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ZnO NANORODS : SYNTHESIS AND APPLICATIONS

[1]SHRINIVAS C. MOTEKAR

[1] *Dept. of Chemistry, Sunderrao Solanke Mahavidyalaya, Majalgaon, Beed.* **(MS) INDIA.**

Abstract: *With the advent of modern technology, ZnO nanorods have been widely studied due to their unique material properties and remarkable performance in electronics, optics, and photonics. Recently, photocatalytic applications of ZnO nanorods are of increased interest in environmental protection applications. This paper presents a review of the current research of ZnO nanorods with special focus on photocatalysis. We have reviewed the semiconducting photocatalysts and discussed a variety of synthesis methods of ZnO nanorods and their corresponding effectiveness in photocatalysis. We have also presented the characterization of ZnO nanorods from the literature. We have highlighted a wide range of uses of ZnO nanorods in various applications in this paper.*

1 Introduction

As we know that nanomaterials have attracted tremendous interest due to their noticeable performance in electronics, optics, and photonics. Nanomaterials are typically classified into three groups: 0-dimensional, 1-dimensional, and 2-dimensional. 0-dimensional nanostructures, referred to as quantum dots or nanoparticles with an aspect ratio near unity, have been extensively used in biological applications [1, 2]. 2-dimensional nanomaterials, such as thin films, have also been widely used as optical coatings, corrosion protection, and semiconductor thin film devices. One-dimensional (1D) semiconductor nanostructures such as nanorods, nanorods (short nanorods), nanofibres, nanobelts, and nanotubes have been of intense interest in both academic research and industrial applications because of their potential as building blocks for other structures [3]. 1D nanostructures are useful materials for investigating the dependence of electrical and thermal transport or mechanical properties on dimensionality and size reduction (or quantum confinement) [4]. They also play an important role as both interconnects and functional units in the fabrication of electronic, optoelectronic, electrochemical, and electromechanical nanodevices [5]. Among the one-dimensional (1D) nanostructures, zinc oxide (ZnO) nanorod is one of the most important nanomaterials for nanotechnology in today's research [6].

ZnO nanostructures have attracted much attention in recent years as they behave differently from their bulk counterpart. For higher catalytic activity, the material should possess the intrinsic properties like optimum band gap, higher crystallanity as well as surface area, and defect free structure. ZnO is a semiconductor material with direct wide band gap energy (3.37 eV) and a large exciton binding energy (60 meV) at room temperature [7]. ZnO is also biocompatible, biodegradable, and biosafe for medical and environmental applications [8]. ZnO crystallizes in two main forms, hexagonal wurtzite and cubic zinc blende. Under general conditions, ZnO exhibits a hexagonal wurtzite structure. The crystalline nature of ZnO could be indexed to known structures of hexagonal ZnO, with a=0.32498 nm, b=0.32498 nm, and c=5.2066 nm (JCPS card no. 36–1451) [9]. The ratio of c/a of about 1.60 is close to the ideal value for a hexagonal cell c/a=1.633 [10]. The structure of ZnO could be described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} stacked alternately along the c-axis (Figure 1(a)). The O^{2-} and Zn^{2+} form a tetrahedral unit, and the entire structure lacks central symmetry (Figure 1(b)). Due to their remarkable performance in electronics, optics, and photonics, ZnO nanorods are attractive candidates for many applications such as UV lasers [11], light-emitting diodes [12], solar cells [13], nanogenerators [14], gas sensors [15], photodetectors [16], and photocatalysts [17]. Among these applications, ZnO nanorods are being increasingly used as photocatalysts to inactivate bacteria and viruses and for the degradation of environmental pollutants such as dyes, pesticides, and volatile organic compounds under appropriate light irradiation [18, 19].

