



ZERO DIMENSIONAL MATERIALS: PROPERTIES, SYNTHESIS AND APPLICATIONS A REVIEW

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Abstract: Reduction in the size and dimensions of the materials brings about a drastic change in their physical and chemical properties making them a powerful tool for advanced research and applications. Increased surface area, quantum confinement effects and good biocompatibility make them applicable in areas of biosensors, solar cells, nanoscale electronic devices, light-emitting nano devices, laser technology and waveguide. The fields are not just limited to the listed one. Research is still going on in the various techniques of synthesis of the nanomaterials that can open the scope further for the wide spread application of nano materials. The present paper deals with the different types of nano materials, their synthesis techniques, unique properties, applications and finally the future challenges in this regard.

Index Terms: Nanomaterials, biocompatibility, quantum confinement effect, semiconductors, sol-gel, hydrothermal.

I. INTRODUCTION

The term “nano” was coined by Norio Taniguchi in 1974 and zero dimensional (0D) nanomaterials are the forerunner of nanotechnology. During last few decades, nano technology has been a rapidly growing field. Researchers all over the world has diverted to this branch owing to the advanced and unique features of nano materials in comparison to the bulk material. Their extremely small size has made them potentially applicable for wide range of industrial, biomedical and electronic use. Because of the smaller size many atoms are at the surface or at the interface making them highly reactive with advanced surface properties, such as energy levels and electronic structure that gives rise to totally different material properties. Nano devices like nanocapsules can open a new dimension in gene therapy, medical diagnosis and drug delivery. Novel properties such as optical stability, wavelength-dependent photoluminescence, chemical inertness, cellular permeability and biocompatibility, 0D nanomaterials offer great adaptability to biomedical applications such as nanomedicine, cosmetics, bioelectronics, biosensor and biochip (Koh I. et al, 2009).

In case of semiconductor materials, reduction in the size increases the surface to volume ratio or quantum size effect resulting in a drastic and, favourable changes in the optical properties and also enhances the conductivity. Such nonmaterial prove vital in the manufacturing of solar cells, sensor technology, display units, biosensors, as catalysts, superabsorbent, parts of automobiles, parts of ammunitions, nanoscale electronic devices like transistors, LEDs, SCRs, diodes. Some of the semiconductor nonmaterial such as Si, Si-Ge, GaAs, AlGaAs, InP, InGaAs, GaN, AlGaN, SiC, ZnS, ZnSe, AlInGaP, CdSe, CdS, and HgCdTe etc., exhibit excellent application in computers, palm pilots, laptops, cell phones, pagers, CD players, TV remotes, mobile terminals, satellite dishes, fiber networks, traffic signals, car taillights, and air bags. (S Iijima,1991) first reported the synthesis of carbon nanotubes with advanced features like strength and stiffness. Carbon nanotubes are thermally stable in vacuum upto a temperature of 2800⁰ C and show conductivity thousand times higher than copper wire. Use of such carbon nanotubes in various components can bring about the revolution in the electronic industry. A nano computer using nanotubes has already developed. Need for the miniaturization of optical devices and electronic sensors have further increased interest of researchers in exploring novel nano semiconductors (Bawendi MG et al, 1990 & Alivisatos A P, 1996). There are practical constraints associated with current technologies; lithographic methods cannot at present be used with a resolution much less than ca. 200 nm. Most semiconducting materials such as the II/VI or III/VI compound semiconductors, show quantum confinement behavior in the 1-20 nm size range, a smaller size than can be achieved, using present lithographic methods. Carbon-based nanomaterials are one of the most widely studied materials in the field of nanotechnology due to their low cost of mass production, low intrinsic toxicity and multifunctional surface fictionalization, (Panwar et al, 2019) .This review paper presents the structures and properties of 0D nanomaterials along with the synthesis techniques.

