SYNTHESIS AND CHARACTERIZATION OF NANO MATERIALS

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ABSTRACT

Engineered nanomaterials are intentionally designed and created with physical properties tailored to meet the needs of specific applications. Non- engineered nanomaterials, on the other hand, are unintentionally generated or naturally produced, such as atmospheric nanoparticles created during combustion. N anomaterials deal with very f ine structures: a nanometer is a billionth of a meter. This indeed allows us to think in both the ' bottom up' or the ' top down' approaches to synthesize nanomaterials, i . e. either to assemble atoms together or to disassemble (break, or dissociate) bulk solids into finer pieces until they are constituted of only a few atoms. Nanomaterials are materials that show promising chemical and physical properties and have various important applications. In this project we have worked on the synthesis, characterization, and applications of nanomaterials. Nanomaterials can be synthesized by using different synthetic techniques. The formation, s tructure, s ize, surface morphology, thermal stability, and surface area of the s ynthesized nanomaterials can be characterized by using different characterization t echniques such as FT- IR, XRD, SEM, TEM, UV-Vis and EDS. Nanomaterials are ver y interesting since they possess characteristics which are connections between bulk material and atomic s t ructures. Synthesis and characterization of nanomaterials can be addressed as a bridge between bulk material behaviors and molecular characteristics. Nanomaterials have size and shape dependent properties which make them totally different from bulk materials.

Keyword : - *Nonmaterial' s, surface, Zero, Classification, wires, and rods etc.*

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1. TYPES OF NANOMATERIALS

Nonmaterial' s can be of various types depending upon the basis of classification. While nonmaterial' s are important in a diverse set of f ields, they can be classified as one of two types: Engineered or Non- engineered. Engineered nanomaterials are intentionally designed and created with physical properties tailored to meet the needs of specific applications. Non-engineered nanomaterials, on the other hand, are unintentionally generated or naturally produced, such as atmospheric nanoparticles created during combustion.[7]
Nanomaterials have extremely small s ize which having at least one dimension 100 nm or less. Nanomaterials can be nanoscale in one dimension (e. g., surface f i lms), two dimensions (e. g., s t rands or f ibers), or three dimensions (e. g., particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and i r regular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. According to Siegel, Nanostructured materials are classified as Zero dimensional, one dimensional, two dimensional, three dimensional nanostructures.

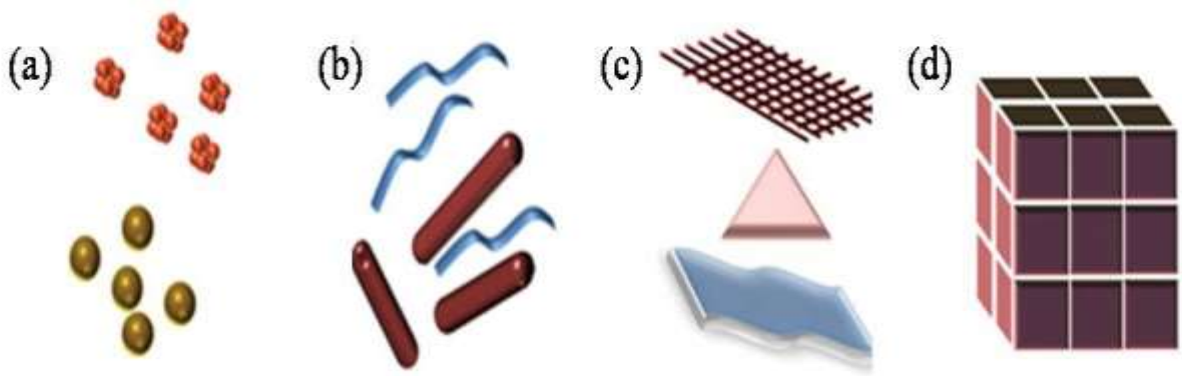

Fig 1.1 Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

1)) Zero dimensional nanostructures, also named as nanoparticles, include s ingle crystal, polycr ystalline and amorphous particles with all possible morphologies, such as spheres, cubes and platelets. In general, the characteristic dimension of the particles i s one hundred nanometres or bellow. I f the nanoparticles are single cr ystalline, they are often referred to as nanocrystals. When the characteristic dimension of the nanoparticles i s sufficiently small and quantum effects are observed, quantum dot i s the common term used to describe such nanoparticles.