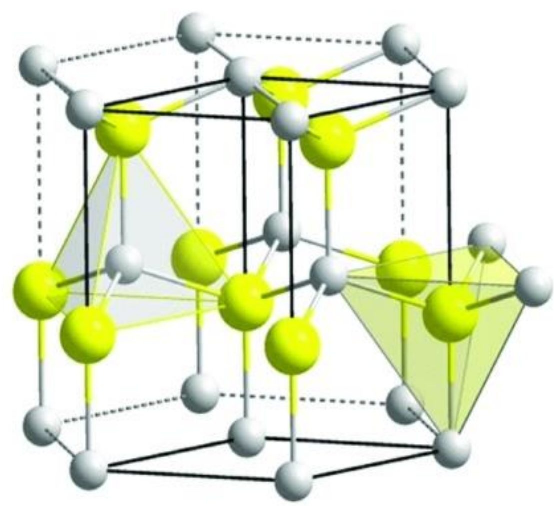

Figure 1: ZnO structure: the wurtzite structure model

This paper reviews recent research in ZnO nanorods with an emphasis on ZnO nanorods used in photocatalysis. In the following sections we have reviewed different semiconductor photocatalysts, compared their properties, and discussed a variety of synthesis methods of ZnO nanorods. We have presented the characterization of ZnO nanorods the literature. Finally, a wide range of ZnO nanorods in various applications is highlighted in this paper.

2 Photocatalysts

Photocatalysis is a promising process for environmental protection because it is able to oxidize low concentrations of organic pollutants into benign products [20–26]. Photocatalysis utilizes semiconductor photocatalysts to carry out a photo-induced oxidation process to break down organic contaminants and inactivate bacteria and viruses [27–29]. Figure 2 illustrates the process of photocatalysis. When photons with energies greater than the band gap energy of the photocatalyst are absorbed, the valence band (VB) electrons are excited to the conduction band to facilitate a number of possible photoreactions. The photocatalytic surface with sufficient photo energy leads to the formation of a positive hole (h^+) in the valence band and an electron (e^-) in the conduction band (CB). The positive hole could either oxidize organic contaminants directly or produce very reactive hydroxyl radicals (OH·). The hydroxyl radicals (OH·) act as the primary oxidants in the photocatalytic system [30], which oxidize the organics. The electron in the conduction band reduces the oxygen that is adsorbed on the photocatalyst.

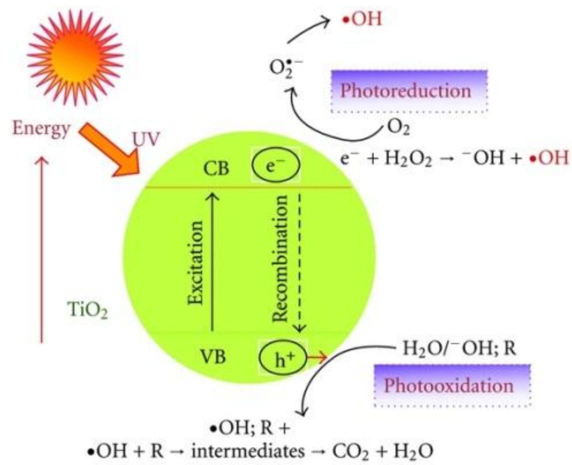

Figure 2: A schematic of the principle of photocatalysis [30]

With the development in the synthesis we have generated number of semiconductors that could be used as photocatalysts, such as TiO_2, ZnO, and WO3, Fe2O3. The band gap energy plays a significant role in the photocatalytic process. Figure 3 shows the band gap energies and the band edge positions of common semiconductor photocatalysts [31–33]. It is necessary to point out that the band gap values of ZnO, reported in the literature, are not all equivalent due to the different levels of the O vacancy in ZnO [34]. Although TiO2 is the most widely investigated photocatalyst, ZnO has also been considered as a suitable alternative of TiO2 because of its comparability with TiO2 band gap energy and its relatively lower cost of production [18, 35, 36]. Moreover, ZnO has been reported to be more photoactive than TiO_2 [37–40] due to its higher efficiency of

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generation and separation of photoinduced electrons and holes [18, 41, 42].