II. CLASSIFICATION OF NANOMATERIALS

When the relative dimension of the material is comparable to the de Broglie wavelength of an electron, the electrons are confined to the regions of one, two or three dimensions. The nanostructures of the crystals having the z direction below this critical value are defined as 2D nanostructures like thin film, layer structure, quantum well. When the dimension both in the x and

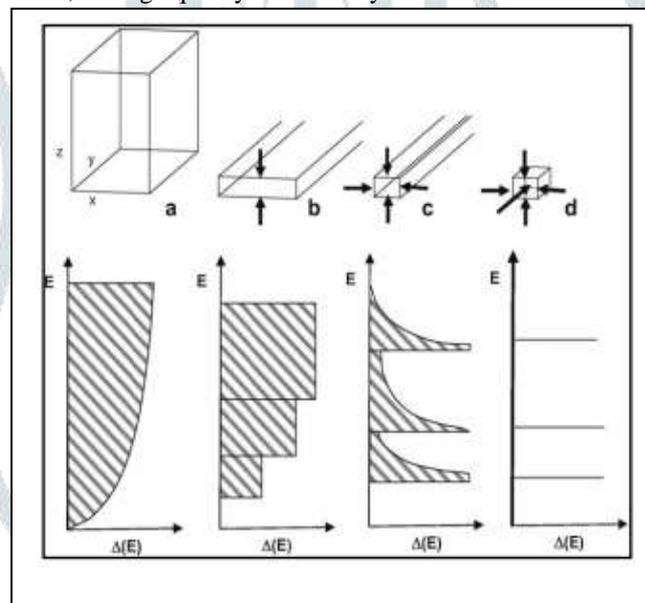
z direction is below this critical value the nanostructures are defined as 1D like linear chain structure, quantum wire and when the y direction is also below this threshold we get cluster, colloid, nanocrystal, quantum dots. These are the 0D materials.

2.1 0Dimensional Nanomaterials

Earlier techniques of synthesizing 0D materials were very basic that gives rise to building blocks of symmetric shapes that can be cuboid or spherical but these materials showed certain disparity in their crystalline structure and size. However (Murray et al, 1993) injected a precursor solution containing dimethylcadmium and trioctylphosphine selenide into a hot trioctylphosphine oxide (TOPO) solution. Through this technique he was successful in developing CdSe nanocrystals of various size ranging from 1.2 to 12nm high monodispersity and crystallinity. Optical spectra of these crystals exhibited size dependent quantum confinement effects, indicating the high monodispersity and high crystallinity of nanocrystals. These crystals were highly soluble in various organic solvents.

2.2 1Dimensional Nanomaterials

Here the dimensions are generally larger than the threshold value and elongation can occur along one main axis. By controlling the variables such as temperature, precursor concentrations, crystalline phases of the nuclei, the choice of capping molecules, and the choice of the regime between kinetically controlled and thermodynamically controlled growth, various nano-building blocks with multi-dimensionality can be produced. The properties changes drastically by change in the dimension of the crystalline materials. Chemseddine and Moritz were successful in synthesizing elongated TiO₂ nanocrystals by hydrolysis and polycondensation of titanium alkoxide [Ti(OR)₄], in the presence of tetramethyl ammonium hydroxide, as a stabilizer and reaction catalyst. (Penn and Banfield, 1993) developed aligned titania nanocrystals under hydrothermal conditions, by adopting an oriented attachment mechanism into the nanocrystal development. The hydrothermal treatment of titanium alkoxide precursors produces diamond shaped anatase titania nanocrystals. The hydrolytic synthesis of II–VI semiconductors also produces one-dimensional rod-shaped nanocrystals, by shape transformations involving oriented attachment processes. The non-hydrolytic high temperature injection method can be effectively utilized, for high quality nanorods synthesis.



Fig(i) showing the concept of system dimensionality: (a) bulk semiconductors (3D); (b) thin film, layer structure, quantum well (2D); (c) linear chain structure, quantum wire (1D); (d) cluster, colloid, nanocrystal, quantum dot (0D). In the bottom, the corresponding density of states [$\Delta(E)$] versus energy (E) diagram.

(Tang et al, 2002) reported a shape transformation from a sphere to a rod by the dipole-induced fusion of CdTe individual nanospheres. (Peng et al, 2000 and Manna et al, 2000) first reported CdSe nanorods via thermal decomposition of dimethylcadmium and trioctylphosphine selenide, in a hot surfactant mixture of trioctylphosphine oxide and hexylphosphonic acid.

2.3 2Dimensional Nanomaterials

2D materials grow under special and controlled manner. All 2D flat nanocrystals possess an overall size in the order of 10 nm. These materials are synthesized by self assembly of solutions and the constituting raw materials of the system are generally metals. The main synthesis methodologies of 2D nanostructures are: (i) anisotropic crystal growth, (ii) surfactant-assisted synthesis and (iii) the assembly of simpler 0D or 1D nanosystems. Discoidal nanocrystals are flat building blocks that are obtained by surfactant assisted synthesis, or anisotropic crystal growth passing through colloidal systems. Photo induced shape changes gives 2D prismatic shapes like silver nano prisms that are obtained by the irradiation of Ag nanospheres with visible light together with an unexpected colour change (from yellow, which is a characteristic surface plasmon band of the spherical particle, to green and finally blue), and a marked change in shape, from nanospheres into nano prisms, (Jin R et al, 2001) . Transition metals like Pd and Ni, or semiconductors such as CdS are used for developing prismatic 2D materials.

