



Chapter 16

Zinc oxide nanostructure and its application as agricultural and industrial material

Satinder Pal Kaur Malhotra* and T.K. Mandal

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Abstract

Nano sized particles of semiconductor materials have achieved great interest in recent years due to their desirable properties and applications in different areas such as agricultural, rubber industries, pharmaceutical and cosmetic, textile industries, electronic industries, sensors, photoelectronic devices and photocatalysts. These nanomaterials have unusual thermal, structural and electronic properties, which are of important scientific interests in the fundamental and applied research fields. Zinc oxide (ZnO) is a promising material which gained increasing interest in recent years owing to its distinctive properties. In this review paper an attempt has been made to elaborate the promising applications of ZnO nanoparticles in various fields.

Keywords: Antibacterial, Biosensors, Photocatalyst, UV- blockers, ZnO nanoparticles

Introduction

Nano sized particles of semiconductor materials have achieved great interest in recent years due to their desirable properties and applications in different areas such as rubber industries, pharmaceutical and cosmetic, textile industries, electronic industries, sensors, photoelectronic

✉ Satinder Pal Kaur Malhotra, Email: malhotrasatinder@gmail.com

Faculty of Science & Technology, ICFAI University Dehradun, Rajawala Road, Selaqui, Dehradun-248197 (Uttarakhand), INDIA

devices and photocatalysts. These nanomaterial's have unusual thermal, structural and electronic properties, which are of important scientific interests in the fundamental and applied research fields (Gancheva *et al.*, 2016, Thirumavalavan *et al.*, 2013). ZnO is a promising, and versatile inorganic material with a broad range of applications. Zinc oxide (ZnO) is usually a semiconductor having wide band gap with an energy gap of 3.37 eV at normal room temperature. Zinc oxide (ZnO), which can exhibit a wide variety of nanostructures, possesses unique semi-conducting, optical, and piezoelectric properties (Wang, 2008, Yang *et al.*, 2010). ZnO is characterized by photo catalytic ability and photo-oxidizing capacity against chemical and biological species. It is a wide band gap semiconductor and this has significant effect on its properties, such as the electrical conductivity and optical absorption. The excitonic emission can persevere higher at room temperature and the conductivity increases when ZnO doped with other metals (Wang, 2004). ZnO-NPs possess unique antibacterial, antifungal properties, high catalytic and high photochemical activities. ZnO possesses high optical absorption in the UV region which is beneficial in antibacterial response and used as a UV protector in cosmetics. ZnO nanoparticles have recently fascinated consideration owing to its unique features. There are potentially numerous promising applications of ZnO nanoparticles in various industries which are summarized below in flow Figure 16.1.

Zinc oxide – properties and agricultural/industrial applications

In rubber industry as fillers and activators for rubber compounds

Between 50% and 60% of ZnO use is in the rubber industry (Moezzi *et al.*, 2012). Zinc oxide along with stearic acid is used in the vulcanization of rubber (Porter, 1991). Zinc oxide is used as additive, it promotes the process of vulcanization in rubber that is used for tire manufacturing. In addition, its good conductivity improves the removal of heat that is generated during the

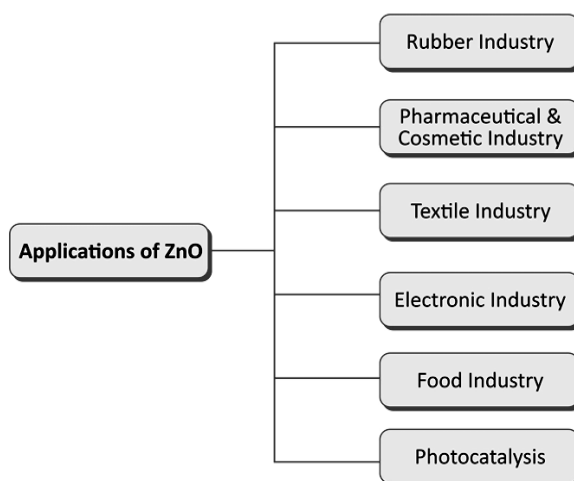


Figure 16.1. Industrial applications of zinc oxide.

churning motion of the tires also protect rubber from fungi and UV light.

