Zinc Oxide (ZnO) Nanoparticles: A Versatile Metal Oxide

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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.

1. Introduction

The nanoparticle synthesis of controlled size, size distribution, shape and surface state is 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 covering 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.

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. The wide range of applications of ZnO nanoparticles is possible because of its three key advantages [3]:

1. 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.

2. Because of its non-central symmetry, ZnO is piezoelectric, which is a key property in building electrochemical coupled sensors and transducers.

3. 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:

1. **Physical methods**: Vapor Phase Oxidation, Thermal Vapor Transport and Condensation (TVTC) or Chemical Vapor Deposition (CVD)

2. **Chemical methods**: Supercritical Precipitation, Sol–gel synthesis or Microemulsion.

3. 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 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.

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.

1.1. Sol gel Synthesis[7], [8]

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 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 0.1 M, 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.
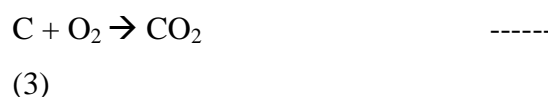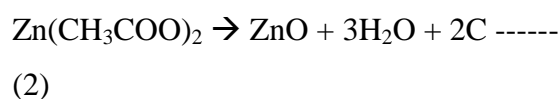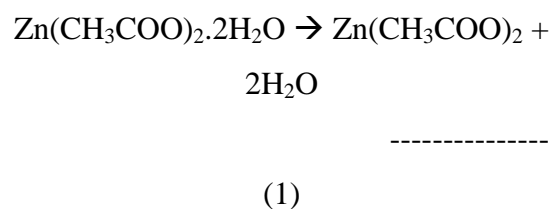
1.2. Ultrasound Assisted Acoustic Cavitation Technique

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 10^{10} 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 (27^0C). 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:

$$Zn(CH_3COO)_2.2H_2O \rightarrow Zn(CH_3COO)_2 + 2H_2O$$

--------------- (1)

$$Zn(CH_3COO)_2 \rightarrow ZnO + 3H_2O + 2C \text{ ------}$$ (2)

$$C + O_2 \rightarrow CO_2 \qquad\qquad \text{------}$$ (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].

2. Characterization techniques for ZnO nanoparticles

X-ray diffraction technique, Transmission electron microscopy, Scanning electron microscopy, UV-Vis spectroscopy,

Photoluminiscence measurements are the general characterization techniques for ZnO nanoparticles synthesized by any method.

2.1. X-Ray Diffraction

Figure 1 shows the XRD pattern of nano-ZnO[12]. All the peaks of the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) reflections can be indexed to the hexagonal wurtzite structure of ZnO. These match well with those in the JCPDS card (Joint Committee on Powder Diffraction Standards, Card No. 89-1397). The strong intensity and narrow width of ZnO diffraction peaks indicate high crystallinity.
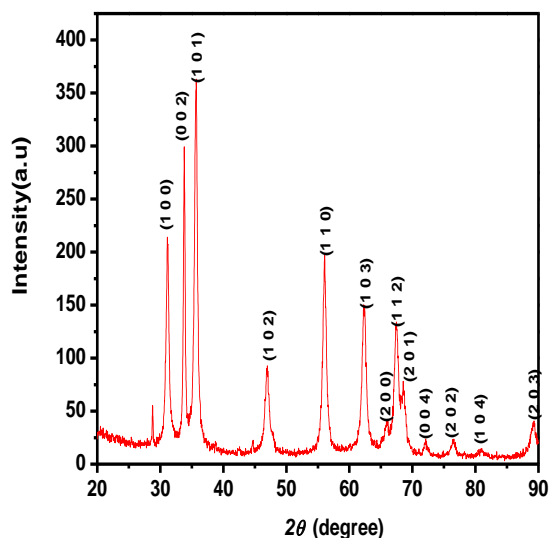