2.4 3Dimensional Nanomaterials

Materials whose size is generally in micrometer or millimeter range and exhibiting nanometric properties due to periodic arrangement of nanosized building blocks are classified as 3D nanomaterials. These materials show totally different molecular and bulk properties. 3D nanocrystals are obtained by stacking of basic building blocks that can belong to 0D, 1D or 2D to have

bigger sized nano structures of innovative shapes. 0D nanosystems, and mainly nanoparticles are the best choice as they can easily lead to the highly ordered 3D closely packed patterns placed together by chemical interparticle interactions. Using a selective evaporation technique from a solution of octane & octanol containing spherical CdSe nanocrystals, super lattices of CdSe nanocrystals can be obtained. These superstructures exhibit novel optical properties that are different from those of diluted CdSe nanospheres in solution.

III TYPES OF 0D NANOMATERIALS

3.1 Carbon Based Nano Materials:

Carbon based nanomaterials are widely used in number of applications like imaging, sensing, drug delivery and other applications due to their low cost of mass production, low intrinsic toxicity and multifunctional surface functionalization. They have inimitable electrical, optical properties, low toxicity and high quantum yield hence are used to produce micro-sensors with superior performance and low power (Zhou et al. 2020 & Ali Etemadi et al, 2014) reported the synthesis, properties, purification and medical application of carbon nanotubes. The strength and flexibility of carbon nanotubes make them of potential use in controlling other nanoscale structures, that will make them to play a significant role in nanotechnology engineering.

3.1.1 Fullerenes:

In 1985 Kroto et al discovered a molecular allotrope of carbon called fullerenes. Fullerenes show high electron affinity, large surface volume ratios and structural stability. Fullerenes also possess good biocompatibility and inertia, and have good affinity with various organic molecules hence are used to construct various biosensors (Afreen et al., 2015). They are used in a diverse range of applications, including electronics, biology and medicine. Fullerenes are often used to construct electrochemical biosensors because of their large electro active surface area, to detect amino acids. The most common fullerene is C60 that consists of five to six sp² hybrid carbon rings, forming a truncated icosahedrons (Carneiro et al., 2019) & (Jaiswal et al,2019) produced a C60-based electrochemical sensor that are essential to the function of central nervous system. The experimental results showed that the C60-based electrochemical sensor could maintain the original performance without current deviation, and was durable in water samples for up to 3 weeks. This sensor had higher detection sensitivity, stability and repeatability than previously reported sensors.

3.1.2 Graphene Quantum Dots

Graphene quantum dots (GQDs) belongs to 0D graphene nanomaterials category and are characterized by their atom-thin graphitized planes not exceeding 2 nanometers in thickness and small transverse dimensions. Various researchers have reported that photo luminescence (PL) is the outstanding property of these nanomaterials and it is a variable one. By changing the dimension, morphology or dopant, the PL excitation and emission wavelength of QGDs can be changed. Because of their unique PL properties, GQD are widely used in the induced enhanced PL sensing system based on magnetic graphene oxide quantum dots (Fe-GQDs) to sensitively and selectively detect arsenic ions in contaminated water. The detection limit of Fe-GQDs for As³⁺ was 5.1 ppb, which is lower than the WHO allowable limit for arsenic in drinking water (10µg/L). In addition, there are plenty of oxygen-rich functional groups at the edge of GQDs, which contributes to their good water solubility and biocompatibility.

3.1.3 Carbon Quantum Dots

Carbon quantum dots (CQDs) or carbon dots (CDs) are quasi-spherical fluorescent particles whose sizes is less than 10nm. CDs have lower content of crystalline sp² carbon and more surface defects hence they show poor crystalinity. CQDs exhibit excellent optical properties like fluorescence, chemiluminescence and electrochemiluminescence, CDs can be synthesized and functionalized quickly and easily by doping or surface functionalization. These processes can further improve the chemical properties, optical properties, surface reaction activity and biocompatibility. Therefore are widely used in fields of bioimaging, drug delivery and biosensing (Molaei et al,2019). CQDs-modified gating electrode for Cu²⁺ detection based on solution-gated graphene transistors are designed and functionalized Fan et al, 2020) For the detection of heavy metal ions in contaminated water, CQDs are used.

