



Synthesis, Characterization, and Applications of ZnO Nanowires : A Review

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Abstract: ZnO is one of the most promising and widely studied materials due to its unique properties and remarkable performance in electronics, optics, and photonics etc. “Meanwhile, doping with selective element offers an effective method to enhance and control the electrical and optical properties of ZnO nanostructures, which is crucial for its practical applications”. Recently ZnO nanowires are used for a number of potential applications such as photocatalysis, solar cells, sensors, and generators. Among the applications of ZnO nanowires, photocatalysis is being increasingly used for environmental protection. In this paper we report a review of the current research on ZnO nanowires with special focus on photocatalysis. We have presented the semiconducting photocatalysts, discussed number of synthesis methods and their corresponding effectiveness in photocatalysis. We have also presented the characterization of ZnO nanowires from the literature. Finally, a wide range of uses of ZnO nanowires in various applications is highlighted there in.

Keywords: TiO₂; Fe₂O₃; NaOH; ZnCl₂.

I. INTRODUCTION

The important properties of nanostructured materials have started motivation among scientists to explore the possibilities of using them in technological applications. The Nanomaterials have attracted great interest due to their noticeable performance in electronics, optics, and photonics etc. Among the nanostructured metal oxides, ZnO is considered to be one of the best metal oxides that can be used at a nano scale level. Nanomaterials are typically classified into three different groups as: 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 (2D) nanomaterials such as thin films, have also been widely used as optical coatings, in corrosion protection, and semiconducting thin film devices. One-dimensional (1D) ZnO nanostructures have been studied intensively and extensively over the last decade for their remarkable chemical and physical properties. One-dimensional semiconductor nanostructures such as nanowires, nanorods, nanofibres etc. have been of intense interest in industrial applications because of their potential as building blocks for other structures [3]. 1D nanostructure are also useful materials not only for investigating the dependence of electrical and thermal transport on dimensionality and size reduction [4], but also play an important role for both interconnects and functional units in the fabrication of electronic, optoelectronic, electrochemical, and electromechanical nanodevices [5].

Among the one-dimensional nanostructures, ZnO (nanowire) is one of the most important nanomaterials used for nanotechnology in today’s research [6]. It is the most promising semiconductor material because of its high mechanical and thermal stability with a direct wide band gap energy (3.37 eV) and a large exciton binding energy (60 meV) at room temperature [7]. ZnO itself has normally a hexagonal or wurtzite structure. Due to their remarkable performance in electronics, optics, and photonics, ZnO nanowires have attracted many applications such as UV lasers [8], light-emitting diodes [9], solar cells [10], nanogenerators [11], gas sensors [12], photo detectors, varistors [6] and photocatalyst with high chemical activity etc.

In this paper we have reviewed the recent research in ZnO nanowires (or nanorods) with its emphasis used in photocatalysis. We have also reviewed different semiconductor photocatalysts, compared their properties, and discussed number of synthesis methods of ZnO nanowires. Simultaneously, we have presented the characterization of ZnO nanowires from the literature. Finally, a wide range of ZnO nanowires in various applications is highlighted there in.

II. PHOTOCATALYSTS

Photocatalysis is a promising process for environmental protection as it is able to oxidize low concentrations of organic pollutants into benign products [13–19]. It utilizes semiconductor photocatalysts to carry out a photo-induced oxidation processes to break down an organic contaminants and inactivate bacteria and viruses [20, 21, 79]. The photocatalysis process is illustrated in figure (1).

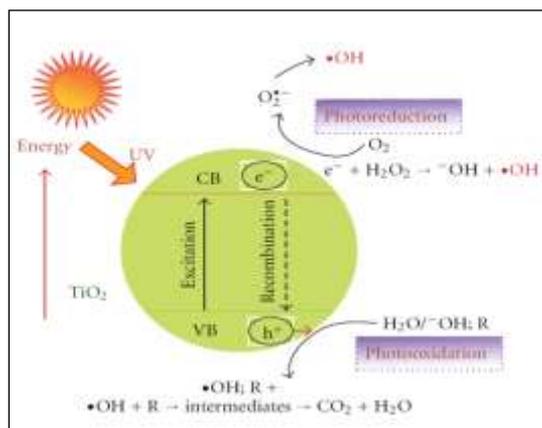


Figure 1: A schematic of the principle of photocatalysis (reproduced with permission from [80] ©2010 Elsevier).

