

Growth of Zinc Oxide (ZnO) Nanorods and Their Optical Properties

L.M. AL-Harbi & E. H. El-Mossalamy

Department of Chemistry, Faculty of science, King Abdul Aziz University
Jeddah 21589, Kingdom of Saudi Arabia
E-mail: sbdmina@yahoo.com & lmajeed2002@yahoo.com

H.M.Arafa

Chemistry Department, Faculty of Science, Tabuk University
P.O.Box 741 Tabuk 71491, Saudi Arabia
E-mail: han.m.a.2008@hotmail.com

A.Al-Owais

Chemistry Department, King Saud University
P.O.Box 272047, Riyadh-11352, Saudi Arabia
E-mail: aowais21@yahoo.com

M. A. Shah (Corresponding author)

Department of Physics, Faculty of science, King Abdul Aziz University
Jeddah 21589, Kingdom of Saudi Arabia
E-mail: shahkau@hotmail.com, sashraf@kau.edu.sa

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Abstract

We herein, report growth of zinc oxide nanorods by a simple reaction of zinc powder and de-ionized water at very low temperature of $\sim 110^{\circ}\text{C}$ without using any organics. The formation of nanorods by the reaction of metals with water is suggested to occur due to the decomposition of water. The decomposed water produces controlled supply of OH^- which further reacts with metal to form ZnO and releases hydrogen. The synthesized ZnO products were characterized in terms of their structural and optical properties. It was observed that the grown nanorods possess good optical property. Compared with other methods, the present method is simple, soft, inexpensive and environmentally benign which will make it suitable for large-scale production for devices and other applications.

Keywords: Soft synthesis, Nanorods, Structural and optical properties

1. Introduction

Zinc oxide (ZnO) is rapidly gaining credibility as a material with excellent possibilities for electronic and photonic devices. Owing to the semiconducting and piezoelectric dual properties, novel applications are introduced which have profound effect in many areas such as self-powdered nanodevices and nanosystems. The demonstration of room temperature ultraviolet lasers, field effect transistors and field emission arrays based on zinc oxide nanorods have stimulated great interest in developing functional nanodevices (C. Klingshrin, 2007)(Z.L. Wang, Z.L. Mater, 2004). Moreover, the wide range of morphological diversity in the nano-regime has made this material a promising candidate in the field of nanotechnology and opened up new possibilities for the fabrication of high performance devices based on these nanostructures. Among the various shapes of nanostructures, one dimensional (1D) nanostructures have received considerable attention due to their potential interests for understanding fundamental physical concepts and for efficient field emission that has enormous commercial applications (Z.W. Pan, Z.R. Dia and Z.L. Wang, 2001)(X. Wang, J. Sang and Z.L.Wang, 2007)(X. Fang, L. Zhang, 2006).

Research in the past have shown that once materials are prepared in the form of very small particles, rods, wires, they change significantly their physical and chemical properties something to the extent that completely new phenomenon are established. While nanomaterials have been generated by physical methods, chemical approaches have proved to be more effective and efficient as they provide better control over the size and shape, which is one of the essential features of nanomaterials. Chemical synthesis of nanomaterials has been reviewed by few authors but innumerable improvements and better methods are being reported continually in the last few years. Among the physical methods, chemical and physical vapour deposition, thermal reduction route, template

based method and pyrolysis have been used for the successful synthesis of ZnO nanostructures (I.W. Park, D.H. Kim, S.W. Jung and C.G.Yi, 2002)(C. X. Xu, X.W. Sun, Z.L. Dong, M.B Yu, T.D.My, X.H. Zhang, S.J. Chua, and T.T. White, 2004)(H. Wie, Y. Wu, N. Lun, and C. Hu, 2005)(Y.H.Yang, D. Wang and G.W.Wang, 2006)(Y.W. Koh and K.P. Loh, 2005). But physical methods generally need expensive equipments, high temperatures and complex producers which restrict further development in actual applications. The chemical methods reported in the literature include decomposition routes of zinc precursor salt, sol-gel, solution, micelles and solvothermal process (R. Muller, L. Madler and S.E Pratginis, 2003)(T. Ahmad, S.Vaidya, N.Sarkar, S.Gosh, A.K.Ganguli, 2006)(Y. Yang, and H. Chen, 2004)(S.C Lyu, Y. Zhang, H. Ruh, H.J. Lee H.W. Shem, E.E. Suh, E.E and C.J. Lee, 2002)(M.N. Kamalasanan and S. Chandra, 1996)(Q. Ahsanulhaq J.H. Kim and Y.B. Hahn, 2007)(M.A.Shah, 2009)(M.A.Shah, 2009)(M.A.Shah, M.Al-shahri and A.M.Assiri, 2009). These approaches generally make use of frequent toxic organics in presence of harmful gases at very high temperatures that can produce unintentional defects and the product can rarely be used for device and other applications.

