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FABRICATION OF NANOMATERIALS BY TOP-DOWN AND BOTTOM-UP APPROACHES – AN OVERVIEW

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ABSTRACT

Nanomaterials fabrication methods can be classified according to whether their assembly followed either the so called *bottom-up* approach or the *top-down* approach. The bottom-up approach is one where smaller components of atomic or molecular dimensions self-assemble together, according to a natural physical principle or an externally applied driving force, to give rise to larger and more organized systems. The top-down approach is where a process starts from a large piece and subsequently uses finer and finer tools for creating correspondingly smaller structures. These two approaches for fabricating nanomaterials are briefly reviewed in this paper.

The paper is an attempt to illustrate the main principles characterizing the two approaches to nanotechnology. On the top-down side, we consider the description of radiation and non-radiation based lithography methods used for fabricating electronic nano-devices; on the bottom-up side we refer to the self-assembly methodology to fabricate polymer nanostructures.

1. INTRODUCTION

Nanotechnology has been steadily receiving significant attention during the past decades both in scientific and engineering communities as well as in popular media. Nanometer-scale materials or 'nanomaterials' often have distinctly different physical and chemical properties in comparison to their bulk form. Indeed several size-dependant phenomena makes nanomaterials attractive in terms of potential applicability compared to their bulk form, justifying the importance and attention such research is receiving. Methods of obtaining nanomaterials vary and mostly depend on the material, its morphology and also the targeted applications. [1-5]. Currently physical techniques are usually limited to specialized vapor deposition techniques for obtaining epitaxial deposition of thin layers and clusters of materials with precision down to atomic layers on various substrates. Other techniques extensively involve solution chemistry and are favored when synthesis of large quantities of nanomaterials at relatively lower costs is required.[6].

In the past decades chemical routes for nanomaterials fabrication have matured and there is a very good control over the size, shape and thus the properties of nanomaterials. Applications of nanomaterials cover a wide range of fields including bio-medicine, electronics, Optoelectronics, water purification, automobile industry etc. Traditionally nanomaterials investigated for (opto/)electronic applications were fabricated by variations of vapor deposition techniques.

Various methods used for fabrication of nanomaterials are shown below in Fig. 1.

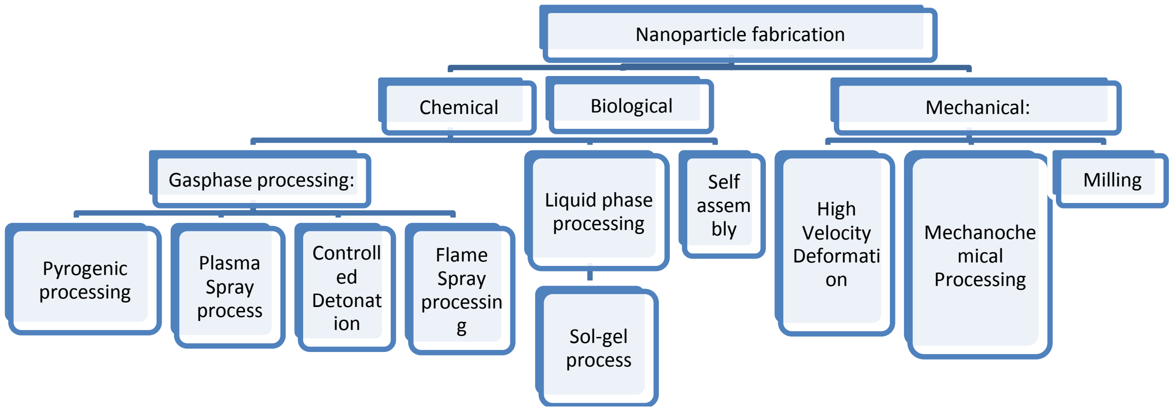

Fig. 1: Fabrication of nanomaterials

1.1 Overview of the two methods:-

The focus of this paper is to investigate the fabrication of nanomaterials by using various techniques and to evaluate their merits and demerits. Fig. 2 shows the two different approaches used for synthesis of nanomaterials.

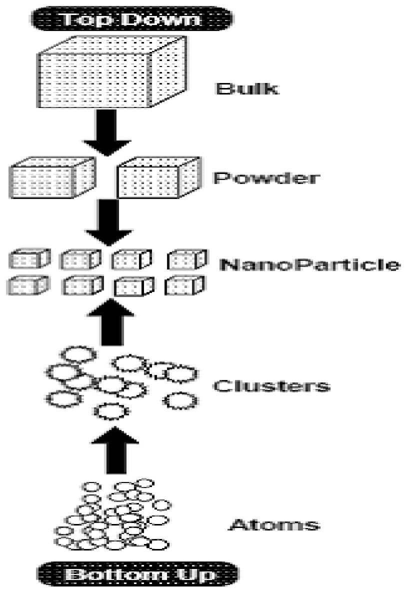

Fig. 2: Top down and bottoms up approach.