When photons with energy greater than the band gap energy of the photocatalyst are absorbed, the valence band (VB) electrons are excited to the conduction band (CB) to facilitate a number of possible photoreactions. The photocatalytic surface with sufficient photo energy leads to the formation of a positive hole (h^+) in valence band and an electron (e^-) in conduction band. The positive hole may either oxidize organic contaminants directly or produce very reactive hydroxyl radicals (OH^\bullet). The hydroxyl radicals (OH^\bullet) acts as a primary oxidants in the photocatalytic system [80], which oxidizes the organic contaminants. The electron in the conduction band reduces the oxygen that is adsorbed on the photocatalyst. There are a number of semiconductors such as TiO_2 , ZnO and Fe_2O_3 which can be used as photocatalysts.

The band gap energy plays an important role in the photocatalytic process. Figure 2 shows the band gap energies and the band edge positions of common semiconductor photocatalysts [22–24]. 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 [25]. Although TiO_2 is the most widely investigated photocatalyst, ZnO is considered as a suitable alternative of TiO_2 because of its comparability with TiO_2 band gap energy and its relatively low cost production [26, 27, 81]. Moreover, ZnO has been reported to be more photoactive than TiO_2 [28–31] due to its higher efficiency of generation and separation of photo induced electrons and holes [32, 33, 81]. In photocatalytic activity the surface area plays a significant role as the contaminant molecules need to be adsorbed on the photocatalytic surface before the reaction takes place. Although nanoparticles offer a large surface area, they have mostly been used in water suspensions, which limit their practical use due to difficulties in their separation and recovery.

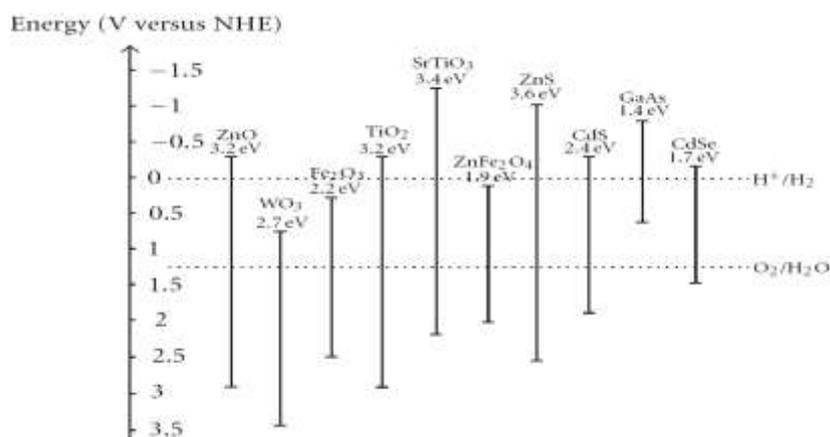


Figure 2: Band edge positions of common semiconductor photocatalysts (data from [23,24,83]).

Table 1 compares different ZnO nanostructures for photocatalytic applications. There are many advantages in nanowire structures that could be used as photocatalysts.



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

Nanoparticles		Nanowires		Nanofilm	
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	Offer larger surface area compared to nanofilm	Lower surface area compared to nanoparticles	Posttreatment for catalyst removal is not required	
	Difficult to recover all the catalyst	Posttreatment for catalyst removal is not required	Lower crystallinity and more defects		

III. SYNTHESIS OF ZnO NANOWIRES

ZnO nanowires can either be grown independently or on certain substrates. However, a vertical aligned growth on a substrate has more advantages in photocatalytic applications. The relative growth rate of crystal faces will determine the final shape and aspect ratio of the ZnO nanostructures. Thus zinc oxide which is a multifunctional material with a large direct band gap created anxiousness in the scientific minds to enhance the research on one dimensional nanostructure especially oxide materials.

The properties of zinc oxide makes the material exists in various shapes in the form of nanostructures exhibiting number of properties like piezoelectricity, optical transparency, conductivity, solar cell, UV and visible photoluminescence, optical nonlinearity and many more. But obtaining various shapes of nanostructures merely depends on different processing techniques. Methods which are related to the synthesis of various shapes of zinc oxide nanostructures are chemical and thermal vapour deposition, vacuum arc deposition, electrochemical, and hydrothermal process. But all these methods reported possesses many complex steps; require sophisticated equipments and rigorous experimental conditions [42]. Thus need for a synthesis technique arises which would be simple, easier and by using it zinc oxide nanostructures can be grown in a laboratory environment and also characterized such structures for a wide range of applications through repeated fabrication and modification.