Figure 1[12]: XRD Pattern of ZnO nanoparticles

2.2. TEM Images

The TEM image of ZnO nanoparticles synthesized by Sol gel method is as seen in **Figure 2.** It illustrates that the three ZnO samples (R=1, 1.5, 2) have similar particle sizes (about 3-4 nm) but their dispersion degrees differ significantly. The ZnO (R = 2) particles are uniform and monodispersed, while ZnO (R = 1) particles aggregate heavily[7].
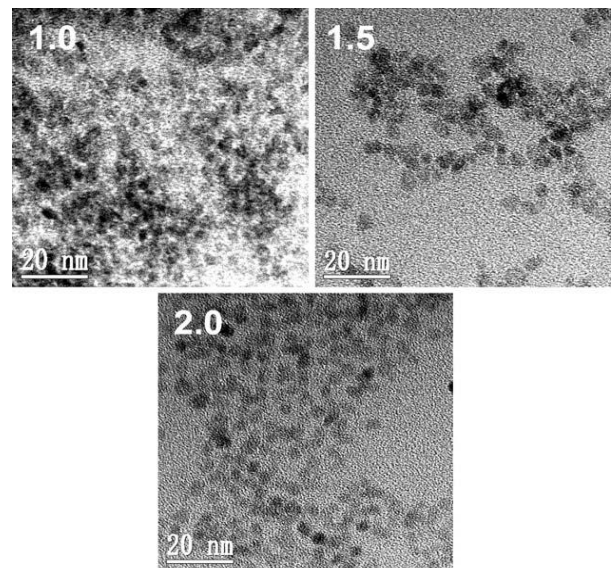

Figure 2[7]: TEM images of ZnO nanoparticles synthesized by Sol-gel technique

Figure 3 shows the TEM image of ZnO nanoparticles synthesized by Ultrasonic cavitation. It can be seen that the uniform nanocrystalline ZnO particles have sphere shapes with weak agglomeration.
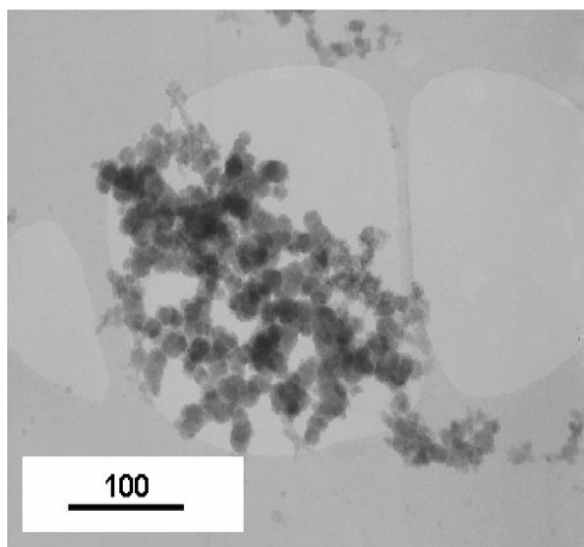
Figure 3[6]: TEM image of ZnO nanoparticles synthesized by Ultrasound Assisted Acoustic Cavitation Technique

2.3. UV-VIS spectroscopy (for sol-gel technique)

Figure 4 indicates the UV-VIS absorption spectrum for nano-ZnO for sol-gel synthesis. These nanoparticles absorb strongly in the region 250-350 nm. Their excitation peaks come into the region of 320-340 nm and emission peaks has redshifting from 480 nm to 540 nm indicating heavy aggregation[7].
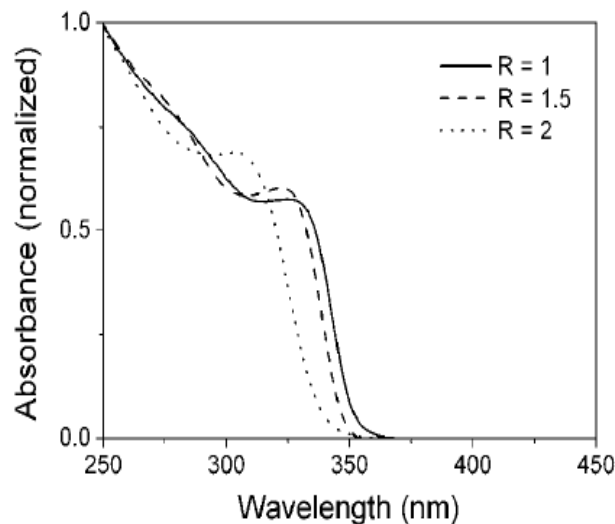

Figure 4[7]: UV-Vis Spectrum

3. Stabilization of ZnO nanoparticles

ZnO nanoparticles tend to undergo spontaneous growth and aggregation as seen from TEM images and UV-VIS absorption spectrum. To avoid this, various attempts have been made some of which are: employing ligands, coating ZnO with polymers and protecting ZnO with inorganic shells such as SiO_2 or ZnS. The Ligands used could be either organic or inorganic. Organic ligands can easily detach from the ZnO surface due to weak bonding whereas the inorganic ligands are porous in nature. Thus, the protection provided by either of the ligands is insufficient and the ZnO nanoparticles coated with them are unstable in water. As a result, the most preferred strategy is coating ZnO with polymers wherein the

polymerization is initiated at the surface of the ZnO nanoparticles. As the polymerization continues more cross-linking occurs forming a tight shell around the ZnO core. Due to presence of cross link sites this shell is difficult to remove and provides better protection to the ZnO nanoparticles.