1.2 Top-Down Methods :

Mechanicanosynthetic Methods :- Mechanical methods offer the least expensive ways to produce nanomaterials in bulk. Ball milling is perhaps the simplest of them all. Ball milling produces nanomaterials by mechanical attrition in which kinetic energy from a grinding medium is transferred to a material undergoing reduction. *Compaction and consolidation* is an industrial scale process wherein nanomaterials are "put back together" to form materials with enhanced properties. Metallic alloys can be made this way. Many top-down mechanical methods are utilized by industry.

Thermal methods form a nebulous category and we try and focus on those that provide heat to a fabrication process. Of these, *electrospinning* is a means to form nanothread materials. *High energy methods* are those that require an excessive input of energy– whether in the form of heat, electricity or solar energy. *Arc discharge* was the first controlled means of making carbon nanotubes. *Laser ablation* and *solar flux* also work well. The problem is control of quality and potential upscale. We include *plasma methods* in this category. Plasmas are created in high-energy situations (high potential bias, etc.). The problem with this and other high-energy methods is upscale potential– with the possible exception of solar flux methods as sunlight is easily available. Top-down *chemical fabrication* methods are always easy to upscale and many, such as *anodizing*, are widespread industrial processes. *Lithographic methods*, as we all know quite well, although energy intensive and requiring expensive equipment and facilities, are top-down methods capable of producing for the most part micron-sized features. Lithography is the means of making printed circuits and computer boards for several decades now. The push to miniaturize in the future is a costly venture as more powerful sources (high energy electron beams and shorter wavelength sources), support equipment and facilities are required. *Nanoimprint lithography* (NIL) is lithography but not according to typical standards. It is more like *template synthesis*. A template material is made first and then stamped into a soft polymeric material to form a pattern. The template stamp is formed by top-down method as is the stamped material. Nanosphere lithography utilizes latex spheres that form a templated matric. So, we can call these techniques template process as well.

1.3 Bottom-Up Methods :

Bottom-up methods start with atoms or molecules to form nanomaterials. *Chemical vapor deposition* is a gas-phase process by which reactive constituents react over a catalyst or pre-templated surface to form nanostructure materials. The economical synthesis of carbon nanotubes is by CVD. Precursors in the form of methane or acetylene or other carbon source gases are passed over Co, Fe or Ni catalyst. Once decomposed into carbon, nanotubes are formed by the catalyst particle. *Atomic layer deposition* is an industrial process that is capable of coating any material, regardless of size, with a monolayer or more of a thin film. *Molecular beam epitaxy* and *MOCVD* are other industrialized processes that are considered to be bottom-up.

Liquid phase methods are also numerous. It is within the liquid phase that all of *self-assembly* and synthesis occurs. Liquid phase methods are upscalable and low cost.*Electrodeposition* and *electroless deposition* are very simple ways to make nanomaterials (dots, clusters, colloids, rods, wires, thin films). *Anodizing* aluminium to make a porous oxide structure is a simple way to make nanomaterials. The porous structure is a nanomaterial as well as any material synthesized within. Porous membranes are in many ways the ultimate template. A new generation of nano bottom-up methods have made the scene. Many of the new methods are both inexpensive and offer high throughput. Disadvantages include establishment of long-range order. The new methods include nanolithography (dip pen method) and nanosphere lithography

2. Sol-gel method:-

The sol-gel process is a versatile soft chemical process, widely used for synthesizing metal oxides, ceramic and glass materials. The ceramic and glass materials can be obtained in a wide variety of forms: ultra-fine or spherical shaped powders, thin film coatings, ceramic fibres, microporous inorganic membranes.[7,8,9].

Sol-gel method normally involves the use of metal alkoxides or organometallic inorganic salts as precursors. In this process, the precursor’s undergoes a series of hydrolysis and polycondensation reaction to form a colloidal suspension or a sol. The sol-gel process involves the transition of a system from a liquid “sol” (mostly colloidal) into a solid “gel” phase Then drying of the gel followed by calcination at different temperatures to obtain the metal oxide nanopowder. In sol-gel method it is possible to control the shape, morphology and textual properties of the final materials. In contrast to high-temperature processes, Sol-gel method has large advantages such as possibility of obtaining metastable materials, achieving superior purity and compositional homogeneity of the products at moderate temperature. Furthermore, this process also influences the particle morphology during the chemical transformation of the molecular precursor to the final oxidic network. Various research groups have reported previously on synthesis of iron oxide and alumina nanomaterials using sol-gel method. An overview of the sol-gel process is illustrated in Fig. 3.

This technique offers many advantages including the low processing temperature, the ability to control the composition on molecular scale and the porosity to obtain high surface area materials, the homogeneity of the final product up to atomic scale. Moreover, it is possible to synthesize complex composition materials, to form higher purity products through the use of high purity reagents.

The sol-gel process allows obtaining high quality films up to micron thickness, difficult to obtain using the physical deposition techniques. Moreover, it is possible to synthesize complex composition materials and to provide coatings over complex geometries.

The starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds, which by hydrolysis and polycondensation reactions form the sol. Further processing of the sol enables one to make ceramic materials in different forms. Thin films can be produced by spin-coating or dip-coating. When the sol is cast into a mould, a wet gel will form. By drying and heat-treatment, the gel is converted into dense ceramic or glass materials. If the liquid in a wet gel is removed under a supercritical condition, a highly porous and extremely low density aerogel material is obtained. As the viscosity of a sol is adjusted into a suitable viscosity range, ceramic fibres can be drawn from the sol. Ultra-fine and uniform ceramic powders are formed by precipitation, spray pyrolysis, or emulsion techniques.

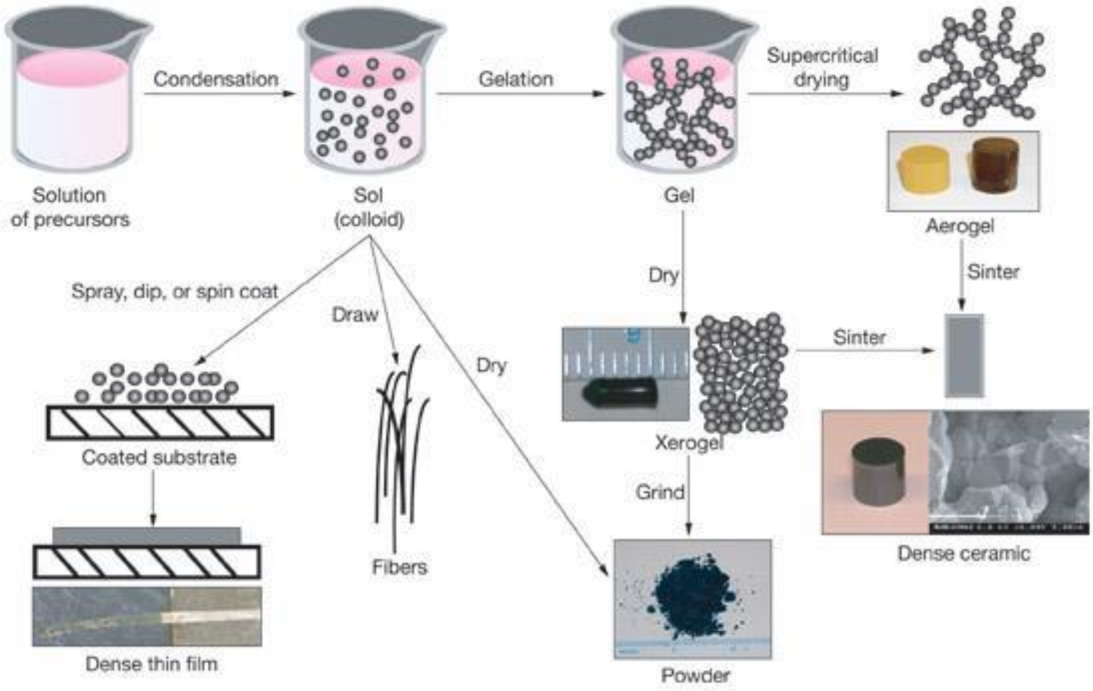

Fig. 3 Sol-Gel Method

3. Hydrothermal method:-

Hydrothermal synthesis is typically carried out in a pressurized vessel called an autoclave with the reaction in aqueous solution [10]. The temperature in the autoclave can be raised above the boiling point of water, reaching the pressure of vapour saturation. Hydrothermal synthesis is widely used for the preparation of metal oxide nanoparticles which can easily be obtained through hydrothermal treatment of peptized precipitates of a metal precursor with water [10, 11]. The hydrothermal method can be useful to control grain size, particle morphology, crystalline phase and surface chemistry through regulation of the solution composition, reaction temperature, pressure, solvent properties, additives and aging time.

4. Gas phase method:-

Gas phase methods are ideal for the production of thin films. Gas phase synthesis can be carried out chemically or physically. Chemical vapour deposition (CVD) is a widely used industrial technique that can coat large areas in a short space of time .During the procedure, metal oxide is formed from a chemical reaction or decomposition of a precursor in the gas phase [12, 13].

Physical vapour deposition (PVD) is another thin film deposition technique. The process is similar to chemical vapour deposition (CVD) except that the raw materials/precursors, i.e. the material that is going to be deposited starts out in solid form, whereas in CVD, the precursors are introduced to the reaction chamber in the gaseous state. The process proceeds atomistically and mostly involves no chemical reactions. Various methods have been developed for the removal of growth species from the source or target. The thickness of the deposits can vary from angstroms to millimeters. In general, these methods can be divided into two groups: evaporation and sputtering. In evaporation, the growth species are removed from the source by thermal means. In sputtering, atoms or molecules are dislodged from solid target through impact of gaseous ions (plasma) [14].

5. Conclusion : The paper describes various methods used for synthesis of nanomaterials .The advantages and disadvantages of these methods is also discussed.The most appropriate technique used for synthesis of nanomaterials basically depends on the material to be used for synthesis. Thus all synthesis techniques stand at par with each other.

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