One such inexpensive method which can be implemented without having any complexes and need for sophisticated equipments is also not desirable is the wet chemical method. Not only the method enable us to fabricate multi-dimensional nanostructures in a large scale but also provides repeated preparation that enables one to varying the process conditions for an investigational study and repeatability in the yield. Till now there were number of reports regarding the fabrication of one dimensional ZnO nanostructures especially nanorods and nanotubes via number of routes.

The Vapor Phase Synthesis: Vapor phase synthesis is probably the most extensively explored approach in the formation of 1D nanostructures [5]. Generally, the vapor phase synthesis process is carried out at higher temperatures from 500°C to 1500°C and produces high-quality nanowires. The typical vapor phase synthesis method includes vapor liquid solid (VLS) growth [35], chemical vapor deposition (CVD) [36], physical vapor deposition (PVD) [38]. Compared to other vapor phase techniques, VLS method is a simpler and cheaper process, and is advantageous for growing 1D ZnO nanowires on large wafers [39].

Chu et al. [40] have synthesized well-aligned ZnO nanowires 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 nanowires with high aspect ratio grew vertically on the substrate at 700 to 750°C; Physical vapor deposition (PVD) technique has also been used to fabricate ZnO nanowires. The advantages of PVD technique are the following: (i) composition of products can be controlled, (ii) there is no pollution such as drain water, discharge gas, and waste slag, and (iii) simple process of making samples [50]. The process of PVD usually is direct thermal vaporation and oxidation of Zn powder at a high temperature and then deposition on the substrate to form the final product [38].

Zhang et al. [50] demonstrate the fabrication of ZnO nanowire arrays on Si substrates by PVD method at a relatively low temperature of about 500°C. In their synthesis process, high-purity Zn powder as source material was placed in a ceramic boat located at the center of a horizontal tube furnace. The Si substrates were placed on top of the boat to collect the products. The system was quickly heated to 500°C under 50cm³/min N₂ flowing at a pressure of about 10–3 torr for 1 hour and then cooled to room temperature. The optical investigation showed that the ZnO nanowires were of high crystal quality and had attractive optical properties.

Mohanta et al. have reported the fabrication of ZnO nanorods grown on P-type GaN/sapphire and silicon-on-insulator substrates by chemical vapour deposition [41]. The nanorods show strong UV band edge emission around 380nm [44-46].

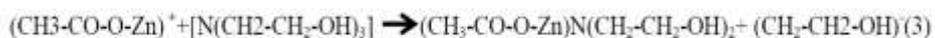
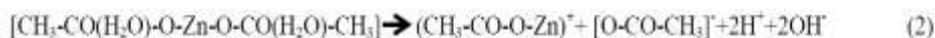
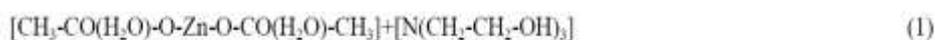
In another report by Ding et al., ZnO nanorods have been grown on various substrates (ceramic, glass, Si, metal) by solution phase growth at 95°C [45]. However there are only few reports on the fabrication of ZnO nanobelts by VLS and thermal evaporation method [46-49]. In another report by Zhang et al. have fabricated ZnO nanobelts by thermal evaporation of ZnCl₂ at 700 °C under flow of Ar and O₂ [48].

Other Solution Phase Synthesis Methods: Other solution phase synthesis methods include the microemulsion and ethanol base methods. Lim et al. [52] reported the preparation of ZnO nanorods by the microemulsion synthesis. The surfactant, such as ethyl benzene acid sodium salt (EBS), dodecyl benzene sulfonic acid sodium salt (DBS), and zinc acetate dispersed in xylene by stirring until a homogenous mixture, was obtained. Then the hydrazine and ethanol mixture solution was added drop by drop to the well-stirred mixture at room temperature. The resulting precursor-containing mixture was subsequently heated to 140°C and refluxed for 5 h. The resultant ZnO nanorods had an average diameter of 80 nm.

In the microemulsion synthesis, the process is referred to as hydrothermal when it is carried out in an aqueous solution [53]. Wu et al. [54] synthesized ZnO nanorods by using a solvothermal base in an ethanol solution. The synthesis process consisted of a NaOH ethanol solution added drop by drop in a Zn(NO₃)₂ ethanol solution and the mixture transferred into a Teflon lined stainless autoclave and heated at 160°C for 12h.

