CHAPTER: 12

OVERVIEW OF SYNTHETIC PROCESSES OF METAL NANOSTRUCTURES FROM VARIOUS METHOD

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ABSTRACT

Nano science is the branch of science that deals with matter on the nano meter scale. By the application of nano science we can manipulate and engineer matter at the nano level. Nano science is an emerging branch of science and engineering that deals with the design, synthesis, and characterization of materials and devices at the atomic level. Any substance behaves differently at the nano scale due to its small size and wide surface area. Any metallic nanostructure has different properties compared to that heavier material structure. There are many methods for synthesis of metallic nanostructures, among which microwave assisted synthesis method has emerged as a new, straightforward and environment friendly method. In this method we have to use a reaction precursor (reagent or salt solution), reducing reagent, stabilizing or capping reagent and a solution in and more voluminous products. With this method we can obtain nanostructures in the range of 1.5 to 550nm, which have wide applications in various fields.

Keywords: *Synthetic Processes, Metal Nanostructures, Method, Nano Science*

1. INTRODUCTION

Metallic nanostructures have garnered significant attention in various fields due to their unique physical, chemical, and optical properties, which differ from their bulk counterparts. These properties make them promising candidates for applications in catalysis, electronics, sensing, and biomedical fields. A plethora of synthetic methods have been developed to fabricate metal nanostructures with precise control over size, shape, composition, and surface properties. In this introduction, we provide an overview of several synthetic processes used for the fabrication of metal nanostructures.[1-2]

1. **Physical Vapor Deposition (PVD):** Physical vapor deposition techniques, such as evaporation and sputtering, involve the deposition of metal atoms onto a substrate under vacuum conditions. In evaporation, metal sources are heated to vaporize and condense onto the substrate, whereas sputtering utilizes ion bombardment to eject metal atoms from a target material. These methods offer excellent control over film thickness and composition, making them suitable for producing thin films and nanostructured coatings.
2. **Chemical Vapor Deposition (CVD):** Chemical vapor deposition methods enable the growth of metal nanostructures by introducing gaseous precursors onto a substrate, where they undergo chemical reactions to form thin films or nanostructures. Techniques such as atomic layer deposition (ALD) and chemical vapor condensation (CVC) allow precise control over film thickness and uniformity, facilitating the fabrication of nanostructured materials with tailored properties.
3. **Chemical Reduction Methods:** Chemical reduction methods involve the reduction of metal ions in solution to form metal nanoparticles. Commonly used reducing agents include sodium borohydride, hydrazine, and various organic compounds. These methods offer versatility and scalability, allowing the synthesis of metal nanoparticles with controlled size, shape, and surface chemistry. Additionally, stabilizing agents such as surfactants or polymers can be employed to prevent nanoparticle aggregation and control their dispersibility
4. **Microwave assisted method :** In the microwave-assisted synthesis of metallic nanostructures, we have used dipolar solvents, because they have electric field potential. In microwave heating electric dipolestructures/solvents are being contact with dielectric heating. These molecules havea partial positive charge at one end and a partial Negative charge atanother end. Microwave ovens work on the Principle of conversion of electromagnetic energy into thermal energy. When a polar molecule falls in the path of electromagnetic radiation. It oscillates to align with them. This causes the energy to be cost from the dipole by molecular friction and collision, resulting in heating.
5. **Biological Synthesis:** Biological methods harness the unique properties of biological molecules, such as proteins, enzymes, and DNA, for the synthesis of metal nanostructures. Biomineralization processes, microbial synthesis, plant-mediated synthesis, enzymatic reduction, and DNA-based nanotechnology offer sustainable and eco-friendly routes for producing metal nanostructures with controlled morphology and composition.

There are three processes which can form metal nanostructures with various mechanism . they are discussed below,

- **Physical processes :** Metallic nanostructures can be formed through various physical processes, each tailored to achieve specific structures and properties. Here are some common methods:[3-4]
- **Physical Vapor Deposition (PVD):** Evaporation: In this process, a metallic material is heated until it evaporates, and the vapor is then condensed onto a substrate, where it forms nanostructures.Sputtering: In sputtering, ions are accelerated onto a target material, causing atoms to be ejected from the target and deposited onto a substrate, forming nanostructures.

Chemical Vapor Deposition (CVD)

- **Atomic Layer Deposition (ALD):** ALD is a cyclic process where gaseous precursors are alternately introduced onto a substrate, allowing for precise control over the deposition of atomic layers, enabling the formation of nanostructures.
- **Chemical Vapor Condensation (CVC):** In this method, vaporized precursors react to form nanostructures on a substrate. Chemical Vapor Condensation offers several advantages such as precise control over nanoparticle size and morphology, scalability, and the ability to synthesize a wide range of materials including metals, metal oxides, and semiconductors. However, it also requires careful control of process parameters and may involve complex equipment setup.

