# Comprehensive Overview on Zinc Oxide Nanostructures

**Shouvik Mitra[*], Saheli Pradhan[**]**

[*]AERU, Biological Sciences Division, Indian Statistical Institute, Kolkata-700108, India.
[**]Department of Botany, B. K. Birla College (Autonomous), Kalyan, Maharashtra
[*]Corresponding author: chemshouvik2009@gmail.com

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## Abstract:

*Zinc oxide is technologically important and ZnO thin layers are widely used in sensors, transducers and catalysts designing. However, after the introduction of nanoscience and nanotechnology the gear has been shifted to its smaller counterpart in contrast to its bulk one. In this review typical synthesis procedure, growth process, classical property, and a few biological perspectives of zinc oxide nanostructures have been highlighted. In coming years new synthetic strategy, benign fabrication will be introduced with plethora of versatile and beneficial applications based on zinc oxide nanostructures.*

**Keywords: zinc oxide nanostructures, synthesis, optical property, optoelectronics, biocides, bioimaging, drug delivery**

## Introduction:

Zinc oxide (ZnO) is a well-known semiconducting and piezoelectric material with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature (Ozgur *et al.*, 2005). ZnO is technologically important and ZnO thin layers are widely used in sensors, transducers and catalysts designing. However, after the introduction of nanoscience and nanotechnology the gear has been shifted to its smaller counterpart in contrast to its bulk one. With the reduction in size unique properties such as chemical, optical and physical properties are being introduced in the structure due to 'nano-effect'. Therefore, ZnO nanostructures emerged its enormous applications in electronic, optoelectronic, electrochemical, and electromechanical devices (Nomura et al., 2003; Nakada et al., 2004), such as UV lasers (Huang et. al., 2001; Govender et. al., 2002), light-emitting diodes (Park et. al., 2004), field emission devices (Zhu et. al., 2003; Wang et. al., 2006), high performance nanosensors (Wei et. al., 2009; Yeh et. al. 2009), solar cells (Law et al., 2005; Clement et al, 2005; Weintraub et al., 2009), nanogenerators (Wang et al., 2006) and nano-piezoelectronics (Wang et al. 2007; 2008). Although these are the main optoelectronic applications of ZnO nanostructures, however applications of ZnO are not only restricted to optoelectronic devices or piezoelectronic materials. ZnO is known as generally recognized as safe (GRAS) by US food and drug administration among the five zinc compounds. Therefore, ZnO is biocompatible, which allowed the researchers to use it for biology-based applications. Sometimes ZnO has been used for filling of medical materials (Wang et al., 2004), but the most interesting property of nano ZnO lies in its biocidal property (Jones et al., 2008; Raghupati et al., 2011). ZnO nanoparticles are used for antifungal, antibacterial property; recently ZnO nanostructures are used for imaging (quantum dots) and drug delivery-based applications (Hong et al., 2011; Muhammed et al., 2011) as well. In this review typical synthesis procedure, growth process, classical property, and a few biological perspectives have been highlighted.

## Structural Diversity:

ZnO has probably the richest variety of different nanostructures which includes nanoparticles, highly ordered nanowire

arrays, tower-like structures, nanorods, nanobelts, nanosprings, nanocombs, hexagonal disc, tetrapods and nanorings etc. ZnO nanostructures are considered to be one of the oldest; therefore immense literatures are available on ZnO nanostructures. A variety of ZnO nanostructure morphologies such as nanoparticles (Luo et al., 2009), nanowires (Huang et al., 2001), nanorods (Liu et al., 2003), tetrapods (Dai et al., 2002), and nanoribbons/ belts (Pan et al., 2001), have

