SYNTHESIS OF NANOPARTICLES

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Introduction

Understanding various techniques for synthesizing nanoparticles is crucial for achieving desired particles with specific sizes and shapes. Nanotechnology encompasses two main synthetic methodologies: the Top-down approach and the Bottom-up approach. Further categorization of synthesis reveals three distinct methods: the physical method, the chemical method, and the biological method.

Before going into the detailed study of the synthetic methods of nanoparticles, there are various factors, which must be taken into consideration while synthesizing and characterizing nanoparticles. They are,

1. **Temperature:** It is an important parameter, which affects the synthesis of nanoparticles by physical, chemical, and biological methods. For physical approaches, high temperatures above 350°C are necessary. Chemical methods work at temperatures below 350°C, while biological methods rely on ambient or under 100°C temperatures. The temperature of the reaction medium dictates the characteristics of the resulting nanoparticles.

2. **Pressure:** Pressure serves as a crucial parameter in nanoparticle synthesis. The pressure applied to the reaction medium directly influences the resulting nanoparticles in size and shape.

3. **Time:** The quality and type of synthesized nanoparticles are determined by the duration of incubation of the reaction medium.

4. **Particle size and shape:** Particle size significantly influences nanoparticle properties. For instance, when the particle size get decreased the melting point of the nanoparticles also decreases, and the colour of the emitted light alters with changes in size. The shape of the synthesized nanoparticles plays a crucial role in their chemical characteristics.

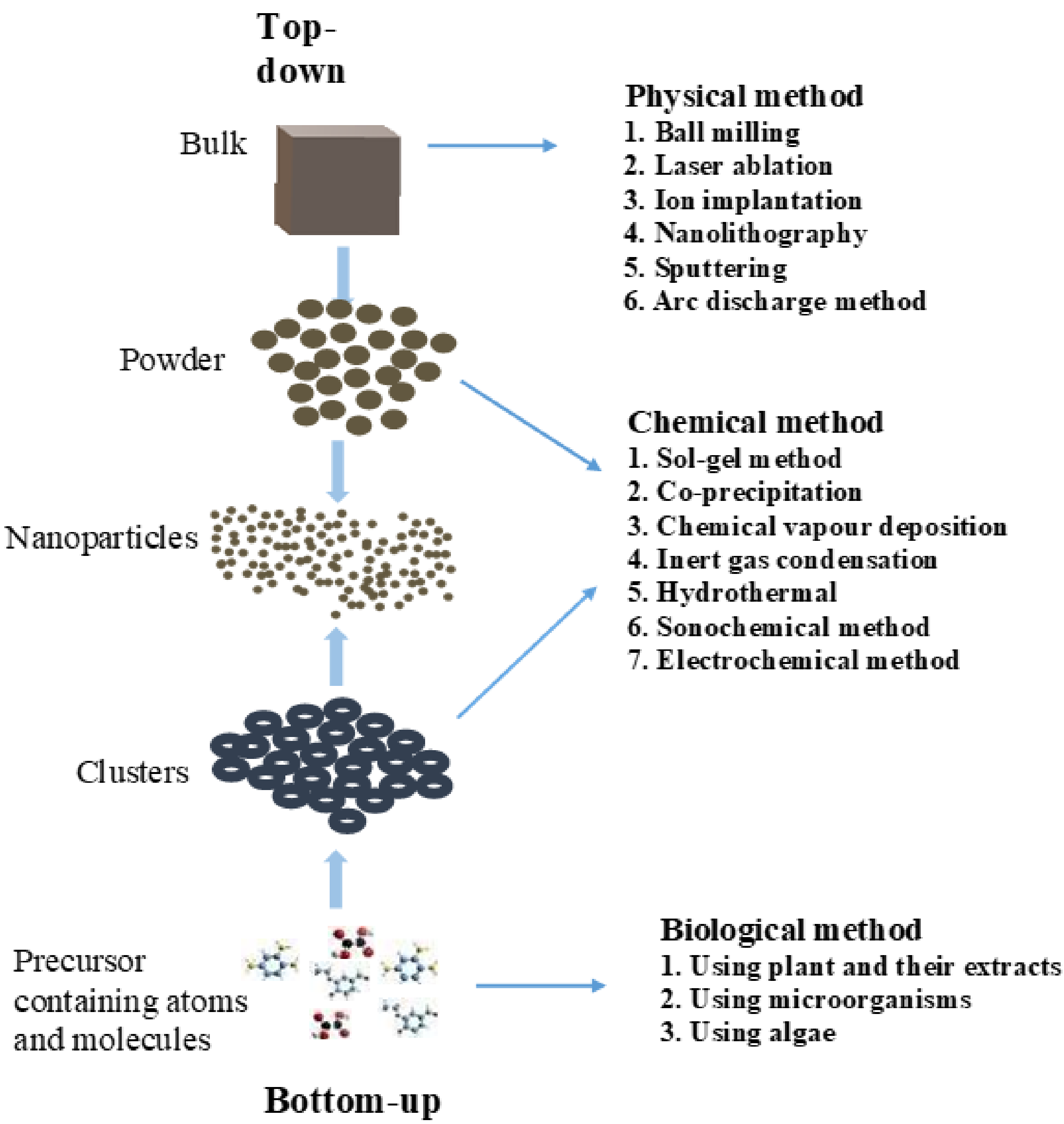
5. **Cost of preparation:** The cost of producing nanomaterials significantly impacts their potential applications. Regulating and controlling synthesis costs is essential to enable mass production and practical use. Chemical methods offer high yields but are not cost-effective, while physical methods are expensive. In contrast, biological synthesis is cost-effective, makingit suitable for large-scale nanoparticle production.