Sol-gel process: The growth of ZnO from zinc acetate dihydrate precursor using sol–gel process generally undergoes four stages, such as solvation, hydrolysis, polymerization and transformation into ZnO. The zinc acetate dihydrate precursor hydrolyzed, regarded as removal of the intercalated acetate ions and results in a colloidal–gel of zinc hydroxide (Eq. (5)), size and activity of solvent have obvious influence on the reacting progress and product. Ethanol has smaller size and a more active OH⁻. Ethanol can react more easily to form a polymer precursor with a higher polymerization degree, which is required to convert sol into gel [78]. These zinc hydroxide splits into Zn²⁺ cation and OH⁻ anion according to reactions (Eq. (4)) and followed by polymerization of hydroxyl complex to form “Zn–O–Zn” bridges and finally transformed into ZnO (Eq. (5)) [77].

Since this chemical method is found to be very simple, cost-effective and quite suitable to adopt in the laboratory. By adapting this method it has been possible to grow ZnO nanobelts at room temperature over a very short duration of growth and without using any surfactant or catalyst. Also this method does not necessitate the maintenance of rigorous experimental conditions as in earlier cases [74-76]. Therefore, overall we can conclude that synthesis of ZnO nanostructures by chemical route not only provides a method for large-scale fabrication of ZnO nanorods with a low cost, but also open a way to the size-controlled fabrication of other materials.



IV. CHARACTERIZATION

Under general conditions, ZnO is single crystalline and exhibits a hexagonal wurtzite structure. The structure of ZnO nanowires could be revealed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Figure 3 shows the XRD pattern of the ZnO nanowire growth on a silicon substrate by using the hydrothermal synthesis method. A dominant diffraction was first solvated in ethanol, and then peak for (002) indicates a high degree of orientation with



the c-axis vertical to the substrate surface. **Figure 4** shows a top down image of ZnO nanowires [55]. Both XRD and SEM demonstrate the hexagonal wurtzite structure of the ZnO nanowires.

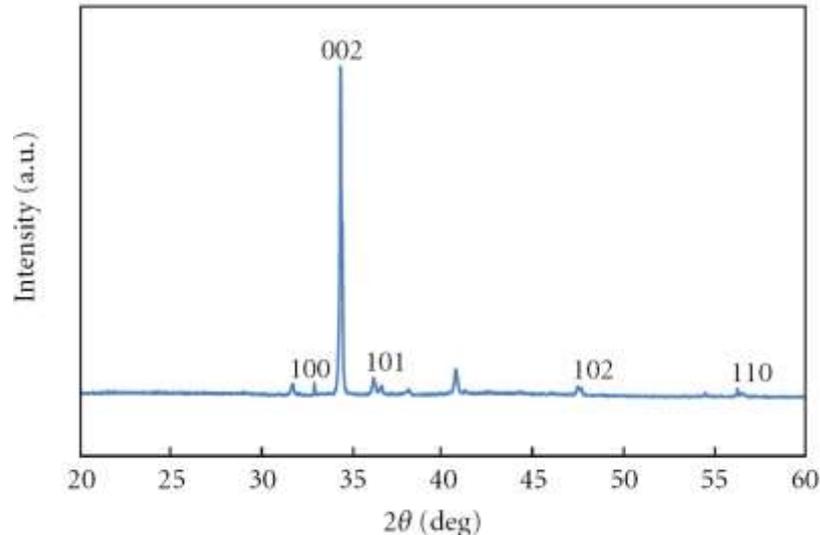


Figure 3: XRD of ZnO nanowires on a silicon substrate growth by the hydrothermal synthesis method (from [56] unpublished)

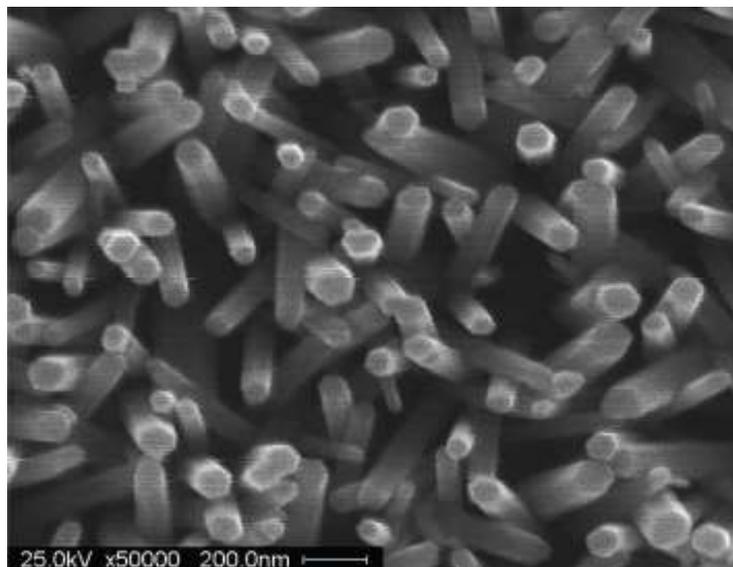


Figure 4: SEM image of the ZnO nanorods array on glass substrate by hydrothermal method (from [56] unpublished).

