



Investigation on the Synthesis and Chemical Properties of Nanomaterials

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Abstract

Nanoscience is assumed to have capability to change the efficiency of the current electronic and electrical devices. So nanotechnology is being developed to achieve the same. Various kinds of nanomaterials are being prepared such that they show tremendous properties at the nanoscale dimensions. Hence, it is worth studying about the synthesis of nanomaterials. The information that we present in this paper corresponds to a basic review on the synthesis and recent work done on nanomaterials. The distinctness of this review is that, the classification and major types of nanomaterials has been reported. The literature was collected through internet, from various available sources. The synthesis methods that have been discussed are sputtering, hydrothermal, microwave assisted, and electrochemical and chemical reduction methods.

Keywords: Materials; Chemical Engineering; Polymers; Nanomaterials;

1. Introduction

Nanoscience and nanotechnology are the terms that have got immense importance in research and development, across the world. There is no precise definition for the terms mentioned above. But the term nanotechnology, may be defined as, “a technical process that involves the preparation and characterization of materials either by reducing their size to nanoscale or using a nano dimensional material” [1]. Nanos, a Greek word, is actually the basis of nano. The Greek word nanos refer to low size or dwarf. The specialty of this particular field is that, it makes the physicists, chemists, solid state scientists, bio-scientists, material scientists, etc. to work together. Because, all the knowledge together contribute to the critical and cutting edge development of nanomaterials. In each and every part of science and technology, nano has got its own importance. Also, it is very important to understand the fundamental difference between nanoscience and nanotechnology [2].

1.1 Basic Terminology

Nanoscience: Investigation of arrangement of atoms and their basic properties at the nano level.

Nanotechnology: Developing the novel nanomaterials for devices, by manipulating the properties of nanomaterials at the atomic level.

Nanomaterial: A material with the size of less than 100 nanometers, for at least one dimension.

1.2 Classification of Nanomaterials

On the basis of size of nano level dimension i.e. < 100 nanometer, nanomaterials are categorized into different categories [1, 3] as shown in figure 1.

0-dimensional: The nanomaterials of all dimensions in nano level. Nanoparticles are the exception in this category.

1-dimensional: The nanomaterials of atleast one dimension in nano level. Other two dimensions will be in any other level. Examples include rods/wires/tubes of nano type.

2-dimensional: The nanomaterials of atleast two dimensions in nano level. Remaining dimension can be in any other level. Examples include films/layers/coatings of nano type.

3-dimensional: The nanomaterials of every

dimension with size of more than 100 nanometers. They are also called as bulky nanomaterials.

Examples include the stack of nanowires/nanorods/nanotubes, etc.

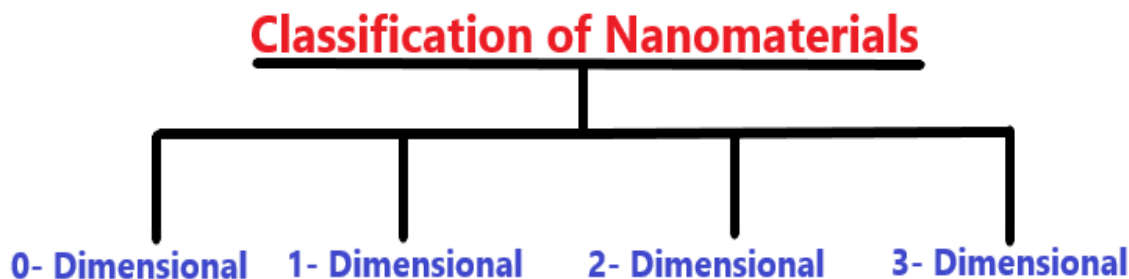


Fig. 1. Classification of Nanomaterials

1.3 Types of Nanomaterials

Based on the size and properties, nanomaterials can be categorized into different types as shown in figure 2.

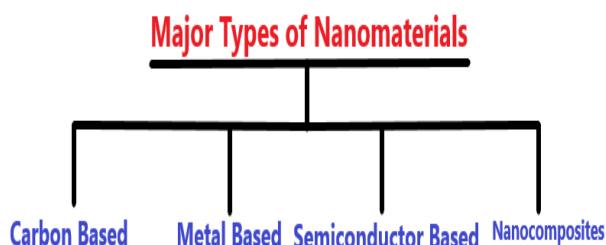


Fig. 2. Types of Nanomaterials

1.3.1 Carbon Nanomaterials

The nanomaterial that contain carbon as the one of its major component, is known as carbon based nanomaterial. Fullerenes and carbon nanotubes come under this category. The carbon nanotubes are incorporated in graphene sheets, and then sheets are rolled into a tube. The mechanical strength of these tubes is very much higher than steel. Fullerenes are the allotropes of carbon [2-3].