ZnO based polymer nanocomposite can be prepared by both Physical as well as Chemical methods. Physical methods involve simple mixing of nanoparticles in polymer solutions or polymer melt. The bonding between polymer and nanoparticles is based on static interactions, Van der Waal's forces or simple Lewis acid-base interactions. Whereas, chemical reactions include bonding via formation of chemical bonds to produce more stable products because of strong interaction between polymer and nanoparticles.

The advantages of chemical methods over physical methods are:

(i)   The products are homogeneous, usually transparent.

(ii)   Their composition is not destroyed by solvent washing, i.e., the products can be isolated from the reaction system by non-solvent methods or centrifugation–redispersion treatment.

(iii)   There is no significant phase separation (ZnO aggregation or polymer crystallization) under TEM or AFM observation.

(iv)   IR spectra show the signals of chemical bonds between polymers and ZnO nanoparticles.

(v)   The decomposition temperature of the products are higher than the polymers themselves [8].

Thus, it can be concluded that, stronger the interaction between polymer and nanoparticles, the more stable nanocomposites will be formed.

3.1. Physical mixtures of polymers and ZnO nanoparticles:

Polymers like Polyvinylpyrrolidone (PVP), Polyaniline (PAni), Polyvinylalcohol (PVA), Polyethyleneoxide (PEO), Polyethyleneglycol (PEG) have been used so far for formation of polymer nanocomposites. 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 conclusion, the various drawbacks associated with this process are:

1. Many polymers are able to quench ZnO visible emission through passivating the ZnO nanoparticle surface;

2. Polymers such as PEO, PVA and PMMA cannot suppress ZnO nanoparticle aggregation effectively;

3. 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

On the basis of structural differences, the chemically synthesized polymer– ZnO nanocomposites are divided into four types:

1. 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:

a. Due to large volume of polymers, the degree of ligand exchange is low.

b. Exchanging the organic groups of the ZnO surfaces by polymer ligands often destroys the ZnO luminescence.

2. 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.

3. 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.

4. The fourth structure is obtained by Bulk polymerization. In this case the polymer is formed by bulk polymerization with the ZnO nanoparticles in the reaction medium. It is very large and can be cast into various forms [8].

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.

3.3. Inorganic shell (SiO₂)

Organic compounds such as long chain aliphatic thiols or amines are used as capping agents for passivating the surfaces of unstable nanoparticles to prevent their aggregation and improve compatibility with the organic matrix. The strategies to control the particle sizes include encapsulating an organic capping agent on the nanoparticle surfaces such as alkylthiols, polymer micelles or using co-ordinating solvent such as dimethly sulfoxide, N,N''-dimethylformamide and tri-n-octylphosphine oxide. However, inspite of this modification there is still some aggregation of nanoparticles observed which seriously affects the photoluminescence.

This problem can be overcome by a new method which involves modification of ZnO nanosurfaces to promote the stability of colloid suspensions and nanocomposites simultaneously preserving its luminescent properties.

As seen in **Figure 5** surface of the nanoparticles is stabilized by the absorption and hydrolysis of an unsaturated aliphatic silane, 3 (trimethoxysilyl)propyl methacrylate (TPM), via a mild sol–gel reaction. The colloidal ZnO nanoparticles are first dispersed in 2-hydroxyethyl methacrylate (HEMA) monomers and then thermally polymerized to form a stable nanohybrid film. Besides, the unsaturated chain of TPM on the ZnO nanoparticles can be polymerized with 2-hydroxyethyl methacrylate, making the particles uniformly dispersed in the poly(2-hydroxyethyl methacrylate) (PHEMA) matrix[9].
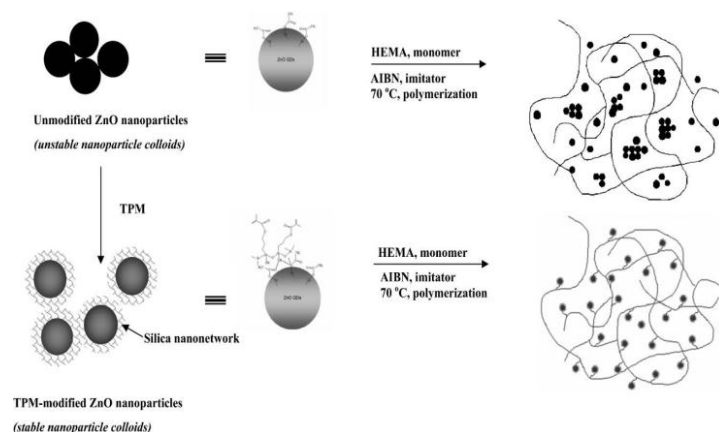

