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Safe and Simple Approach to Prepare Hexagonal ZnO Nanostructures in Water

O.A.Al-Hartomy[1,2] and M. A. Shah[1,3]
[1]Department of Physics, Faculty of Sciences, King Abdul Aziz University, Jeddah,
Kingdom of Saudi Arabia
[2]Department of Physics, Faculty of science, Tabuk University, Tabuk,
Kingdom of Saudi Arabia
[3]Electron Microscopy Centre, Department of Physics, Faculty of science, National Institute of Technology, Srinagar-190006,
India
sashraf@kau.edu.sa

***Abstract*—Nanosciences is regarded and acknowledged as a triumph of human ingenuity and the development of man is always marked by technological breakthroughs. The emerging field of nanotechnology is leading to a technological revolution in the world. It is the next industrial revolution and almost all industries will be radically transformed by it in a few years and this technology would directly benefit a common man when it comes to commercial use. It has already established a beachhead in the economy. The challenge is the mass production through economical routes.**

In this paper, we will present a novel and bio-safe synthesis of hexagonal zinc oxide (ZnO) nanostructures at very low temperature of ~120oC simply by using metallic zinc foil and de-ionized (DI) water without harmful organics. The technique does not require of any additives, surfactants or toxic chemicals. The synthesized ZnO products were characterized in terms of their structural and optical properties. The EDS and XRD pattern confirmed the composition and crystallinity of the grown nanostructures and revealed that the grown products are pure ZnO with the wurtzite hexagonal phase. The reported method is new, economical, fast, environmentally benign and free of toxicity, which will make it suitable for biomedical applications.

Keywords-ZnO; nanorods, X-ray Diffraction, Medicine and Energy

I. Introduction

Zinc oxide is rapidly gaining credibility as a material with excellent possibilities for electronic and photonic devices. It exhibits a wide band gap (3.37eV), large excitation binding energy (60meV), biocompatibility, and high melting temperature (2248K), presenting itself a promising material for wide range of well known technological applications which are well documented [1-4]. Among the various nanoforms, 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 such as field emission flat panel displays, x-ray sources, parallel beam electron microscopy and vacuum microwave amplifiers [5].

Among the physical methods, chemical and physical vapour deposition, metallorganic vapour phase epitaxy, thermal reduction route, template based method and pyrolysis methods have been used for the successful synthesis of 1D ZnO nanostructures [6-10]. 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 and solvothermal process [11-15]. But most of the pathways suggested for the synthesis involve environmentally malignant chemicals which are toxic and not easily degraded in the environment. Environmental friendly chemical synthesis requires alternative solvents such as ionic liquids, liquid and water. Water is particularly attractive because it is inexpensive, environmentally benign and bestowed with many virtues especially under supercritical conditions [16]. In our preliminary studies reported earlier, we have obtained nanorods of different geometries by varying the time and temperature of the reaction [17]. It was proposed that the growth of nanostructures with different morphologies, sizes, compositions was mainly controlled by temperature and duration of reaction process. Encouraged by the results, the present studies have been carried out keeping the time and temperature constant.

In this paper, a versatile and expedient route to grow zinc oxide nanorods by a simple reaction of zinc metal with water at very low temperature of ~120^{o}C without using organics/amines has been presented. The morphological and structural investigations revealed that the as-grown ZnO nanorods are hexagonal and possessing well crystallinity with wurtzite hexagonal phase.

II. Experimental

A. Materials

Zinc powder as well as foils were used as a source of zinc and were cleaned by ultra-sonication in acetone and water for 10 minutes in each solvent. A closed cylindrical Teflon lined stainless steel chamber was used for the synthesis.

B. Synthesis

In a typical synthesis, 2mg of zinc metal powder was taken with 40 ml of de-ionized water in a Teflon-lined stainless steel chamber with 50 ml capacity. The prepared reaction mixture was kept at 120°C in an oven for 24 hours. After the desired time, the system was allowed to cool down naturally and the resulting mixture was centrifuged. The zinc foils, collected from the reactions vessels, were washed with de-ionized water several times and finally dried in air.

C. Characterization of samples

Phase structure and the purity of the as prepared samples were characterized by powder X-ray diffraction (XRD) taken on a Philips (X'Pert PRO PW-3710) diffractometer with 2θ ranging from 10-80°, using Cu Kα (λ =0.15141 nm) radiation operated at 40kV and 30mA. The morphology of the products was carried out using Field Emission Scanning Electron Microscope (FEI SEM, NNL 200, Japan), coupled with energy dispersive X-ray spectrometer EDX (Gensis).

III. RESULTS AND DISCUSSIONS

A. Structural information

The XRD patterns of the as-prepared samples synthesized at 120°C shown in Fig. 1 reveal diffraction peaks of (100), (002), (101), (102), (110) and (112), which are characteristic of the pure ZnO with the wurtzite hexagonal phase. All the peaks in the pattern can be indexed to hexagonal wurtzite structure with space group $P6_3mc$ and lattice constants a = 0.3249 nm, c= 0.5206 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 inset in Figure 1 shows the EDX pattern which again shows that the product is pure and contains only zinc and oxygen.

