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Nanomaterials: Methods of Preparation, Properties and their **Applications**

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Introduction

The formation of nanostructures in the first meteorites marks the beginning of the history of nanomaterials, which dates back to the big bang. Later, many more nanostructures like skeletons and seashells appeared in nature. Nanoscale smoke materials were created by early humans using fire. The scientific history of nanomaterials, however, started considerably later. The colloidal gold nanoparticles created by Michael Faraday in 1857 are among the earliest scientific publications. Precipitated and fumed silica nanoparticles were being produced and offered as an alternative to ultrafine carbon black for rubber reinforcements in the USA and Germany by the early 1940s. Despite the fact that nanomaterials have a lengthy history, significant advances in nanoscience have just recently emerged. Researchers from various academic disciplines, including biology, medicine, chemistry, mechanics, and materials science, collaborate on research on nanoparticles. According to reports, a heterogeneous catalyst was the first nanoparticle-based technology to be created in the early nineteenth century, which was then followed by the usage of silver halide nanoparticles in photography. In Greek, the word "Nano" signifies dwarf. Normally, the prefix "nano" is used to denote a billionth part (10-9) of any unit, such as a second or metre. Approximately the length of a few atoms lined up shoulder to shoulder, a nanosecond is one billionth of a second, and a nanometre is one billionth of a metre. From the extremely small scale of nanometers, a world of objects is constructed. In modern physics, the atom is regarded as the tiniest particle and nanomaterials as the tiniest components of nature. In order to create nanostructured materials, different modulation dimensionalities can be used, such as zero (for example, atomic clusters, quantum dots, and cluster assemblies), one (for example, multilayers), two (for example, ultrafine-grained over layers or buried layers/nanotubes), and three dimensional materials (e.g. bulk materials). Oswald was the first to recognise that materials of this size and shape ought to exhibit unusual and intriguing features. However, inorganic compounds made of a few hundred or a few dozen atoms, known as clusters, have only attracted substantial attention in the recent two decades. Because nanoparticles displayed unique features that set them apart from similar macro-crystalline materials, interest has been expanded to a wide range of metals and semiconductors. It has been widely categorised and fully explained how bulk materials made of atoms and molecules work. Nanomaterials are divided into various categories according to their dimensions, composition, and shapes. These categories are discussed below.

One Dimensional nanomaterials: Nanoscale materials, such as the circuitry in computer chips and the anti-reflection and hard coatings on eyeglasses, are typically thin films or surface coatings. For decades, thin films have been manufactured and employed in a variety of industries, including engineering, chemistry, and electronics. Different techniques can be used to deposit thin films, which can be controlled to grow until they are only one atom thick, or monolayers.

Two Dimensional Nanomaterials Nanometer-scale two-dimensional nanomaterials have two dimensions. Among them are 2D nanostructured films, which have nanostructures securely affixed to a substrate, or nanopore filters, which are employed for the filtration and separation of small particles. Free particles with



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Vol 1, No. 03, 2022

diameters in the nanoscale range and a high aspect ratio are also regarded as 2D nanomaterials. An illustration of a 2D nanoparticle is asbestos fibres.

Three Dimensional nanomaterials Three-dimensional (3D) nanomaterials are substances that are nanoscale in all three dimensions. These include colloids, free nanoparticles with different morphologies, and thin films deposition under circumstances that provide atomic-scale porosity.

Nanocomposites Nanomaterials can be composites of many materials or can just have one main constituent ingredient. While pure materials of a single composition can now easily manufactured using a number of techniques, the nanocomposites seen in nature are frequently agglomerations of materials with different compositions. Nanoparticles are essential to modern technology, but their applications are restricted, hence nanocomposites are used to expand the usefulness of materials. It has generated a lot of interest from both a theoretical and practical standpoint. Materials with the necessary reaction can be created by combining the physical features of nanocomposites. When particle sizes are reduced to extremely small dimensions, optical or magnetic properties change, which are generally of great interest in the field of nanocomposites materials. Composites have great qualities like a high melting point, high hardness, low density, low coefficient of thermal expansion, high thermal conductivity, good chemical stability, and improved mechanical qualities like a higher specific strength, better wear resistance, and a higher specific modulus. They also have a good future in a variety of industrial fields.