In pharmaceutical and cosmetic industry as a component of sunscreen, lotions, powders, dental pastes, etc., absorber of UV radiation

Nanoparticulate zinc oxide is the broadest spectrum UVA and UVB absorber that is approved for use as a sunscreen by the U.S. Food and Drug Administration (FDA), and is completely photostable (Mitchnick *et al.*, 1999). ZnO is basically included in some cosmetic lotions as it is also known to maintain UV blocking and absorbing capabilities. In sunscreen applications, because of the ingredient of bulk ZnO, it leaves a whitish tint when applied to the skin, but when ZnO nanoparticle is used in sunscreen application due to its transparent nature, it doesn't leave any tint on the skin while applying. Compared to titanium dioxide (TiO₂), ZnO is considered to be a good ingredient in sunscreen applications because of its wide band gap due to which they can block UVA rays which are at the wavelength range of 320-400 nm. Compared to titanium dioxide zinc oxide is considered to be non-irritating, non-allergenic, and non-comedogenic. Zinc oxide also imparts the optical and biochemical properties and therefore it is used by the pharmaceutical industry for manufacturing zinc ointments, zinc pastes, adhesive tapes, and bandages for skin and wound treatment. When mixed with eugenol, a ligand, zinc oxide eugenol is formed, which is used as a restorative and prosthodontic in dentistry. Zinc oxide is widely used to treat a variety of skin conditions, including dermatitis and acne. It is used in products such as baby powder, calamine lotion, and barrier creams to treat diaper rashes, anti-shampoos and antiseptic ointments. ZnO can also be used as the astringent for wounds healing, anti-hemorrhoids, itching due to eczema and excoriation in the human medicine. Zinc oxide tape used by athletes as a bandage to prevent soft tissue damage during workouts (Hughes and McLean, 1988). Researches have shown that nano ZnO which has the average size between 20 nm and 45 nm can enhance the antibacterial activity of ciprofloxacin against *Staphylococcus aureus* and *Escherichia coli* in vitro (Banoee *et al.*, 2010).

In textile industry as antibacterial and UV blocker

The incorporation of nanoparticles like ZnO, TiO₂ or clay nanoparticles into textiles are becoming more demanding, as they provide protection from harmful UV radiation. Fine particles of the zinc oxide have deodorizing and antibacterial properties and for this reason they are added into materials including cotton fabric. In comparison to conventional UV absorbers (organic and inorganic), nanoparticles are more efficient at absorbing and scattering UV radiation, because they have a larger surface area per unit mass and volume than the conventional materials. Textiles coated with nanoparticles keep the UV blocking property more time than conventional materials. Hence, these nanoparticles increase the effectiveness of blocking UV radiation. Zinc oxide provides an excellent UV-protection when cotton fabrics are treated with zinc oxide nanorods of 10 to 50 nm in length. ZnO nanoparticles inlaid in polymer matrices (e.g., soluble starch) have a good potential for applications such as UV protection ability in textiles. In fact,

ZnO is said to have the broadest spectrum absorption range among many inorganic UV absorbers. However, ZnO suffers from poor chemical stability. It can dissolve under both high and low pH conditions. TiO₂ has excellent chemical stability, but the UV-absorption range is narrower than ZnO so that it often relies on light scattering effects in addition to light absorption effects to block UV light. Due to these reasons, zinc oxide seems to be ideal for the preparation of highly UV-absorbing, nanosol-based coatings.

Textile and clothing are carriers of microorganisms such as bacteria and fungi because of the adhesion of these organisms on the fabric surface. Antibacterial finishes are applied in sport clothing, inner wears and medical textiles as a safe and effective means against various bacteria, fungi and chlamydia. These textiles are generally treated with silver ions, but also with zinc oxide (ZnO) nanoparticles, copper oxide (CuO) nanoparticles, aluminum oxide (Al₂O₃) and magnesium oxide (MgO) nanoparticles. The influence of ZnO nanoparticulate fillers on antibacterial effects of various polymer nanocomposites against both grampositive and gram-negative bacteria, represented mostly by *Staphylococcus aureus* and *Escherichia coli*, respectively, have been proven by many authors. ZnO NPs are added to polymers such as polyurethanes (Ma and Zhang, 2009, Li *et al.*, 2009) polypropylene (Altan and Yildirim, 2012), high density polyethylene (Li and Wang, 2010) or poly(vinyl chloride) (Geilich and Webster, 2013), where all authors observed reduction of bacterial species as compared to the initial untreated polymer samples. The use of 0.6% nano-ZnO for coating can be sufficient to provide antimicrobial property to wearable cotton textiles, whereas 1% of nano-ZnO is recommended for medical textiles due to its high antimicrobial activity. ZnO nanoparticles scores over nano-silver in terms of cost-effectiveness, whiteness and UV-blocking property.