The surface area plays a significant role in the photocatalytic activity. The contaminant molecules need to be adsorbed on the photocatalytic surface before the reactions take place. Nanoparticles offer a large surface area, but they have mostly been used in water suspensions, which limit their practical use due to difficulties in their separation and recovery. Moreover, additional equipment is needed for catalyst nanoparticle separation. Photocatalyst supported on a steady substrate can eliminate this issue. One-dimensional nanostructures, such as nanorods grown on a substrate, offer enhanced photocatalytic efficiency due to their extremely large surface-to-volume ratio as compared to a catalyst deposition on a flat surface [28, 44]. Table 1 compares different ZnO nanostructures for photocatalytic applications. There are many advantages in nanorod structures that could be used as photocatalysts.

TABLE 1: Comparison of different ZnO nanostructures used in photocatalytic applications.

Nanoparticles		Nanorods		Nanothin film	
Advantages	Disadvantages	Advantages	Disadvantages	Advantages	Disadvantages
Could be suspended in a solution	Particle aggregation in a solution leads to a reduced surface area	Growth could be well aligned on most substrates	Growth conditions are more restricted	Coated on certain substrates	Lower performance because of small surface area
High performance because of larger surface areas	Posttreatment for catalyst removal is required	O? er larger surface area compared to nanothin film	Lower surface area compared to nanoparticles	Posttreatment for catalyst removal is not required	
	Di? cult to recover all the catalyst	Posttreatment for catalyst removal is not required			
		Lower crystallinity and more defects			

3. Synthesis of ZnO Nanorods

ZnO nanorods can be either grown independently or grown on certain substrates. However, a vertical aligned growth on a substrate has more advantages in photocatalytic applications. The anisotropy of the ZnO crystal structure assists the growth of nanorods. The most common polar surface is the basal plane (0 0 1) with one end of the basal polar plane terminating in partially positive Zn lattice points and the other end terminating in partially negative oxygen lattice points. The anisotropic growth of the nanorods takes place along the *c*-axis in the [0 0 0 2] direction [45]. The growth velocities under hydrothermal conditions along the different directions are following the pattern V (0001) > V (1011) > V (1010) [46]. The relative growth rate of these crystal faces will

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determine the final shape and aspect ratio of the ZnO nanostructures.

The synthesis methods of ZnO nanorods could mainly be classified as vapor phase and solution phase synthesis.

3.1. The Vapor Phase Synthesis. It is the most extensively explored approach in the formation of 1D nanostructures [5]. A typical vapor phase synthesis method takes place in a closed chamber with a gaseous environment. Vapor species are first produced by evaporation, chemical reduction, and gaseous reaction. After that, the species are transferred and condensed onto the surface of a solid substrate. Generally, the vapor phase synthesis process is carried out at higher temperatures from 500˚C to 1500˚C and produces high-quality nanorods. The typical vapor phase synthesis method includes vapor liquid solid (VLS) growth [47], chemical vapor deposition (CVD) [48], metal organic chemical vapor deposition (MOCVD) [49], physical vapor deposition (PVD) [50], molecular beam epitaxy (MBE) [51], pulsed laser deposition (PLD) [52], and metal organic vapor phase epitaxy (MOVPE) [53]. Among the vapor phase synthesis methods, VLS and MOCVD are two of the most important methods for the ZnO nanorods synthesis. Compared to other vapor phase techniques, VLS method is a simpler and cheaper process, and is advantageous for growing ZnO on large wafers [54]. The VLS process has been widely used for the growth of 1D nanorods and nanorods. A typical VLS process is used with nanosized liquid metal droplets as catalysts. The gaseous reactants interact with the nanosized liquid facilitating nucleation and growth of single crystalline rods and wires under the metal catalyst. Typical metal catalysts in the VLS process are Au, Cu, Ni, Sn, and so forth. ZnO nanorods have been successfully grown on sapphire, GaN, AlGaN, and ALN substrates through the VLS process [55]. The quality and growth behavior of the ZnO nanorods are strongly affected by the chamber pressure, oxygen partial pressure, and thickness of the catalyst layer [56, 57]. Chu et al. [58] synthesized well-aligned ZnO nanorods using VLS mechanism on Si substrate with chamber temperature varying from 600 to 950˚C and pressure from 0.75 to 3 torr. They showed that ZnO nanorods with high aspect ratio grew vertically on the substrate at 700 to 750˚C, the density of nanorods decreased when the temperature was higher than 800˚C, and the growth rate and length of nanorods were decreased with increasing total chamber pressure.