Further structural characterizations can be carried out by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). **Figure 5(a)** shows a low-resolution TEM image of ZnO nanowires with a homogeneous diameter size that does not vary significantly along the wire length. The HRTEM pattern measured for one individual nanowire is shown in **Figure 5(b)**. The crystal lattice fringes spacing in the HRTEM image are 0.52nm and fringes perpendicular to the wire axis is 0.26 nm. This measured plane spacing is characteristic of the (002) planes, showing the ZnO nanowire with a perfect lattice structure and verifying that the nanowires grow along the c-axis direction [57].

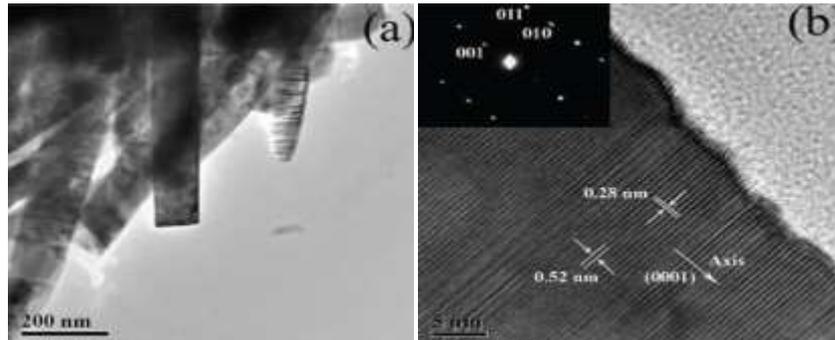


Figure 5: (a) TEM of ZnO nanowires on an ITO substrate showing a general view. (b) HRTEM image showing individual nanowires with $[0\ 0\ 2]$ growth direction. Inset shows selected electron diffraction (SAED) patterns (reproduced with permission from [57] ©2010, Elsevier).

The ZnO nanowires obtained at different reaction times and examined by Raman spectra are presented in **Figure 6**. The peaks of the ZnO nanowires at 327, 378, 437, 537, and 1090 cm^{-1} were observed in all the samples. A narrow strong band at 437 cm^{-1} has been assigned to E2 modes involving mainly a Zn motion corresponding to the band characteristic of the wurtzite phase. The band at 378 cm^{-1} (A1T mode) indicates the presence of some degree of structural order disorder in the ZnO lattice. The band bands at 327 cm^{-1} should be assigned to the second-order Raman spectrum. A band at 537 cm^{-1} is the contribution of the E1 (LO) mode of ZnO associated with oxygen deficiency.

The envelope of bands above 1090 cm^{-1} can be attributed to overtones and/or combination bands [58]. **Figure 7** shows the UV-Visible absorption spectra of ZnO nanoparticles, ZnO nanowires, and ZnO/Fe nanowires. ZnO nanowires showed a larger enhancement absorption in the visible range as compared to ZnO nanoparticles. The ZnO/Fe nanowires exhibit even stronger absorption than the ZnO nanowires and nanoparticles in both the UV and the visible range implying that ZnO/Fe nanowires could more be fully utilized, most of the UV and visible light than the other two. **Figure 8** shows the FTIR spectrum of ZnO nanorods in the range of 2000–300 cm^{-1} . There is only one significant spectroscopic band around 417 cm^{-1} associated with the characteristic vibrational mode of Zn–O bonding [59]. The X-ray photoelectron spectroscopy (XPS) result Zn(2p) of the ZnO nanorods is shown in **Figure 9**. The peaks at 1021.4 and 1044.6 eV in the spectrum corresponding to the doublet of Zn (2p_{3/2}) and (2p_{1/2}), respectively, can be attributed to the formation of hexagonal ZnO nanorods [82]. **Figure 10** shows the photopotential response of a ZnO nanowire electrode under UV irradiation. When the UV light is switched on, electron-hole pairs are generated and produce a photocurrent. The UV irradiation changes the current abruptly with some variation, and the photo-potential is sharply reduced when the light is switched off [26]. In addition to the above characterizations, ZnO nanowires also exhibit many other unique chemical and physical properties for many applications such as large surface areas, piezoelectric, piezotronic, and optical.

