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ZINC OXIDE (ZNO) NANOPARTICLES: A VERSATILE METAL OXIDE FOR WASTEWATER TREATMENT

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ABSTRACT

In recent years, various metal oxide nanoparticles have gained significant importance due to their characteristic properties. Nano Zinc Oxide is the most important of all the metal oxide nanoparticles because of its varied properties. This paper focuses on methods of synthesis and characterization of ZnO nanoparticles, its properties, advantages over other materials of similar properties and applications in various fields. Also, various methods to stabilize the ZnO nanoparticles have been discussed.

Keywords: *ZnO nanoparticles, ZnO capping agents, Photoluminescence*

INTRODUCTION

The nanoparticle synthesis of controlled size, size distribution, shape and surface state recognized to be of prime importance as their properties are essential for successful application. Among all nanomaterials, nanoparticles of metal oxides are very attractive as their unique characteristics make them the most diverse class of materials with properties overing almost all aspects of solid-state physics, materials science and catalysis. Indeed, the crystal chemistry of metal oxides, i.e. the nature of the bonding, varies from highly ionic to covalent or metallic [1].

Besides catalysis, metal oxides represent therefore an essential constituent in technological applications such as magnetic storage, gas sensing, and energy conversion. As a wide band gap semiconductor, ZnO has found many applications such as transparent electrodes in solar cells, varistors, electro- and photo luminescence devices, chemical sensors, catalysts, UV absorbers and anti bacterials. Semiconductor nanoparticles have attracted much interest because of their size-dependent optical and electrical properties. The properties of nanoparticles depend on the particle size as well as several other factors: structures, shapes, and surface states of the particles. For these applications, the nanoparticles need to be dispersed homogenously in different matrices and a number of new synthesis strategies have been developed in order to prevent particle agglomeration and to increase the stability of ZnO nanoparticles dispersions [2]. The wide range of applications of ZnO nanoparticles is possible because of its three key advantages

- It is a semiconductor with a direct wide band gap of 3.37 eV and a large excitation binding energy of 60 MeV. It is an important functional oxide, exhibiting excellent photo catalytic activity.
- Because of its non-central symmetry, ZnO is piezoelectric, which is a key property in building electrochemical coupled sensors and transducers.
- Finally, ZnO is biosafe, biocompatible and can be used for biomedical applications without coating. With these three unique characteristics, ZnO is one of the most important nanomaterial in future research and applications.

Many methods have been proposed for the synthesis of ZnO nanoparticles [3-4]:

- Physical methods: Vapor Phase Oxidation, Thermal Vapor Transport and Condensation (TVTC) or Chemical Vapor Deposition (CVD)
- Chemical methods: Supercritical Precipitation, Sol–gel synthesis or Microemulsion.
- Ultrasound assisted synthesis of semiconductor ZnO nanoparticles.

Most of the above methods like Vapour phase oxidation, Chemical vapour deposition [CVD], Supercritical precipitation require very high temperatures for synthesis, long reaction time, use of toxic and highly sensitive compounds and employ extremely sophisticated apparatus. Additionally, in case of vapour phase oxidation, the ZnO nanoparticles undergo cluster interaction to form aggregates which is undesirable. Critical control over partial pressure of oxygen for Vapour phase deposition is required. Control over gas flow rates in Vapour phase deposition and CVD is equally essential. Compared to these techniques Sol-gel synthesis results in higher yield and is easier [2].

Ultrasound assisted Acoustic Cavitation technique is a recently developed simple, green, and cost-effective approach. It has evident advantages due to good compositional control, good homogeneity of liquid precursors, low equipment cost, and lower crystallization temperature. Thus, Sol-gel technique and Ultrasound assisted Acoustic Cavitation are the most preferred methods for synthesis of ZnO nanoparticles.

2.0 NANOPARTICLE SYNTHESIS TECHNIQUES [3-6]

2.1. Sol gel Synthesis

Sol-gel technique is an effective method for synthesis of nanoparticles with visible fluorescence at low cost. The ZnO nanoparticles resulting from sol-gel method show sharp and clear visible emission, which accounts for the fact that the ZnO nanoparticles have high concentration of surface defects, small diameter, amorphous in nature and well protected by ligands or shells.