2)) One dimensional nanostructures have been called by a variet y of names including: whiskers, f ibres or f ibrils, nanowires and nanorods. In many cases, nanotubules and nanocables are also considered one dimensional structures. Although whiskers and nanorods are in general considered to have smaller l ength to thickness ratio (aspect ratio) than f ibres and nanowires, the definition is a l i t t l e arbitrary. Therefore, nanostructures with large aspect ratio are addressed as " nanofibres".

3)) Thin films are two dimensional nanostructures, another important nanostructure, and have been a subject of intensive study for almost a century, and many methods have been developed and improved.

4)) Three dimensional nanostructures include powders, f ibrous, multilayer and polycrystalline materials in which the 0D, 1 D and 2 D s t ructural elements are in close contact with each other and form interfaces. An important type of three- dimensional nanostructured materials is a compact or consolidated (bulk) polycr ystal with nanosize grains, whose entire volume is f i l l ed with those nanograins.[7]

Semiconductor nanomaterials is one of the richest class of nanomaterials. Examples of semiconductor nanomaterials are Cu S, Pb S, Ga As, Ga P, etc. Semiconductor has governed a s ignificant role in progressing research in nanoscience and nanotechnology, which results in novel classes of semiconductor materials. Usually in conductors current i s considered to f low due to electrons only but here in semconductor materials i t i s caused by both electron as well as hole movements. Semiconductor materials do not belong onl y to crystal solids but are of the nature of amorphous and l iquids too. A pure semiconductor is called as intrinsic semiconductor. The electronic properties and the conductivity of semiconductor can be changed in a controlled manner by addinig very small quantities of other materials called dopants. The f ield i s expected to open new avenues for science and technology. Preparation and applications of the metal oxide nanostructures is one of the classes belonging to Semiconducting nanomaterials and nanotechnology. Metal oxide proved to be ver y promising for a variet y of practical applications. The good thermal and chemical stability of these inorganic materials enable them to be widely used. Metal oxides play a very important role in many areas of chemistry, ph ysics, and materials science. Examples of metal oxide nanomaterials are ZnO, CuO, NiO, Ga_2O_3, Al_2O_3, etc.[8]

2. . NANOMATERIAL SYNTHESIS

Nanomaterials deal with very fine structures: a nanometer is a billionth of a meter. This indeed allows us to think in both the ' bottom up' or the ' top down' approaches (Fig. 1 . 3) to synthesize nanomaterials, i . e. either to assemble atoms together or to disassemble (break, or dissociate) bulk solids into finer pieces until they are constituted of only a few atoms.[6]