Recently, an interesting and encouraging result (M.A.Shah, A. Towkeer, 2010) provides motivation to synthesize zinc oxide nanorods without additives or organics at low temperatures. Interestingly, high quality nanorods of zinc oxide were obtained by simple reaction of zinc powder and de-ionized water at 110°C. The morphological and structural investigations revealed that the as-grown ZnO nanorods are hexagonal and possessing well crystallinity with wurtzite hexagonal phase. In addition to this, good optical property was observed for the grown nanorods. The reported method besides being organics free is economical, fast and free of pollution, which will make it suitable for large scale production.

2. Experimental

2.1 Nanomaterial preparation

Zinc powder (Ranbaxy Chemicals, > 5 μ m) has been used without any preheated producer or any further purification and de-ionized water has been prepared in laboratory. For the synthesis of nanorods, a closed cylindrical Teflon lined stainless steel chamber of 50ml capacity was used.

2.2 Preparation of ZnO

In a typical synthesis, 5 mg of zinc powder was taken in a vial containing 30 ml of de-ionized water and was well sonicated for 30 minutes before placing at desired temperature in a Teflon bomb. The reaction mixture was transferred to teflon-lined stainless steel chamber and has been kept at 110°C in an oven for 12h. After the desired time, the system was naturally cooled to room temperature. The reaction mixture was centrifuged to reclaim the precipitated sample and was washed with distilled water. After drying in air, the final powder was obtained.

2.3 Characterization

The morphology and the size of the products was carried out using high resolution FE-SEM (FEI NOVA NANOSEM-600) coupled with energy dispersive x-ray spectrometer (EDX). The obtained powders were characterized by X-ray powder diffraction (XRD) using Siemens D 5005 diffractometer using Cu K α radiation (λ =0.15141 nm) in the 2 theta range from 25-65° with 0.02°/min. The optical properties of the ZnO nanorods were measured with JASCO V-550 UV/Vis spectrophotometer at room temperature.

3. Results and discussion

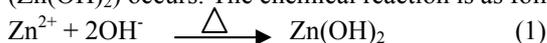
The general morphologies of the as-grown structures, obtained after the reaction of zinc foil with water at 110°C for 12h, was observed by FESEM and demonstrated in figure 1 which confirms that the grown products are hexagonal nanorods. Figure 1 (a) and (b) show the low and high magnification FESEM images of the nanorods and confirms that the nanorods are grown in a very high density over the whole foil substrate. The typical lengths of the grown nanorods are $2 \pm 1 \mu\text{m}$. The nanorods are hexagonal in shape and possessing smooth and clean surfaces throughout their lengths. The typical diameters of the as-grown nanorods are $\sim 60 \pm 10 \text{ nm}$. The nanorods are exhibiting hexagonal surfaces and facets throughout their lengths which confirm that the nanorods are well-crystalline and possessing wurtzite hexagonal phase.

To check the composition of the as-grown nanorods, EDX analysis was performed. Figure 2 demonstrates the typical EDX analysis of the as-grown ZnO nanorods. It is confirmed from the EDX analysis that the grown nanorods are composed of zinc and oxygen only. The molecular ratio of Zn:O of the grown nanorods, calculated from EDX and quantitative analysis data, is close to that of 1:1. Except Zn and O, no other peak for any other element has been found in the spectrum which again confirmed that the grown nanorods are pure ZnO.

To identify the crystallinity and crystal phases of the as-grown structures, X-ray diffraction (XRD) analysis was performed and shown in figure 3. Figure 3 shows the typical XRD pattern of the as-grown nanostructures on zinc foil. All the peaks in the pattern can be indexed to hexagonal wurtzite structure with space group P6₃mc and lattice constants $a = 0.3249 \text{ nm}$, $c = 0.5206 \text{ nm}$, (JCPDS card no. 36-1451). No diffraction peaks arising from any impurity can be detected in the pattern confirms that the grown products are pure ZnO.

The UV-vis absorption spectrum of the ZnO nanorods is shown in figure 4. The absorption spectra have a narrow peak near the band edge in the exciton absorption region (at about 376 nm) and blue-shifted relative to the bulk exciton absorption (380 nm). The stronger exciton effect is an important character of quantum confinement effect.

