Shape Control in Zinc Oxide nanostructures by Precipitation Method

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Abstract. Zinc oxide nanostructures are of eminent importance for the field of chemical sensors, field effect transistors, transparent conductors and ultraviolet light emitting devices. Work in this project is focused on the synthesis and characterization of nanoparticles and nanorods of zinc oxide (ZnO) by precipitation method. The morphology of the samples can be controlled by adjusting the amount of NaOH and citric acid in the NaOH or citric acid/water system. X-ray diffraction (XRD) analysis reveals the single phase of ZnO hexagonal wurtzite structure. The Fourier transform infrared spectroscopy (FT-IR) was used to classify functional groups and types of chemical bonds of the samples. The morphology of the samples was investigated by Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). UV-vis spectroscopy was also performed to study the optical properties of ZnO nanostructures. The estimated band gap of ZnO samples was in the range of 3.68-3.71 eV.

1. Introduction
Zinc oxide (ZnO) is an important semiconductor with a direct band gap of 3.37 eV [1]. ZnO nanostructures have found wide applications in optoelectronic devices, energy storage, sensors transistors and drug release [2]. The properties of ZnO are highly dependent on its morphology and specific surface area, as well as on the uniform size and density of the crystal [3]. Therefore the control on morphology, size and chemical composition of synthesized ZnO nanostructures have been one critical issue in the field. ZnO with different morphologies has been synthesized by various methods including hydrothermal [4], sol-gel [5], chemical vapour deposition [6] and double-solvothermal methods [7]. Among these methods, a simple effective route to synthesize ZnO nanostructures by utilization of nontoxic and environmentally benign solutions is still the key issue. The solution base synthesis, such as precipitation method, are attractive because the process are very simple and low cost.

In this work, we report the synthesis of ZnO nanostructures with distinct morphologies by a simple precipitation method. By adjusting the ratio of NaOH and citric acid, different morphologies of ZnO can be controllably synthesized. The synthesized ZnO nanostructures were investigated by XRD, FT-IR, FESEM, TEM and optical absorption measured by UV-vis was carried out to estimate the band gap energy ($E_g$). This method can also be used to prepare nanoscale oxide of other interesting materials.

2. Experimental procedure
2.1 Synthesis of ZnO nanostructures
ZnO nanoparticles and nanorods were synthesized by a simple precipitation method. Zn(NO$_3$)$_2$.6H$_2$O, NaOH and citric acid were used as starting chemicals. In typical procedure for ZnO nanoparticles, 0.15 mol Zn(NO$_3$)$_2$.6H$_2$O solution prepared in 5 ml deionized water was stirred for 30 minutes at room
temperature. 5 ml of 0.05 mol citric acid solution was mixed into the solution of Zn(NO$_3$)$_2$•6H$_2$O under constant stirring. Then 10 ml of 0.125 mol NaOH solution was slowly added into the mixed solution under constant stirring at room temperature. For ZnO nanorods, 0.03 mol Zn(NO$_3$)$_2$•6H$_2$O solution prepared in 10 ml deionized water was stirred for 30 minutes at room temperature. 10 ml of 0.07 mol NaOH solution was slowly added to the Zn(NO$_3$)$_2$•6H$_2$O solution. The mixed solution was stirred with magnetic stirrer at room temperature. Throughout the whole process described above, no pH adjustment was made. The homogeneous solution was transferred to an ultrasonic bath and the reaction was kept at constant temperature of 80°C for 6 h. The precipitates were filtered and washed several times with deionized water and ethanol separately. The product was then dried in a vacuum at 90°C for 4 h. The final product was calcined in air at 400°C for 2 h to obtain ZnO powders.

2.2 Characterization of ZnO nanostructures

The calcined samples were characterized for crystal phase identification by powder X-ray diffraction (XRD) using a Philips X-ray diffractometer (PW3710, The Netherlands) with CuK$\alpha$ radiation ($\lambda=0.15406$ nm). The Fourier transform infrared (FT-IR) spectra of the powders (as pellets in KBr) were recorded using a Fourier transform infrared spectrometer (Spectrum GX FT-IR spectrometer, Perkin Elmer Instrument, England) in the range of 4000-400 cm$^{-1}$ with a resolution of 1 cm$^{-1}$. The morphology of ZnO powders were characterized by field emission scanning electron microscopy (FEI Helios nanolab G3 GX) and transmission electron microscopy (Hitachi H8100 200kV). The optical absorption spectra were measured in the range of 200-800 nm using a UV-vis spectrometer (T80/T80t, PG Instruments Limited, UK).