In agriculture and electronic industry in the manufacture of LEDS and solar cells, field emitters, photo diodes, sensors, etc.

There are different electronic components, for example piezo-electric converters, transparent conducting oxides, sensors, luminous diodes, and optoelectronic or spintronic components, that at present are barely conceivable without zinc oxide. Zinc oxide-based semiconductors are used as transparent conductive layers in blue light-emitting diodes, liquid-crystal screens, and thin-film solar cells.

Light emitting diodes and solar cells: Since ZnO semiconducting NPs possess a wide band gap of about 3.37 eV and a large exciton binding energy at of 60 ev at room temperature, their electronic and luminescent properties have been extensively studied in connection with the potential applications in light emitting devices (LEDs). Within this field, most of the attention has been devoted to low dimensional structures such as ZnO quantum dots, nanorods or nanowires. ZnO can be combined with GaN for LED-applications since ZnO overlap with that of GaN, which has a similar bandgap (~3.4 eV at room temperature). Compared to GaN, ZnO has a larger exciton binding energy (~60 meV, 2.4 times of the room-temperature thermal energy), which results in bright room-temperature emission from ZnO. Moreover, organic light emitting diodes

(OLEDs) utilize a nanocomposite layer composed of a semiconductive polymer and luminescent ZnO nanoparticles (Willander *et al.*, 2010).

Dye sensitized solar cells (DSCs): DSSCs are the devices which convert visible light into electricity based on sensitization of wide band gap semiconductor. ZnO has been considered as a promising candidate for DSSCs due to its carrier mobility and direct band gap, and position of conduction band but in spite of these advantages, the efficiencies of zinc oxide based DSSCs are usually low. Continuous improvement of dye sensitized solar cells (DSCs) represents one option for harvesting energy from the light. For this purpose, DSCs based on ZnO hierarchical nanostructures manifested maximum conversion efficiency up to 5.4 % (Zhang *et al.*, 2009).

Field effect transistor: The zinc oxide (ZnO) nanostructures nanowire-based field-effect transistors (FETs) are the basic element for nano-electronics applications (Makhniy and Melnik, 2003). Also, the ZnO nanowires FETs are the fundamental building blocks for many nanoscale electronic devices. Early studies of zinc oxide (ZnO) nanowire FETs have focused only on their device performance, and photo detection (Jain *et al.*, 2016; Al-Sabahi *et al.*, 2016; Shan *et al.*, 2016). The interface roughness plays a prominent role in the electronic transport for transistors. The zinc oxide (ZnO) nanowires FET shows excellent properties, such as good transparency to visible light, excellent uniformity, and high mobility compared with traditional amorphous/polycrystalline silicon devices.

Photo diodes: The zinc oxide (ZnO) nanostructures are synthesized and fabricated as photo diodes also. There are increasingly plenty of scientific and industrial applications of photo diodes at nanoscale (Marie *et al.*, 2015; Kim *et al.*, 2014). The experimental analysis of zinc oxide (ZnO) reported that the nanostructures of ZnO heterojunction photodiodes consisting of p-Si and n-ZnO nanowire core and shell structures. The conformal coating made by an n-type ZnO layer that encircled a p-type silicon (Si) nanowire is applied in many photo diode applications. These photodiodes present enhanced ultra violet (UV) and visible responsivities compared to other planar thin film photodiodes (Singh *et al.*, 1984).

Biosensors: Biosensors (e.g. photometric, calorimetric, electrochemical, piezoelectric, among others when categorized based on the detection principles) are widely used in healthcare, chemical/ biological analysis, environmental monitoring, agriculture and food industry. Nanomaterials, alone or in combination with biologically active substances, are attracting ever-increasing attention since they can provide a suitable platform for the development of high performance biosensors due to their unique properties (Yakimova *et al.*, 2012). For example, the high surface area of nanomaterials can be employed to immobilize various biomolecules such as enzymes, antibodies, and other proteins. In addition, they can allow for direct electron transfer between active sites of the biomolecules and the electrode. Besides semiconducting properties, ZnO nanomaterials also exhibit various desirable traits for biosensing such as high catalytic efficiency, strong adsorption capability, and high isoelectric point (IEP; ~9.5) which are suitable for adsorption of certain proteins (e.g. enzymes and antibodies with low IEPs) by electrostatic interaction (Wang *et al.*, 2006). Furthermore, high surface area, good biocompatibility/stability,

low toxicity, and high electron transfer capability also make them promising nanomaterials for biosensors (Kumar and Chen, 2008). The majority of reported ZnO-based biosensors are for the detection of various small molecule analytes such as glucose, phenol, H₂O₂, cholesterol, urea, etc.