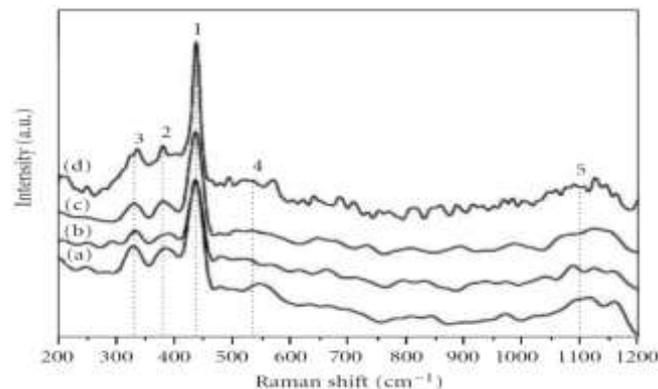


Figure 6: Raman spectra of the ZnO structures obtained by the hydrothermal method at 130°C for (a) 30min, (b) 60min, (c) 120 min, and (d) 180 min (reproduced with permission from [58] ©2010 Elsevier).

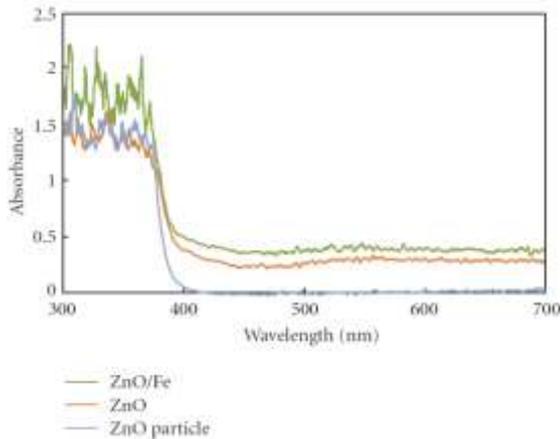


Figure 7: UV-Visible absorption spectra of ZnO nanoparticle, ZnO and ZnO/Fe nanowires (from [56] unpublished).

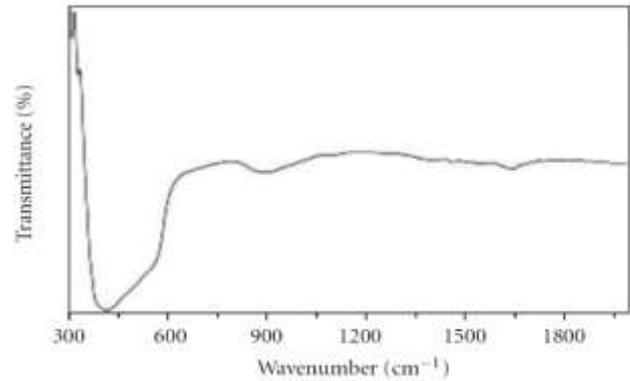


Figure 8: FTIR spectrum of ZnO nanorods prepared at 200°C for 20 h using NaOH (reproduced with permission from [84] ©2010Elsevier).

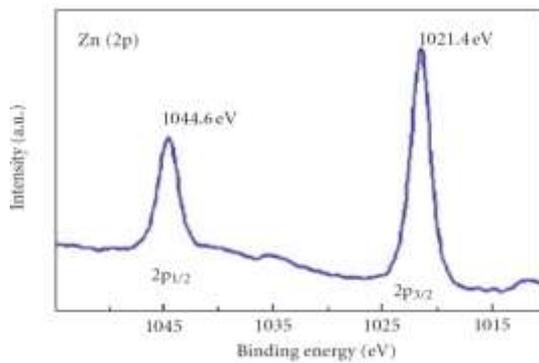


Figure 9: Zn(2p)XPS spectrum of synthesized ZnO nanorods on a ZnO thin film (reproduced with permission from [85] ©2011Elsevier).

