mechanical properties, biological properties, thermal properties, electrical conductivity, optical absorption, melting point) concerning bulk of same chemical composition.[6,7] Hence, the design and production of novel applications can be accomplished by monitoring the shape and size of the nanometer scale. A wide range of applications of nanomaterials concerning their size and shape-dependent nature ranges from bio-sensing and catalysts to optics, antimicrobial activity, computer transistors, chemical sensors, electrometers, and wireless electronic logic and memory schemes. These nanoparticles have applications in medical imaging, nanocomposites, filters, drug delivery, and hyperthermia of tumors [8–12]. For instance, geranium quantum dots of size less than 10nm can be produced in fixed proportion for a novel optoelectronic device for single electron transistors (SETs) and light emitters [13].

Metal-based nanoparticles also have wide applications in the field of medicine and pharmacy. For instance, gold and silver-based nanoparticles are commonly used in biomedical and nano-biotechnology (one of the most promising interdisciplinary fields[14]. Recent development in the formation of nanoparticles shows a peculiar role of microorganisms and biological systems in the production of metal-based nanomaterials due to their growing success, ease of formation, and environmentally friendly method (green chemistry) without involving harsh, toxic, and expensive chemicals [15–18].
The characteristics of production of highly stable and monodispersed nanoparticles are as follows

Selection of suitable organisms

To determine the potential of organisms before selecting their intrinsic properties like enzyme activities and biochemical pathways are studied. For instance, plants with heavy metal accumulation and detoxification serve as the best candidate for nanoparticle synthesis.

Requisite conditions for enzyme activity and cell growth

The growth is associated with factors like nutrients, light, temperature, pH, and buffer strength, which should be optimized to promote growth. The presence of these substrates in sub-toxic levels from the start of the development would eventually accelerate enzymatic activities.

Reaction conditions

For the industrial-scale synthesis of metal-based nanomaterials, the production rate and yield play a vital role in maintaining and monitoring the reaction conditions. Bio-reduction conditions like substrate concentration, the bio-catalyst concentration, electron donor and its concentration, pH, temperature, exposure time, buffer strength, mixing speed, and light is monitored and optimized [19]. However, some scientists have used complementary aspects like visible light, microwave irradiation, and boiling to affect the morphology, size, and rate of reaction.

2. Principles of sustainable and green chemistry

Green or sustainable chemistry deals with reducing or eliminating the production and use of toxic substances. The growth and development in science and technology have advanced and are rapidly increasing daily as per the living standard of humanity. Such accelerated progress leads to drastic changes like environmental degradation, depletion of the ozone layer, climate change, and global warming affecting life on earth. So to overcome such shortcomings, green chemistry came into the picture to balance the judicial use of natural resources considering economic growth and environmental conservation [20]. There is a slight difference between Green Chemistry and Environmental Chemistry as the latter deals with the identification of the source, elucidation of mechanism, and quantifying the problems associated with the environment. In contrast, green chemistry deals with designing an alternative pathway or technology safe enough to overcome the shortcomings of Environmental chemistry [21].
Figure 1. Green chemistry principles

Green chemistry aims to protect the environment using methods like catalysis, biocatalysis, alternative renewable raw materials, reaction media, and reaction conditions. The basis of the green chemistry framework stands on twelve principles used to create a safe passage to design molecules, materials, reactions, and processes.[22,23] Paul Anastas and John Warner, in their book named “Green Chemistry Theory and Practice book, 1998” explain every term related to the development of the green chemistry principle. The principle highlights the removal of dangerous and hazardous substances (Fig. 1) as follows

**Prevention:**

The first principle suggests that it is relatively more efficient and wise to prevent the generation of waste and toxins than to treat or clean afterward. The prevention process is more viable for humans and the environment as it is considered cheaper and less tedious than eliminating waste after generation. For instance, the over-exploitation of natural resources like coal and petroleum products and extensive usage results in the release of sulfur and nitrogen oxides to the atmosphere by contributing as a main source of acid rain [24].
Atom economy

The principle of Atom Economy is initially linked to waste management as it involves maximum utilization of raw materials and production of desired product, generating the least amount of byproducts. When we look for the proper meaning of atom economy, we say it is the ratio of the relative molecular masses of the product we desire to the relative molecular masses of all the reactants participating in the reaction expressed in percentages. This means we need to design the synthesis process so that the generation of waste material is reduced and the amount of product we desire is maximized; for instance, the ancient method (boots process) of synthesis of ibuprofen had low economic cost as the input of raw material was confined only up to 40% while in the newly developed method (Hoechst synthesis) involving three steps utilizes almost all (up to 99%) the raw materials used thereby eliminating the generation of waste material. This new method is cost-effective with a high atom economy, contributes to preventing pollution, and, subsequently, is environmentally friendly [25].

