ISBN: 978-93-94570-00-9

9. Nanomaterials - Synthesis, Classification and Properties: Strategies Towards Sustainable Development

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9.1 Introduction:

Nanomaterials (NMs) are particles with a size of nanometers in at least one dimension. Many researchers are interested in nanomaterials because they offer unique qualities such as high physical and chemical stability, flexible chemistry for functionalization, and a large surface area. Nanomaterials on the scale of 1 to 100 nm have radically different chemical properties than materials on the micro- and macroscale. The surface area of a material grows as its size decreases. For the binding procedures, this characteristic is critical. On the nanomaterial surface, there are more binding sites. NMs are employed in a variety of fields, including biological sciences, aircraft, electronics, chemical production, and agriculture, due to their small size. Many inorganic nanoparticles are used as NMs, including carbon nanotubes, which are commonly used as carriers; iron nanoparticles, which are widely used due to their magnetism; and silica nanoparticles, which have attracted research attention due to their abundant pore structure and large specific surface area. Other research has focused on nanoparticles made of copper, gold, or silver [1]. Polymers and liposomes are organic carriers for insecticides that are renewable, biodegradable, and environmentally beneficial [2, 3]. The majority of applications for these materials are focused on increasing efficiency and productivity. They are also known as nanostructured materials (NSMs) or engineered nanomaterials (ENMs).

Nanomaterials are divided into 0D, 1D, 2D, and 3D nanomaterials based on numerous characteristics such as shape, homogeneity, dimensionality, and aggregation. These nanoparticles are used in a variety of nanotechnology applications, including the diagnosis of various diseases and the manufacturing of different processors with integrated circuits in small sizes and higher efficiency, due to their various features. As a result of this reduction, laptops are becoming lighter, cell phones are becoming smaller, and an aspect of optical fiber has replaced bundles of heavy copper wire, resulting in a technological improvement.

Because nanomaterials give increased sensitivity toward the target molecule in environmental samples and lower detection and quantification limits, they have been successfully used in a variety of environmental applications. However, significant challenges must be overcome before these nanomaterials can be commercially available in the near future. The preparation of robust, repeatable, nontoxic, biocompatible, environmentally friendly, and low-cost nanomaterials are the key challenges. Other difficulties include large-scale manufacturing and commercialization of nanomaterial-based products. We show the latest developments, problems, and industrialisation trend of NMs in many domains in this chapter.

9.2 Dimensional Structures of Nanomaterials:

A nanomaterial is a broad term that refers to all forms of nanoscale materials with unit sizes ranging from 1 to 100 nanometers. They can be found naturally or manufactured chemically, mechanically, physically, or physiologically with a variety of structures. The following is a simplified taxonomy of nanomaterials based on their structures:

9.2.1 Zero-Dimensional Nanomaterials:

All three dimensions of the materials in this category are negligibly small. Artificial atoms, often known as quantum dots, have separate energy states. Silver and gold nanoparticles are metallic nanoparticles; nevertheless, quantum dots of Cadmium selenide (CdSe) and cadmium sulphide (CdS) are included in semiconductor nanoparticles. Nanoparticles in the 150 nm range can have a variety of forms, including cubic, polygonal, and spherical.

Fullerene is one of the most well-known examples, as it is the smallest and most stable structure due to its symmetric structure. The fullerene molecule has a shape similar to that of a soccer ball. The particles are free to rotate due to weak intermolecular connections. Fullerene has the lowest surface energy due to its 0D structure [4].

9.2.2 One-Dimensional Nanomaterials:

The materials in this study have two nanometer scale dimensions, one of which is greater than the other two, implying that they have micrometer scale lengths and nanometer range diameters. Nanotubes, nanofibers, and metal or oxide whiskers, for example, are examples. They have bigger surface areas and higher aspect ratios, making them ideal for nanocomposites.

9.2.3 Two-Dimensional Nanomaterials:

These include materials having one dimension on the nanoscale scale and the other two on the micrometer scale being substantially larger than the first. 2D nanomaterials include graphene, Nano films, Nano sheets, Nano platelets, and Nano clays. Different deposition procedures are used to create thin films, which are used in a variety of fields including electronics, sensor devices, and magneto-optical devices [5]. The created Nano films have a covering or area of several square centimeters, with a thickness in the 1100 nm range.