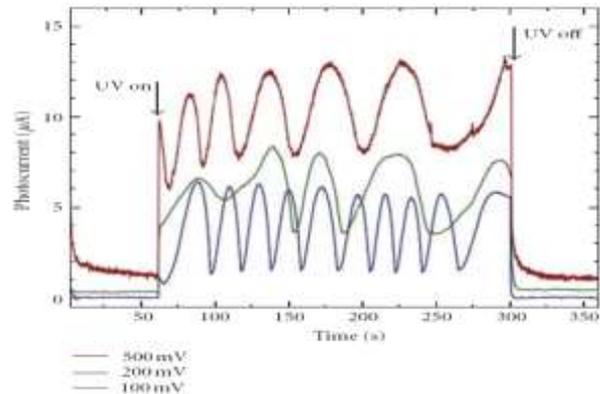


Figure 10: Photocurrent response to UV light at different DC biases (reproduced with permission from [19] ©2011 American Chemical Society).

V. PROPERTIES/APPLICATIONS

Compared with bulk materials, low-dimensional nano scale materials, with their large surface areas and possible quantum-confinement effects, exhibit distinct electronic, optical, chemical and thermal properties. In many cases, 1D nanostructures are superior to their counterparts with larger dimensions. The ZnO nanoparticles are characterized by means of the modern testing techniques such as XPS, ESR, SPS and PL.

Jing, Liqiang and Yuan have reported the relationships of surface oxygen vacancies (SOV) with photoluminescence (PL) and photocatalytic performance. The results show that the smaller the particle size, the larger the SOV content, the stronger the PL signal, the higher the photocatalytic activity, indicating that the SOV, PL and photocatalytic activity have inherent relationships. This was because of the reasons that the PL signal is attributed to the free and binding excitons resulting from the SOV, while the SOV is favorable for a photocatalytic oxidation reaction since the SOV can easily capture the photoinduced electrons, and the captured electrons had strong interactions with the adsorbed oxygen.

5.1. Gas Sensor: ZnO is one of the earliest discovered and most widely used oxide gas sensing materials. ZnO functions as a gas sensitive material due to its electrical conductivity that can be dramatically affected by the adsorption or desorption of gas molecules on its surface [60]. 1D nanostructured devices such as nanowires are more sensitive and selective due to their high aspect ratio giving rise to a large surface area. Recently, Oh and Jeong [61] fabricated CO sensors based on aligned ZnO nanorods on a substrate and exhibited high sensitivity to CO gas with the low detection limit of 1 ppm at 350°C.

5.1.2. Biosensor: Now days, ZnO nanostructures have attracted interest in biosensor applications due to many advantages, including nontoxicity, biosafety, bio-compatibility, high electron-transfer rates, and combination with immobilized enzymes [62]. In addition, ZnO has high ionic bonding (60%), and it dissolves very slowly at normal biological pH environments. Liu et al. [63] have constructed an ampere-metric glucose biosensor based on aligned ZnO nanorod films formed directly on the surface of ITO glass.

5.3. UV Laser: Room temperature of ZnO-nanowire-based UV lasing has been recently demonstrated [64]. Figure 11 shows a typical room temperature photoluminescence (PL) spectrum of ZnO nanorods with an excitation wavelength of 325nm at room temperature [65]. The spectrum exhibits two bands including a strong ultraviolet emission at 378nm (or 3.28 eV) and a weak spectral band in the visible region. The UV emission was contributed to the near band edge emission of the wide band gap of ZnO. Visible emission is due to the presence of various point defects such as oxygen vacancies.

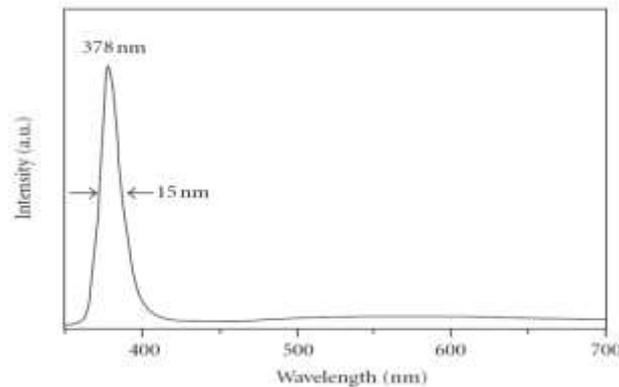


Figure 11: Room temperature PL spectra of ZnO nanorods ($\lambda_{exc} = 325$ nm) (reproduced with permission from [86] ©2009 Elsevier)

5.4. Light-Emitting Diode: The output power of GaN LEDs with ZnO nanotip arrays can be enhanced by up to 50% times [66]. A heterojunction LED could be fabricated by the growth of vertically aligned ZnO nanowires on a p-GaN substrate and employed indium tin oxide (ITO)/glass to combine and package [67, 68]. Figure 12 shows the electroluminescence (EL) spectra of ZnO NWs/p-GaN/ZnO nanowire heterostructure at a DC current of 20mA. A UV-blue electroluminescence (EL) emission was observed from the nanowire-film heterojunction diodes. Most of the currently developed ZnO LEDs are based on heterojunctions. However, a ZnO rod p-n homojunction LED with an ion implanted P-doped p-type ZnO could also be fabricated [69].