Less hazardous chemical synthesis

This principle involves the design of chemical processes and methods to be done so that the product we obtain has less toxicity or is dangerous to the environment and human health. Most of the synthesis we carry out, or design involves multiple steps wherein we use a lot of toxic chemicals and reagents. Despite the product being less toxic, the risk of contamination becomes high due to multiple-step synthesis. It is a task in green chemistry to redesign such environmentally friendly methods. Biological enzymes can replace toxic chemicals, making the processes cleaner and cheaper. For instance, Asahi Kasei’s polycarbonate synthesis is simpler when toxic carbonyl dichloride (COCl₂) is replaced with carbon dioxide (CO₂) resulting in the removal of dichloromethane (CH₂Cl₂) as solvent promoting green synthesis as it is more toxic compared to carbon dioxide (CO₂) [26].

Designing safer chemicals

Clearly to achieve this goal of maintaining the particular function and efficiency for designing safer products is a task that can be accomplished by having knowledge not only about chemistry but also the principles of toxicology and environment. As the name suggests, the principle deals with designing chemicals with high selective nature while carrying out the specific desired function, thereby minimizing the toxicity aim is to minimize the usage of chemicals which are carcinogenic, mutagenic, and neurotoxic, ensuring the risk and toxicity caused by such chemicals is reduced. The application of this principle in various fields is not hidden from all. It is widely used to develop insecticides and pesticides specific to certain organisms (target specific). Another example is the production of polymers of polyphenylene sulfone (PPSU), a new-age engineering plastic used in underground trains and indoor airplanes, as it provides environment safety without mechanical and flame-resistant properties [27].
Safer solvents and auxiliaries

Using auxiliaries, solvents, and separating agents should be avoided wherever possible. If it is supposed to be used, then the substances having nature as nontoxic, non-hazardous, non-carcinogenic, non-explosive materials should be used. For any given chemical reaction, the use of auxiliaries and solvents is predominant. So by reducing the number of such chemicals in use, we are generating less waste and keeping the environment clean and safe. The conventional solvents used are primarily toxic, corrosive, and flammable, and their recovery involves a large amount of energy loss; therefore, the development of environment-friendly solvents is necessary concerning current demand. The substitution of conventional solvents with environment-friendly solvents is done based on worker safety, environment safety, process safety, and sustainability. The most important characteristics these solvents should possess are that they must be easy to use and recycle, physically and chemically stable, and have low volatility. For instance, certain chemicals like pyridine, dichloromethane, chloroform, and dimethoxyethane are some of the chemicals that are harmful for both health and the environment. Instead of these solvents, green solvents like methyl ethyl ketone, propan-2-ol, butan-1-ol, and acetone can be used as they are less toxic [28].

Design for energy efficiency

Energy efficiency is one of a chemical reaction's basic or fundamental roots. As the name suggests, this principle deals with energy efficiency and the requirements of a chemical reaction. The energy efficiency and need for a chemical reaction should be designed so that by consuming less energy, the process can proceed to make it environment-friendly, efficient and viable. It is expected that these kinds of processes should be carried out at an ambient temperature and pressure as the major aim of this principle is to save energy or, in other words, to exploit every bit of power to the fullest supplied to complete the same chemical process minimizes the use by avoiding wastage, the chemical industries and institutions have adopted various methods. Also, catalysts can be used to carry out certain chemical reactions to lower the activation energy of the reaction and thereby minimize the energy requirement [29].

Use of renewable feedstock

Renewable resources came into the picture when the concept of sustainable development was enlightened due to rapid growth, worldwide demand, and development. With the increase in population, the requirement of growth and production increased to overcome that, and the principle of use of renewable feedstocks was promoted. We depended on non-renewable sources like coal, petroleum, and natural gases for ages. Still, due to their over-usage and exploitation, the levels of non-renewable resources are coming down day by day, and the formation of this coal and petroleum requires years and years. Instead of these non-renewable energy sources, we can use renewable resources as a predominately available alternative.[21]
Reduce derivatives

The central concept of green chemistry revolves around synthesizing the target molecule in an environment-friendly method. The term derivatization means modifying the chemical and physical state of chemical species through eiting a blocking group or through protection or deprotection. This principle of green chemistry highlights the concept of minimizing or avoiding the excessive formation of derivatives as the formation and removal of the exact needs extra reagents as the steps increases and can contribute to generating waste to avoid the formation of derivatives; the physical-chemical processes can be replaced by biological processes for synthesis as the waste produced in such cases can easily be degraded with the help of biological processes of waste management [30].

Catalysis

A catalyst is a chemical substance that enhances the reaction rate by lowering the activation energy of a reaction. It is used in small quantities and recovered by the reaction's end[31]. If you consider stoichiometric reagents, they are used in excess amounts and are difficult or not recovered at the end of the reaction [32]. The principle behind this is to use less energy, reduce the generation of waste, and minimize the use of water. All catalysts are enzymatic, homogeneous, or heterogeneous; the major role is to accelerate the reaction without affecting relative energy between the products, reactants, or the participating reaction. Catalyst has high chemical selectivity, specificity, and stereochemistry, but the only drawback is they lack heat sensitivity and poor stability.

Design for Degradation

This principle deals with designing the reaction so that the desired product and waste material obtained are not harmful in nature and must be easily degraded by natural means without accumulating in the environment. This principle's goal is to avoid forming harmful toxic substances and recycle the waste as much as possible to return to production [33].