Nanoparticles uniformity and agglomeration Nanoparticles can exist as suspended/colloids, as agglomerates, or as dispersed aerosols depending on their chemistry and electro-magnetic characteristics. For instance, unless their surfaces are covered with a non-magnetic substance, magnetic nanoparticles have a tendency to aggregate and create an agglomeration state. Depending on the size of the agglomeration, nanoparticles may act like larger particles while they are in an agglomerate form. So it follows that when deciding whether to consider health and environmental regulation of novel materials, nanoparticle aggregation, size and surface reactivity, along with shape and size, must be taken into consideration.

Methods of synthesis of nanomaterials: Bottom-Up and Top-Down Approaches

A review of the literature suggests that top-down and bottom-up fabrication processes are primarily used to create nanomaterials. The top-down approach begins with a bulk substance and uses mechanical, chemical, or other types of energy to break it down into smaller pieces. As opposed to the bottom-up strategy, which uses chemical reactions, etc. to create nanomaterials from atomic or molecule species. Researchers, scientists, and engineers are interested in managing the size, shape, distribution, composition, and degree of agglomeration of nanoparticles and nanostructure materials (NMs) for a variety of purposes. While colloidal dispersion is a good illustration of a bottom-up strategy for the synthesis of nanoparticles/nanomaterials, attrition or milling is a typical top-down method for creating nanoparticles/nanomaterials. Three-dimensional photonic crystals can be made on a large scale and at a low cost by using top-down holographic laser lithography in photo resists and bottom-up self-assembly of colloidal sub-micron spheres. Lithography can be thought of as a hybrid method because bottom-up creation of thin films is different from top-down etching, although bottom-up methods are more frequently used in nanolithography and nanomanipulation. There aren't many benefits and drawbacks to these methods. Because it adheres to classic object-oriented design, which contends that complexity is best understood by starting with an abstraction and breaking it down into smaller components, the top-down approach is frequently adopted. Working with an abstraction might be difficult at times, and it is more effective to start small and work your way up. The surface structure is imperfect, which is the main issue with the top-down approach. The processed patterns can suffer severe crystallographic damage from traditional top-down processes like ball milling and lithography, and in the case of lithography, additional defects may be added even during the etching phases. For instance, lithographically produced nanowires have a rough surface and may have several impurities and structural flaws. Given that nanostructures and nanomaterials have a very high surface to volume ratio, such flaws would significantly affect their physical characteristics and surface chemistry.

The term "bottom-up approach" describes the process of creating a substance atom by atom, molecule by molecule, or cluster by cluster. We know that linking different monomers together forms polymers, according to organic chemistry and/or polymer science. After colliding with the growth surface during crystal growth, growth species such atoms, ions, and molecules sequentially organise into the crystal structure. The bottom-up methodology has been crucial in the study of nanostructures and nanomaterials. This is due to a



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Vol 1, No. 03, 2022

number of factors. There isn't much room for a top-down strategy when structures are on the nanometer size. A better possibility of obtaining nanostructures with fewer flaws, more uniform chemical composition, and better short and long range ordering is also promised by the bottom-up strategy. This method's main drawback is that an object may be divided into several sections, some of which may cause the item and background to blend together. The aforementioned methods can also be divided into physical and chemical methods. Physical technique is, broadly speaking, based on a method of transferring growth species from a source or target. The process starts at the atomic level and largely excludes chemical reactions. For the elimination of growing species from the source or target, numerous techniques have been devised. However, chemistry is quite rich in chemical technology, and many different kinds of chemical reactions are involved.