9.2.4 Three-Dimensional Nanomaterials:

The materials in this class have three dimensions that are all outside the nanometer range. Nanocrystals or equiaxed nanoparticles are other names for these particles. All of their dimensions are greater than 100 nanometers.

Nanostructured bulk materials, also known as bulk nanomaterials, have no dimensions on the nanometer scale but are divided into equal portions on the nanometer size or contain diverse configurations of crystals on the nanoscale.

9.3 Classification of Nanomaterials Based On Chemical Composition:

Nanomaterials are classed according to their origin (natural or manmade), chemical composition (organic and inorganic), production (biogenic, geogenic, anthropogenic, and atmospheric), size, shape, and features, and research and industrial applications.

They can be categorized into many categories based on their chemical composition, such as the following:

- Metals make up the majority of metal-based materials (e.g., silver, gold, and copper nanoparticles). Metal oxide nanomaterials, such as titania, silica, and alumina, are formed of metal and oxygen.
- Nanotubes, fullerenes, graphene, and Nano spheres are carbon-based nanomaterials that include carbon in various configurations.
- Dendrimers are materials made up of highly branching macromolecules with nanoscale dimensions. Dendrimers have multiple chains on their surfaces that can be changed to perform certain activities.
- Quantum dots are auto fluorescent semiconductor nanocrystals used in in vivo biomedical imaging. They have certain unique and exciting optical properties due to their quantum confinement, such as sharp and symmetrical emission spectra, high quantum yield, distinctive chemical properties, and excellent photo stability. Binary metal complexes, such as CdSe, CdS, and CdZn, are examples.
- Nanocomposites are particular kinds of materials made by mixing two phases of distinct materials, and they tend to maintain the properties of each material employed in their development. They are classified as multiphase materials with at least one dimension in the nanoscale. Chemical properties, high thermal and mechanical stability, multifunctionality, chemical functionalization, and a large interphase zone are all features of these materials. As a result, they can be used in a variety of fields of science and technology, such as catalysis, Nano sensor and Nano probe production, sorption processes, chemical and biological applications, fuel cells, nonlinear optics, bio ceramics, high-power batteries, environmental protection, and anticorrosion agents.

9.4 Synthesis of Nanomaterials:

In general, there are two methods for making nanomaterials: (1) the bottom-up method and (2) the top-down method.

9.4.1 Bottom-Up Approaches:

The nanoparticles are first generated at the atomic level and then incorporated into the appropriate material in the bottom-up technique. Nanoparticles can be made from colloidal dispersion, and powders can be made using the sol-gel process followed by integration.

9.4.2 Top-Down Approaches:

The top-down method begins with a bulk material at the macroscopic level, which is then trimmed to the required nanoparticles. Etching and ball milling are two examples.

9.5 Characterization of Nanomaterials:

To explain the morphology of composites, crystalline phases, and average size, many techniques for characterization of nanomaterials can be used. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM), can be used to examine the composites' morphology. FTIR, Raman spectroscopy, XPS, and EDX can all be used to look for functional groups on the surface of nanotubes. The thermogravimeter (TGA) can be used to investigate thermal stability. Physisorption and chemisorption analyzers can determine the surface area, porosity, pore size, and pore distributions. By measuring the amount of gas desorbed at various temperatures, temperature programmed desorption (TPD) analyses establish the number, type, and strength of active sites available on the surface of a nanomaterial. The gas desorbs at different temperatures if there are multiple active ingredients present. The amount of reducible metal species presents in the nanomaterial and the temperature at which reduction occurs are determined via temperature programmed reduction (TPR). This can be done by determining how much analysis gas (such as hydrogen) reacts with the catalyst at various temperatures. The amount to which nanomaterials can reoxidize is determined by temperature programmed oxidation (TPO).