Real-time analysis for pollution prevention

This principle focuses on analyzing the methods of chemical synthesis and their analysis to monitor the production of the desired product. It also aims to prevent the formation of toxic, dangerous substances for human health and the environment. This also includes the development of analytical methods considering the in-process monitoring and control before the formation of toxins at any stage. Previous methods used were tedious and used analysis of the sample in bulk quantity, along with the use of solvents and energy in large amounts. But with the advances in technology, the sample size to analyze has been reduced, and the amount of solvent employed is also minimized.

Inherently benign chemistry for accident prevention

The agenda behind this principle is that the substances used in the process and the ones produced should not be prone to cause any accidents. Selecting safe substances minimizes the potential for chemical accidents, explosions, and accidental fires. For instance, the widely used supercritical CO₂ replaced the organic solvent.
3. Synthesis of nanoparticles via green route

Nanoparticles can be synthesized in various ways, but their synthesis is categorized into two main types: namely traditional methods and green methods. The traditional methods have their own benefits such as extensive scalability [34], extensive control over morphology of nanoparticles [35–37], energy storage or conservation [38–40], and target specific disease therapy [41,42]. Despite having a lot of advantages, traditional methods also employ a lot of demerits like these methods involve organic solvents for the synthesis which not only contributes to neurobehavioral and reproductive health-related stress but also due to the use of drastic conditions (high pressure and heat) for the synthesis process also compromises the health and the working conditions [43–48]. While working with organic solvents, the concern for volatile vapors also arises due to their low boiling point along with the concern of excessive production of carbon dioxide which is responsible for environmental changes like global warming and greenhouse effect [49–51]. As a result of these irreversible risks involved in synthesis using traditional form for both the environment and the scientist, these methods have fallen out of favor irrespective of the benefits they provide. Due to these shortcomings, the concept of green synthesis came into picture considering the climatic condition, fast-growing and developing world (Fig. 2).

Moving towards green chemistry and green techniques for nanomaterial production have been recently brought into picture to avoid toxic, hazardous, and non-eco-friendly substances which promoted scientist and researchers to develop keen interest towards biological approaches to synthesize nanomaterials [52].

![Flow chart of synthesis of nanoparticles via green route](image-url)

*Figure 2. Flow chart of synthesis of nanoparticles via green route*
Green synthesis brings a clean, safe, cost effective, sustainable and environment friendly method to synthesize nanoparticles [53]. Green method of synthesis includes replacing hazardous toxic chemicals while developing new strategies to minimize or eradicate harmful chemicals and byproducts hazardous to health and environment [52]. Green methods include microorganisms like bacteria, algae, fungi, yeast species as well as plants. The final size and the morphology of the nanoparticles are determined by different active molecules and precursors like metal salts that are employed while synthesis. Green methods provide a lot of benefits from microbial action to natural reducing and stabilizing properties [54]. The synthesis of nanomaterials can be done using physical, chemical and biological approaches. Physical method includes cracking a superstructure and restricting their nanosize margin and chemical method includes reaction of chemical compounds. Physical methods are tedious compared to chemical methods whereas chemical methods use toxins and hazardous chemicals. Some of these methods are condensation, sol-gel method, chemical vapor deposition and other biochemical approaches [55]. Biological methods for synthesis includes synthesis of nanoparticles using plant extracts, microorganisms, (bacteria, fungi, yeast, algae) and bio-molecules (enzymes, sugar and proteins) and also whole cells [52].

The most widely used methods for synthesis are top down approach and bottom up approach. The top down approach to synthesize nanoparticles involves larger bulk materials (superstructure) broken into very small nano-sized particles (atomic or molecular level), while the bottom up approach involves individual atoms brought together to form larger nanomaterials [54]. Top down method includes few techniques like lithographic, etching, sputtering and grinding in a ball mill, while bottom up method includes growing of nanoparticles from simpler molecules. Size and shape of the nanoparticle can be monitored by using target precursors concentrations, reaction media or conditions (temperature, pH), and surface functionalization along with templates utilization, a bottom up approach. Surface functionalization has a crucial aspect when synthesizing nanomaterials with respect to certain applications like high chemical activity and large surface promotes aggregation. Hence, aggregation is avoided by functionalization of nanoparticles using certain chemicals to increase their stability during storage, transportation and application (Fig. 3) [56].
3.1 Top down approach

The top down method includes the breakdown of huge bulk matter into tiny nano sized particle. It is a subtractive method includes breaking of superstructure bulk matter and confining it to smaller structures by chemical or mechanical means. Some techniques that involves top down approaches are mechanical grinding, attrition, milling [52]. Top down approaches are simple yet they produced irregular shaped extremely small particles and since there is a difficulty face to maintain a proper size and shape of the particles is the major downfall of this approach [57]. The following are few methods, which are employed under top down approach.