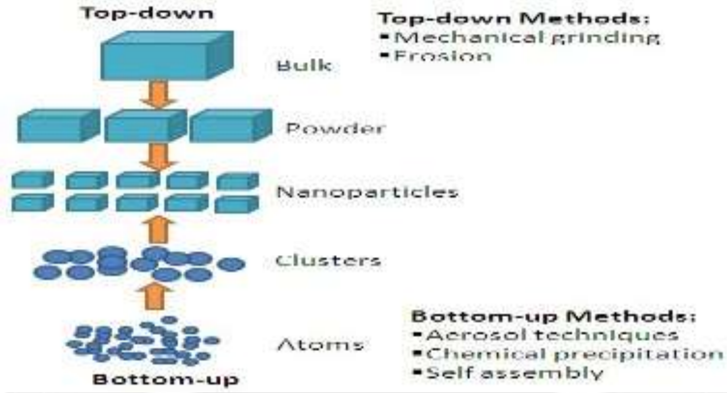

Fig 1.2 Schematic illustration of the preparative methods of nanoparticles

The bottom- up approach of nanomaterials synthesis first forms the nanostructured building blocks (nanoparticles) and then assembles these into the final material. An example of this approach is the formation of powder components through aerosol and sol- gel techniques and then the compaction of the components into the final material. In the top- down approach, nanoscale devices are created by using larger, externally controlled devices to direct their assembly. The top- down approach often uses the traditional workshop or microfabrication methods in which externally controlled tools are used to cut, mill and shape materials into the desired shape and order. Attrition and milling for making nanoparticles are typical top- down processes. An approach where both these techniques are employed is known as a hybrid approach. Lithography is an example in which the growth of thin film is a bottom- up method whereas itching is a top- down method. The bottom- up approach generally produces nanostructures with fewer defects as compared to the nanostructures produced by the top- down approach. The main driving force behind the bottom- up approach is the reduction in Gibbs free energy. Therefore, the materials produced are close to their equilibrium state. In top- down techniques such as lithography, significant crystallographic defects can be introduced to the processed patterns. For example, nanowires made by lithography are not smooth and can contain a lot of impurities and structural defects on its surface. Since the surface area per unit volume is very large for the nanomaterials, these defects can affect the surface properties, e. g., surface imperfections may cause reduced conductivity and excessive generation of heat would result. In spite of the defects, the top- down approach plays an important role in the synthesis and fabrication of nanomaterials. The present state of nanoscience can be viewed as an amalgamation of bottom- up chemistry and top- down engineering techniques.[7]

There are two broad categories of nanomaterial synthesis:

1)) Vapor phase growth process and 2) Solution phase growth process. Vapor phase growth process can be either vapor- liquid- solid (VLS) process or vapor- solid (VS) process. The various synthesis techniques of nanomaterials are:

a) Vapor Phase growth Process
b) Thermal Evaporation Process
c) Pulsed Laser deposition Process
d) Sputtering Process
e) Metal- organic chemical vapor deposition (MOCVD) process
f) Cyclic feeding chemical vapor deposition (CFCVD) process
g) Spark discharge generation
h) Solution Phase Growth Process
i) Sol- gel deposition process
j) Electrochemical deposition process k)
Sonochemcial method

l) Chemical precipitation method m)
Hydrothermal growth process

3. NANOMATERIAL AS CATALYSTS

Catal ysts are species that are capable of directing and accelerating thermodynamically feasible reactions while remaining unaltered at the end of the reaction. The performance of a catalyst is largel y measured in terms of i t s effects on the reaction kinetics. Catalysts may be used primaril y to give high reaction selectivity rather than high conversion rate. Some catalysts because of their selective nature are used when we want a particular reaction product. Catal ysis is described as homogeneous when the catal yst i s soluble in the reaction medium and heterogeneous when the catalyst exists in a phase distinctly different from the reaction phase of the reaction medium. Almost all homogeneous catal ytic processes are l iquid phase and operate at moderate temperatures (< 150 ° C) and pressures (< 20 atm). Corrosion of reaction vessels by catalyst solutions, and difficult and expensive separation processes are common problems. Traditionall y, the most commonly employed homogeneous catalysts are inexpensive mineral acids, notably H_2SO_4, and bases such as KOH in aqueous solution. The chemistry and the associated technology i s well established and to a large extent well understood.[24]

More recently, there have been significant scientific and technological innovations through the use of heterogeneous catalysis, involving a solid catalyst that i s brought into contact with a gaseous phase or l iquid phase reactant medium in which the catalyst is insoluble. This has led to the expression " contact catalysis" sometimes used as an alternative designation for heterogeneous catal ysis. Higher surface area available with the Nanomaterial counterparts, nano- catal ysts tend to have exceptional surface activity. For example, reaction rate at nano-aluminum can go so high, that i t is utilized as a solid- fuel in rocket propulsion, whereas the bulk aluminum i s widely used in utensils. Nano- aluminum becomes highly reactive and supplies the required thrust to send off pay loads in space. Similarly, catalysts assisting or retarding the reaction rates are dependent on the surface activit y, and can ver y well be utilized in manipulating the rate controlling step.[24]