3.1.4 Quantum dots

SiQDs are a new type of heavy metal-free QDs developed in recent years. Fluorescent semiconductor nanocrystals, quantum dots (QDs) are generally prepared with atoms from group II-VI or III-V in the periodic table. QDs, such as CdTe, CdSe, and InP, have potential applications in various biomedicine fields. They are used to develop a variety of fluorescence, chemiluminescence and bioluminescence sensors because of their unique optical properties such as enhanced brightness, resistance to photo bleaching, large absorption coefficient, narrow emission spectrum and size tunable light emission (Ma et al., 2019).

3.2 Other Nanomaterials

Polymer dots generally possess high fluorescence brightness and high photo stability. (Chunlei Xia et al,2019) observed the effect of synthesis on the structure and properties of CDs and also reported the effects of synthesis conditions of the bottom-up methods in terms of the structures and properties of Carbon Polymer Dots. Insights into formation process and nucleation mechanism of CPDs are also offered. A brief about the future development of CDs and with critical insights into facilitating their potential in various application fields is presented.

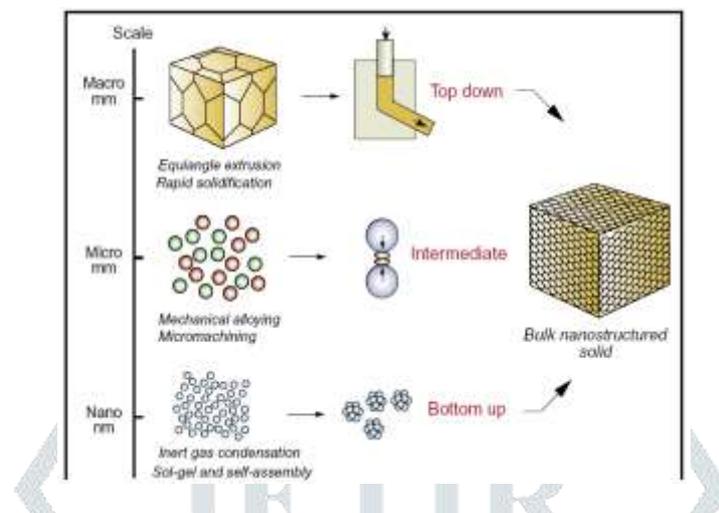
3.2.1Magnetic nanoparticles (MNPs)

They have a size range of 1-100 nanometers, are composed of materials with high saturation magnetization, such as pure metals (Fe, Co, Ni), alloys (FeCo, permalloy, alnico) and oxides (Fe₃O₄, CoFe₂O₄). Due to their superparamagnetism property, they have attracted the researchers all over the wide for their potential use in different fields. The correlation between density and specific surface area of ZrO₂ nanoparticles were studied by (Agnieszka Opalinska et al, 2015). They synthesized the nanoparticles using a hydrothermal process involving microwave heating. The material was annealed at 1100 °C which resulted in an increase in the average grain size of the ZrO₂ NPs from 11 to 78 nm and a decrease in the specific surface area from 97 to 15m²/g. At the same time, the density increased from 5.22 g/m³ to 5.87 g/m³. A strong correlation was reported between particle size and density of the nanomaterials.

3.2.2 Gold nanoparticles and silver nanoparticles have advanced physical and chemical properties hence are commonly used in medical diagnosis. They are conductive materials with a large surface area and unique optical properties (Kurochkina et al, 2018). In addition, Ag nanoparticles have attractive electrical properties. Compared with Au nanoparticles of the same dimension, they have higher extinction coefficient and are more prone to electrochemical oxidation, (Bahrami et al.2016).

IV SYNTHESIS TECHNIQUES

Smaller components and machines are always in demand because of their lower consumption of power and lesser use of raw materials. Besides such materials are compatible with the human cells and tissues and prove helpful in the diagnosis of different diseases and detection of tumors. All these lead to the exploration of new and advanced techniques for synthesis of nanoscale materials. Two main general approaches available for the synthesis of nanometer materials are bottom-up and top-down techniques. Bottom-up method involves use of atoms or molecules as building blocks. Here, a complete structure is created, organic or inorganic by using atom to atom or molecule to molecule to form a arrangements in a functional form to give macroscopic systems.