The traditional sol–gel route of preparing ZnO nanoparticles involves hydrolysing zinc acetate in ethanol, which requires refluxing zinc acetate in absolute ethanol for 3 hrs, followed by reacting it with LiOH under

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sonication. The as-prepared ZnO nanoparticles are not very stable because the small acetate groups cannot protect the ZnO sufficiently. As a result, the emission color of the obtained colloids turns rapidly from blue to green within a few minutes and then slowly from green to yellow within several days.

Thus, another method used involves dissolving $Zn(Ac)_2.2H_2O$ and $LiOH.H_2O$ together in triethylene glycol (TEG) at room temperature in beakers by stirring. The concentration of zinc is fixed at 0.1M, while the molar ratio of [LiOH]:[Zn] is varied as 1, 1.5 and 2 respectively. The solutions are exposed to air and stirred for a month. For thermal analyses and IR spectrum measurements, excess ethyl acetate is added into each TEG solution to precipitate the white ZnO gel. The gel is washed with ethyl acetate and centrifuged, followed by drying in a vacuum oven at 100^0C.

In this technique the molar ratio of [LiOH]:[Zn] (designated as R), plays a key role in determining the emission colour and particle size of the nanoparticles. For R values between 0.1-10 ZnO colloids are transparent and quiet stable for at least a week. Also, for R< 0.5 the ZnO luminescence is rather weak, for R >1.8 ZnO nanoparticles do not precipitate but exhibit strong blue emission while for R >2 the solution turns gradually yellow, indicating a red shift and some unknown reactions.

2.2. Ultrasound Assisted Acoustic Cavitation Technique

During sonication, ultrasonic longitudinal waves are radiated through the reaction solution causing alternating high- and low-pressure regions in the liquid medium. Millions of microscopic bubbles form and grow in the low-pressure stage, and subsequently collapse in the high-pressure stage. Hot spots that are localized regions of extremely high temperatures, as high as 5000K, and pressures of upto 1800 atm can occur from the collapsing bubbles, and cooling rates can often exceed 1010 Ks^{-1} The energy released from this process, known as Cavitation, would lead to enhanced chemical reactivity and accelerated reaction rates.

This is a novel and very simple method to prepare extremely pure nanocrystallites of ZnO with hexagonal structure using aqueous solution of zinc acetate dehydrate in absolute ethanol as a capping agent with the help of ultrasound irradiation in normal laboratory conditions at room temperature (270^0C). Zinc acetate dehydrate, thiophenol and absolute ethanol are the precursors used. The proposed mechanism is as follows:

Zinc acetate can easily be dissolved in water and adding thiophenol solution would cap the dissolved zinc acetate colloids by the help of ultrasonic irradiation. The formation of the ZnO nanoparticles can be proposed employing the following thermal decomposition:

$Zn(CH_3COO)_2.$ $\longrightarrow$ $2H_2O$

$Zn(CH_3COO)_2 + 2H_2O$ (1)

$Zn(CH_3COO)ZnO + 3H_2O + 2C$ (2)

$C + O_2 \longrightarrow CO_2$ (3)

The sonication time is a key parameter to control the shape and morphology of the nanostructure. Increased sonication time, leads to deterioration of nanoparticles [4].

3.1. PHYSICAL MIXTURES OF POLYMERS AND ZNO NANOPARTICLES

Polymers like Polyvinylpyrrolidone (PVP), Polyaniline (PAni), Polyvinyl alcohol (PVA), Polyethyleneoxide (PEO), Polyethyleneglycol (PEG) have been used so far for formation of polymer nano-composites. However, this process resulted in decreased photoluminescence and increased UV emission. When ZnO nanoparticles are incorporated into an already luminescent polymer like Poly (phenylene vinylene) (PPV), a charge separation into electrons and holes arising from the PPV chains takes place at the polymer-nanoparticle interface. This phenomenon results into quenching of polymer fluorescence [8].