The growth of the nanorods could be understood on the basis of the following mechanism. At room temperature, zinc does not react with water molecules. When the temperature was raised to 110°C and pressure was generated in Teflon-lined stainless chamber, the zinc reacted with water and formation of zinc hydroxide (Zn(OH)₂) occurs. The chemical reaction is as follows:



Moreover, as the concentration of the Zn²⁺ and OH⁻ ions exceeds a critical value, the precipitation of ZnO nuclei starts. The Zn(OH)₂ can be transformed into the ZnO crystals via the simple chemical reactions mentioned below:



The precipitates of Zn(OH)₂ are more soluble as compared to the ZnO precipitates, therefore, the formed Zn(OH)₂ precipitates tend to continuously produce Zn²⁺ and OH⁻ ions which form the ZnO nuclei. The formed ZnO nuclei are the building blocks for the formation of the final products. With increasing the reaction time, the deposition over the ZnO nuclei increases in uni-direction and finally ZnO nanorods were formed. The newly formed ZnO species form nucleation centers. These nuclei gradually grow in the lateral as well as longitudinal directions. According to the growth habit of ZnO crystals, a single source ZnO nucleus was bounded by top (0001), bottom (0001⁻) and six (0110) side facets. Due to the polar nature of ZnO nanocrystals, the (0001) facet is the Zn terminated (+ve surface) whereas the (0001⁻) face is the O terminated (-ve) surface. Thus these polar surfaces attract newly formed ZnO species as well as the opposite charges (OH⁻ or Zn²⁺) towards it. Thus the polar nature of ZnO crystals and the coordination ability of water molecules with Zn atoms guide the one dimensional growth of ZnO crystals, resulting in the formation of nanorods. Moreover, water at elevated temperatures plays an essential role in the precursor material transformation because the vapor pressure is much higher and the state of water at elevated temperatures is different from that at the room temperature. The solubility and the reactivity of the reactants also change at high pressures and high temperatures and high pressure is favorable for crystallizations. The high temperature and high pressure might have helped some water molecules to dissociate into OH⁻ ions, resulting in non-aligned nanorods. From our experiments and analysis, it suggests that the growing mechanism of ZnO nanostructures may be simple hydrothermal process, but it still have large space to be studied.

4. Conclusion

In this paper, we report an efficient and expedient route for the synthesis of hexagonal ZnO nanorods at low temperature without surfactants and substrates. The proposed single source and catalyst-free method is simple, cheap and environmentally benign. The mechanism for the formation of nanorods is briefly described in accordance with decomposition of metal with water giving out hydrogen. The UV-vis absorption spectrum reveals that the ZnO nanorods are of excellent optical quality, exhibiting very strong UV emission at 376 nm. Furthermore, it is well expected that such a technique would be extended to prepare many other important semiconductor metal oxide nanostructures.

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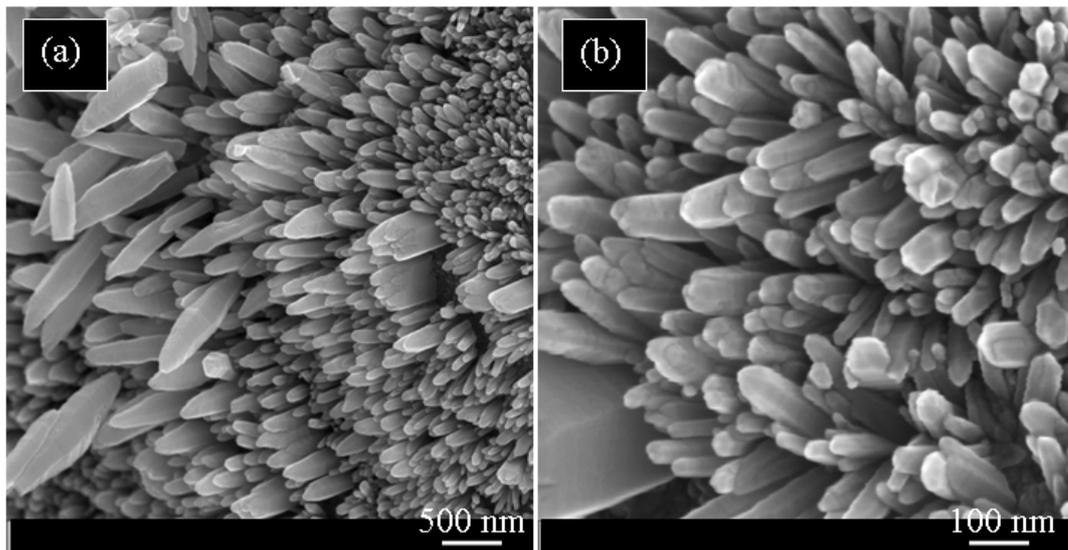


Figure 1. (a and b) shows the low and high magnification of FESEM images of nanorods obtained by the reaction of zinc metal powder with water at 110°C for 12 h.