Chemical and Physical Methods

Chemical Methods: Nanoparticles are frequently created via chemical processes. The creation of new materials with cutting-edge properties has been greatly aided by chemistry. Chemical synthesis has the advantage of being flexible in the design and synthesis of novel materials that can be improved into the finished product. Since chemical synthesis allows for molecular-level mixing, the main advantage chemical techniques have over other processes is in obtaining good chemical homogeneity. But there are certain challenges with chemical processing. The chemistry in some preparations is intricate and dangerous. Another source of contamination is the byproducts or unintended consequences of a chemical reaction. Agglomeration can significantly change the characteristics of the materials and can also be a major cause of concern at any point in the synthetic process. It is not always easy for all systems, but many chemical processes are ideal for inexpensive production.

Physical Methods: The synthesis of nanostructured materials and their commercial manufacture now employ a variety of physical techniques. This section discusses several experimental methods, beginning with physical methods.

Mechanical grinding

In the "top-down" method of synthesis of nanomaterials, mechanical attrition/milling is a typical illustration. In this method, the material is generated not by cluster construction but rather by the structural disintegration of coarser-grained structures as a result of extreme plastic deformation. In this procedure, tiny steel balls are allowed to revolve inside a drum before falling with the force of gravity onto a solid contained inside the drum. Due to its ease of use, the low cost of the equipment required (on a laboratory scale), and its potential to be used to the synthesis of virtually all kinds of materials, this technique has grown in popularity for producing nanocrystalline materials. The ability to easily scale up to tonnage quantities of material for various purposes is frequently cited as the technique's main benefit. Another important benefit of this approach is that it is low-cost, large-scale, and an old, well-established process with a possible resolution of 2–20 nm. This method has significant drawbacks, including the generation of asymmetric nanoparticles, the introduction of flaws, the entrance of contaminants from the balls, and the introduction of milling additives. Usually, tumbler mills or high-energy shaker planetary balls are used to perform mechanical milling. The amount of energy that refractory or steel balls impart to the powder relies on the rotational (vibrational) speed, size, and quantity of the balls, the mass ratio of the balls to the powder, the milling period, and the milling environment. The brittleness of the powders can be significantly increased during milling in cryogenic liquids, which can affect the fracture process. As with any process that yields high-quality materials, effective measures to stop oxidation are required. Due to the need for the milling to occur in an inert atmosphere and the handling of the powder components in an appropriate vacuum system or glove box, this process is particularly constrained for the synthesis of non-oxide compounds. This type of synthesis can be used to create powders that are either elemental or complex, amorphous or nanocrystalline alloy materials, etc.

Sputter deposition

Sputtering, or ejecting material from a source or "target," deposits thin layers onto a "substrate," such as a silicon wafer, using the physical vapour deposition (PVD) technique. The energy distribution of the sputtered atoms that are ejected from the target is very broad. The sputtered ions can ballistically fly from the target in straight lines and impact energetically on the substrates or vacuum chamber, causing re-sputtering (the re-sputtering is reemission of the deposited material during the deposition process by ion or atom bombardment). Alternatively, at higher gas pressures, they can collide with the gas atoms that act as a moderator and move diffusively, reaching the substrates or vacuum chamber. Frequently, an inert gas is the



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Vol 1, No. 03, 2022

sputtering gas. Neon is preferred for sputtering light elements because it is near to the target's atomic weight, whereas krypton or xenon is used for heavy elements since it will transmit momentum more effectively. Compounds can also be sputtered using reactive gases. Depending on the process settings, the compound may be produced on the substrate, in flight, or on the target surface. Sputter deposition is a complicated process, but the availability of numerous controllable parameters gives professionals a great deal of control over the growth and microstructure of the film. Sputtering is widely employed in the semiconductor sector to deposit thin coatings of different materials for use in processing integrated circuits. Sputtering is the best technique for depositing contact metals for thin film transistors since it uses low substrate temperatures. Even materials with the highest melting points can be easily sputtered, but it is impossible to evaporate these materials in a resistance evaporator. This is a significant benefit of sputter deposition. Sputtered films usually adhere to the substrate better than evaporated films. Sputtering's main drawback is that it is more challenging to combine with a lift-off method for structuring the film.

