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Synthesis of ZnO nanoparticles without catalysts and their photoluminescence

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In this paper, we demonstrate a novel and direct synthesis of high quality zinc oxide (ZnO) nanoparticles by a versatile and a simple approach without using catalysts. The approach is based on a simple reaction of zinc powder and de-ionized (DI) water at relatively low temperatures of 200°C. The formation of ZnO nanoparticles by the reaction of metals with DI water is suggested to occur due to the oxidation of metallic zinc in presence of water. The nanoparticles have diameters varying between 50 to 90nm, with an average diameter of 70 nm. The synthesized ZnO products were characterized in terms of their structural and optical properties. Photoluminescence (Pl) measurements were adopted to analyze the optical properties of nanoparticles; both a strong UV emission and weak deep level emissions were observed. The reported method besides being catalyst free is economical, fast, environmentally benign and free of pollution, which will make it suitable for large scale production.

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1. Introduction

In recent years, the synthesis and characterization of zero and one dimensional semiconductor nanostructures have attracted much interest, because of their unique optical, electrical, mechanical and thermoelectric properties. Nanodevices based on 0D semiconductors have been used in the realm of light emitting devices, biological and chemical sensors [1-2]. Among various nanostructured materials, zinc oxide (ZnO) is rapidly gaining credibility as a material with excellent possibilities for electronic and photonic devices. It exhibits a wide band gap (3.37 eV), large excitation binding energy (60meV) and high melting temperature (2248 K), presenting itself a promising material for wide range of well known technological applications which are well documented and reported time to time [3-5]. It is suitable for short wavelength optoelectronic applications and is recognized as a promising photonic material in the blue-UV region [6].

Up to now many methods have been used for preparing ZnO nanoparticles. Among them, physical vapor deposition, vapor phase transport, chemical vapor deposition, surfactant assisted hydrothermal method and soft solution methods have been employed for the preparation of zinc oxide nanoparticles [7-12]. Catalyst or template based methods have also been used to prepare nanoparticles in which catalyst act as the energetically favored sites for an adsorption of gas phase reactants while the template is used to direct the growth of 1D structures [13]. However, the addition of catalyst or template of the reaction system involves a complicated process and may result in impurity in the products. Moreover, most of the above methods involve environmentally malignant chemicals and organic solvents which are toxic and not easily degraded in the environment.

To this end, we present a versatile and an expedient process to synthesize ZnO nanoparticles by a simple reaction of zinc powder with de-ionized water at very low temperature of 200 °C without use of any catalyst. To the best of our knowledge, the synthesis of nanoparticles without catalyst has not been reported so far. The nanoparticles are spherical in shape and have diameters varying between 50 to 90 nm, with an average diameter of 70 nm. The structural and optical properties were analyzed. Detailed and systematic studies would be necessary to optimize the conditions for obtaining nanoparticles of desired dimensions. The reported method besides being catalyst and organic free is fast, economical, reproducible.

2. Experimental

In a typical synthesis, 2 mg of Zn metal powder was added to 10 ml of de-ionized water in a glass veil and the reaction mixture was sonicated for about 20 minutes. The reaction mixture was transferred into a stainless steel autoclave and sealed under inert conditions. Few drops of ethylenediamine were also added dropwise to the reaction mixture, which acts as dispersing agent. The mixture was heated slowly (2°C/min) to 200 °C and maintained at this temperature for 24 hours. The resulting suspension was centrifuged to retrieve the product, washed and then finally vacuum dried.

Field emission scanning electron microscope (FESEM) images were recorded with a FEI NOVA NANOSEM 600 coupled with EDX. X-ray diffraction patterns of the samples were recorded with Siemens D 5005 diffractometer using Cu Kα (λ =0.15141 nm) radiation. The optical property of as-grown nanoparticles was studied by room-temperature photoluminescence (PL) spectroscopy measured with He-Cd laser (325nm) as an optical pumping source.

3. Results

To identify the crystallinity and crystal phases of the as-grown structures, X-ray diffraction (XRD) analysis was performed and shown in figure 1. Fig. 1 shows the typical XRD pattern of the as-grown nanostructures on zinc metal. 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.