6. **Pore size:** Nanoparticle quality and applications are significantly impacted by their porosity, especially in applications like drug delivery, such as in cancer treatment.

7. **p^H Value:** p^H plays a significant role in nanoparticle synthesis by chemical and biological methods. It has been noted that the p^H of the solution medium impacts nanoparticle size and texture. This allows for size control by adjusting the solution's pH, particularly in the biological method.

8. **Environment:** The surrounding environment greatly affects the nature of the nanoparticles synthesized. Environmental factors like absorption and reactions impact nanoparticle formation. For instance, in biological synthesis, nanoparticles develop a coating that results in increased thickness and larger size.

Synthetic Methodologies



A. Top- Down Approaches

The top-down approach involves starting with larger structures and reducing them to nanoparticles through a sequence of controlled operations. However, these methods have notabledrawbacks, primarily due to their need for extensive installations and significant capital investment for setup. They have proved to be expensive and unsuitable for large-scale production, making them better suited for laboratory experimentation. This approach relies on a grinding process, making it less suitable for soft samples. Moreover, this method can cause imperfections in surface structure, and substantially impact the physical and other properties of nanoparticles. The common methods involved in the top-down approach are as follows, , Chemical vapour deposition, Physical vapour deposition , , Electron beam lithography, and X-Ray lithography Ion implantation

B. Bottom-Up Approaches

The bottom-up approach involves constructing nanomaterials by assembling molecules by molecules, atoms by atoms, and clusters by clusters. Physical forces drive particles to combine, resulting in larger structures. This technique is favored for creating complex nanostructures due to its precise control over particle size, leading to enhanced optical, electronic, and other properties. This method, also known as the constructive approach, entails building material from atoms to clusters to nanoparticles.

Bottom-up approach relies on a concept called molecular recognition (self-assembly, self-assembly is when things of the same kind come together naturally). Starting materials for this method can be either liquids or gases. Compared to the top-down method, bottom-up approaches can create devices at once and are more affordable, but they become challenging when thedesired structure gets larger and more complex. The common methods involved in the bottom-upapproach are as follows, Colloidal precipitation, Sol-gel synthesis, Hydrothermal synthesis, Electrodeposition, and Organometallic chemical route.

Method Of Synthesis

1. **Physical methods**: There are number of physical methods for the synthesis of nanoparticles. These techniques operate at elevated temperatures, usually greater than 350°C.

2. **Chemical methods**: These are simple and affordable methods for producing nanoparticles. They typically involve working at temperatures below 350°C. The production of large amounts of materials is possible featuring a variety of particle sizes and shapes.

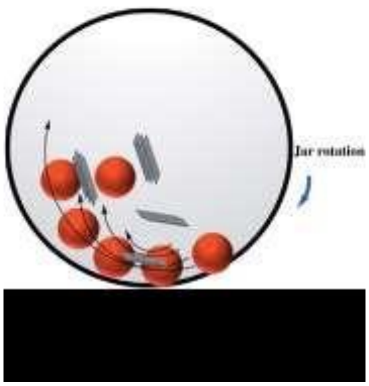
3. **Biological methods**: Biological methods involve utilizing microorganisms such as fungi,bacteria, yeast, etc., plant extracts (or enzymes), or templates such as DNA, viruses, and membranes. This approach is also called "green synthesis" because of its minimal toxicity and eco-friendly nature.