3.1.1 Mechanical milling or ball milling process

Ball milling is a fundamental and effective top-down method that produces nanomaterials by transferring kinetic energy from the grinding media to the material that is being reduced. This method is useful to produce various nanoparticles and metal alloys using different materials. The interaction of balls, and between balls and vessel walls, produce drastic phase transformation at high temperature and pressure.
The ball milling process have repercussions on various factors such as crystal size, particle size and surface, mechanical dislocation and modification of meta-stable phases. Milling process can be used for growth and compression of the size of nanoparticles as well as change in structure, agglomeration of nanoparticle, mixing of two or more phases [58–63]. There are certain merits of these techniques which includes high capacity, safety, simplicity, reliability, long term maintenance and universality [64–66]. With merits come certain limitations like energy wastage, destructive/destroying/disordering crystal structure, noise and contamination while working, sturdy weight (Fig. 4).

3.1.2 Thermal evaporation

In this method chemical link in a molecule breaks down due to heat as the process is endothermic [67]. Thermal evaporation methods give rise to monodispersed suspensions promoting production of inorganic nanoparticles [68]. In the center of heating zone an alumina crucible having powder is placed where a resistive heating method is employed with a 20 cm consistent gap between source and substrate is maintained. Substrates are cleaned with acetone and ethanol before placing it in the evaporator. PID (proportional integral derivative) controller and a digital display used to measure and control the temperature at source and substrate respectively. Deposition time is controlled by a shutter fixed at the entrance of crucible while glass slides before being used for deposition is cleaned in soap solution followed by acetone and de-ionized water ultrasonically [69–72].
Thermal evaporation method has a lot of advantages for synthesizing and fabrication of nanomaterials, for instance, fabrication can be carried out in solvent free mode. Similar to advantages we also have certain shortcomings to thermal evaporation method like low quality source material, difficulty in depositing alloy compositions and combinations (Fig. 5) [73–75].

3.1.3 Laser ablation

A powerful electromagnetic beam that has been increased by encouraging radiation emission is referred as laser and the hypothesis was first introduced by Einstein [76]. Laser ablation technique for the synthesis of nanoparticles from diverse solvents is quite a simple process [67]. In 1960, Mainman was the first to build practical laser, now used in multiple fields like information transmission, industry, medical treatment, and military services [77]. Removal of molecules from surface of substrate to create micro/nano structure is done with the help of pulsed laser which indeed has wide applications in metals, ceramics, polymers and glasses. A substance is eliminated from substrate by focusing a laser beam, via which the energy is absorbed in order to melt or evaporate or vanish, ablation occurs. In the entire laser machining applications laser ablation is constant which basically means the process which deals with both vaporization as well as melts ejection [76]. Traditional micro-processing methods are replaced by laser due to processing speed which is widely used in various techniques by irradiating solid target dipped in liquid by laser beam to produce nanoparticles altering its particle size, morphology, composition by adjusting laser
settings and liquid medium [78–80]. This method has a lot of merits like it promotes the production of ligand-free noble particles and energy loss is low, with merits there comes short coming of the method which involves high energy requirement due to high efficiency in ablation, due to dispersion of laser source in industrial scale the capability to form nanoparticles reduces [81].

3.1.4 Lithographic methods

This method of synthesis of nanoparticle require expensive equipment and instrument, and are also dreadful with respect to energy requirement but are capable enough to make micron sized particles. Since ages lithographic techniques were used for producing computers and printed circuits but now a days we use nanoimprint lithography method which is different from the conventional lithographic, initial step involves formation of template material followed by stamping of soft polymeric method to form patterns. The formation of template matrix requires latex sphere through nanospheres lithography method. Various types of lithographic techniques are used now a day out of which some are photo-lithography (proximity printing and projection printing), electron beam lithography, soft lithography, nanoimprint lithography, focused ion lithography, and dip pin lithography [82].

3.2 Bottom up approach

The bottom up approach is an additive method where smaller units (atoms or molecules) serves as building blocks, combine to form nanostructures. Some techniques that involves bottom up approaches are sol-gel method, chemical vapor deposition, plasma spraying, micro-emulsion method and laser ablation. Chemical method involves bottom up approach to synthesize nanomaterials [52]. Bottom up approach is also described as constructive technique as it involves formation of an assembly using smaller units. Quite the opposite of top down approach, the output have well defined shape, size and chemical composition as, a self-assembly of atoms and molecules as building units are formed [57].

3.2.1 Chemical vapor deposition

Chemical vapor deposition is a successful and a distinct method for the synthesis of nanoparticles, in the era of microelectronics, chemical vapor deposition is still one of the most promising synthesis methods since decades overcoming all the limitations employed by modern technology. In this method simple materials are used, and in reaction chamber, a thin coating of gaseous reactant is placed on the surface of substrate, and when the gas comes in contact with the heated substrate surface, chemical reaction occurs. In order to increase the deposition process and to maintain the stability there are various parameters that need to be controlled for instance, gas phase reactants delivery, and enclosed reaction chamber to be employed, proper discharge of gases, monitoring reaction pressure, energy source employed for chemical reactions, cleaning of exhaust gases to accomplish safety and nontoxic goals and automation process [83–85]. The chemical vapor deposition method have various advantages for nanostructure growth and fabrications such as finest degree of control, dense and pure material production, repeatable synthesis process,
regulation in growth rate, production of hard, robust, homogeneous and pure nanoparticles, large scale fabrication with purity, fine crystal quality, and few substrate flaws, and parameter control can result in regulating crystal structure, morphology, and orientation. With advantages come disadvantages of using chemical vapor deposition method like poisonous, flammable or explosive precursors, expensive precursors, raise fabrication costs, poisonous gaseous byproducts, and limited substrate use due to high deposition temperature. [83,86,87]