Figure 5[9]: Stabilization of ZnO nanoparticles using inorganic shell (SiO₂)

The TPM modified ZnO nanoparticles have high dispersion stability in organic solutions and have very little tendency to aggregate even over long periods of time. The room temperature PL measurements indicate that this method preserves the

superior luminescence of ZnO in both the initial solutions as well as the nanohybrid films.

4.1. Properties

a. Photoluminescence in ZnO

Photoluminiscence [PL] is a phenomenon in which a substance absorbs photon (electromagnetic radiation) resulting in excitation to higher energy state and then it returns to a lower energy state by emission of this photon. This transition occurs in a very short period of time typically in the order of 10 nanoseconds. The photoluminescent ZnO nanoparticles are non-toxic, cheap and very stable under ambient conditions towards sunlight, water and air.

The photoluminiscence of ZnO nanoparticles has two components: One is the photo-generated electron recombination with holes in the valence band or in traps near the valence band. This process produces UV light of about 370 nm because the ZnO band gap is 3.37 eV at room temperature. The other component is visible emission (also called deep level emission) related with oxygen vacancies. Two popular mechanisms for the ZnO visible emission that have been

suggested are shown in **Figure 6**: One is recombination of a shallowly trapped electron with a hole in a deep trap and the other is recombination of an electron in singly occupied oxygen vacancies (i.e., deeply trapped) with a photo-generated hole in the valence band. (A) represents - Typical exciton emission, (B) represents recombination of a shallowly trapped electron with a deeply trapped hole, and (C) represents recombination of a shallowly trapped hole with a deeply trapped electron. In order to simplify the maps, the shallow traps near the valence band (VB) and the conductance band (CB) are not marked [8].
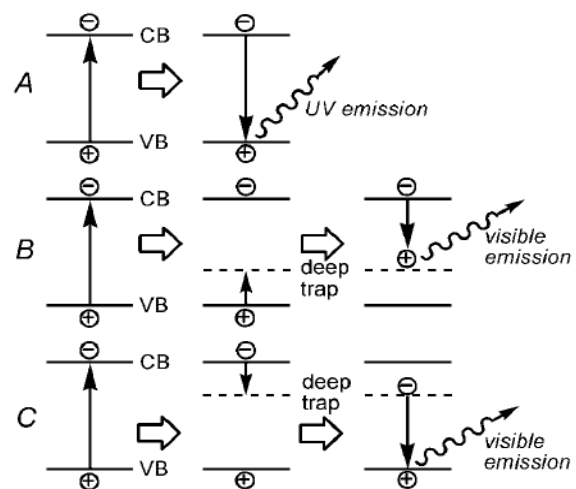

Figure 6[8]: Mechanism for ZnO visible emission

4.2. Piezoelectric Property

The piezoelectric property of ZnO has been extensively exploited in various applications like force sensing, acoustic

wave resonator, acousto-optic modulator etc. The crystal structure of ZnO with oxygen atoms and zinc oxide atoms bonded tetrahedrally, form the basis of the piezoelectric nature. In such a non-centrosymmetric structure, the center of positive charge and negative charge can be displaced due to external pressure induced lattice distortion. This displacement results in local dipole moments, thus a macroscopic dipole moment appears over the whole crystal.

The piezoelectric coefficient of ZnO nanobelts is measured by AFM (atomic force microscopy) with conductive tips. ZnO nanobelts are deposited on a conductive substrate, then the whole substrate is coated with 5 nm thick Palladium [Pd] serving as top electrode on the nanobelt. After the nanobelt is located by AFM, piezoresponse force microscopy is used to measure the effective piezocoefficient of the surface of the nanobelt. As the result, the effective piezocoefficient of nanobelt is observed to be frequency dependent [10].

4.3. Magnetic Doping

Spin Polarized Dilute Magnetic Semicord (DMS) overcomes the conductance mismatch associated with semiconductor devices. With Co, Fe and Mn as dopants, ZnO is a promising host material for ferromagnetic doping. Because of its wide band gap, ferromagnetic ZnO is regarded as an excellent material for short wavelength magneto-optical devices. These studies enable the use of magnetic ZnO nanowires as nanoscale spin-based devices [10].