- **Physical Methods:** Ball Milling: In ball milling, mechanical energy is used to break down bulk materials into nano-sized particles. Ball milling is a mechanical process used to produce fine powders and even nanoparticles from relatively coarse materials. It involves the use of a ball mill, a rotating cylindrical chamber or container, filled with spherical or cylindrical grinding media. The material to be milled is placed into the chamber along with the grinding media, and the whole system is rotated at a certain speed
- **Laser Ablation:** A laser is used to vaporize a target material, and the resulting vapor condenses to form nanostructures. Laser ablation offers several advantages for nanomaterials synthesis, including precise control over composition, size, and morphology, as well as the ability to synthesize a wide range of materials without the need for additional chemical precursors. However, careful control of laser parameters such as pulse energy, pulse duration, and repetition rate is essential to achieve desired outcomes, and the process may also generate heat, requiring cooling measures to prevent undesirable effects such as thermal damage to the target material.

Gas Phase Synthesis

- **Flame Synthesis**: Nanostructures are formed through chemical reactions in a flame, where precursors react and form particles that subsequently aggregate into nanostructures. Flame synthesis offers several advantages for nanomaterials production, including scalability, relatively low cost, and the ability to produce a wide range of materials with controlled properties. However, careful control of flame parameters such as temperature, residence time, and precursor concentration is essential to achieve desired outcomes and ensure reproducibility. Additionally, safety considerations must be taken into account when working with flammable gases and high temperatures
- **Plasma Synthesis:** A plasma is used to generate reactive species, which then react to form nanostructures in the gas phase. Plasma synthesis offers several advantages for nanomaterials production, including precise control over composition, morphology, and properties, as well as the ability to deposit materials onto a variety of substrates. Additionally, plasma processes can be conducted at relatively low temperatures, allowing for the synthesis of materials that are sensitive to high temperatures. However, careful control of plasma parameters and precursor chemistry is essential to achieve desired outcomes and ensure reproducibility.

Chemical processes [5-7]

Chemical processes offer versatile routes for synthesizing nanostructures with precise control over size, shape, composition, and surface properties. Here are several common chemical methods for synthesizing nanostructures:

- **Sol-Gel Process**:Sol-gel chemistry involves the conversion of a precursor solution (sol) into a solid network (gel). By controlling parameters such as precursor concentration, pH, and temperature, various nanostructured materials like metal oxides, silica, and hybrid organic-inorganic materials can be synthesized. in the synthesis of silica-coated silver nanoparticles, a sol-gel process might involve mixing silver nitrate and tetraethyl orthosilicate (TEOS) in a solvent such as ethanol, followed by hydrolysis and condensation. By controlling the ratio of reactants and reaction conditions, nanoparticles with specific sizes and shapes can be obtained.
- **Hydrothermal/Solvothermal Synthesis**:In hydrothermal/solvothermal synthesis, nanomaterials are formed by chemical reactions in high-temperature and high-pressure aqueous or organic solvents. This method is widely used for synthesizing metal oxides, sulfides, and other inorganic nanostructures with controlled morphology and crystallinity.In this method, zinc precursor salts such as zinc nitrate or zinc acetate are dissolved in a solvent along with a base (such as sodium hydroxide or ammonia) and sometimes a surfactant. The solution is then sealed in a high-pressure vessel and heated under autogenous pressure to temperatures typically ranging from 80°C to 200°C for a certain duration of time, ranging from several hours to several days. This process leads to the formation of ZnO nanoparticles through the hydrothermal reaction.

a typical synthesis procedure might involve dissolving 0.1 mol of zinc acetate dihydrate ($Zn(CH3COO)2 \cdot 2H2O$) in 100 mL of ethanol or water, followed by the addition of 0.2 mol of sodium hydroxide (NaOH). The resulting solution is then transferred to a Teflon-lined stainless-steel autoclave and heated at 150°C for 12 hours. This could result in the formation of ZnO nanoparticles with an average size of around 20-50 nm, depending on the reaction conditions.