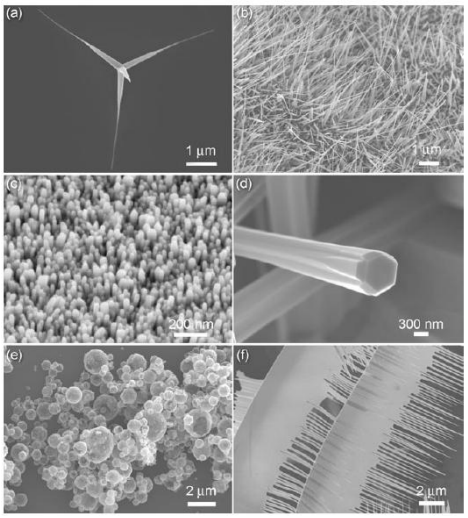



**Figure 1**. Different morphological features of ZnO nanostructures, (a)-(f) shows different morphology of ZnO nanostructures under scanning electron microscope; adapted from Small, 2006, 2, 944.

been reported. ZnO nanostructures have been fabricated by various methods, such as thermal evaporation, metal–organic vapor phase epitaxy, laser ablatio, hydrothermal synthesis, and template-based synthesis (Pan et al., 2001). Recently, novel morphologies such as hierarchical nanostructures (Lao et al., 2002), bridge-/nail-like nanostructures (Lao et al., 2003), tubular nanostructures (Xing et al., 2004), nanosheets (Park et al., 2004), nanopropeller arrays (Gao et al., 2004), nanohelixes (Kong et al., 2004), nano-rings (Kong et al., 2004) and nano-pyramid (Liu et al., 2012) have also been introduced. The other variations in ZnO nanostructures are ZnO quantum dots (Shi et al., 2011) and porous ZnO nanostructures (Barick et al.). Some of the possible ZnO nanostructure morphologies are shown in Figure 1. Although it is difficult to integrate all possible synthetic methodology, a more generalized synthetic strategy has been depicted here.

## Synthetic Processes:

Usually ZnO nanostructures can be readily synthesized using two methods; one is the wet chemical synthesis while the other one is the physical techniques. Wet chemical synthesis consists of hydrothermal method, solution phase synthesis or even surfactant directed synthesis.

### Wet chemical synthesis:

Wet chemical synthesis provides a facile chemical manipulation under relatively low temperature conditions. Depending upon the nature of the reaction one can easily manipulate its scale up version. Zinc salts are readily hydrolyzed to corresponding hydroxyl or amine complexes which are used for the growth of ZnO nanostructures. Amine compounds usually grow along c-direction while citrate restricts the growth along c-direction. A wide variety of morphological features are revealed in wet chemical synthesis. However, reactants, stoichiometry and pH of the reaction play pivotal role behind the morphology (Zhang et al., 2005). Sometimes ethanolamine plays the dual role of stabilizing agent as well as growth directing agent (Razali et al., 2011). Structure directing amine controls the architecture of ZnO (Du et al., 2012), depending on preferential adsorption at sites. Usually tetrapod, urchin, flower and rod like morphologies are obtained under alkaline pH (pH>8) (Arya et al., 2012). Zinc nitrate [$Zn(NO3)_2$], zinc chloride [$ZnCl_2$], zinc acetate [$Zn(OAc)_2$], zinc sulfate [$ZnSO_4$] are the commonly used zinc precursors. In contrary hexamethylenetetramine, ammonia, citric acid, NaOH/KOH is used as a growth/structure directing agents (Arya et al., 2012). Zinc salt and structure directing agents are added in solution phase with the mixture is allowed to react under heating conditions either in refluxation reaction or by solvothermal reactions (Gu et al., 2009). Sometimes ultrasonications are also used to produce ZnO nanostructures (Gu et al., 2009).

These reactions produce a wide variety of nanostructures including nanoparticles, nanorods, nanowires, nanoflowers, waxberry balls, nanoflakes, hollow sphere and even needle like structure depending upon the nature of precursors used. For the production of 3D nanoflower like assembly seeding method is used, sequential Lamer type nucleation-growth and Ostwald ripening are the main reason behind such assembly. Now a days sonochemical synthesis provides the reaction under mild condition (Hou et al., 2007) for the growth of ZnO nanostructure.