1.3.2 Metal Nanomaterials

Metal ions of +2 and +3 valency are used as the raw materials to prepare metal based nanoparticles. Preparation can be done through chemical synthesis or photochemical reaction. These metal ions are simplified into metal based nanoparticles, with the help of chemical reductants. The resulting nanoparticles contain large surface areas. Also, it is possible to prepare the new nanoparticles by combining more than two single nanoparticles [2-3].

1.3.3 Semiconductor based Nanomaterials

These kind of nanomaterials are extensively used in catalysis and some electrical applications. Some of the most widely investigated semiconductor nanomaterials are zinc sulphide (ZnS), ZnO, cadmium sulphide (CdS), cadmium selenide (CdSe), etc. They exhibit both metallic and non-metallic characteristics. Their properties can be finely tuned by using graphene [1].

1.3.4 Nanocomposite Materials

Nanocomposite is a solid substance that possess different phases where at least one phase size should be less than 100 nanometers. Nanocomposites can be further divided into ceramic/metal/polymer matrix composites. These materials has got significant importance in solar cells, and catalysis applications [1].

During the period of earlier decades, development of nanoscience and nanotechnology is exceptionally well, and it should be acknowledged. Distinct nanomaterials having 1-/2-/3-dimension(s) have been developed for the applications such as sensors (both electrical and bio), energy devices (storage and harvesting), catalytic applications, etc. [4-5]. In the technology of sensors and energy devices, nanomaterials of following characteristics are essentially required:

- Large porosity
- High surface energy
- Large surface area (specific surface area)

Because, the above properties hold a key role in the chemical processes occurring at surfaces and interfaces.

Transition metal oxide based nanomaterials exhibit the following features that are quite useful in the applications of electrochemistry [4].

- Catalytic activity
- Easy reinforcement in noble metal nanoparticles
- Large abundance
- High energy storage capacity
- Non-degradation for long time
- Low cost preparation
- Less toxic in nature

One of the most widely used nanomaterial is zinc oxide (ZnO), for several optical and piezoelectric applications. The bandgap of ZnO nanomaterial is nearly 3.37 eV. Nanodevices fabrication, became effective, with the use of ZnO nanomaterials in the form of spheres, rods, wires, arrays, etc. Because they show good piezoelectric, dielectric, and optical properties. The incorporation of transition metals, in ZnO nanostructures, resulted in tremendous electrical properties that could be useful for devices based on spin [6]. Also, the magnetic properties can be induced and altered with the introduction of cation of magnetic nature. For instance, chromium (Cr) doped ZnO exhibit the good magnetic properties. Cr is identified as one of the suitable modifier for ZnO, for following reasons [7-8]:

- Stable ferromagnetism in Cr-doped ZnO
- Low ionic radius than Zn
- Can easily replace Zn position
- Paramagnetic nature at high temperatures
- Antiferromagnetic nature at low temperatures

In this review paper, we present a basic understanding on the different preparation methods of nanomaterials, and the recent work done.

2. Discussion and Analysis

This section deals with the different preparation methods of nanomaterials of different kinds. Nanomaterials based on iridium metal, are quite useful in electrical/optical/catalytic applications. Hence, it is worth to have basic understanding on the preparation techniques (majority techniques are shown in figure 3) of Iridium based nanomaterials.

2.1 Preparation through Sputtering

Sputtering is one of the deposition technique that can be done physically i.e. sputtering is a physical vapor deposition technique. Under the subject of

an external and alternating electric field, the charged ions can be accelerated in a specified direction, through sputtering. When these charged ions collide with the target surface, atomization of surface takes place. Then the substrate surface will be sputtered with the neutral atoms, and hence, nano (particles or films) materials are said to be formed. Through this method, nanomaterials of relatively high melting points can be produced. Also, nanocomposites can produced with the usage of multiple sputtering targets. Moreover, the narrow size distribution of nanoparticles can be achieved through this method. Niwa and other researchers, realized an electrode made of Iridium/carbon nanocomposite [9]. It has been identified that the Iridium nanoparticles, which are dispersed on carbon nanofilm, exhibit a size of nearly 2 nanometers. Hence, the surface morphology can be altered/controlled with sputtering method.

2.2 Electrochemical Preparation

This method is based on redox reaction. Under the application of electric potential, the dissolved cations (metallic) get discharged, and become crystals on the cathode. With the control of voltage and current, the physical properties of nanomaterials can be disciplined. Through this method, single nanocrystalline materials can be produced on the single crystalline substrates. Using the iridium chloride (IrCl_3 -solution type) electrolyte, Iridium nanoparticles are electrochemically deposited. Deposition has been done on the film of carbon nanotube [10]. On average, the size of nanoparticle is approximately around 100 to 180 nanometers [10].