9.6 Properties of Nanomaterials:

9.6.1 Nanomaterials for Water Treatment:

Scientists have studied the adsorption of contaminants from aqueous solutions onto a variety of adsorbents, including activated carbons, agricultural by-products, minerals, polymers, and metal oxides. Two important properties of an efficient sorbent with high capacity and quick rate adsorption are (1) functional groups and (2) big surface area. Nanotechnology advancements present leapfrogging prospects for improving next-generation water supply systems. Nanoparticles and nanocomposites have a lot of promise for improving water and wastewater treatment efficiency and augmenting water supply through the safe use of unusual materials. Nanotechnology's extremely efficient, modular, and multifunctional processes are expected to provide high-performance, low-cost water and wastewater treatment operations that are less reliant on huge infrastructures. Nanotechnology-enabled water and wastewater treatment is projected to overcome current treatment issues and bring new treatment capabilities that could allow for the cost-effective use of unconventional water sources to extend the water supply. Adsorption, membrane processes, photocatalytic destruction of pollutants, disinfection and microbial control, and pollutant detection and monitoring are only a few of the possibilities for nanomaterials in water treatment. The role of nanomaterials in adsorption and membrane processes-based applications will be discussed in the following sections.

9.6.2 Nanomaterials in Adsorption:

Adsorption is a technique in which a material termed an adsorbent is used to remove a soluble substance from water called an adsorbate. It is the mass transfer of adsorbate from a fluid phase to a porous surface of a solid phase via intermolecular attraction, resulting in the formation of an adsorbate film on the adsorbent surface. Nanomaterials' surface atoms are more reactive and can attract more adsorbates due to the large proportion of atoms on the surface and the increase in surface energy. Nanomaterials have a significant number of atoms with varying morphologies and the ability to act as an adsorbent for chemical species, lowering the system's free energy. Because of their: increased adsorption efficiency, greater adsorption capacity, and faster kinetics, nanomaterials offer considerable improvements in adsorption efficiency, higher adsorption capacity, and faster kinetics. Extremely high specific surface area (the nanoscale effect is attributed to a change in surface structure that creates new adsorption sites) Associated sorption sites and a larger number of surface reaction sites, such as corners, edges, and vacancies (for example, as the particle size of nanomagnetite decreased from 300 to 11 nm, its arsenic adsorption capacity increased more than 100 times [6]. Metal-based nanoadsorbents, carbon-based nanoadsorbents, and polymeric nanoadsorbents are the three types of nanomaterials used as adsorbents.

9.6.3 Nanomaterials for Pesticide Formulations:

Pesticides are critical in preventing biological disasters and increasing crop productivity. Pesticide AIs are mostly lipid-soluble [7]. NMs employed in pesticide manufacture are mostly involved in the development of nanopesticide formulation methods to improve AI bioavailability. AIs' stability is improved by NMs. Under the protection of NMs, AIs that are easily photolyzed and degraded can be stabilized. NMs can be utilized to release AIs in a targeted and controlled manner at the optimal working concentration. NMs could reduce pesticide toxicity to non-targets by taking advantage of the material's isolating effect on AIs and organisms, which is useful for expanding the pesticide's application area. Because of their antibacterial and insecticidal capabilities, NMs could be employed as nanopesticides directly. NMs have a modest size yet a large surface area effect. As carriers, NMs improve AI solubility while also protecting them from volatilization and degradation [8].

9.6.4 Nanomaterials for Fertilizer Applications:

Chemical fertilizers are currently preferred by farmers [9] because they are more effective and cost-effective than alternative fertilizers. Chemical fertilizers, on the other hand, can be overused and even squandered, resulting in soil degradation, reduced food yields, and pollution. For example, urea, which is particularly water-soluble and prone to loss, meets 80% of plant need for N-fertilizers [10]. NMs have been employed in a variety of fertilizer formulations. They're made as tunable and controllable fertilizers, and they're used to reduce fertilizer waste. These formulations improve nutrient absorption by improving soil nutrient management, assisting in the creation of a nutrient cycle in agriculture, reducing nutrient depletion, and reducing the impact of nutrient disorder on crop output and the environment. NMs are now used as bio-fertilizers, as well as trace element fertilizers like Fe and Zn, major element fertilizers like N, P, and K, and medium element fertilizers like Si, Ca, Mg, and S. Organic fertilizer also contains NMs.