Metal oxides have wide industrial applications in catalysis f i eld by serving as active compositions or as supports. There are a lot of opportunities in modifying nanostructures to improve substantiall y the catalytic activity and selectivity of existing catalysts. Such endeavours are particularly f ruitful when a fundamental approach i s adopted, whereb y the design of the catal yst composition and microstructure i s targeted towards solving the bottleneck of specific reaction.[24]

4. METAL OXIDE SUPPORTED AU CATALYSTS

I t is noted that the metal oxide supported noble metal nanoparticles i s a class of ver y important catalysts. Numerous investigations using supported gold catalysts on metal oxides were carried out during last two decades s ince the pioneer work by Haruta et al. Before this, gold was regarded as catalytic inactive. I t becomes an incredible active material when subdivided into nanoscale. Catalysis by supported gold catalysts has rapidly become a hot topic in chemistry, and has found widel y applications in reactions such as selective oxidation of alcohols, oxidation of CO, reduction of selective reduction of nitro groups. I t i s generally agreed that the catalytic activity of gold catalysts depends on the size of the gold particles s ince the Au catalyst is totally inactive when the particle size i s larger than ~ 8 nm in diameter. Developing practical methods for the preparation of supported- Au catalysts with good control of Au particle s ize and s tability s t i l l remains a challenge. Various methods such as deposition- precipitation (DP), co- precipitation (CP), and impregnation (IP) have been developed to prepare controllable gold particles uniforml y supported on substrates.

A support with large specific surface area allows well dispersion of Au particles on the support surface. Nanofibres and nanotubes are suitable to serve as supports because of their large surface area. Zhu et al. loaded gold particle on TiO_2 (anatase) nanotubes and nanofibres using deposition- precipitation (DP) method, in which small gold particles and high catalytic activity for CO oxidation are obtained as a result.[24]

Moreover, the nature of oxides is also of great importance as the activities are related to i t . Metal oxides, such as ZrO_2, Al_2O_3, TiO_2 and SiO_2 are widely used catalyst supports. Oxides

supported gold catalysts are active towards many reactions, including oxidation of CO, selective oxidation (alkenes, alcohols and even alkanes), water- gas shift, and removal of atmosphere pollutants (NO_x , VOCs).
The supports used are classified as reproducible and i rreproducible supports.[24]

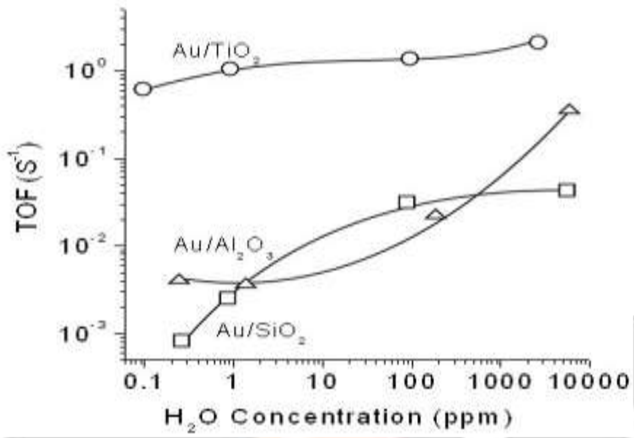

Fig 1.1. Turnover frequencies (TOF) per surface gold atom at 273 K for CO oxidation over a) Au/TiO_2, b) Au/Al_2O_3 and c) Au/SiO_2 as a function of moisture concentration.