- **Emulsion-Based Methods:**Emulsion-based methods, such as microemulsion and emulsion polymerization, involve the dispersion of immiscible phases (e.g., oil and water) stabilized by surfactants or polymers. These methods enable the synthesis of nanoparticles with controlled size, shape, and surface properties, including metal nanoparticles and polymer nanoparticles.
- **Chemical Reduction**:Chemical reduction involves the reduction of metal ions in solution to form metallic nanoparticles. Common reducing agents include sodium borohydride, hydrazine, and various organic compounds. This method is widely used for synthesizing metal nanoparticles such as gold, silver, and platinum. In this method, metal ions are reduced to form metal nanoparticles using a reducing agent such as sodium borohydride (NaBH4) or hydrazine. In the synthesis of gold nanoparticles, a typical procedure might involve mixing 1 mL of a 0.01 M gold precursor solution with 10 mL of water and then adding 0.5 mL of a 0.1 M NaBH4 solution. This could result in the formation of gold nanoparticles with an average size of around 10 nm, depending on factors such as the concentration of reactants and reaction time.
- **Precipitation Methods**:Precipitation methods involve the controlled mixing of two or more precursor solutions to induce the formation of insoluble compounds, which precipitate as nanostructures. Examples include co-precipitation, reverse micelle precipitation, and homogeneous precipitation. This approach is used for synthesizing metal oxides, sulfides, and hybrid materials.
- **Template-Directed Synthesis:**Template-directed synthesis involves using templates or scaffolds to control the size and shape of nanostructures. Templates can be organic molecules, polymers, or inorganic materials. By depositing or growing materials within the template structure, nanostructures with defined dimensions and architectures can be obtained. Examples include mesoporous materials, nanoporous membranes, and DNA scaffolds. in the synthesis of gold nanorods using a template-assisted method, gold ions might be reduced within the channels of a porous alumina membrane. By controlling the pore size and deposition conditions, gold nanorods with aspect ratios (length-to-width ratios) ranging from 2 to 10 or higher can be obtained.

Biological processes[8-9]

Biological processes offer unique and sustainable routes for synthesizing nanostructures, often leveraging the inherent self-assembly capabilities of biological molecules. Here are several biological methods for nanostructure synthesis:

- **Biomineralization:**Biomineralization is a biological process where organisms control the nucleation and growth of inorganic minerals within biological matrices. This process is observed in organisms such as mollusks, diatoms, and corals. By manipulating the environmental conditions and biological templates, researchers can engineer nanostructured materials with controlled composition, morphology, and organization.
- **Biosynthesis by Microorganisms:**Certain microorganisms, including bacteria, fungi, and algae, have the ability to reduce metal ions to form metallic nanoparticles. This process typically involves the secretion of biomolecules such as enzymes, proteins, and polysaccharides, which act as reducing agents and stabilizing agents. Microbial synthesis is a sustainable and eco-friendly method for producing metal nanoparticles with controlled size and shape.
- **Plant-Mediated Synthesis:**Plants possess a variety of biomolecules, such as phytochemicals, polyphenols, and enzymes, which can facilitate the reduction and stabilization of metal ions. Plant extracts are often used as reducing agents in solution-phase syntheses of metal nanoparticles. By optimizing reaction conditions and plant species, researchers can

control the size, shape, and surface properties of the synthesized nanoparticles. in the green synthesis of silver nanoparticles using plant extracts, fresh leaves of a plant such as neem or Aloe vera might be boiled in water to obtain an extract, which is then mixed with a silver nitrate solution. The reduction of silver ions by phytochemicals in the extract results in the formation of silver nanoparticles. The size and morphology of the nanoparticles can vary depending on factors such as the type of plant extract used and reaction conditions

- **Enzymatic Synthesis**:Enzymes exhibit remarkable specificity and catalytic activity, making them valuable tools for nanostructure synthesis. Enzymatic reactions can be used to produce nanoparticles through the reduction of metal ions or the polymerization of monomers. Examples include the use of enzymes such as horseradish peroxidase, glucose oxidase, and lipases for the synthesis of metal nanoparticles, quantum dots, and polymeric nanoparticles.
- **Protein-Based Synthesis:**Proteins exhibit a wide range of structural and functional diversity, making them attractive candidates for nanostructure synthesis. Protein-based approaches involve engineering or modifying proteins to control their interactions with inorganic materials or to serve as templates for nanoparticle assembly. Examples include the use of ferritin as a template for synthesizing magnetic nanoparticles and the incorporation of peptide sequences for directing mineralization processes.

Biological methods for nanostructure synthesis offer several advantages, including biocompatibility, sustainability, and scalability. These approaches hold great promise for the development of advanced materials for applications in biomedicine, catalysis, sensing, and environmental remediation.