3.2.2 Hydrothermal

A high-temperature, high-pressure reaction between a solid substance and an aqueous solution in a reaction vessel followed by deposition of small particles is termed as hydrothermal synthesis. This method employs solution reaction-based approach where water is used as a solvent; it is carried out in an autoclave (steel pressure vessel) by adjusting temperature and pressure. To attain vapor saturation the temperature of the vessel is increase beyond the boiling point of water. Hydrothermal process works as a great achievement in the field of science and technology as it employs homogeneous precipitation, cost effective, environment friendly, easy scale up and pure final product. The morphology of crystal produced under hydrothermal conditions depends on the growth conditions of the crystal. To monitor the morphology of crystal produced, the pressure of the system is controlled which indeed is dependent on the vapor pressure of the main reaction composition. By this hydrothermal process we can prepare solids such as luminescence phosphorus, super-ionic conductors, and microporous crystals as well as it can also help to synthesize distinct condensed material such as thin films, nm particles and gels [88–94]. High temperature and pressure, reaction time and solvent type plays a key role in hydrothermal process of synthesis [95]. Hydrothermal processes of synthesis also have certain merits for instance, the size of the nanoparticles can be controlled precisely,

**Figure 6. Schematics of hydrothermal technique**
and nanocrystals produced have high crystalline nature [88,96]. Hydrothermal method of synthesis also have limitations such as the instrument that is the autoclave used for this process is expensive, and while synthesizing the nanoparticles the growth of the crystal cannot be monitored directly (Fig. 6) [88,91,96].

3.2.3 Co-precipitation

![Figure 7. Schematics of co-precipitation technique](image)

One of the ancient wet chemical processes to synthesize nanomaterials is co-precipitation method which is simplest, basic and widely used method. The precipitate obtained at the end of synthesis consists of both product and impurities which are eventually separated using filtration and washing. This method is employed to obtain composition of two or more cations in a homogeneous solution having an advantage to form homogeneous nanomaterials with small sizes and size distribution. The method involves drop by drop addition of one solution into another solution (containing dissolved precipitating agents) directly. Widely used precipitants in this approach are hydroxides, chlorides, carbonates and oxalates. The advantages of this method include energy efficiency, easy and quick method, and homogeneity of particle is maintained throughout. Similarly the disadvantages includes difference in precipitation rates, impurities produced along with product numerous chemicals are employed which is neither environment friendly but is also hazardous to human health (Fig. 7) [89,97–102].
3.2.4 Sol-gel method

![Schematics of sol-gel technique](image)

The word sol-gel consists of two words one is sol and the other is gel. It is one of the easiest methods to synthesis nanoparticles as it is simple. A colloidal solution made with the help of solid particles suspended in it is sol while, a solid macromolecule dissolved in liquid is gel. This sol gel technique involves few steps namely hydrolysis followed by polycondensation followed by aging followed by drying and at the end calcination. In the first step the precursor (metal alkoxides) undergoes hydrolysis in presences of water or alcohol forming hydroxide solution. The reaction medium determines the approach for instance if the medium is water then the approach is called as aqueous sol-gel approach but if the medium is an organic solvent then the approach is called as non-aqueous sol-gel approach. The second step involves the removal of water and alcohol forming metal oxide bonds through condensation of neighboring molecules. Increased solvent viscosity caused by polycondensation creates porous structures that retain a gel-like liquid phase. In the third step the gel network re-precipitates due to continuous polycondensation within the localized solution resulting in reduction of porosity of colloidal particles and increasing thickness between them, hence it is called aging. The gel is then dried which is very difficult as the separation of water and organic components disrupts the structure and so drying is carried out. Final step involves calcination to get rid of water and residues from the sample. There are multiple advantages for this method like high product purity, cost effective, homogeneous character of the produced material, and simple technique to synthesize complicated nanostructures. Similarly disadvantages includes tedious process,
health hazardous due to use of organic chemicals and post treatment to purify sample is mandatory (Fig. 8). [67,89,97–99,103,104]

### 3.2.5 Pyrolysis

The most popular method for synthesis of nanoparticles in industries is pyrolysis where the precursor (liquid or solid state) used to synthesize nanomaterial is burned using flame. In order to recover the nanoparticles formed the precursor is transferred into furnace at high pressure. High temperature employed in this process of pyrolysis supports easy evaporation of the precursor and to achieve that we use laser or plasma sometimes. The advantages of pyrolysis includes that this process is simple, cost effective, continuous, efficient with high yield of the nanoparticles [105].