The gold samples loaded on reproducible samples show high activity toward CO oxidation. An interesting fact found on supported gold catalysts is that moisture plays an essential role in low- temperature CO oxidation, by contributing to the formation and regeneration of the surface active sites. Haruta et al. reported that this effect of the moisture is dependent on the catalyst support. As is shown in Figure 4 . 5 , the enhancement of activity with the increasing moisture concentration was observed on the different types of supports involving insulating Al_2O_3 and SiO_2 as well as semiconducting TiO_2 . However, so far a detailed mechanism involving the role of moisture and that of catalyst supports have not been well addressed. In a recent coupled TG- FTIR study on Au/ α- Fe_2O_3 catalysts for CO oxidation, it was proven that at low temperatures, small Au nanoparticles cannot activate the oxygen of the support lattice directly, and thus the lattice oxygen doesn’ t participate in the reaction; instead, it is molecular oxygen species that are responsible for the low temperature CO oxidation. Meanwhile, there are a lot of reports showing that the activation of molecular O_2 occurs mainly on the catalyst support, and are probably related to the surface OH groups and to the surface O- vacancy concentration and distribution. On the other hand, the extensive studies on the photocatalytic water splitting reaction on TiO_2 surface have shown that water molecules can either dissociate at oxygen vacancies (defects) on the TiO_2 surface, yielding surface OH groups, or physically adsorb on these sites. Theoretical studies have revealed that surface OH- groups on TiO_2 can facilitate adsorption and activation of molecular oxygen. Based on the above knowledge, a logical hypothesis could be proposed, in which the defect sites on TiO_2 surface may play a key role in the catalytic oxidations using molecular O_2 as oxidant. The enhanced O_2 and H_2O adsorption due to these defects results in increased activity. Therefore, a systematic study of the surface structure and the activity are necessary to explain this phenomenon.[24]

5. CONCLUSIONS

Nanomaterials are materials that show promising chemical and physical properties and have various important applications. In this project we have worked on the synthesis, characterization, and applications of nanomaterials. Nanomaterials can be synthesized by using different synthetic techniques. The formation, structure, size, surface morphology, thermal stability, and surface area of the synthesized nanomaterials can be characterized by using different characterization techniques such as FT- IR, XRD, SEM, TEM, UV- Vis and EDS. Nanomaterials are very interesting since they possess characteristics which are connections between bulk material and atomic structures. Synthesis and characterization of nanomaterials can be addressed as a bridge between bulk material behaviors and molecular characteristics. Nanomaterials have size and shape dependent properties which make them totally different f rom bulk materials. Bulk materials have f ixed properties regardless of their s ize but nanomaterials are totally different. Synthesis of nanomaterials can be done by twoapproaches either by top- down approach or bottom- up approach. In case of top- down approach we t ake a bulk material and by i tching or milling reduce i t to the s ize of nanoscale. In case of bottom- up approach we start f rom atoms or molecules and assemble them until they reach the size of nanoscale. Recently there have been many developments in the preparation and use of nanomaterials, more specifically i solated nanoparticles of s imple and compound oxides. The properties and applications of nanomaterials are determined by the morphology and structure. Considerable efforts have been focused on the synthesis of novel nanostructures with tailored morphology. The ability of shape control over the crystals is s t i l l rather l imited due to a lack in understanding the principles and mechanics about the formation of multi dimensional nanostructures. The synthetic methods have many disadvantages and onl y a ver y few can be considered as " user- f r iendly". Most of the methods require high temperature and solid templates. Majority of the raw materials used are extremely toxic, unstable and expensive. Some methods require sophisticated equipments and inert atmospheres. Also the reactions are not easy to control or to reproduce and have no diversit y. Many of them generate a lot of pollutants harmful to the environment. Hence alternative routes should include less expensive and simpler approaches with diversity, which are environmentally benign. I t i s important to consider the consumption of raw materials and energy and the generation of waste when a s ynthesis procedure i s designed whether i t i s an original one or an alternative approach.

As a prelude to the project a detailed l i terature surve y on nanomaterials was done and is presented in the f i rst chapter. This chapter covers the introduction about synthesis, characterization, properties, applications, and importance of nanomaterials. The second chapter is a specific review on synthesis t echniques of nanomaterials.

This chapter describes the synthesis of nanomaterials by different methods. The methods include Hydrothermal method, Vapor phase growth process, thermal evaporation process, Pulsed laser deposition process and many more. The third chapter describes the characterization of nanomaterials by various techniques. The methods discussed in this chapter are SEM, TEM, XRD, EDS, RS, FTIR, and UV- Vis. The fourth chapter deals with the applications of nanomaterials. The few important applications of nanomaterials which are discussed in this chapter include Microbial fuel cell in which carbon nano tubes are used, Next generation computer chips, Sensors, Catalysts and Solar cells.

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