Humidity sensors: ZnO nanocomposites also find applications as humidity sensors (Zainelabdin *et al.*, 2012). Humidity sensors are inserted into the textile along the weft direction as a replacement for weft yarn. Warp threads are replaced by conductive yarns to contact the sensors inside the textile. Humidity sensors have a detection range from 25 to 85% with 10% sensitivity. Several approaches of humidity sensor development via smart textile technology for healthcare applications as ulcer prevention, monitoring of sweat rate and moisture in wounds are put into use.

Gas sensors: Many researches have focused on the preparation of metal oxide semiconductor gas sensors in the form of thin films. These operate upon the change of the resistance of metal oxide nanoparticles due to the adsorption of reducing gases (Lee, 2009). Selectivity to hydrogen gas was achieved by sputtering Pd clusters on the nanorod surface. The addition of Pd is effective in the catalytic dissociation of hydrogen molecules into atomic hydrogen, increasing the sensitivity of the sensor device. The sensor detects hydrogen concentrations down to 10 parts per million at room temperature, whereas there is no response to oxygen in a similar way, ZnO based sensors designed for nitrogen dioxide (Chen *et al.*, 2011), ammonia and ethanol (Zhang *et al.*, 2011) were successfully fabricated.

In food industry as an antibacterial agent and food packaging

ZnO shows photocatalytic properties and therefore it acts as an excellent antibacterial agent. This material can be activated by UV and visible light to form the electron-hole pairs. The holes thus formed can split the H₂O molecule (from suspension from ZnO) to OH⁻ and H⁺. Dissolved oxygen molecules on could be converted to superoxide radical anions ($\bullet\text{O}_2^-$) which react with H⁺ to produce (HO₂ \bullet) radicals. The collisions of (HO₂ \bullet) with electrons produce the hydrogen peroxide anion (HO₂⁻). These species react with hydrogen ions to produce H₂O₂ molecules that can penetrate the cell membranes and kill the bacteria (Padmavathy and Vijayaraghavan, 2008).

One of these essential applications is in food industry; as an antibacterial agent in food packaging and towards foodborne pathogen. Some of the main benefits of using NPs in food nanotechnology are the addition of NPs onto food surfaces to inhibit bacterial growth, also using of NPs as intelligent packaging materials and for nano-sensing (Chaudhry and Castle, 2011). Among these NPs, ZnO-NPs developed as a successful candidate in the food industry. The antibacterial influence of ZnO-NPs against foodborne pathogens stimulates proficient applications in food packaging, and can be introduced in food nanotechnology. Researches have showed that ZnO-NPs can inhibit and kill common as well as major foodborne pathogens. The bactericidal activity of ZnO-NPs (8-10 nm size) against *E. coli DH5a* and *S. aureus* was examined and found to be effective at 80 and 100 lg mL⁻¹. These concentrations disrupted the cell membrane causing cytoplasmic leakage (Kaur *et al.*, 2011). Narayanan *et al.*, 2012 tested the antibacterial activity of

ZnO-NPs against some human pathogens such as *P. aeruginosa*, *E. coli*, *S. aureus*, and *E. faecalis*. They emerged with the result that ZnO-NPs have strong antibacterial activity toward these human pathogens. Likewise, the antimicrobial activity of ZnO-NPs was studied (Chitra and Annadurai, 2013) toward *P. aeruginosa* and *E. coli* which were isolated from mint leaf extract and frozen ice cream, and ZnO was prepared using wet chemical method, yielding spherical morphology with smooth surface, of concentrations 20, 50, and 100 L. Both bacteria showed decreased growth rate at the highest concentration 100 L, and they explained the growth inhibition as a result of cell membrane damage through penetration of ZnO-NPs. Protection of food from microbial pollution is one of the main purposes in food packaging. The emergence of nanotechnology assisted to present novel food packaging materials with antimicrobial properties and with novel nano-sensors to trace and monitor the food. Several studies have addressed the antibacterial properties and potential applications of ZnO-NPs in food processing. For example, ZnO has been included into a number of food linings in packaging to avoid spoilage plus it maintains colors. ZnO-NPs provide antimicrobial activity for food packaging. Once they are introduced in a polymeric matrix, it permits interaction of food with the packaging possessing functional part in the conservation. The use of polymer nanotechnology in packaging was introduced by Silvestre *et al.* (2011) to achieve novel way of packaging that mainly meet the requirements of protection against bacteria. These materials with improved antimicrobial properties permit also tracking of food during storage and transfer.