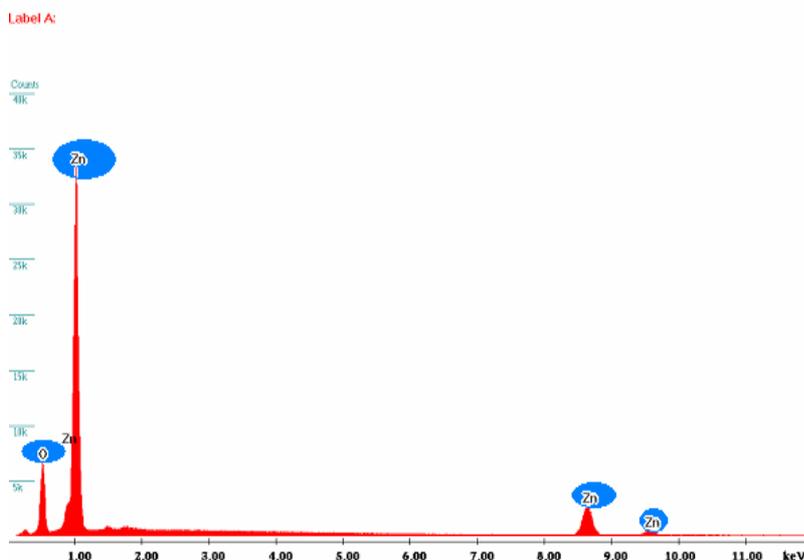


Figure 2. The EDX analysis confirming the existence of all elements involved in sample preparation.

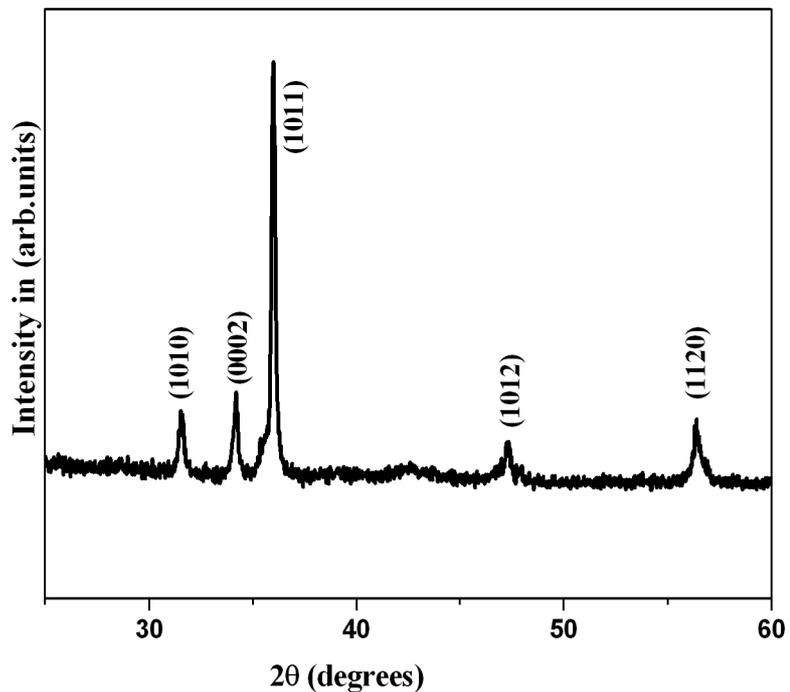


Figure 3. XRD pattern of the ZnO nanorods

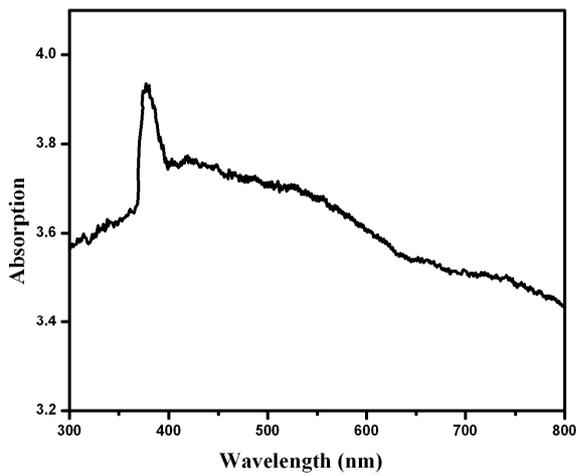


Figure 4. UV-vis absorption spectra of ZnO nanorods