3. Results and discussion

The structure of the ZnO samples was primary examined by XRD. XRD patterns of the samples in Figure 1 show the single phase of ZnO hexagonal wurtzite structure as compared to the standard data (JCPDS 36-1451). There is no diffraction peak originating from impurity phase in the XRD pattern, indicating that ZnO was successfully synthesized by these procedure.

![Figure 1. XRD patterns of ZnO nanostructures of calcined at 400 °C for (a) ZnO nanoparticles and (b) ZnO nanorods](image)

![Figure 2. FT-IR spectra of the synthesized ZnO samples for (a) ZnO nanoparticles and (b) ZnO nanorods](image)

The functional groups and the types of chemical bonds of the ZnO nanostructures were performed by FT-IR. The FT-IR spectra of the ZnO samples are shown in Figure 2. There are several bands present in the wavenumber range 4000-400 cm$^{-1}$. The absorption bands in the range $\sim$3150-3146 cm$^{-1}$ and $\sim$1632-1596 cm$^{-1}$ have been assigned to the vibration of hydroxyl groups due to the absorbed water on surface of the samples and show a stretching vibrational mode of O-H groups, respectively. The peaks at $\sim$2374 (ZnO nanorods) and 2368 cm$^{-1}$ (ZnO nanoparticles) are assigned to the absorption of
atmospheric carbon dioxide. The peak at \( \sim 1399 \text{ cm}^{-1} \) correspond to the C=O stretch [1]. The bands noticed at around 1064 and 1058 cm\(^{-1}\) were correlated to the vibrations of carbonate in the ZnO samples. The strong peak between \( \sim 477 \text{ (ZnO nanoparticles) and 483 cm}^{-1} \text{ (ZnO nanorods) correspond to the stretching vibrations of Zn-O bands, which indicates that the samples are well crystallized [8].} \)

![Figure 3. FESEM images of ZnO samples calcined at 400 °C for (a) ZnO nanoparticles (b) ZnO nanorods](image)

![Figure 4. TEM images with corresponding selected area electron diffraction (SAED) patterns of ZnO nanostructures for (a) ZnO nanoparticles and (b) ZnO nanorods](image)

![Figure 5. FT-IR spectra of ZnO samples for (a) ZnO nanoparticles and (b) ZnO nanorods](image)
Figure 3 represents the FESEM of ZnO prepared by adjusting the ratio of NaOH and citric acid. As shown in Figure 3(a), ZnO synthesized from 2.5:1 of NaOH and citric acid solution have an agglomerated spherical particles. Nanorod morphology was visualised for ZnO synthesized from NaOH solution (Figure 3(b)). The nanoparticles and nanorods tend to agglomerate during synthesis or delivery process due to their high surface area and surface energy [9, 10]. In addition, the morphology and structure of ZnO samples were investigated by TEM as shown in Figure 4. Figure 4(a)-(b) show TEM bright field images of nanoparticles and nanorods of ZnO. The ZnO nanoparticles have average size of ~25 nm. The length and width of ZnO nanorods are around 685 and 120 nm, respectively. The corresponding SAED patterns of the ZnO samples (inset in Figure 4(a) and (b)) reveal spotty ring patterns typical of polycrystalline materials of the hexagonal wurzite structure of ZnO, which is in agreement with the XRD results and no secondary phases exist. Figure 5(a)-(b) shows UV-vis absorption spectra of ZnO nanostructures. Absorption peak for ZnO samples is observed around 300 nm. The optical band gap of the samples can be obtained by extrapolating the linear portion of the plot ($\alpha h\nu$)$^2$ versus $h\nu$. The inset of Figure 5 (a) and (b) shows the extrapolation of the linear portion of the curves toward absorption equal to zero ($y = 0$) give $E_g$ for direct transitions [11]. The band gap values are found to be 3.68 eV and 3.71 eV for ZnO nanoparticles and nanorods, respectively. The band gap of ZnO reported in this work is close to that reported in the literatures [1, 12].

4. Conclusion
ZnO nanostructures have been synthesized by a simple precipitation method using Zn nitrate, NaOH and citric acid. The XRD patterns and FT-IR spectra suggested the formation of hexagonal wurzite structure in the ZnO samples. The nanoparticles with particle size of ~25 nm and nanorods with the width of ~120 nm and 685 nm in the length, obtained by TEM. The band gap was determined to be 3.68 and 3.71 eV for nanoparticles and nanorods ZnO samples. The current simple synthesis method can be extended to prepare nanostructures of other interesting metal oxides.

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