To eliminate the possible incorporation of catalytic impurities and to produce high-purity Catalyst free metal organic chemical vapor deposition (MOCVD) is another important synthesis method for ZnO nanorods [49, 59]. One more advantage is that the growth temperature of catalyst-free MOCVD is lower than a typical VLS growth temperature [60]. The ability to grow high-purity ZnO nanorods at low temperatures is expected to greatly increase the versatility and power of these building blocks for nanoscale photonic and electronic device applications [5]. Zeng et al. [61] reported that well-aligned ZnO nanorods were prepared by MOCVD on Si substrate without catalysts. In their grown process, high-purity diethyl zinc (99.999%) and N_2O (99.999%) were used as zinc and oxygen sources, respectively, and N_2 as the carrier gas. The base pressure of the reactor chamber and the working pressure were 10^{-5} and 50 torr, respectively. A thin nucleation layer of ZnO was grown at a low substrate temperature of 400˚C at the beginning. After annealing the nucleation layer, ZnO nanorods were grown on the nucleation layer at the substrate temperature of 650˚C.

Physical vapor deposition (PVD) technique is convenient and popular method to fabricate ZnO nanorods. Comparatively PVD techniques are suitable because of the following reasons: (1) composition of products can be controlled, (2) there is no pollution such as drainwater, discharge gas, and waste slag, and (3) simple process of making samples [62]. The process of PVD usually is direct thermal evaporation and oxidation of Zn powder at a high temperature and then deposition on the substrate to form the final product [50]. Zhang et al. [62] demonstrate the fabrication of ZnO nanorod arrays on Si substrates by PVD method at a relatively low temperature of about 500˚C. The Si substrates were placed on top of the boat to collect the products. The system was quickly heated to 500˚C under 50 cm^3/min N_2 flowing at a pressure of about 10^{-3} torr for 1 h and then cooled to room temperature. The optical investigation showed that the ZnO nanorods were of high crystal quality and had attractive optical properties.

3.2. Solution Phase Synthesis. Solution phase synthesis has many advantages when compared to vapor phase synthesis, such as low cost, low temperature, scalability, and ease of handling. Generally, solution phase reactions occur at relatively low temperatures compared to vapor phase synthesis methods. Thus, solution synthesis methods allow for a greater choice of substrates including inorganic and organic substrates. Due to the many advantages, solution phase synthesis methods have attracted increasing interest. In solution phase synthesis, the growth process could be carried out in either an aqueous or organic solution or a mixture of the two [63, 64].

3.2.1. Hydrothermal Method. Generally, solution phase synthesis is carried out in an aqueous solution, and the process is then referred to as the hydrothermal growth method [65, 66]. Hydrothermal methods have received a lot of attention and have been widely used for synthesis of 1D nanomaterials. In addition, hydrothermally grown ZnO nanorods have more crystalline defects than others primarily due to oxygen vacancies [28]. Nanorods with inherent defects are capable of exhibiting visible light photocatalysis even without doping with transition metals [67]. The general process for vertically aligned ZnO nanorods grown on a substrate by the hydrothermal method is the following.

(a) A thin layer of ZnO nanoparticles is seeded on a certain substrate. The seeding layer promotes nucleation for the growth of nanorods due to the lowering of the thermodynamic barrier [68].

(b) An alkaline reagent (such as NaOH or hexam-ethylenetetramine) and Zn^{2+} salt ($Zn(NO_3)_2$, $ZnCl_2$, etc.) mixture aqueous solution is used as a precursor (or growth solution).