### Physical methods:

Physical techniques are the dry methods to obtain ZnO nanostructures; although precise control of morphology is possible, but reaction conditions are a bit difficult. Carbothermal reduction, thermal evaporation, vapor phase transport falls in this category (Ahmad et al., 2009). In general a seed is formed first followed by the growth of structures along a particular direction on to it. Of late electrochemical synthesis are gaining interest for the synthesis of ZnO nanostructures (Stafinaik et al., 2011). In this method seed layer is not required. The most common method for the electro-deposition of ZnO involves the reduction of oxygen or nitrate on the substrate in the presence of a zinc salt at neutral pH and elevated temperature. An increase in surface pH via generation of hydroxyl ions during reduction drives the formation of ZnO nanostructures in electrochemical methods.

## Synthesis Mechanism:

Chemical reactions in aqueous systems are considered to be present in a reversible equilibrium. Usually, an alkaline solution is required to produce ZnO nanostructures. Normally divalent metal ions do not hydrolyze in acidic environments (Li et al., 1999), therefore strong alkali such as NaOH and KOH is required. As the base concentration is increased the solubility of ZnO nanostructures are increased, meanwhile KOH is thought to be preferable than NaOH during hydrolysis reaction. Lattice incorporation of impurity is one of the known phenomenons during the hydrolysis reaction. As K+ has a larger ion radius than Na+, a lower probability of incorporation into the lattice by former one is observed (Liu et al., 2004). Even sometimes Na+ hinders the crystal growth by forming virtual capping layers. The generalized reaction by using a zinc salt precursor is as follows:

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2$$
$$Zn(OH)_2 + 2OH^- \leftrightarrow [Zn(OH)_4]^{2-}$$
$$[Zn(OH)_4]^{2-} \leftrightarrow ZnO_2^{2-} + 2H_2O$$
$$ZnO_2^{2-} + H_2O \leftrightarrow ZnO + 2OH^-$$
$$ZnO + OH^- \leftrightarrow ZnOOH^-$$

The O2– present in ZnO comes from the base, hence growth of ZnO does not necessarily require $H_2O$. Therefore, a wide range of organic solvents are also capable to execute the reaction (Cheng et al., 2004).

## Properties:

#### Optical and PL property:

In most of the cases UV-Vis spectra of ZnO nanostructures are obtained in the region of 350-370 nm depending on the nature of substrate (Patra et al., 2012), the absorbance appears as a characteristic hump. ZnO quantum dots or porous ZnO scaffolds do exhibit a characteristic UV-Vis absorbance in that particular region. Therefore nano ZnO is expected to exhibit characteristic absorbance meanwhile room temperature PL emission of ZnO nanostructures is well documented. Some of the studies have shown variable-temperature photoluminescence of the samples. Room temperature PL spectra of ZnO consist of a UV emission and possibly one or more visible bands due to defects and/or impurities. Two peak PL curve was obtained one centered at 380 nm and the other in the region of green emission (Patra et al., 2012). Among the two bands, the lower band is attributed to the recombination of excitons as reported by Vanheusden et al. 1999, while the broad peak can be indexed to singly ionized oxygen vacancy in ZnO.

### Electrical Property:

The fundamental study of the electrical properties of ZnO nanostructures is crucial for developing their future applications in nanoelectronics. Electrical transport measurements have been performed on individual ZnO nanowires and nanorods (Liu et al., 2003). Using standard procedure they are configured as field effect transistor (FET). Briefly they are first dispersed in isopropanol to form stable suspension, deposited on to a $SiO_2$/Si substrate. Photolithography is used at this stage to define contact electrode array and back gate electrode. Due to the presence of defect sites such as oxygen vacancy and zinc interstitials, they exhibit n-type semiconductor behavior. A characteristic I-V curve is obtained against different back gate voltages. Furthermore, the electrical properties of FETs can also be studied using conductive AFM by mapping the local electrical potential (Fan et al., 2005). A scanning tip is capable to switch on and off the conductance periodically, indicating the potential application for a nano-electromechanical system.