### 3.2.6 Sputtering

Sputtering is widely used method among bottom up approaches as it involves non-thermal vaporization method which can be achieved at <0.67 Pa, maintained by vacuum pump. The components of sputtering method involve (Fig. 9):

![Figure 9. Components of sputtering method](image)

The method involves deposition of nanomaterials on the surface of substrate by particle ejection using high energy ions. This method employs surface coating, thin layer deposition and surface etching applications [106–109]. The simplest source for sputtering is plasma ions produced by applying electric potential between the electrodes in gas phase, and when
the glow discharge sources [110]. The advantages of sputtering method is it works at low temperature by coating large surface area uniformly on elements, alloys, and compounds [111,112]. Just like the advantages there are certain shortcomings to this method for instance, low purity, energy conversion into heat which should be removed and sputtering rates are low with respect to thermal evaporation [112,113].

4. Role of plants in synthesis of green nanoparticles

Synthesis of green nanoparticles is the simplest, cost-effective, reliable, reproducible resulting in production of more stable products. Microorganisms can be employed for the synthesis of nanoparticles via green route but the process is quite slow and tedious with only limited number of size and shapes possible compared to the synthesis route based on plant based materials. Using green method for synthesis the fewer parameters like high pressure, energy, temperature and toxic chemicals can be avoided or completely eliminated making the process environment friendly. Now a days the researchers and scientists are hooked on to engaging them to avoid using synthetic method for synthesis as plant based materials not only produce highly stable nanoparticles but also involve in straight forward reaction to scale up along with low risk of contamination by impurities (Fig. 10).

![Figure 10. Synthesis and characterization of green nanoparticles](image)

Hence, plants and their parts are used to synthesize nanoparticles as an alternative route for synthesis of nanoparticles instead of synthetic route due to the tremendous advantages these methods bring, out of which the most important advantage or impact is nature friendly method they employ. These methods have a lot of merits and so are the new topic of interest for researchers and their extensive work using plants and their parts, some benefits are
larger production due to availability of the precursor in bulk quantity most of the time, scaling up can also be easily carried out, apart from that this method is budget friendly as the precursor or source material is available in nature, lastly it is an environment friendly method. Nanoparticles synthesized using extract of green tea leaves [114–116], Terminalia chebula fruit extract [117], extract of Oolong and black tea leaves [118,119], extract of banana peel and Colocasia esculenta leaves [120], extract of Sorghum bran [121], and extract of Eucalyptus leaves [122] have already been used (Fig. 11).

Figure 11. Plant and microorganisms for the source of nanoparticles

5. Role of microorganisms in green synthesis of nanoparticles

5.1. Microbes

Microbes have excellent defense mechanism as the bacterial cells have resistance for reactive ions in the surrounding which indeed is responsible for the synthesis of nanoparticles as high concentration of ions are toxic for bacterial cells in general. In order to prevent their death due to hostile condition, their cellular machinery promotes the conversion of highly reactive ion into stable atoms. This peculiar property exhibited by bacterial cell is exploited by researchers and scientist for bio-synthesis of nanoparticles. Cell destruction may occur if the nanoparticles are produced in high concentration. Microbes live in an ambient condition irrespective of variation in parameters like pH, temperature, and pressure but it has certain limitations which arise due to potential
contamination caused by the reaction period between metal nanoparticles and organisms, which could cause cell structure to be destroyed [123,124].

5.2 Algae

The synthesis of nanoparticles synthesized by algae based precursor is rapidly growing due to its variety of applications and its distinct characteristics. Synthesis of gold stable nanoparticles using Sargassum wightii was demonstrated [125]. The only limitation this process employs is limited size and number of nanoparticles will be cooperative to carry out the applications.

5.3 Fungi

Using fungi based precursor is one of the most prominent and also most popular means of synthesizing nanoparticles due to the ease to handling biomass, their economically affordability as well as an efficient source of extracellular enzymes leading to large scale production of enzymes. But due to contamination it sometimes invites the creation of genetic mutation or genetic manipulation of organisms [126]. The synthesis rate is slow to handle the entire biomass produced, research are going to overcome these short comings.

6. Types of green nanoparticles

Variety of nanomaterials are found in nature and for our convenience they have been categorized in various class such as metals, metal oxides, carbon based, polymers, nanocomposites, but majorly it is classified as zero dimensional which involves clusters, one dimensional which involves nanotubes, fibers, rods, similarly two dimensional which includes films and coats and lastly it is three dimensional which includes poly-crystals.

The framework or the backbone or the basic structure of these types of nanomaterials is carbon atoms and hence they are called as carbon based nanoparticles. These nanoparticles are special as they exhibit distinctive properties like different hybridization as well as allotrophic forms. These nanoparticles are very sensitive for commotion in synthesis parameters and factors allowing tailored manipulation on a large extent are unmatched till date by inorganic based nanostructures [127,128]. Most of the substances found on the earth surface consist of carbon and due to which the synthesis and applications of these distinct carbon based nanoparticles have numerous applications and stands as one of the most promising areas of science and technology drawing the attention of young scientist and researchers [129]. The synthesis of carbon based nanoparticles by synthetic route have been practiced since decades but the switch towards greener approach is seen as it supports eco-friendly nature and is also cost effective [130]. In order to synthesize these carbon based nanoparticles researchers and scientist are using either a green precursor or green condition for the synthesis [131]. The structural conformation and its hybridization determine the physicochemical and electronic properties of carbon based nanomaterials [127]. At high temperature and high pressure carbon thermodynamically favors tetrahedral sp³ conformation of a diamond but at lower heat of formation it favors planar sp²
conformation forming graphite sheets. Graphite sheets are more stable thermodynamically compared to two dimensional forms[127]. During the formation of nanoparticles through top-down approach, the planar graphite sheet curvature produces strain energy compensating the reduction of thermodynamically unfavorable dangling bonds of graphite layers [132]. Based on shape of nanoparticles it sub-categorized for instance, Carbon Nanotubes (CNT) are tube like shaped, nano-horns are horn shaped particles, fiber like shape give rise to nanofibers and ellipsoids or sphere like structure belongs to the group named as fullerenes [133].