(c) The ZnO seeded substrate is kept in the growth solution at a certain temperature and a certain period of time.

(d) The resultant substrate and growth layer is washed and dried.

When hexamethylenetetramine ($(CH_2)_6N_4$, or HTMA) and $Zn(NO_3)_2$ are chosen as precursor, the chemical reac-tions can be summarized in the following equations [35]

Decomposition reaction:

$$(CH_2)_6N_4 + 6H_2O \longrightarrow 6HCHO + 4NH_3 \quad (1)$$

Hydroxyl supply reaction:

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^- \quad (2)$$

Supersaturation reaction:

$$2OH^- + Zn^{2+} \longrightarrow Zn(OH)_2 \quad (3)$$

ZnO nanorod growth reaction:

$$Zn(OH)_2 \longrightarrow ZnO + H_2O \quad (4)$$

One of the key parameters for the growth of ZnO nanorods is controlling the supersaturation of the reactants. It is believed that high supersaturation levels favor nucleation and low supersaturation levels favor crystal growth [3]. If a lot of OH^- is produced in a short period, the Zn^{2+} ions in the solution will precipitate out quickly due to the high pH environment, and, therefore, Zn^{2+} would contribute little to the ZnO nanorod growth and eventually result in the fast consumption of the nutrient and prohibit further growth of the ZnO nanorods [69]. Thus, the concentration of OH^- should be controlled in the solution to maintain low super-saturation levels during the whole nanorod growth process.

Effect of the ZnO Seeding Layer. Typical preseeding methods include thermal decomposition of zinc acetate, spin coating of ZnO nanoparticles, sputter deposition, and physical vapor deposition. In order to seed ZnO particles on the sub-strate, ZnO seeds must be annealed at certain temperature to improve ZnO particle adhesion to the substrate and nanorod vertical growth alignment. Greene et al. [70] studied the minimum temperature required to form textured seeds from zinc acetate on a silicon substrate from 100 to 350°C. The results suggest that temperatures between 150 and 200°C are needed for seed alignment, whereas higher temperatures promote seed crystallinity and growth. Baruah and Dutta [71] have reported that a very uniform thin layer of ZnO nanoparticles could be observed when ZnO seeds are annealed at a temperature of

350˚C. However, when the annealing temperature was further increased to 450˚C, ZnO crystallized into nanoparticles as well as nanorod-like structures. The authors hinted that ZnO seeds annealing at a temperature of about 350˚C could give the best results for the ZnO nanorod growth.

The crystal size texture and thickness of ZnO seed layers also affect the quality of ZnO nanorod growth [72–75]. Ghayour et al. [72] reported the effect of seed layer thickness on alignment and morphology of ZnO nanorods. The results showed that the diameter increased, the density decreased, and the length of the nanorods slightly decreased when the thickness of the seed layer increased. Wu et al. studied the effects of seed layer characteristics on the synthesis of ZnO nanorods. The SEM images showed the density of nanorods decreased from 35 to 12 μm^{-2} when the thickness increased from 106 to 191 nm and the diameter of the nanorods was found to increase with the seed layer (002) grain size. Ji et al. [75] found that the average diameter of nanorods is increased from 50 to 130 nm and the density is decreased from 110 to 60 μm^{-2} when the seed layer thickness is changed from 20 to 1000 nm. Baruah and Dutta [71] reported that the nanorods grown on seeds crystallized from a zinc acetate solution have a higher aspect ratio (of the order of 3) than those grown using nanoparticle-seeded substrates. Without a ZnO seeding layer, ZnO nanorods could be grown on an Au/substrate by introducing a suitable content of ammonium hydroxide into the precursor solution [76]. Au is used as an "intermediate layer" to promote the growth of ZnO nanorods [76].