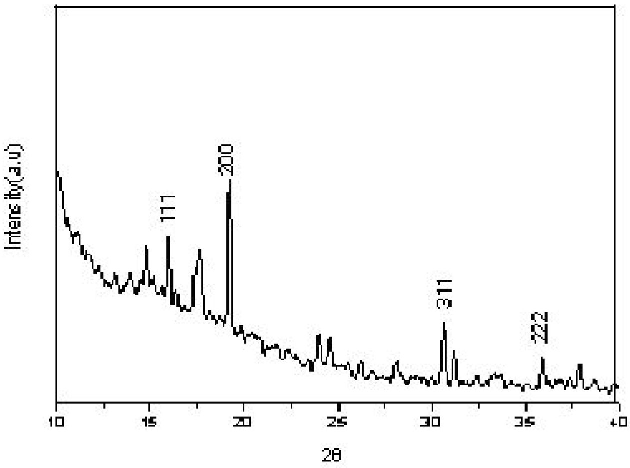
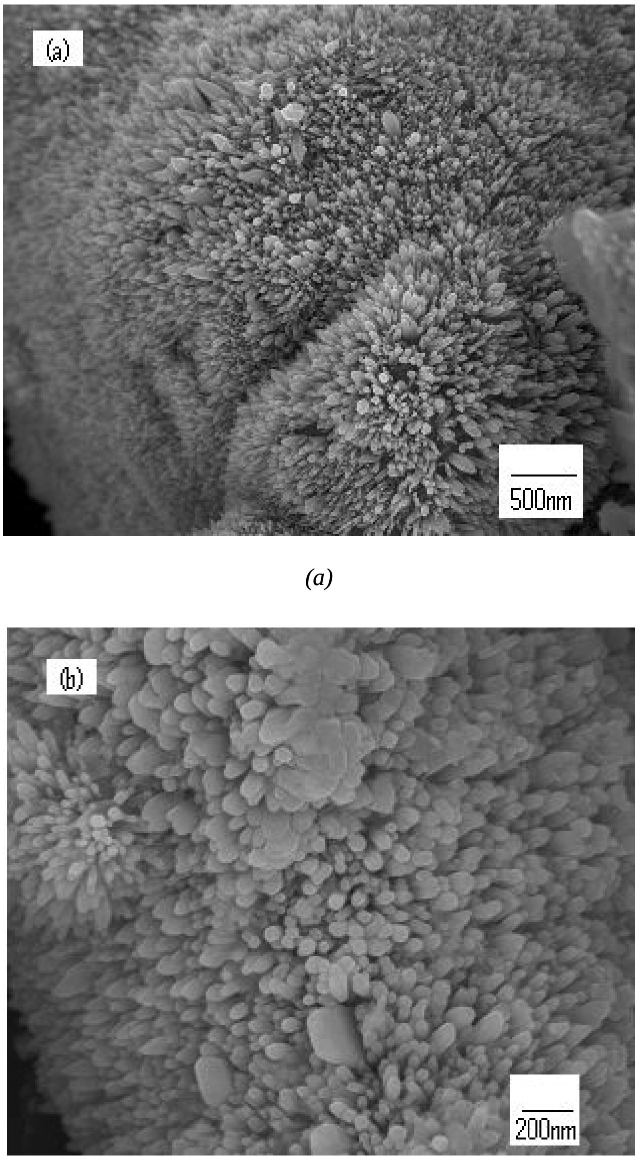


Fig. 1. Typical XRD pattern of as-grown ZnO nanoparticles obtained by the reaction of zinc metal powder with water at 200 °C for 24h.

The general morphologies of the as-grown structures, obtained after the reaction of zinc powder with water at 200 °C for 24 h were observed by FESEM. Fig. 2 (a) and (b) show the low and high magnification FESEM images of the nanoparticles and confirms that the nanoparticles are grown in a very high density. The nanoparticles have diameters varying between 50 to 90 nm, with an average diameter of 70nm. The influence of reaction conditions on physical properties of synthesized nanoparticles as well as mechanism is yet to be investigated. This work, however, in its preliminary stage has ruled out the role of catalysts and substrates in the formation of ZnO nanostructures.



(a)

(b)

Fig. 2. (a and b) shows low and high magnification FESEM images of nanoparticles obtained by the reaction of zinc metal powder with water at 200°C for 24h.

The EDX measurement on the nanoparticles indicates that the nanostructures are composed of Zn and O as shown in Fig. 3, which supported XRD results. The molecular ratio of Zn/O of the nanostructures, calculated from EDX and quantitative analysis data is close to that of bulk ZnO.

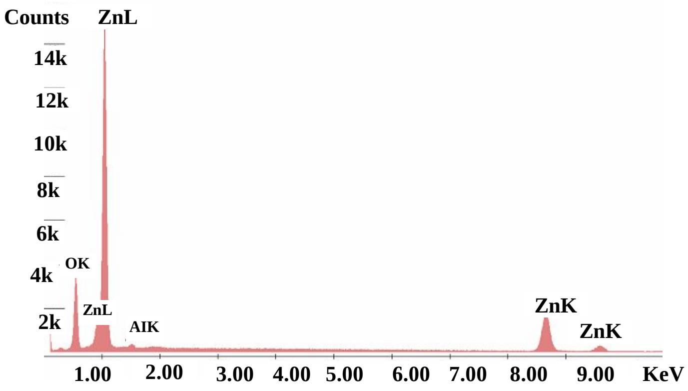


Fig. 3. Typical EDX spectrum of the as-grown ZnO nanoparticles obtained by the reaction of zinc metal powder with water at 200 °C for 24h.