6.1 Carbon nanotubes

Based on their structural characteristics, carbon nanotubes are divided into two groups: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). The diameter of these synthetic nanometers ranges from a few micrometres to millimetres, with lengths as long as 550 mm [134,135].

6.2 Fullerenes

The molecular form of carbon or the \(C_n\) clusters (\(n>20\)) of carbon arranged in spherical shape is popularly known as fullerene family. It consist of a cage like structure having 12 five membered rings and an unspecified number of six membered rings[136].

6.3 Graphenes

A two dimensional hexagonal crystal lattice having mono-layer framework of carbon atom consisting of sp\(^2\) hybridized atoms are known as graphenes [136].

6.4 Carbon nanofibers

Graphene nanofoils are used to create the thread-like nanostructures known as carbon nanofibers, which are twisted into a cup or cone shape as opposed to the more conventional cylindrical tube shape [136].

7. Nanoparticles applications

Nanotechnology is a rapidly developing field of study with multiple applications in areas like biomedicine, physical science, chemical science, and environmental research. The following consist of general discussion on wide range of applications of green nanoparticles (Fig. 12) [137]:

7.1 Antimicrobial agents

Numerous studies have been conducted and carried out to determine the antimicrobial activities of green nanoparticles. In recent studies, it was reported that the positively charged silver nanoparticles (AgNPs) have more affinity to negatively charged bacterial cells. The mechanism of this process can both be extra-cellular as well as intracellular. The extra-cellular mechanism by green nanoparticles includes aggregation of silver
nanoparticles on the surface of bacterial cell inhibiting cellular transport and cell signaling while the intracellular mechanism deals with altering the bacterial activity by entering the cell cytoplasm of bacteria through cell membrane releasing silver ions. Similar to bacterial cell synthesis the silver nanoparticles can be synthesized by *Melia azedarach* leaf extract showing antifungal activities against *Verticillium dahlia* in *Solamum melongena L* (728 eggplants) both *in vitro* and *in vivo* medium. The results of the action of silver nanoparticles on *Verticillium dahlia* in *in vitro* conditions with concentration 60 mg/L reduced the growth effectively while *in vivo* condition only 20 mg/L showed growth reduction by 87% causing vascular discoloration by 97% compared to control. In another study of antibacterial activity of biogenic iron oxide nanoparticles synthesized by the extract of *Skimmia laureola* on pathogen *Ralstonia solanacearum* was carried out it was found that the growth is inhibited by cell degradation at nanoparticle concentration 6mg/L [137–139].

![Figure 12. Applications of green nanoparticles](image)

### 7.2 Cellular imaging

In vivo self-bio-imaging of cancer cells using fluorescent gold nanocluster synthesized intracellularly by reducing chloroauric acid inside the cytoplasm of cancerous cell into gold nanoparticle (AuNP) which helps in diagnosing cancerous cells. Similarly carbon nanoparticles synthesized using advance green method yields blue coloured photoluminescence nanoparticles having low cytotoxicity, bio-compatible, high water
solubility and quantum yield serving as a good candidate for cellular imaging showing cellular uptake by Human HeLa cells [137].

### 7.3 Catalyst

Gold nanoparticles produced from the egg shell extract of *Anas platyrhynchos* was used as a catalyst to remove toxic dye (*Eosin Y*) based on photodegradation method resulted removal of 96.1% of dye. Spherical shaped gold nanoparticles was synthesized with the help of *Eucommia ulmoides* bark extract used for decolorization of two model compounds (reactive yellow 179 and Congo red) in NaBH₄ presence acts as an efficient catalyst by reducing both the model compounds within 20 minutes [137].

### 7.4 Remediation of environmental pollutants

Green nanoparticles have shown a promising potential to adsorb/co-precipitate/reduce/oxidize the contamination arises from soil and water because of their high surface area to mass ratio. Various iron precipitates like magnetite (Fe₃O₄), siderite (FeCO₃) and vivianite (Fe₃(PO₄)·8H₂O) are extracted from microbial consortium serve as a useful tool to act as an adsorbent for As, Cr, Cu, and Zn generated from, waste water. Swine water remediation with high concentration of N and P, is removed in presence of iron nanoparticles produced using extract of *Eucalyptus* leaves and to prevent eutrophication of water. Removal of halogenated herbicide (quinclorac), by synthesizing green gold particles using yeast (*Saccharomyces cerevisiae*) is employed, which basically converts quinclorac to 8-quinoline-carboxylic acid hence confirms dechlorination [137].