### Piezoelectric property:

One of the important characteristic property and signature of ZnO nanostructures are their piezoelectric property which is extensively used for various applications in force sensing, acoustic wave resonator, acousto-optic modulator, etc. (Corso et al., 1994). Piezoelectricity is the accumulation of charge in materials due to presence of external stress. The origin of piezoelectricity in ZnO nanostructures is due to its crystal structure with oxygen atoms and zinc atoms are tetrahedrally bonded. In presence of external stress such a lattice structure can undergo distortion with displacement of positive and negative charge. This results generation of local dipole moments, and a macroscopic dipole moment appears over the whole crystal. In fact, nano ZnO retrieves high piezoelectric property amongst tetrahedrally bonded semiconductors (Kong et al., 2003). The piezoelectric property of ZnO nanostructures is investigated for their potential applications in nano-electromechanical systems. The piezoelectric coefficient of ZnO nanostructures can be measured by AFM with conductive tips.

### Cytocompatibility:

ZnO is known to be as safe, it is one of the five zinc compounds which are generally recognized as safe (GRAS) by US food and drug administration for biomedical applications (Patra et al., 2012). Owing to its biocompatibility ZnO nanoparticles has been used widely in sunscreen formulation. Even ZnO has been used in filling of medical materials. Though some of the researchers have raised the issue of toxicity due to generation of reactive oxygen species (ROS) (Applerot et al., 2009); overall, it is biocompatible to be used in biomedical purposes.

## Properties:

### Sensors designing:

ZnO nanostructures have been widely used for sensing applications because of their high sensitivity to the chemical environment. Small sized nanostructures possess high surface area in contrast to its bulk counterpart which influences electronic as well as optical property. ZnO nanowires have demonstrated high sensitivity even at room temperature. The sensing process is governed by oxygen vacancies on the surface that influence the electronic properties of ZnO. When oxidizing gas molecules such as $NO_2$ is adsorbed at vacancy sites, electrons are withdrawn leading to a reduction of conductivity. In contrary reducing molecules such as $H_2$ react with surface-adsorbed oxygen, generates electron leading to a higher conductivity. A ZnO nanorod based $H_2$ sensor has been developed (Lupan et al., 2007), however selectivity should be introduced at this stage. In order to improve sensitivity metal deposition is used on ZnO surface, for instance Pt-coated ZnO nanorods are used for higher sensitivity (Ozturk et al., 2012). Similarly, $O_2$, $NO_2$, and $NH_3$ gas sensors have also been demonstrated separately (Fan et al., 2004). Ethanol sensing by ZnO can also be done (Bie et al. 2007). Apart from chemical sensing ZnO nanostructures

are widely used in biosensing applications, the most important step is to immobilize the nanostructure within the matrix. ZnO nanostructure matrix are widely used to bind with GOx, ChOx, uricase, horseradish peroxidase (HRP), microperoxidase and tyrosinase etc. (Ahmad et al., 2010) for their sensitive detection. Apart from these biosensors ZnO nanostructures-based glucose biosensor, $H_2O_2$ biosensor, uric acid biosensor and super oxide dismutase biosensors are also used widely (Dai et al., 2009). For a glucose-based biosensor the negatively charged glucose oxidase enzyme is immobilized on positively charged ZnO through electrostatic forces. At an applied potential of +0.8 V versus Ag/AgCl reference electrode, the glucose biosensor shows a linear response (Wei et al., 2006).