5. Applications

a. 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 don't get absorbed into the skin and are compatible with skin. **Table No. 1** compares the UV blocking effect of nano-ZnO with other blocking agents.

Sunscreen Ingredients	Amount of Ray Protection		Chemical (C) or Physical (P)
	UV A	UV B	
Aminobenzoic acid [PABA]	○	●	C
Octyl salicylate	○	●	C
Phenylbenzimidazole	○	●	C
Titanium dioxide	◐	●	P
Zinc oxide	●	●	P

Protection Level: ○ Minimal;

◐ Considerable; ● Extensive

Table 1[17]: UV blocking effect by various sunscreen ingredients

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 [17].

b. 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.

5.3. Antimicrobial activity in textiles

Zinc oxide–soluble Starch nanocomposites were impregnated onto cotton fabrics. These ZnO nanoparticles were found to absorb strongly at 361 nm due to the quantum confinement effect, improving the UV-stabilization of the fabric. The cotton fabrics impregnated with these nanocomposites showed excellent antibacterial activity against two representative bacteria, *Staphylococcus aureus* (Gram positive) and *Klebsiella pneumoniae* (Gram negative), hence showing a very good antimicrobial activity [14].

5.4. Weatherability and Leach Resistance of Wood Impregnated with Nano-Zinc Oxide [13]

To test the effectiveness of ZnO based wood preservatives, the test specimens prepared from sapwood portion of southern pine tree, were vacuum impregnated with nano-ZnO treatments. These specimens were treated with aqueous solutions of 30 nm ZnO in water with concentrations of 1, 2.5, and 5% based on metal oxide. Untreated specimens were also tested. These treated specimens were dried for 3 days and then were used for further testing.

5.4.1. Weathering

Treated and untreated specimens were weathered outdoors for 12 months and visually evaluated for UV damage (i.e. splitting, chalking and graying). The specimen surface in direct light was considered the exposed surface, and the underside of each specimen was considered the unexposed surface for reporting results.

The following results were observed-

After 12 months of outdoor weathering, a specimen without any treatment was found to be damaged badly. Specimens treated with nano-ZnO were visibly brighter than untreated specimens particularly on the unexposed surface. Especially at higher treatment concentrations, the least chalking and least graying of surface was observed. Water repellency rated by visible water beading on wood surfaces only lasted for 8 weeks. Also, water repellency was found to be higher in case of highly loaded nano-ZnO specimens. This is useful characteristic to prevent bacterial and fungi growth on specimen.

5.4.2. Chemical Leaching

For this test, five specimens (19 × 19 × 19 mm) per treatment were

placed into 500-mL beakers, submerged in 100 mL of DI water and subjected to a vacuum to impregnate the specimens with the leaching solution. These samples were mildly agitated for 14 days. The leachates were collected after 6 hrs, and 1, 2, 4, 6, 8, 10, 12 and 14 days. Leachates were analyzed for zinc with ICP-AES and expressed as ppm zinc for the average leach rate of the 5 blocks per treatment concentration.

It was observed that, the surface with only zinc sulfate was readily leached where as no leaching of nano-ZnO occurred at any treatment concentration. Hence, this shows that the ZnO nanoparticles help to promote the antimicrobial properties to the specimen.

c. Finger –printing

Nanostructured ZnO particles are being used as a fluorescent powder for detection of finger prints on a non-porous surface in forensic department. The ZnO nanoparticles preferentially adhere to the fingerprint marks giving a contrast between the fingerprint features and the background surface. ZnO has been used as White Small Particle Reagent (SPRs). SPRs are particles which adhere to sebaceous or fatty substances in latent finger prints. In the SPR method, ZnO powder was dispersed in distilled water containing a surfactant. The specimens are immersed in the suspension, washed with distilled water, and then dried at room temperature before imaging. On illumination with long wave UV light, a visible luminescence of ZnO provides a contrast between fingermarks and surface substrates. This method is strictly used in case of non porous substrates like polyethylene, glass and aluminium foil. Major advantage associated with this process is that there is minimal background staining on non-porous surfaces. The SPR is significantly more effective on polyethylene and on aged prints than the dry powder technique. As an improvement in the technique, ZnO nanoparticles doped with Lithium ions were used to enhance the visible luminescence [11].

6. Conclusion

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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