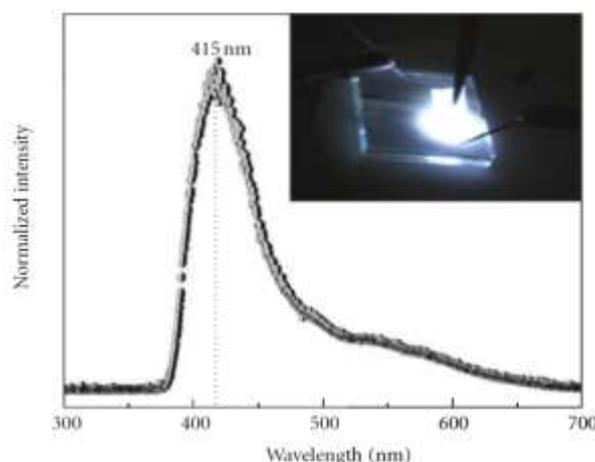


Figure 12: EL spectra of ZnO nanowires/p-GaN/ZnO nanowires heterostructure at a DC current of 20mA. The inset is a photograph of the emission of blue light by the heterojunction LED under dc bias (reproduced with permission from [51] ©2009 American Institute of Physics).

5.5. Photocatalysis: ZnO nanowires used as photocatalysts have been recently reported by many research groups [70-73]. Sugunan et al. [70] described a continuous flow water purification system by the fabrication of ZnO nanowires grown on flexible poly-L-lactide nanofibers. The continuous flow photocatalytic decomposition of organic compounds in water has no need for separation of the photochemically active material from the reservoir, and the purified water can



be directly collected from the reservoir (Figure 21). The various organic pollutants that have been tested and removed under UV light illumination include methylene blue, monocrotophos, and diphenylamine. The results demonstrated that simultaneous photocatalytic decomposition of more than one organic contaminant is possible by using the polymer-ZnO nanostructure. The authors also stated that the fabrication can be easily scaled up and the whole photocatalytic water treatment setup can easily be adapted either as a point of use system or centralized large-scale water purification system. Surface properties such as surface defects and oxygen vacancies of photocatalysts play a significant role in the photocatalytic activity. ZnO nanowire crystalline defects exist primarily due to oxygen vacancies [21]. Nanoparticles with crystalline defects are capable of exhibiting visible light photocatalysis even without doping with transition metals [51].

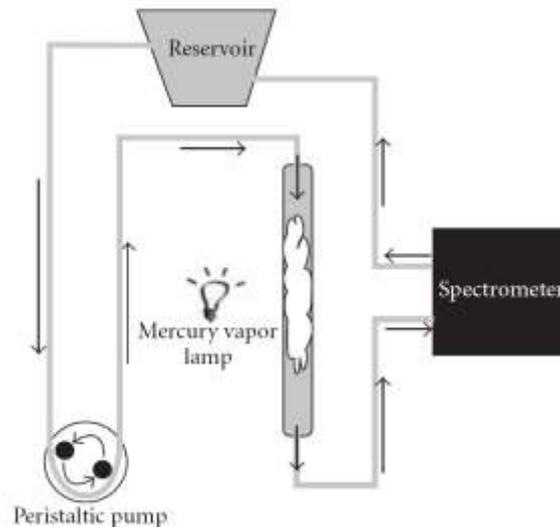


Figure 13: Schematic of a continuous-flow photocatalytic water treatment system (reproduced with permission from [87] ©2010 The American Ceramic Society).

VI. CONCLUSION

ZnO is one of the most promising and widely studied material due to its unique properties and remarkable performance in electronics, optics, and photonics etc. Meanwhile, doping with selective element offers an effective method to enhance and control the electrical and optical properties of ZnO nanostructures, which is crucial for its practical applications. Recently ZnO nanowires are used for a number of potential applications such as photocatalysis, solar cells, sensors, and generators. Among the applications of ZnO nanowires, photocatalysis is being increasingly used for environmental protection.

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