## Optoelectronics:

One of the important optoelectronic applications of ZnO nanostructures is designing of light-emitting diode (LED). Bao et al. constructed a single nanowire LED (Bao et al., 2006). There ZnO nanowires were dispersed on a Si substrate followed by spin coating with poly(methyl methacrylate) thin film, finally current-voltage characteristics, photoluminescence, and electroluminescence of this device has been studied. A ZnO homojunction LED was fabricated on a single-crystal GaAs substrate by ultrasonic-assisted spray pyrolysis (Du et al., 2006). The LED exhibited a threshold voltage of ~4 V under forward bias. Meanwhile a hybrid light-emitting p-n junction diode was also formulated using ZnO nanorods as the n-type material and poly-2, 4-ethylene dioxythiophene poly(styrenesulfonate) as the p-type material. In the electroluminescence spectrum which exhibited a threshold bias of 3V (Thomas et al., 1957). These are e few examples of using ZnO nanostructures in devising LED, which demonstrates that suitable functionalization can lead to generation of LED.

## Solar Cells, Photocatalytic Property:

Of late ZnO nanostructures are being used in dye-sensitized solar cells as an electrode material (Bedja et al., 1997). Dye sensitized solar cells coupled with ZnO nanostructures exhibit ultrafast electron injection on to the conductance band of ZnO (Chou et al., 2007). The important criteria of the nanostructures used to couple with dye sensitized solar cells should exhibit a wide band gap, high charge carrier mobility, high surface area for efficient dye-sensitization and light harvesting. Usually, ZnO nanostructures demonstrate aforementioned characteristics and hence widely used for fabrication of dye sensitized solar cell applications. Therefore, ZnO seems to be a promising material for solar cell applications and has the advantage over other metal oxides as ZnO nanostructure can be synthesized easily with controlled size and shape. Dye-sensitized solar cells usually have an electrolyte to regenerate the dye by electron donation to its ground state after excitation.

Another important application of ZnO nanostructure lies in its photocatalytic property. ZnO is known to exhibit photocatalytic property depending on the band gap as well with their capability to produce reactive oxygen species (Wang et al., 2009). This photocatalytic property (Deng et al., 2008) is widely used in organic dye degradation (Hong et al., 2009; Wang et al., 2007). Sometimes mixed nanocomposites are being used to execute the photocatalytic property. Suitable doping can induce synergistic effect for photocatalytic applications (Ullah et al., 2008).

## Biocidal applications:

The supreme biomedical application of ZnO nanostructures lies in its biocidal property against different kind of microbial systems. Antibacterial activity of ZnO of size ranging from nanometer to micrometer range was established by Ohira et al. 2008, interaction between prokaryotic cells and ZnO was investigated by Yan et al. 2011, electrostatic interactions between Pseudomonas aeruginosa and ZnO was studied by Feris et al. 2010, even interaction between bacterial envelope and ZnO nanoparticles was observed by Jiang

et al. 2010. Antibacterial property was studied by Padmavathy et al. 2009 and others (Dutta et al., 2012; Leung et al., 2012) while applications of ZnO nanoparticles on a few fungal systems were also studied (Sharma et al. 2010). Applerot et al. 2009 proposed that ROS is responsible behind the toxicity. Similarly, Yin et al. 2010 investigated the cytotoxicity of ZnO through ROS generation. Interestingly transition metal doped ZnO is effective against E. coli as shown by Dutta et al. 2010. Therefore, most of the ZnO nanostructures are effective against microbial system and ROS is supposed to be the formal

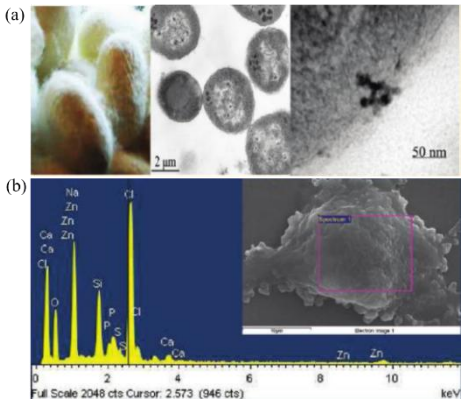



**Figure 2.** A typical bioavailability study of ZnO nanoparticles within cellular system, (a) Transmission electron microscopic image demonstrating cellular internalization, (b) SEM and EDX analysis of ZnO nanoparticle treated cells; adapted from Langmuir, 2011, 27, 13206