Laser ablation

In this procedure, high-power laser pulses are used to cause the substance to vaporise. Nanoparticles and particulate films have been created using laser ablation on a large scale. The main excitation source of ablation in this method, which produces clusters directly from solid samples for a wide range of applications, is a laser beam. Given that nano-particulate web-like structures have novel features that can be used in new technological applications, the possibility of creating them over a large sample area is particularly intriguing. Line-Spark Atomization (LSA) is a brand-new method of solids atomization that is based on laser spark atomization. In a nutshell, the LSA can evaporate material off a solid target at a rate of around 20 g/s when it is in an argon environment. The LSA is a very effective tool for the fabrication of ceramic materials and coatings due to the small dimensions of the materials and the ability to generate thick films. Additionally, the carrier gas flow rate can be adjusted to change the porosity of the thick films produced by the laser spark atomizer, which allows for control over the microstructure of the coatings. The nanomaterials produced with this method make good candidates for membrane technology, catalysis, and lithium-ion battery applications. Due to the benefits listed above, this method has been mostly employed to create single-walled nanotubes (SWNT).

Ion Beam Deposition Techniques (Ion-Implantation)

Ion-implantation is a method of material engineering in which ions of one material are inserted into another solid, altering the solid's physical characteristics. Ionimplantation is utilised for a variety of purposes in materials science research as well as the manufacture of semiconductor devices and metal polishing. There are numerous instances where the production of nanoparticles involves the utilisation of ions with energies ranging from a few KeV to hundreds of KeV or lower (200eV). A particular ion gun made to manufacture metal ions is typically used to create the ions of interest, which are then accelerated at high or low energy toward a substrate that has been heated to a few hundred degrees Celsius. Different processes, including sputtering and the production of electromagnetic radiation, may occur depending on the energy of the incident ions. This technique can be used to create compounds and alloys of multiple elements as well as nanoparticles of a single element. Sometimes post-calcination is performed to increase the crystallinity of the materials. According to some tests, the ion-implantation approach can be used to produce doped nanomaterials. Making nanoparticles with quick heavy ions (few MeV energy) and ion accelerators like a pelletron accelerator is another option.

Electric Arc Deposition

Using a powerful arc discharge between electrodes, this is one of the most straightforward and practical methods for producing fullerenes and carbon nanotubes on a large scale. The electrodes are kept in a vacuum chamber that is water cooled in order to produce a powerful arc. The source of material is the positive electrode itself. For discharge action, the introduction of inert gas or reactive gas is required. Typically, there is a 1mm gap between the electrodes, and a low voltage power source transmits high current of 50 to 100 amps (12-15 volts). Material for the anode evaporates when an arc is created. As long as the



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Vol 1, No. 03, 2022

discharge is kept up, this is possible. As one of the electrodes burns and the gap widens as a result, it becomes imperative to regulate the electrode gap without rupturing the vacuum. The arc between the two graphite electrodes can produce a significant amount of fullerenes, which causes the temperature to increase to as much as 35000C. Compared to the pressure utilised for the creation of nanotubes, fullerens form at a lower helium pressure. Additionally, fullerens are made by purifying soot that has been collected from the vacuum chamber's inner walls, whereas nanotubes are only discovered to form under conditions of high He gas pressure and in the cathode's centre. The chamber walls contain no carbon nanotubes. The area where nanotubes are generated is frequently surrounded by some carbon nanoparticles. This process should theoretically allow for the production of various nanocrystals or tubes made of different materials. However, fullerens or carbon nanotube deposition are discovered to be the most common applications for this technique.