Applications of metal nanometarails [10-13]

Metal nanoparticles and nanostructures having applications across various fields due to their unique properties. Here are some common applications:

1. **Catalysis**:Metal nanoparticles serve as highly efficient catalysts due to their high surface area-to-volume ratio and unique electronic properties. They are used in catalytic converters, fuel cells, and various organic transformations in the chemical industry.
2. **Biomedical Applications**:Metal nanoparticles, such as gold and silver nanoparticles, are used in biomedical imaging, drug delivery, and therapy. They offer tunable optical properties for imaging and photothermal therapy and can be functionalized for targeted drug delivery.
3. **Electronics and Optoelectronics:**Metal nanoparticles are incorporated into electronic devices, such as conductive inks, transparent conductive films, and sensors. They are also utilized in plasmonics for enhancing light-matter interactions, leading to applications in sensors, photodetectors, and solar cells.
4. **Environmental Remediation:**Metal nanoparticles are employed in environmental applications for pollutant detection, monitoring, and remediation. They can catalyze the degradation of organic pollutants, remove heavy metals from wastewater, and detect environmental toxins with high sensitivity.
5. **Energy Storage and Conversion**:Metal nanoparticles are utilized in energy storage devices, such as batteries and supercapacitors, to enhance their performance by improving conductivity and charge transfer kinetics. They are also used in catalytic processes for hydrogen generation and fuel cells.
6. **Surface-Enhanced Raman Spectroscopy (SERS):**Metal nanoparticles exhibit strong localized surface plasmon resonance, making them ideal substrates for enhancing Raman scattering signals. SERS is used for sensitive detection and identification of molecules in various fields, including biomedical diagnostics, environmental monitoring, and food safety.

7. **Textiles and Coatings:** Metal nanoparticles are incorporated into textiles and coatings to impart antimicrobial properties, UV protection, and stain resistance. They are also used for coloration and printing applications due to their tunable optical properties.

8. **Nanocomposites:** Metal nanoparticles are embedded in polymer matrices to produce nanocomposites with enhanced mechanical, electrical, and thermal properties. These nanocomposites find applications in aerospace, automotive, packaging, and construction industries.

Characterization of metal nanomaterials [14-16]

Techniques name	Description	Application
1. Scanning Electron Microscopy **(SEM)**	SEM provides high-resolution images of the surface morphology of nanomaterials by scanning a focused electron beam across the sample surface. It can provide information about particle size, shape, and distribution	Morphological analysis, size determination, surface roughness measurement.
2. Transmission Electron Microscopy **(TEM)**	TEM uses a focused electron beam transmitted through the sample to provide detailed images of internal structures and ultrafine details of nanomaterials. It offers high resolution, allowing visualization of individual nanoparticles	Nanoparticle size, shape, crystal structure, lattice imaging
3. X-ray Diffraction **(XRD)**	XRD measures the diffraction pattern produced when X-rays interact with the crystal lattice of nanomaterials. It provides information about crystal structure, phase purity, and crystallite size.	Phase identification, crystal structure determination, grain size analysis
4. Fourier Transform Infrared Spectroscopy **(FTIR)**	FTIR measures the absorption of infrared radiation by functional groups in nanomaterials. It can provide information about chemical composition, bonding, and molecular structure	Chemical composition analysis, identification of functional groups, detection of surface modifications
5. UV-Visible Spectroscopy **(UV-Vis)**	UV-Vis spectroscopy measures the absorption of ultraviolet and visible light by nanomaterials. It is used to analyze electronic transitions and optical properties	Bandgap determination, quantification of nanoparticle concentration, assessment of optical properties
6. Dynamic Light Scattering **(DLS)**	DLS measures the Brownian motion of nanoparticles in suspension to determine their size distribution. It provides information about hydrodynamic diameter and polydispersity.	Particle size distribution analysis, determination of zeta potential, stability assessment.
7. Atomic Force Microscopy **(AFM)**	AFM uses a sharp tip to scan the surface of nanomaterials with high spatial resolution. It provides information about surface topography, roughness, and mechanical properties	Surface morphology analysis, measurement of surface roughness, mechanical property characterization.

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2. CONCLUSION

In conclusion, the synthetic processes for fabricating metal nanostructures are diverse and offer tailored approaches for controlling their size, shape, composition, and properties. Biological methods for nanostructure synthesis offer several advantages, including biocompatibility, sustainability, and scalability. These approaches hold great promise for the development of advanced materials for applications in biomedicine, catalysis, sensing, and environmental remediation. By selecting appropriate synthesis methods, researchers can design and engineer metal nanostructures with desired functionalities for a wide range of applications, including catalysis, electronics, photonics, and biomedicine. Continued research in this field promises to unlock new opportunities and advance the development of next-generation nanomaterials

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