The choice of nanoparticle synthesis methods depends on specific requirements. Each method has its own advantages as well as disadvantages, and the selection depends on available resources. Physical methods are good for small-scale production, while chemical methods are chosen for cost-effective production. Biological methods have their own unique significance.

1. **Physical Method**

Mechanical Method

Ball Milling



The ball milling method presents a straightforward and cost-effective approach for synthesizing nanoparticles. In this method, a mill chamber, typically constructed from stainless steel, contains numerous small balls made of materials such as iron, hardened steel, tungsten carbide or silicon carbide. These balls rotate inside the mill, facilitating the synthesis process. The chamber is filled with either inert gas or air and rotated rapidly around its central axis. Material is converted into nano-size by compressing it between the container walls and balls. The ball-to-material mass ratio is normally maintained at a 2:1 ratio. The process is not so sophisticated, therefore the shape of the nanomaterial is irregular and produces crystal defects.

Laser Ablation (LA)

Laser ablation is a complex top-down approach where laser light penetrates a sample's surface, causing the removal of electrons from the material. The interaction between generated free electrons and bulk sample atoms transfers energy, leading to surface heating and vaporization. With high laser flux, the material transforms into a plasma state containing atoms, molecules, ions, and clusters. The pressure contrast between seed plasma and atmosphere drives rapid plasma expansion and cooling. LA takes place in a vacuum or gaseous environment and can be improved using a tube furnace to control growth conditions better.

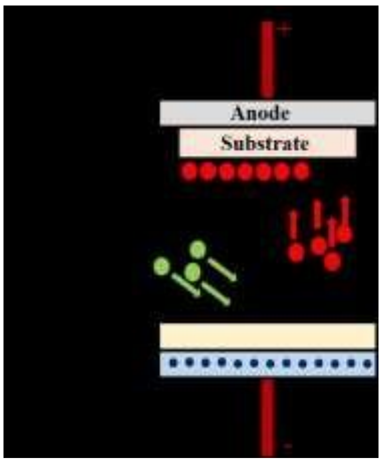
Ion Implantation

Ion implantation is employed to alter the existing surfaces of materials. This technique involves directing high-energy ions with electrostatic charges (ranging from 10 to 100 Kev) toward the surface. These ions carry kinetic energies much greater than the binding energy of the host material, allowing them to be implanted in a surface layer, often several nanometers in thickness.

Nanolithography

Lithography is a top-down approach, which involves patterning a sample by removing certain parts or arranging materials on a suitable substrate. Often combined with deposition and etching, it achieves high-resolution topography. Lithography can be categorized as masked or maskless. In the realm of masked lithography, patterns are generated through the utilization of masks or molds, encompassing techniques like photolithography, soft lithography, and nanoimprint lithography. Conversely, mask less lithography methods, such as electron beam lithography, scanning probe lithography and focused ion beam lithography produce arbitrary patterns directly without the need for masks or molds. Nanolithography's key advantage is producing desired shapes and sizes, from single nanoparticles to clusters. However, complex equipment and costs are drawbacks.

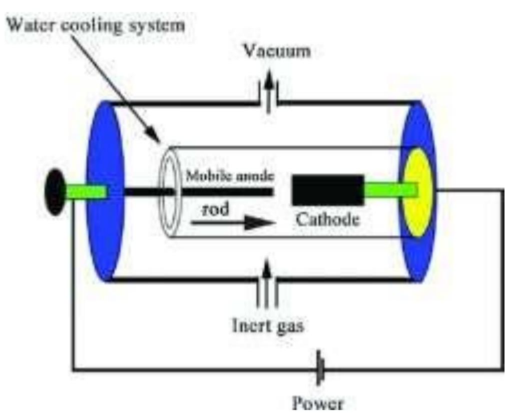
Sputtering



Sputtering

Sputtering involves depositing nanoparticles onto a surface through the collision of particles with ions, ejecting them from thesurface. This often leads to the deposition of a thin nanoparticle layer followed by annealing. Typically, argon plasma is used for this process. Factors like layer thickness, annealing conditions, substrate type, etc., determine the nanoparticle's size and shape.