B. Morphology examinations

The general morphologies of the as-grown structures, obtained after the reaction of zinc metal with water at 120°C for 24h, was observed by FESEM and demonstrated in figure 2 which confirms that the grown products are hexagonal nanorod shaped. Figure 2 (a) and (b) show the low-magnification FESEM images of the nanorods and confirms that the nanorods are grown in a very high density over the whole foil substrate. The nanorods are hexagonal in shape and possessing smooth and clean surfaces throughout their lengths. The typical diameters of the as-grown nanorods are ~ 80 ± 10 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.

C. The formation mechanism

The formation of ZnO nanorods on zinc powder in the presence of water can be explained by various chemical reactions. As initially, zinc does not react with water molecules but at 120°C and under pressure in Teflon-lined stainless chamber, the zinc reacted with water and forms a protective zinc hydroxide ($Zn(OH)_2$) layer with dissolved hydroxide ions onto the surfaces of the zinc foil. As the concentration of the Zn^{2+} 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

$$Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$$

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 Zn^{2+} and OH^- ions which form the ZnO nuclei as shown schematically in Figure 3. The formed ZnO nuclei are the building blocks for the formation of the final products. Even though a plausible growth process for the formation of ZnO hexagonal-shaped ZnO nanorods are described here but more studies are needed to clearly explain the growth process for the formation of these nanorods. Due to crystal habits of ZnO, the nuclei have a hexagonal shape.

IV. CONCLUSION

An efficient and expedient route has been explored for the synthesis of hexagonal ZnO nanorods at low temperature of 120°C without additives and surfactants. Furthermore, it is expected that such a technique would be extended to prepare many other important semiconducting metal oxide nanorods. The method reported is safe and the production of hexagonal shape has been exciting during this work.

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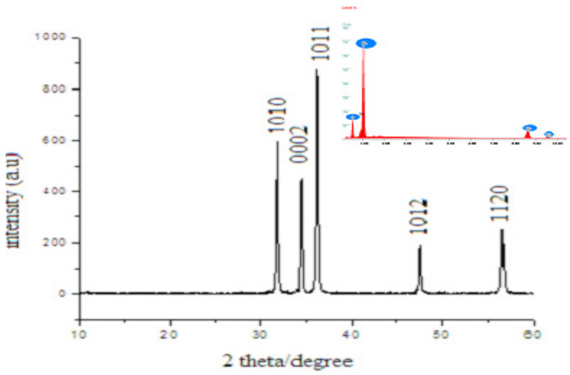

Figure 1. The XRD pattern of as-grown ZnO nanorods.

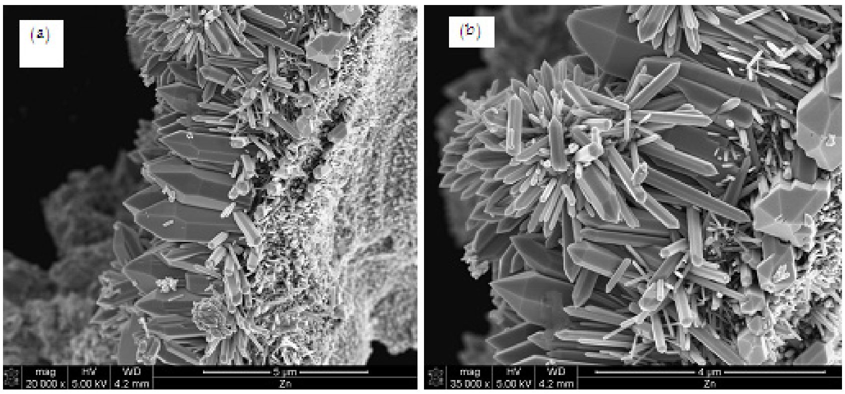

Figure 2. The typical (a and b) low and (c and d) high-resolution FESEM images of nanorods obtained by the reaction of zinc metal powder with water at 120°C for 24h.

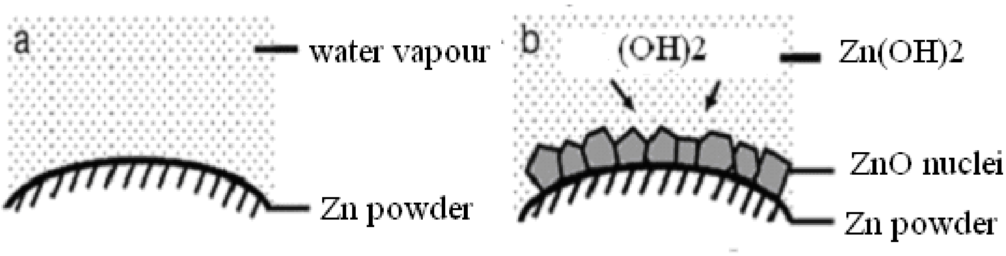

Figure 3. The schematic illustration of the growth (a) Zn particles and water vapour co-exists. (b) Layer of Zn(OH)2 formed on the particle surface and subsequent decomposition to ZnO