2.3 Hydrothermal Preparation

Under the elevated high temperature and pressure conditions, aqueous preparation of nanomaterials is generally referred as hydrothermal method. The preparation is done in a separate closed system where environment pollution is avoided. But still, observing the nanocrystals is quite difficult. Because, the reactions will not stop at high pressure. Nanoparticles based on Iridium, have been prepared through hydrothermal synthesis, in hydroxyethyl piperazineethanesulphonic acid. The temperature condition is 180 °C [11].

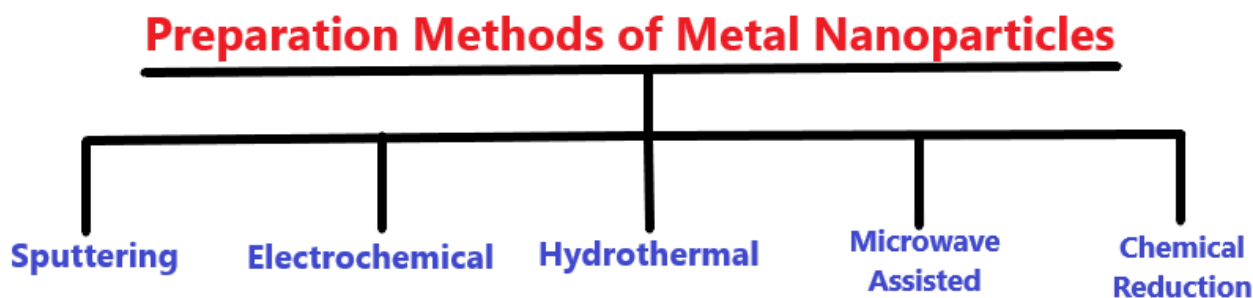


Fig. 3. Different Preparation Techniques of Metal Nanoparticles

2.4 Microwave assisted Preparation

It is one of the rapid technique to produce materials of nanoscale. In the span of very few minutes, nanomaterials can be prepared effectively and efficiently. The frequency (electromagnetic) ranges from 300 megahertz to 300 gigahertz. When the source of microwave is switched off, the reactions are stopped immediately. In the presence of argon atmosphere, iridium nanoparticles have been prepared through microwave assisted method. $\text{Ir}_6(\text{CO})_{16}$ and 1-butyl-3-methylimidazoliumtetrafluoroborate have been used as the precursor and reaction medium respectively. Uniformly distributed nanoparticles can be produced through this method.

2.5 Preparation through Chemical Reduction

It is one of the common technique to prepare the noble metal based nanoparticles. It is basically referred as a one-step method. Because, the reactants are chemically reduced in a single reactor, and still the desired compound can be achieved. No advance steps/procedure are/is required to separate and purify the intermediate substances. This method helps to produce the desired product in short time. Also, this method involves faster reaction rate.

In one of the work [12], iridium nanoparticles of size between 2.25 and 4.25 nanometers have been prepared by reducing chemically the lithium triethylborohydride. The following chemical substances have been utilized:

- Precursor: H_2IrCl_6
- Media: tetrahydrofuran
- Stabilizer: octadecanethiol

The as prepared nanoparticles were found to be crystalline in nature, and exhibit face centered cubic packing. The preparation has been done under ambient atmosphere. In another work [13], iridium nanoparticles of size nearly 3 nanometers

have been produced. The method of preparation is chemical reduction. Precursor used is IrCl_3 -ethylene glycol. The reduction was very mild, for obtaining the Iridium nanoparticles.

3. Literature on Nanomaterials/Nanoparticles

Recently [14], oxide of composition $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Co}_{0.12}\text{Ni}_{0.12}\text{O}_2$, has been prepared with distinct morphology. It means that the material synthesized is in the form of micro-sphere/rod, nanoplate and nanoparticle. It was found that the electrochemical properties were completely dependent on the morphology. Also, it was identified that microrods and nanoparticles exhibit high and low electrochemical properties respectively. The high electrochemical performance of microrods was may be due to the Lithium active ion sites originated from porosity of the structures. Also, the contact area between the electrolyte and electrode is very large.

Cobalt quantum dots exhibit good electrocatalytic features. In one of the work [15], cobalt nanocomposite has been prepared. The dimensional size is around 3.2 nanometers. It exhibit the properties that are shown in table 1.