Effect of an Alkaline Reagent. Some alkaline reagents that have been used to supply OH^- during the reaction process are NaOH, hexamethylenetetramine (HMTA), Na_2CO_3, ammonia, and ethylenediamine. When NaOH, KOH, or Na_2CO_3 is chosen, the synthesis process is carried out at elevated temperatures and pressures in a Teflon-sealed stainless autoclave [77–80]. When HMTA, ammonia, or ethylenediamine is chosen, the synthesis process can be carried out at temperatures below 100˚C and at atmospheric pressure. However, HMTA is the most often used due to its advantage in producing high-quality ZnO nanorods [81]. HMTA plays different significant roles during the synthesis process. First, HMTA supplies the OH^- ions to drive the precipitation reaction by thermal degradation [82]. Second, HMTA acts as a pH buffer by slowly releasing OH^- ions through thermal decomposition The hydrolysis rate of HMTA is decreased with an increase in pH and vice versa. Third, HMTA attaches to the nonpolar facets of the ZnO nanorods and prevents access of the Zn^{2+} ions to them thus leaving only the polar (001) face for epitaxial growth [68].

Effect of Precursor Concentration. To ascertain the relation-ship between the precursor concentration and the ZnO nanorod growth, Wang et al. [83] carried out a series of experiments by varying the precursor concentration and different ratios of [$Zn(NO_3)_2$]/[$C_6H_{12}N_4$]. The effect of the concentration of the precursor on the growth of ZnO nanorods is to increase the average diameter of ZnO nanorods almost linearly from 43 to 70 nm and the average length from 65 to 320 nm, as the precursor concentration increases from 0.008 to 0.04M (Figure 4). The corresponding aspect ratio of the ZnO nanorods increases from 1.8 to 5.8 and then slightly decreases to 4.6 (Figure 4 insert). Changes in the [$Zn(NO_3)_2$]/[$C_6H_{12}N_4$] ratio did not have a significant effect on the diameters of the ZnO nanorods (Figure 5). The aspect ratio of the ZnO nanorod arrays reached a maximum value of 7.25 when the [$Zn(NO_3)_2$]/[$C_6H_{12}N_4$] ratio was set to unity (Figure 5 insert). Xu et al. [69] studied the nanorod density by varying the precursor concentration with equal molar concentrations of the zinc salt and HMTA. The experimental results showed that the density of the nanorods is closely related with the precursor concentration. From 0.1 to 5 mM, the ZnO nanorod density was increased from 55/100 μm^2 to 108/100 μm^2. When the precursor concentration is further increased, the density of ZnO nanorods remains approximately steady with a slight decreasing tendency. The authors explained that the zinc chemical potential inside the body of the solution increases with zinc concentration. To balance the increased zinc chemical potential in the solution, more nucleation sites on the substrate surface will be generated, and, therefore, the density of the ZnO nanorods will increase. However, a continuous increase in the solution concentration may not increase the density of the nanorods when its density is larger than the saturation density. Kim et al. [84] reported that the density and diameter of ZnO nanorods are especially sensitive to the concentration of the reactants. Furthermore, the structural transition is shown by increasing the concentration. There are several reports available on the photon assisted degradation of organic dye molecules using semiconductor metal oxide ZnO [85-87] of different morphologies. At the lowest concentration of Zn^{2+}, the ZnO nanorods grow as single crystals with a low density and variable orientations. On the other hand, at the highest concentration, the nanorods grow as polycrystals due to the supersaturated Zn^{2+} source.

Conclusions

This paper provides an overview of the synthesis, characterization, and applications of ZnO nanorods. The hydrothermal synthesis method is simple and efficient and it has received increased attention. A mixture of zinc nitrate and hexamine as precursor is the most popular. Due to the unique properties of the material, ZnO nanorods are attractive for a number of potential applications such as photocatalysis, solar cells, sensors, and generators. Among the applications of ZnO nanorods, photocatalysis is being increasingly used for environmental protection. Further research is needed to improve the quality of ZnO nanorods and large-scale produce ZnO nanorods for practical industrial applications. Based on this paper, ZnO nanorods promise to be one of the most important materials in photocatalytic as well as others applications.

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