Arc Discharge Method



Arc Discharge method

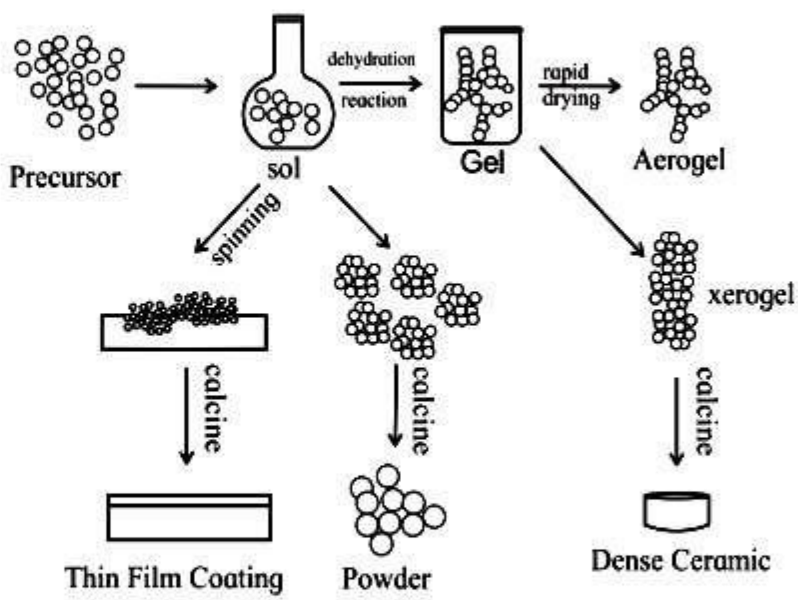
Arc discharge method is a popular technique for synthesizing nanoparticles. It involves creating a high-energy electrical discharge between two electrode materials in an inert gas environment. The intense heat generated by the arc vaporizes the electrode materials, producing a plasma plume rich in vaporized atoms and ions. As the plasma cools down rapidly, these species condense and nucleate, forming nanoparticles. The method is widely used for producing carbon-based nanoparticles like carbon nanotubes and fullerenes. It offers control over nanoparticle size, structure, and composition by adjusting experimental parameters such as electrode materials, discharge conditions, and gas environment.

2. Chemical Method

Sol-Gel Method

The sol is a liquid-phase mixture with suspended solid particles, while the gel is a solid structure immersed in a solvent. Sol-gel is a favored bottom-up approach due to its simplicity and wide applicability for nanoparticle synthesis. It falls under the liquid phase synthesis category and is particularly suitable for creating oxide nanoparticles and composite nano powders. The sol-gel technique involves various steps:

- Formulating a consistent solution involves decomposing metal-organic precursors within an organic solvent or organic salt solution.
- Transforming precursor oxide into a robustly interconnected solid structure.
- Hydrolysis yields a sol, wherein colloidal particles disperse in a liquid medium through the introduction of suitable reagents, commonly water.
- Sequential condensation processes lead to the formation of a gel, which evolves into a sturdy interconnected organic network.



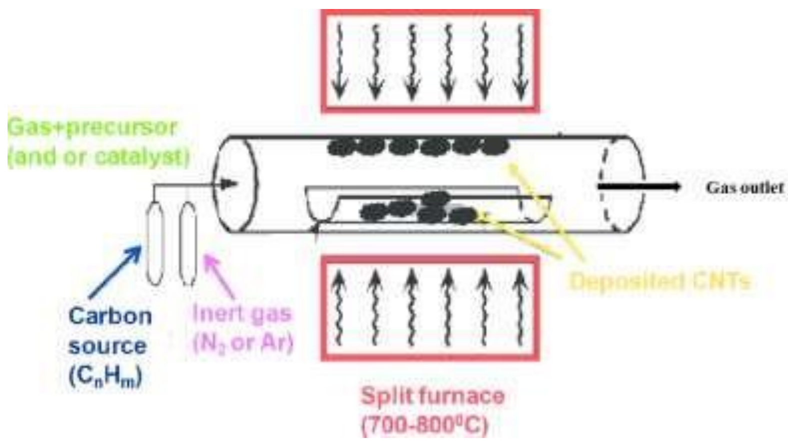
Sol-Gel

Co-precipitation

Co-precipitation is a frequently employed wet chemical method widely used for its simplicity, cost- efficiency, and reproducibility. It is also referred to as the solvent displacement method. For preparing nanoparticles, key components include a polymer phase, synthetic or natural, and a solvent like ethanol, acetone, and hexane, alongside a nonsolvent polymer. Nanoparticles are created by swiftly diffusing the polymer solvent into a nonsolvent polymer phase while mixing the polymer solution. The interfacial tension between these phases maximizes the surface area, leading to the spontaneous precipitation of nanoparticles.