Fig(ii) top-down, intermediate and bottom-up synthesis techniques for nanomaterials

In the design of novel advanced functional nanomaterials, the uniformity of the shape and size of the nanoparticles is a key issue. The development of soft inorganic chemistry processes like hydrothermal and sol-gel have given rise to the concept of organic-inorganic hybrids at the recent times. The low temperature processing characteristics of this process allow the chemical design of organic-inorganic hybrid materials through the incorporation of low molecular weight organic molecules with appropriate functionalities into inorganic materials. The temperatures are generally low so that the organic matter is not destroyed. Synthesis of nano materials can be achieved through a physical or chemical process involving solid, liquid or gases. Physical process generally use top-down approach in which nano particles are synthesized by decreasing the size of the constituents of the bulk material. Chemical process involves bottom-up technique controlling of cluster of atoms or molecules at a nanoscale. Wet chemical techniques are widely incorporated in the synthesis as this method offers several advantages over the conventional methods. Some of the benefits of this method are like, better control on the shape and size of the nanoparticles, cost effective, good reliability and agglomeration of the products can be alleviated by functionalization with different capping ligands. Following wet chemical methods have been successfully used for synthesis of different types of nanoparticles:

1. Solvothermal/hydrothermal
2. Sol-Gel

4.1.Hydrothermal/Solvothermal

“A chemical reaction carried out in a closed system in the presence of a solvent (aqueous and non-aqueous solution) at a temperature higher than that of the boiling point of the solvent is called hydrothermal or solvothermal.” Nanomaterials or micro particles of different morphology can be obtained by using solvothermal techniques. A solvothermal process involves high pressures. Depending on the target material to be obtained, the temperature of the reaction is selected. With different aims and objectives, hydrothermal technique is employed to obtain the desired nanomaterials. (Hosaka M,1991) synthesized gem stones and studied their characteristics. (Habashi F,2005) used this technique for mineral extraction from leaching. Using hydrothermal method (Gogotsi Y.G et al,1994) developed carbon thin films on the substrate of carbides. Well defined, fine particles in size and morphology of oxides and chalcogenides were synthesized by employing this technique (Rajamathi M et al, 2002). There are number of factors that control the solvothermal processes like chemical and thermodynamical. Solvothermal reactions are mainly characterized by different chemical parameters (nature of the reagents and of the solvent) and thermodynamical parameters (as temperature, pressure, etc.).

4.2 Sol Gel

A ‘sol’ is a dispersed system that consists either of solids or discrete “globules” or oligomers in the form of chains in a dispersion medium. The medium can be any other liquid or the universal solvent i.e. water. A gel is a stiff mass of a continuous phase, similar to a viscous liquid. The sol can be prepared by controlled hydrolysis and poly condensation reactions of alkoxides, which then form the network of the resultant glasses. The method is based on the phase transformation of a sol obtained from metallic alkoxides or organo metallic precursors. The advantages of the sol-gel method are its versatility and the possibility to obtain high purity materials, whose composition is perfectly controlled.

Sol gel technique offers two main advantages i.e., it can produce compositions that cannot be created with conventional methods and secondly, the mixing level of the solution is retained in the final product, up to the molecular scale. The process is carried at low temperatures using inorganic precursors to give ceramics and glasses of better quality, homogeneity and purity than other methods carried at higher temperatures. As the process shows a promising potential in the fabrication of wide variety of novel nonmaterial that are applicable in different fields as electrosensors, biosensors, catalysts, biodetectors, etc., it has become the center of interdisciplinary research. Sol gel method offers the benefit of controlling the mechanism and kinetics of the proceeding

chemical reactions at each step hence a modification at single stage can affect the final structure of the materials, (Dimitriev Y et al, 2008). Besides, the sol-gel process is undoubtedly the simplest and the cheapest one.

V CONCLUSIONS

Researchers all over the world are in search of new innovative, reliable and low cost techniques in the synthesis of novel nanomaterials because of their outstanding properties in comparison to their bulk counterparts. These materials are applicable in different sensors as photoluminescence sensor, electrochemical sensor, electronic sensor, etc. Owing to their smaller size and biocompatibility, non toxic nano materials find space in the detection of cancerous tissues, as sensors in detection of tumours and also in the treatment of it. There is wide range of applications of these materials in almost all the branches of engineering technology. However the current synthesis techniques doesnot allow controlling the structure of the materials at atomic level hence there is certain limitation related to the synthesis accuracy. But the research and innovative methods are still going on hence one can expect better applicability of these materials.

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