9.6.5 Nanomaterials Applications in Agrochemicals:

Many eco-friendly agrochemicals, such as bio-pesticides, have received a lot of attention in recent years as a result of the environmentally friendly control strategies advocated by Integrated Pest Management, the rapid rise of organic farming, and the increased awareness of environmental protection and food safety. NMs are then applied to these chemicals [11].

9.6.6 Nanomaterials for Bio-Pesticide Applications:

Bio-pesticides are more environmentally friendly than chemical pesticides, and they are becoming more popular for pest and disease control in plants. Bio-pesticides are now gaining market share in the following categories [12].

- Microbial pesticides
- Viral pesticides
- Plant-derived pesticides
- Biochemical pesticides

9.6.7 Nanomaterial-Mediated Nucleic Acid Pesticides System:

Because of their high specificity, low research cost, and safety, RNA pesticides are both safe and environmentally benign. As a potential environmentally benign and effective pesticide for plant protection, these insecticides fit current standards for sustainable agriculture. RNA insecticides, on the other hand, are unstable, quickly destroyed, and decay before reaching their target. NMs are used in RNAi delivery methods to preserve siRNA and increase the efficiency with which it enters bugs [13].

9.6.8 Nanomaterials Applied in Plant Growth Regulators:

NMs and PGRs are primarily used to detect trace concentrations of plant hormones in plants and to regulate hormone levels flexibly to get the best output value. NMs also aid in the absorption and transport of PGRs into plants.

9.6.9 Nanomaterials Applied in Pheromones:

Attract-and-kill through pheromones is one of the most potent approaches to integrated pest management [14], and continuous release of pheromone active substances is required during the pest capture period. However, due to the volatile nature of pheromones, their duration is usually very short, and frequent replacements are needed during field application. This is a major disadvantage of pheromones that needs to be solved. Larson et al. developed a controlled release polyethylene dispenser for the controlled release of pheromone AIs [15]. The gel system was a three-dimensional nanoscale supramolecular network structure, providing high pheromone retention capacity.

9.7 Nanomaterials in Membrane Processes:

Membrane technology is used in a variety of separation processes, including wastewater treatment, gas separation, and desalination [16]. The selective transport of the target molecule through the membrane structure is the basis for membrane separation [17]. For the treatment of wastewater samples, Nano filtration and reverse osmosis membranes are commonly used. However, their water flux behaviour is hampered by a thick separating layer. Nanomaterials (graphene, fullerenes, carbon nanotubes, and nanoparticles) can be incorporated into the membrane structure to offset this disadvantage. The combination of membranes with nanoparticles that have great physical and chemical properties gives outstanding physical and chemical stability, as well as high rejection of the target substance to be isolated from the sample.

9.7.1 Carbon Nanomaterial-Based Membranes:

Carbon nanoparticles are widely used in the construction of innovative nanocomposite membranes because they offer unique properties such as excellent mechanical, chemical, and thermal stabilities, large surface area, superior optical properties, and decreased density. Nanocomposite membranes are frequently developed by incorporating carbon nanomaterials such as graphene, carbon nanotubes, and fullerenes into the membrane structure [18]. The integration of nanoparticles with membranes not only provides excellent physical and chemical stability, as well as high rejection and flux behaviours, but also introduces diverse traits such as catalytic and antibacterial properties to the produced nanocomposite membranes [19].

9.7.2 Graphene-Based Membranes:

Graphene was discovered by Geim and Novoselov in 2004 [20]. Since then, so much efforts were put into the design and development of new graphene-based functional materials. Owing to the excellent hydrophobic feature of graphene, it was widely used in the preparation of functional materials with superhydrophobic features. Recently, these superhydrophobic functional materials were efficiently applied for the separation of water oil mixture [21].

9.7.3 Carbon Nanotubes-Based Membranes:

Many researchers have concentrated on the usage of CNTs in various applications since their discovery in 1991 [22]. Carbon nanotubes (CNTs) are cylindrical structures made up of coiled graphene sheets that are classified as MWCNTs or single-walled carbon nanotubes. CNTs have a number of advantages, including great oleophobicity and hydrophilicity [23], as well as outstanding mechanical, electrical, and thermal properties [24, 25]. The design and preparation of innovative nanocomposite membranes can be successfully carried out by combining these unique properties with membrane systems.