Molecular Beam Epitaxy (MBE)

This method of deposition can be used to deposit quantum dots, wells, wires, and other structures in a very controlled way, whether they are elemental or compound. High vacuum, typically 10–10 torr, is required to achieve high levels of purity in materials. In addition to the ultrahigh vacuum system, MBE primarily comprises of real-time structural and chemical characterization capabilities, such as Auger electron spectroscopy, X-ray photoelectric spectroscopy, and reflection high energy electron diffraction (RHEED) (AES). The growth of films can be transferred to the chamber without being exposed to the environment if additional analytical instruments are added to the deposition chamber or to a separate analytic chamber. Under such a low pressure in the MBE, the evaporated atoms or molecules from one or more sources do not interact with one another in the vapour phase. Molecular beams of the constituent elements are obtained using special deposition sources called effusion cells. In order to achieve adequate element mobility on the substrate and layer-by-layer growth to produce nanostructures, the rate of deposition is kept very low and the substrate temperature is very high. A highly pure film can be easily created since the ultra high vacuum environment ensures the absence of impurity or contamination. The chemical composition of the deposit can be precisely controlled at any given time thanks to individually controlled source evaporation.

Electrodeposition

Electroplated materials have been created using this method for a very long time. The weight of the substance moved can be estimated in accordance with Faraday's rules of electrolysis by carefully regulating the number of electrons transmitted. According to this, the quantity of electrons given immediately correlates to the number of moles of product that the electric current produces. The basic goal of nanoscience and nanotechnology is to electro-deposit a single layer on a surface in a very controlled manner. For accurate findings, the current and time must be precisely monitored, and any additional variables that may affect how currents are consumed, such as contaminants, must be thoroughly understood. The need for extremely clean rooms results from this. Platinum films with nanostructures can be created by electro-depositing liquid crystalline combinations. The films that are produced are incredibly flat, consistent, and lustrous. The idea of electroplating from liquid crystalline mixtures can be applied to various metals, such as semiconductors, palladium (Pd), Ni, and Au oxides. For a variety of uses, including solar cells, batteries, fuel cells, and windows that can disperse heat and change properties depending on the environment, nanostructured films made of liquid crystals are of great interest due to their distinctive nature. The electrode substrate's surface properties have a significant impact on the main benefit of this, and these properties also affect how the deposits are shaped and sized.

Some Important Applications of nanomaterials

Making new, multifunctional products that can be used in a much better way in the future is now possible thanks to materials' ability to drastically alter their properties at the nanoscale. In just a few years, they have made significant entry into the global market because to quick advances in synthesis and in understanding the properties of nanomaterials. Therefore, several significant uses of nanomaterials are briefly covered in this section. The three-dimensional displays, single electron transistors, spin valves, and magnetic tunnel junctions (MTJ) are conceptually novel electronic devices based on nanomaterials. These devices



Vol 1, No. 03, 2022

typically have dimensions of a few nanometers. Crystal at the nanoscale affects how materials behave chemically, electronically, and optically. In the fields of toys and sporting goods, nanomaterials are also crucial. Tennis balls made of nano clay have improved pore filling and air pressure retention capabilities. Balls last longer as a result of this. The toy industry has been prepared to accept nanoparticles. The use of nanoparticles in the textile industry has generated a lot of interest. Nanoparticles are crucial in cosmetics as well. Small, uniformly sized zinc oxide and titanium oxide nanoparticles can absorb UV radiation and shield the skin from it. Given their well-known uses, nano-based cosmetics are growing in popularity. Due to their well-known antimicrobial qualities, silver nanoparticles are employed in refrigerators, air purifiers or air conditioners, water purifiers, and photography. Due to their functional properties, such as the very low density materials known as aerogels, which are excellent for use of various applications in spacecrafts and defence for reducing the weight of application instrument, scientists in the fields of space and defence are also attempting to adopt nanomaterials as alternative materials and to replace the conventional materials by nanomaterials. Aerogels can be used to create specialised lightweight clothing items like jackets, coats, and more since they can be used to create fabrics with poor heat conductivity. The utilisation of nanomaterials causes a significant change in the fields of biotechnology and medical science. Initial test results demonstrate the viability of using nanomaterials for a variety of drug delivery systems, cancer tumour therapy, or cancer tumour detection. Such materials demonstrated a significant impact on the resolution of numerous healthrelated issues. There is a lot of nanotechnology-based research being done to assist patients with HIV and diabetes. Work is ongoing to better understand how nature operates and mimics human behaviour. Thus, nanoparticles have a number of beneficial uses including the fire-retardancy and UV protection of fabrics.

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