Table.1. Properties of Cobalt Nanocomposite

S. No.	Material	Property	Value
1.	Cobalt Nanocomposite	Mass activity	1250 A/g
2.		Tafel slope	37 mV/dec
3.		Overpotential	0.37 V

Further, the nanocomposite also exhibit large dispersion, enhanced electron transfer mechanism and low dimension. Therefore, cobalt quantum dots distributed on reduced graphene oxide possess exceptional electrocatalytic properties.

Noble and stable metals like gold, silver, iridium, platinum, etc. possess tremendous properties like

electrical/optical/mechanical/magnetic properties. Especially at the nanoscale, they are said to be stable, active catalysts, and exhibit corrosion resistance [16-22]. As per the existing literature, the metal based nanoparticles can be used as the catalysts. The chemical characteristics of Iridium nanoparticles is mainly based on composition, and surface morphology. It was identified that, the surface enhanced Raman scattering was studied well for Iridium nanochains than Iridium nanoparticles [23-24].

Nanomaterials based on transition metals and noble metals show versatile chemical properties. Mudusu and others [25], have developed the Tinsulphide (SnS) nanomaterials with 1-dimension. The developed SnS nanostructures high single crystalline nature, and exhibit growth (1 0 0) plane direction. These nanostructures may be useful for making SnS based photovoltaics, batteries, etc. The SnS nanowires preparation is briefly shown, as follows:

- Catalyst: Sapphire, modified by gold
- Substrate: Silicon
- Technique: chemical vapour deposition
- Temperature range: 500-950 °C
- Growth Mechanism: Vapor → Liquid → Solid

Metal oxide nanoparticles of hollow spheres, have been prepared for the devices of electrochemical energy storage [26-29]. The nanoparticles include nickel oxide (NiO), tungsten oxide (WO₃), titanium oxide (TiO₂), etc. The size of NiO nanomaterials is nearly 28 nanometers. Through hydrothermal method, cobalt oxide (Co₃O₄) quantum dots have been prepared [30]. The crystallite size of these quantum dots is approximately 2 nanometers. Transition metal based nanostructures are found to be alternate candidates for platinum and other noble metal catalysts. On the titanium foil, Co₃O₄ nanomaterial is fully grown. It exhibit rod structure with a sharp tip. On average, the diameter of the rods is 400 nanometers and length is around 10 micrometers. These properties were altered when Co₃O₄ was doped with zinc (Zn⁺²).

From the existing literature, we found that, nanoparticles of size < 10 nanometers can be produced through hydrothermal method. But still, chemical reduction is an effective method to synthesize nanoparticles. Because, the

electrochemical properties are high for the nanomaterials prepared through chemical reduction. Cobalt quantum dots have been prepared by dispersing them in graphene nano sheets. The size of the prepared cobalt quantum dots is 3.2 nanometers, on average [15].

In one of the recent work [6], Cr doped ZnO nanomaterials have been prepared through hydrothermal route. The XRD analysis indicated that materials exhibit Wurtzite hexagonal structure. The space group of the structure is identified as P36mc. The magnetization values (x) at 27 °C and -263 °C are given in table 2.

Table.2. Magnetization Values of Cr doped ZnO, at Different Temperatures

S.No.	Material	X at 27 °C (emu/g)	X at -263 °C (emu/g)
1.	Zn _{0.97} Cr _{0.03} O	0.038	0.40
2.	Zn _{0.95} Cr _{0.05} O	0.055	0.90
3.	Zn _{0.93} Cr _{0.07} O	0.148	1.26

The magnitude of field (Coercive field (C)) required to make magnetization zero, and the values of remanant magnetization (M_r) is shown table 3 and table 4 respectively.

Table. 3. Magnetization Properties of Cr doped ZnO, at 100 K

S.No.	Material	C (Oe)	M _r (emu/g)
1.	Zn _{0.97} Cr _{0.03} O	45	0.00030
2.	Zn _{0.95} Cr _{0.05} O	126	0.0029
3.	Zn _{0.93} Cr _{0.07} O	137	0.0041

Table. 4. Magnetization Properties of Cr doped ZnO, at 10 K

S.No.	Material	C (Oe)	M _r (emu/g)
1.	Zn _{0.97} Cr _{0.03} O	49	0.00088
2.	Zn _{0.95} Cr _{0.05} O	230	0.0093
3.	Zn _{0.93} Cr _{0.07} O	261	0.0121

Conclusions

Based on the review that has been done in this work, the following conclusions and recommendations have been made:

- For electrochemical applications, nanomaterials based on transition metals are quite useful.
- Very low size (< 10 nm) nanomaterials can be prepared through the process of sputtering.
- Chemical reduction is mostly used to prepare noble metal based nanomaterials.

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