The Pl spectrum of the nanoparticles is presented in Fig. 4. The excitonic peaks of the spectrum are clearly resolved. It is well known that there are two kinds of emissions bands of UV and visible spectrum in ZnO crystals. The emission in the UV region is attributed to the recombination between electrons in conduction band and holes in valence band. The visible emission is related to the defects related deep level emission such as oxygen vacancies and Zn interstitials.

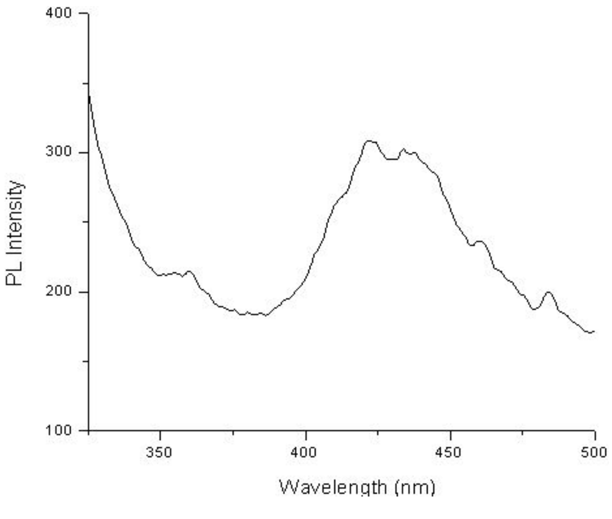


Fig. 4. Typical room-temperature photoluminescence (PL) spectrum of as-grown ZnO nanoparticles obtained by the reaction of zinc metal powder with water at 200 °C for 24h.

In this study, a sharp, strong and dominant UV emission at 325nm and a broad green emission at 425nm are observed. It is believed that the blue emission corresponds to the singly ionized oxygen vacancies and results from recombination of photon generated hole with single ionized charge state of this defect. Ying et al. have reported that if the concentration of oxygen vacancies is reduced in the synthesized products then it results in the appearance of a sharp and strong intensity near band edge and a short or suppressed green emission [14]. In our synthesized ZnO nanoparticles, a strong and a sharp near band edge emission is observed which confirmed as that the as products have good optical properties with very less structural defects. Therefore, a study of PL property of ZnO nanoparticles can provide valuable information on the quality and purity of this material.

4. Discussion

The growth of the nanparticles could be understood on the basis of the following reaction mechanism.

$$Zn(s) + 3H_2O\,(l) \rightarrow ZnO\,(s) + 3H_2\,(g) \qquad (1)$$

Here (s), (l) and (g) refer solid, liquid and gas phases respectively. A similar study has been reported recently in case of iron oxide nanorods [15]. As the concentration of Zn^{2+} and OH^- ions exceeds a critical value, the precipitation of ZnO nuclei starts, the $Zn(OH)_2$ can be transformed ZnO crystals. The precipitates of $Zn(OH)_2$ are more soluble as compared to ZnO precipitates, therefore, $Zn(OH)_2$ precipitates formed tend to continuously produce Zn^{2+} and OH^- ions, which form the ZnO nuclei. The zinc oxide nuclei formed are the building blocks for the formation of final products. Due to crystal habits of ZnO, the nuclei have a hexagonal shape. In the wurtzite hexagonal phase, ZnO has polar and nonpolar faces. In polar ZnO crystals, the zinc and oxygen atoms are arranged alternately along the c-axis and the top surfaces are zinc terminated (0001) and are catalytically active while the bottom surfaces are O-terminated (0001) and are chemically inert [16]. The zinc metal on reaction with water slowly gives out hydrogen (g) and the liberated oxygen reacts with metal to give oxides as shown in the above reaction. The Zn reacts with oxygen and forms ZnO nuclei, which further serve as seeds for ZnO nanoparticles growth. Finally, the Zn nuclei grow to form ZnO nanoparticles. Moreover, water at elevated temperatures plays an essential role in the precursor material transformation because the vapour pressure is much higher and the state of water at elevated temperatures is different from that at 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.

5. Conclusions

The nanoparticles of zinc oxide have been synthesized by a very simple route at 200°C. The technique is based on a simple reaction between zinc powder and de-ionized water without using any catalyst. The UV emissions suggest that the nanoparticles could be used for optoelectronic devices. This facile, reproducible and effective low cost approach should promise us a future large scale synthesis of ZnO nanostructures for many applications in nanotechnology. The approach is expandable and extendable to other metal oxides.

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