### 7.5 Sensor

The field of nanoscience have tremendous popularity as this field is not only associated with other subjects but also have wide applications on large scale such as high sensitive sensor used for the determination of various environmental parameters. *Murraya koenigi* extract helped to synthesize silver nanoparticles are highly sensitive towards calorimetric detection of mercury (II). The detection of mercury (II) is based on a linear relation between intensity of band of surface plasmon resonance and it various concentration (50 nM-500μM) of mercury (II). Additionally mercury (II) in silver nanoparticle solution, disappearing the colour and SPR band reduction shifting towards blue region [137].

### 7.6 Oily sewage re-mediating agent

Oil sewage in marine ecosystem makes the life of aquatic organisms hostile which in directly affects human life and mother nature, in this process Melamine sponge came into picture with the qualities such as it is highly stable, low costing, highly porous, with low surface energy and strong adhesion. The merits of using Melamine sponge is that it helps in complete removal of oily sewage associated with selective absorption of layered oil/water mixture having really high separation efficiency (99.9%) and fair permeation flux (1300 Lm⁻²h⁻¹). The determination and removal of total petroleum hydrocarbons (TPHs) from water can be achieved by the iron nanoparticles formed from *Vaccinium floribundum*,
as the iron nanoparticles provide the condition to reduce or to remove total petroleum hydrocarbons by 88.34% [137].

7.7 Antimicro fouling agent

In recent times studies shows the use of biogenic nanomaterials as anti-fouling agents in health care facilities, food production and processing industries, shipping industries and for membrane based separation techniques to forbid the formation of bio-film. The antimicro fouling capacity of gold and silver nanoparticles derived from Turbinaria conoides was compared and the results shows that silver nanoparticles are more skilled in controlling biofilm formed by E. coli, Salmonella sp., Serratia liquefaciens and Aeromonas hydrophilia. The silver nanoparticles derived from Turbinaria ornate exhibited maximum inhibition for E. coli (71.9%) out of 15 bio-film under study. Synthesis of silver nanoparticles produced by Bacillus vallis mortis and its action against micro-algal strains and marine bio-film forming bacteria was studied which indicated reduction in the formation of bio-film at 0.5-1 nM concentration [137].

8. Challenges and future perspectives

Nanomaterials and nanoscience is the topic of interest amongst the researchers and scientist, due to growing demand worldwide, due to this the synthesis of nanoparticles and advance applications in various field of science have drawn the attention of the researchers. As per the survey literature surveys various bio-molecules plays key role as a capping agent for the synthesis of nanomaterials, which includes several aspects to look into which includes temperature, particle size, concentration of extract, pH and the effect of synthesis. Size variation of nanoparticles may arise due to various factors like the concentration of capping agent, pH alternations, the size and shape of nanoparticles can be monitored controlled through investigating various aspects and parameters via experimental methods. For instance, pH of the reaction mixture can be measured at the initial phase of the reaction as well as throughout the reaction process followed by end. When the pH of the mixture is acidic (low pH) the agglomeration by nucleation of nanoparticles occurs, while at high pH (alkaline) the nanoparticles produced are stable. Hence, acidic medium leads to formation of nanoparticles with poor stability and will form clusters that agglomerate, while alkaline medium leads to formation of pearl like stable nanoparticles consisting large diameter and the process is a fast process [118,140,141]. At high temperature the growth dynamics would be fast in the same span of time but the major drawback here would be the formation of defects thereby affecting the quality of crystal. Nucleation process controls the size of the nanoparticles, the smaller the time for nucleation the better size controlled nanoparticles will be formed. Optimization of pH, temperature, time of reaction, ratio of solvent is necessary for production of nanoparticles. Surface charge is also an important aspect to study and characterize nanoparticles as the nature and intensity of surface charge determines the interaction of nanoparticles with its environment. Due to the growing applications of nanoparticles in various field have also increased their demand and production and with repeated production of nanoparticles there comes the risk of
contamination of environment. In order to protect the environment the greener methods of synthesis is practiced and promoted by the scientist and the researchers which is a simple process, being cost effective and environment friendly minimizing the harmful toxins production which in a way required less efforts and is less tedious as it doesn’t involve elimination of toxins. The principle of green chemistry covers all aspects related to environment and safe practices but the swing towards green chemistry also required the recycling and reusing of energy sources and chemicals so as to make it cost effective improving the quality of life, human health and environment. Recent studies focus on the synthesis, characterization and behavior of nanomaterials along with their wide applications in various fields of science and technology including pharmacology and medicinal sciences, agriculture, water treatment, air treatment, electronics and telecommunication. The technique used to synthesize these materials is now considered to be available in the local vicinity and must be techno-economically feasible. Also the biochemical modification in the synthesis process has now begun a sustainable evolution of green methods for synthesis. It is expected that the shortcomings or the challenges faced by this generation will be soon endured in near future due to advancement of instruments, methods and techniques along with modernization, deep understanding and fast development.

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