Chemical Vapour Deposition (CVD)

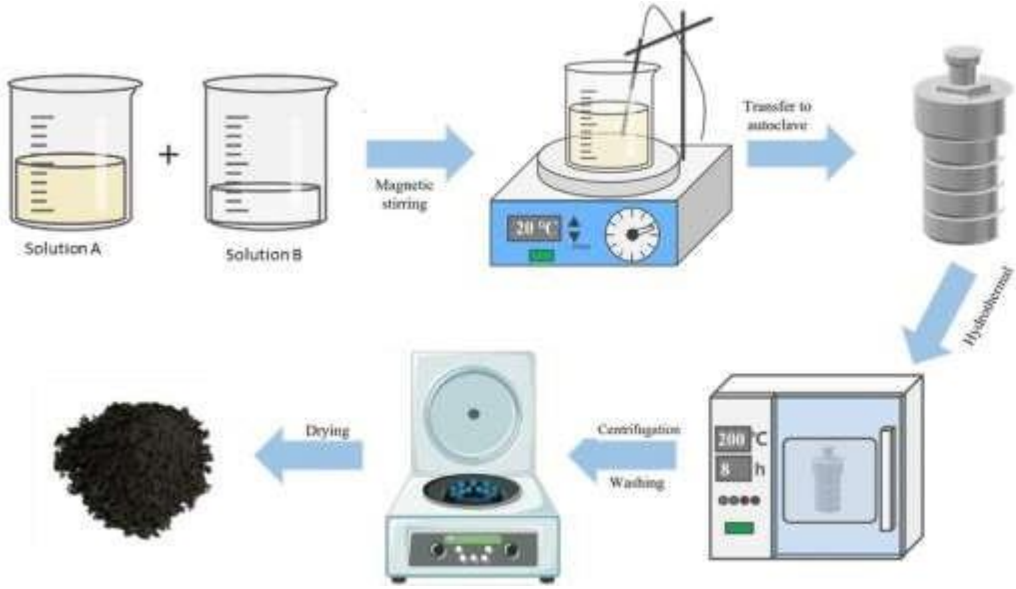
CVD is a top-down method employed to create nanostructures. It involves a chemical reaction between a heated substrate and a combining gas in a reaction chamber at room temperature, resulting in a thin film forming on the substrate's surface. The temperature of the substrate affects the process. CVD offers benefits like highly pure, uniform, durable, and robust nanoparticles. However, drawbacks include the need for specialized equipment and the production of highly toxic gaseous by-products.



Chemical Vapour Deposition

Inert Gas Condensation

This method is widely used for creating metal nanoparticles, where metallic sources evaporate in the presence of inert gas to produce fine nanoparticles at reasonable rates and attainable temperatures. This process is suitable for creating copper metal nanoparticles where, metal is vaporised inside a chamber filled with inert gases like argon, helium, or neon, causing the vaporized atoms to lose energy upon collision with the inert gas. The vapor undergoes cooling by liquid nitrogen, yielding nanoparticles with a size range of 2 to 100 nm.



Hydrothermal Synthesis

Hydrothermal Synthesis

Hydrothermal synthesis is a widely employed method to create nanomaterials and relies on a solution reaction approach. This process involves crystal nucleation and growth, resembling crystallization. Hydrothermal synthesis involves a broad temperature from room temperature to very high levels. Morphology control is achieved through low-pressure or high-pressure conditions based on the main composition's vapor pressure in the reaction. Temperature, pH, and reactant concentrations can be adjusted to influence particle morphology.