In nutshell, the various drawbacks associated with this process are:

- Many polymers are able to quench ZnO visible emission through passivating the ZnO nanoparticle surface
- Polymers such as PEO, PVA and PMMA cannot suppress ZnO nanoparticle aggregation effectively
- Some polymers such as PVP and PPV themselves have fluorescence so as to interfere with ZnO emission, resulting in undesirable effects.
- To overcome these difficulties various chemical modifications are employed to improve ZnO visible emission.

3.2. CHEMICAL HYBRIDS OF POLYMERS AND ZNO NANOPARTICLES [2-5]

- On the basis of structural differences, the chemically synthesized polymer–ZnO nanocomposites are divided into four types:
- The first type involves grafting of polymer on ZnO surface as independent organic ligand. It resembles a hair on head structure and hence the name. It is synthesized by hydrolyzation of zinc salts or ligand exchange. The two disadvantages associated with this type are:
  - ✓ Due to large volume of polymers, the degree of ligand exchange is low.
  - ✓ Exchanging the organic groups of the ZnO surfaces by polymer ligands often destroys the ZnO luminescence.
- The second structure resembles an olive with one core and a thin orbicular shell of crosslinked polymer ligand. It is synthesized strictly by ATRP initiated on nanoparticle surface. The polymeric ligands on ZnO surface are cross-linked by ATRP to form a tight shell around ZnO.
- The third structure resembles watermelon with a polymer forming a microsphere (100nm – 10nm) comprising of many ZnO nanoparticles inside. This structure is obtained by emulsion or solution polymer and occurs as a suspension in water.
- The fourth structure is obtained by Bulk polymerization. In this case the polymer

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is formed by bulk polymerization with the ZnO nanoparticles in the reaction medium. It is very large and can be cast into various forms.

- The method of preparation of polymer ZnO nanocomposites has profound effect on the final properties of ZnO. The surface state, dispersity, crystallinity and purity of ZnQD could be changed during preparation. So, the resulting polymer ZnO nanocomposites with the same compositions would exhibit quite different optical properties.

5. APPLICATIONS [7-8]

Sunscreen lotion

Nano-ZnO particles are transparent in the visible region of the spectrum. They act as physical filters against the UVB and especially UVA radiation of the sun. As these particles are very minute and crystalline in nature, they reflect the UV rays and hence act as sun-blocking agents for skin. Because of their small size, they dont get absorbed into the skin and are compatible with skin.

The high photoreactivity of nano-ZnO makes the safety of zinc oxide nanoparticles a controversial subject nowadays. However, a new method to cover the ZnO nanoparticles with special coating called as, Z-coat with dimethicone, improves the stability of them and helps to reduce their photoreactivity. So, ZnO nanoparticles are the most effective to use as UV blocking agents in Body Lotions than the other ingredients [7].

UV protection in textiles

Bioactive or antimicrobial and UV-protecting textiles are in great demand nowadays. The textiles coated with metal oxide nanoparticles is an approach to the production of highly active surfaces to have UV blocking, antimicrobial, water repellant and self-cleaning properties. Zinc oxide (ZnO) nanoparticles embedded in polymer matrices like soluble starch is a good functional nanostructure. When, clothing is treated with nano-ZnO its UV-protection ability as well as the antimicrobial properties get enhanced. This principle is nowadays majorly used in synthesis of textiles used in the medical field. The UV-blocking property of a fabric is enhanced with an ultraviolet absorber finish that absorbs ultraviolet radiation and blocks its transmission through fabric to the skin. Nano-ZnO has increased surface area and also has intense absorption in UV-region. It is more stable than other organic UV-blocking agents.

CONCLUSIONS

Over the past few years, ZnO nanoparticles of varied shapes like- nanorods, nanotubes, nanocombs, nanopropellers and nanoflowers- have been reported. Nano-ZnO of different shapes gives different properties. By merely changing the synthesis process and the capping agents, it is possible to manipulate the properties of ZnO nanoparticles. Its wide applications ranging from opto-electronic devices to sunscreen lotions make them exciting for future research and applications. Thus, the versatility of ZnO nanoparticles make them a promising host for advancements in various applications like light emitting diodes, varistors, dye-sensitized solar cells, electro and photo-luminescence devices, chemical sensors etc. in the near future.

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