Photocatalysis for waste water treatment

Nanostructured metal-oxide semiconductors are promising candidates for photocatalytic environmental remediation (Lines, 2008; Arivalagan *et al.*, 2011). Many kinds of semi-conductor oxides such as TiO₂, ZnO, Fe₂O₃, ZrO₂, have been widely used as photocatalysts in waste water decontamination (Padmavath *et al.*, 2008). Among those metal-oxide semiconductors, zinc oxide has attracted much attention for its high photosensitivity, environmental friendliness, low cost, and strong oxidizing power (Li and Li, 2010; Vijayakumar *et al.*, 2010; Qamar, *et al.*, 2015). In the field of photocatalysis, titanium dioxide (TiO₂) is undoubtedly the material most extensively studied (Asahi *et al.*, 2001; Maeda *et al.*, 2006). However, ZnO has been reported to exhibit photocatalytic activity comparable or sometimes even better to TiO₂ and is considered as a very promising alternative. Moreover, ZnO is cheap, low-toxic material that can be prepared by a large variety of methods (Rolison, 2003; Kim *et al.*, 2005). As the photocatalytic activity of semi-conductors generally depends on crystal size, surface area, morphology and native defects, the abundances in morphologies makes ZnO representative material in the research field of photocatalysis (Arai *et al.*, 2007; Ang *et al.*, 2013). However, there are some non-ignorable faults in the wide band gap semiconductors (such as TiO₂ and ZnO) as photocatalysts because they can only be excited for photocatalysis under UV light irradiation (Linsebigler *et al.*, 1995; Han, 2005). It is noted that visible light with spectral wavelength between 400 and 700 nm accounts for about

45% of the total energy of the solar radiation, while UV light occupies less than 10%. Thus, it is of great interest to improve the photocatalytic activity for practical photocatalytic applications under visible light. Besides, the fast recombination rate of the photogenerated electron-hole pairs in the monocomponent semiconductors restricts their photocatalytic efficiency (Hoffmann *et al.*, 1995). Semiconductor/semiconductor heterostructure photocatalysts may increase the photocatalytic activity by extending the photo-responding range and increasing the charge separation rate (Serpone *et al.*, 1995). ZnO hollow spheroids were successfully used for the complete photocatalytic degradation of aqueous solution of rhodamine B (as the model organic dye used for textiles colouring) under UV light within minutes. Neither in the presence of ZnO spheroids and absence of UV light nor with UV illumination and without the ZnO, did any photocatalytic degradation of rhodamine B took place (Sinha *et al.*, 2010). Similarly, another group of authors synthesized nanorods assembled flowers which demonstrated 91 % and 80 % degradation of methylene blue and rhodamine B dye, respectively, within 140 minutes (Rahman *et al.*, 2013). In addition, the effect of morphology of ZnO particles prepared by microwave assisted solvothermal synthesis on photodegradation of methyl orange was evaluated among six different samples. The best result represented by 98% degradation of methyl orange within 40 min was manifested by hierarchically structured spheres; the authors' explanation was related to the highest specific surface area (Zhang and Zhu, 2009).

Conclusion

The properties of ZnO at nanoscale, applications in industries can be applied to many industrial applications. ZnO nanostructure material has gained much interest owing to its wide applications for various devices such as solar cells, transistors, transducers, transparent conducting electrodes, sensors and catalysts. ZnO nanoparticles are one of the most abundantly used nanomaterials in consumer products and biomedical applications due to their specific properties, e.g. transparency, high isoelectric point, biocompatibility and photocatalytic efficiency. ZnO nanoparticles used as antimicrobial agents in food packaging materials show good antimicrobial activity. ZnO nanoparticles are known for their anti-bacterial activity and hence it finds application in various commercial products such as cosmetics and sunscreens. The ZnO-based textile exhibit excellent photocatalytic and antibacterial activities, and it shows a promising sensing response. The combination of sensing, photocatalysis, and antibacterial properties provided by ZnO NRs is used in the concept of smart textiles for wearable sensing without a deodorant and antibacterial control. Advanced technologies included incorporation of moisture, temperature, pressure sensors, drug release, and fiber optics powered by textile-based batteries.

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