Sonochemical Synthesis

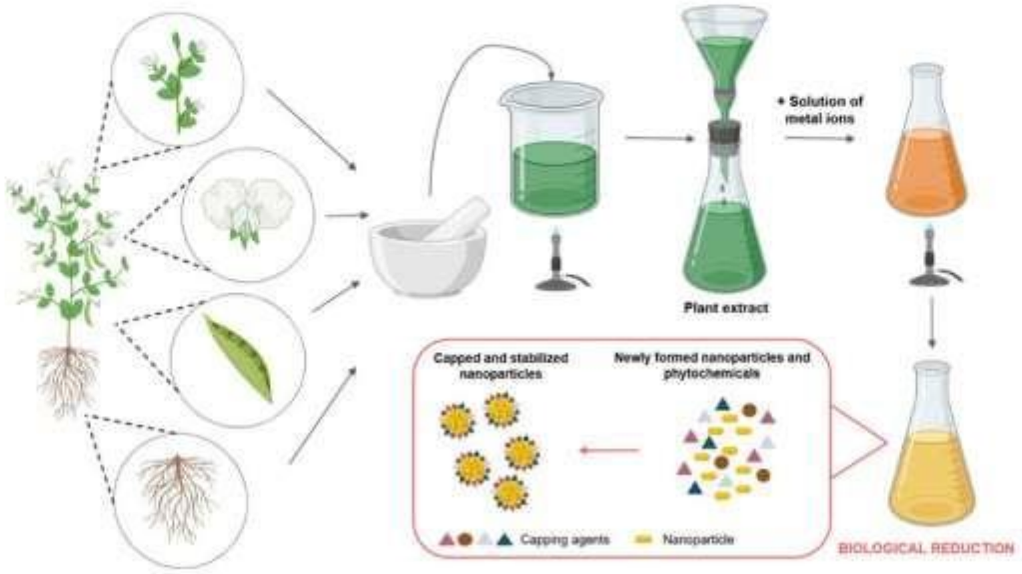
Sonochemistry, among the initial methods employed, entails chemical reactions prompted by intense ultrasound radiation ranging from 20 kHz to 10 MHz. This technique relies on acoustic cavitation to drive the process. Ultrasound proves to be a convenient means for synthesizing nanomaterials, offering distinct advantages in various nanomaterial-related domains: (1) generating amorphous products; (2) integrating nanomaterials into mesoporous materials; (3) applying nanoparticles onto ceramic and polymeric surfaces; and (4) managing the morphology of nanomaterials

Electrochemical Method

The electrochemical method for synthesizing nanomaterials involves the application of voltage to initiate chemical reactions within an electrolyte solution. This technique is adaptable to various materials and is employed in the production of metallic nanoparticles, whether with or without nanoporous hard templates. These templates, such as track-etched polymers or anodized aluminum oxides, are coated with a metal film that serves as a cathode for the electroplating process. The reduction and deposition of metal ions occur within the template pores, providing control over nanoparticle size and morphology through the adjustment of electrodeposition parameters. Electrochemical synthesis is particularly advantageous for crafting multicomponent nanowires. Additionally, electrospinning and electrodeposition serve as versatile methods for creating nanofibers from polymers, composites, and ceramics. This includes subsequent processes like calcination or carbonation.

3. Biological Method Synthesis using plant extracts

Plant extracts play a significant role in the biosynthesis of nanoparticles, a process known as green synthesis. Extracts from different plant parts like leaves, flowers, seeds, barks, fruits, and roots are used for creating nanoparticles, including silver nanoparticles. These plant extracts can also act as stabilizing and reducing agents during the synthesis process.



Nanoparticles synthesis from plant extracts

Synthesis Using Microorganisms

In recent times, the synthesis of nanoparticles using microorganisms has gained significant attention because of its economical nature and environmentally sustainable characteristics. Two methods for synthesizing nanoparticles from microorganisms are extracellular biosynthesis and intracellular biosynthesis. Some microorganisms have the ability to sequester metal ions, and various reductase enzymes present in these microorganisms can store and neutralize heavy metals. The process of nanoparticle formation by microorganisms includes capturing metal ions, enzymatic reduction, and capping. Initially, the metal ions are captured on the surface or inside the microbial cells, and subsequently, enzymes are employed to reduce them into nanoparticles.

Synthesis Using Algae

Algae-based nanoparticle synthesis is environmentally friendly, cost-effective, and has applications in various fields. This method involves preparing algae to extract in either aqueous or organic solvent through heat or boiling. A molar solution of an ionic metallic complex is then prepared. The algae solution and the metallic complex solution are incubated with or without stirring under controlled conditions. The synthesis of nanoparticles depends on the type of algae and is influenced by various factors, including biomolecules like peptides, pigments, and polysaccharides that contribute to metal reduction. Silver and gold nanoparticles are commonly synthesized using this approach.

Conclusion

The top-down approach is costly and unsuitable for soft samples. While it's not practical for large-scale production, it's well-suited for lab experiments. On the other hand, the bottom-up method depends on molecular recognition and involves building nanostructures atom by atom, molecule by molecule, or cluster by cluster. Various nanoparticle synthesis methods were explored.

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