mechanism behind the scenes. A lot of efforts have been paid in order to evaluate the origin of ROS (Li et al., 2011). ZnO nanostructures are usually bio-available to the microbial system, readily internalized within cellular systems and then generate ROS for the response. A typical bioavailability of ZnO nanoparticles inside cells were investigated by EDX and TEM analysis, when ZnO nanoparticles exhibit antimicrobial effect it results the rupture of cell membrane. With this unique antimicrobial property of ZnO nanostructures, they are successfully used in formulation of antimicrobial matrix, fabrics and clothing. A schematic representation bioavailability of ZnO nanoparticles inside cells has been demonstrated in Figure 2.

## Bioimaging:

Bioimaging applications of ZnO nanostructures are rare. As ZnO quantum dots exhibit PL property (Sun et al., 2012); they can be used as bioimaging agent. Hong et al. have demonstrated intrinsically fluorescent ZnO nanowires can be adopted for molecularly targeted imaging of cancer cells, after they are functionalized to render water solubility, biocompatibility, and low cellular toxicity. Optical imaging of integrin Rvβ3 on U87MG human glioblastoma cells has been achieved with

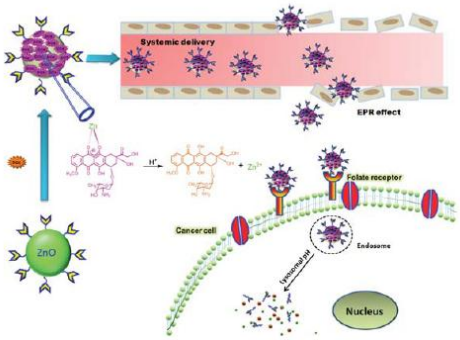



**Figure 3.** A schematic representation of targeted drug delivery-based applications of ZnO quantum dots for the delivery of doxorubicin; adapted from J. Mater. Chem., 2011, 21, 13406

RGD peptide-conjugated green-fluorescent ZnO nanowires, which has opened up new avenues of research for investigating ZnO nanowire based agents in tumor vasculature-targeted molecular imaging and drug delivery. Properly fabricated ZnO nanostructures with tunable size can also be used as a bioimaging agent as shown by Zhang et al. 2012.

## Drug delivery:

Though ZnO nanostructures have been used widely in biocidal applications, sensor designing, catalysis and gas sensing; successful application of these nanostructures in drug delivery is still in a nascent stage. Previously Ostrovsky et al. 2009 have addressed selective destruction

of cancer cells by ZnO nanoparticles; the similar has been reported by Rasmussen et al. 2010 where ZnO nanoparticles are found to destroy tumor cells selectively. Zhang et al. 2011 and Hariharan et al. 2012 demonstrated multimodal cancer treatment using ZnO nanoparticles loaded with daunorubicin/doxorubicin by means of photodynamic therapy. However, lack of suitable targeting to tumor cells limits their applications. So drug loaded targeted nanocarrier will be an exclusive alternative. In this context, Barick et al. reported high drug loading efficiency of three dimensional (3D) mesoporous ZnO which could be effective in drug delivery systems. Later Muhammad et al. and Yuan et al. 2010 addressed the potentiality of acid degradable Mg doped ZnO quantum dots and ZnO quantum dots for targeted drug delivery. Similarly, a sustain release of captopril from mesoporous ZnO nanospheres has been noted to promote a drug delivery system (Bakrudeen et al., 2013). A typical schematic representation of ZnO quantum dot based targeted drug delivery platform has been demonstrated in Figure 3. Another important biomedical application is gene delivery-based application, although the report of using ZnO nanostructures in gene delivery is limited. Nie et al. 2006 used three-dimensional tetrapod like ZnO nanostructures for plasmid DNA delivery.

In coming years new synthetic strategy, benign fabrication will be introduced with plethora of versatile applications in terms of biological perspectives.

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