9.7.4 Fullerene-Based Membranes:

Fullerenes are a type of carbon allotrope with 60 carbon atoms arranged in hexagons and pentagons. The form of fullerenes and carbon nanotubes is the primary distinction. In the nanoscale, fullerenes are cage-like structures, whereas CNTs are tube-like structures [26,27]. Fullerenes were utilized as effective nanomaterials in membrane architectures, and the fullerene-based nanocomposite membranes generated were successfully used to remediate environmental samples such as wastewater. Chen and colleagues, for example, created a nanocomposite membrane made of polyvinyl butyral/polyvinylidene fluoride and fullerene covered with F-127 [28].

9.7.5 Nanoparticle-Based Membranes:

Nanoparticle-based membranes are another prominent material for separation operations. Yu et al., for example, developed a polysulfone membrane based on yttrium nanoparticles and modified with polyvinyl alcohol for the effective separation of arsenate from water [29]. Gold nanoparticle-based polydopamine (pDA)-polyethyleneimine nanocomposite membranes for the efficient removal of salts from water samples were produced in another fascinating study [30]. The generated gold nanoparticle-based composite membranes also demonstrated outstanding antibacterial efficacy against Escherichia coli and Staphylococcus aureus, according to the findings. The production of polyethylene nanocomposite membranes with silica nanoparticles for humic acid removal from water samples was described by Akbari and colleagues [31].

9.7.6 Molecularly Imprinted Polymer-Based Membranes:

MIPs are custom-made materials with specialized binding sites for the molecule of interest [32]. MIPs are made by polymerizing appropriate functional monomers with a cross-linker and the desired molecule, often known as a "template". Designing and constructing new membranes with excellent selectivity and penetration behaviour toward the target compound/s remains a critical and difficult task. Recent research has shown that combining membrane technology and molecular imprinting technology to build composite membranes is an excellent strategy. These composite membranes can be used to effectively separate target molecules [33].

9.7.7 Metal Nanoparticles:

Metal nanoparticles [such as silver (Ag) and gold (Au) nanoparticles] are promising materials as efficient adsorbents in environmental analysis because they have excellent features such as very small dimensions and large surface area to volume ratios, which ensure excellent adsorption capacities for target compounds in environmental samples.

Silver nanoparticles, for example, are effective materials with excellent antibacterial properties due to their very toxic effects on various microorganisms such as viruses and bacteria. As a result, Ag NPs have been effectively used to identify and separate microorganisms from contaminated environmental samples such as water.

Due to their ease of synthesis with reducing agents such as hydroxyl amine and citrate, gold nanoparticles (Au NPs) are also efficient nanomaterials similar to Ag NPs. To improve their binding efficacy toward the target chemical, Au NPs can be implanted into various adsorbents.

9.7.8 Biomimetic Materials:

Biomimetic materials are created by creating artificial duplicates of biomaterials found in nature. These biomaterials are utilized in tissue culture, cell development, biotechnological manufacturing, and other applications where the original materials have failed to perform their roles or are used to maintain the environment. Several peptides and proteins are made using biomimetic materials, which are created or have designs borrowed from nature. A variety of polymers have been developed to improve mechanical characteristics and strength [34]. The first stage in a biomimetic method is to discover the performance of biomaterials found in natural systems, and then to figure out how they work, which can be done using scanning probe microscopy.

9.8 Conclusion:

This chapter provides a comprehensive summary of nanomaterials' recent progress in several domains. The rapid growth of nanomaterials has opened up new possibilities for the design and fabrication of innovative nanomaterials in environmental sciences, such as Nano sensors, Nano sorbents, Nano tools, and portable Nano devices. To avoid unwanted repercussions on natural ecosystems, safety assessments of artificial nanomaterials in systems other than no target, including biological systems, should be closely investigated. Studies of their destiny and behaviour in natural environmental settings, such as soil and water, would aid in the management of nanomaterials with potential toxicological implications. It is envisaged that successful examples of nanomaterials-based products in the environmental sciences will be commercially available in the future, thanks to the efforts of researchers from various departments of study such as chemistry, medicine, pharmacy, biology, and material science engineering.

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