

The effect of doping V_2O_5 on crystallization and physical properties of ZnO nanoparticles

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Abstract : In this work, zinc oxide nanoparticles and vanadium doped zinc oxide were synthesized by wet chemical and wet incipient method, respectively. Zinc oxide nanoparticles were heated at 650 and 750 °C for 3 h in air and then characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive (EDX) analysis and photoluminescence (PL). The XRD patterns showed that the zinc oxide samples have a wurtzite structure (hexagonal phase) and vanadium doped is in V_2O_5 crystalline structure. Their structural characteristics and physical properties were investigated and compared. XRD and SEM data show that the size of nanoparticles increased from 24.3 to 32.6 nm when the annealing temperature was increased. Also, the results indicate that increasing the degree of crystalline improved the physical properties of the nanoparticles.

Keywords : ZnO, V_2O_5 , wet incipient method, photoluminescence.

Introduction

Semiconductors are a class of materials defined primarily by their electronic properties. During the past two decades, nanocrystalline semiconductor particles have attracted considerable because of their novel properties, such as large surface-to-volume ratio and the three dimensional confinement of the electrons¹⁻⁴.

Zinc oxide semiconductor is an important member of semiconductors because of their favorable electronic and optical properties for optoelectronic applications. It has a wide band-gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature. Zinc oxide is transparent to visible light and can be made highly conductive by doping⁵⁻⁹. It is potentially useful in various optoelectronic applications such as optical sensors and light emitters. Also, zinc oxide has been used widely in surface acoustic wave devices, gas sensing devices, piezoelectric devices and catalysts⁹⁻¹³.

Nanocrystalline ZnO can be prepared by various methods such as sputtering¹⁴, chemical vapor deposition

(CVD)¹⁵, molecular beam epitaxy (MBE)¹⁶, spray pyrolysis¹⁷, pulse laser deposition¹⁸ and the sol-gel process^{19, 20}.

The properties and application of nano structured semiconductors are strongly dependant on their crystalline quality, crystal phase, size, composition and shape. Therefore synthesising of highly tuned nanocrystals has been a challenging topic.

In this work, the wet incipient method is used for preparation of vanadium doped zinc oxide nanoparticles. Also, the effects of the vanadium amount and heat treatment on the structural characteristics and physical properties of ZnO nanoparticles have been investigated.

Experimental

All reagents were analytical grade and purchased from Merck Company. Reagents were used without any further purification.

Preparation of zinc oxide nanoparticles via wet chemical method (undoped ZnO) :

In a typical synthesis, a solution of 5 mmol zinc acetate dihydrate in 30 mL absolute ethanol was added to a

solution of surfactant CTAB ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ to CTAB molar ratio was equal to 1) in 30 mL of absolute ethanol under stirring. Then, 20 mL of NaOH (0.3 M) solution was added to the above solution under continuous stirring in order to get the pH value of solution about 10. The new solution was kept in a water bath at 70 °C for two hours. It was observed that the solution started precipitating after one hour in water bath. After cooling the system to room temperature, the product was separated by centrifugation, washed with absolute ethanol and deionized water for several times, and then dried under vacuum at 70 °C for 10 h. Finally, the nanoparticles were calcined at two different temperatures to understand the effect of annealing temperature (650 and 750 °C for 3 h).

Preparation of vanadium doped zinc oxide nanoparticles by wet incipient method :

A uniform suspension of ZnO nanoparticles (prepared sample at 750 °C) and deionized distilled water was provided. Then, the amount of ammonium metavanadate (V/Zn = 0.05, 0.1 and 0.15) was added to this suspension under vigorously stirring at 70 °C until the yellow paste obtained. The products dried under vacuum at 70 °C for overnight, and then calcined at 400 °C for 2 h.

Characterization :

The crystal phase and particle size of the synthesized products, after purification, were characterized by X-ray diffraction (XRD) using FK60-04 with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) in 2θ ranges from 20 to 80°, and with instrumental setting of 35 kV and 20 mA. The morphology of the nanostructures was observed by emission scanning electron microscopy (SEM, Philips-XL ϕ 30). Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu-840S spectrophotometer using KBr pellet. The photoluminescence (PL) spectra were measured on a spectrofluorometer (VARIAN-CARY ECLIPSE) at room temperature at an excitation wavelength of 325 nm.

Results and discussion

The XRD patterns of ZnO samples calcined at 650 and 750 °C temperatures for 3 h are shown in Fig. 1. All peaks can be well indexed to wurtzite structure (hexagonal phase) with lattice constants of $a = 0.32495 \text{ nm}$ and $c = 0.52069 \text{ nm}$ (JCPDS, No. 36-1451). No other crystalline phase was found in the XRD patterns, indicating the high purity of the products. Both of the ZnO samples

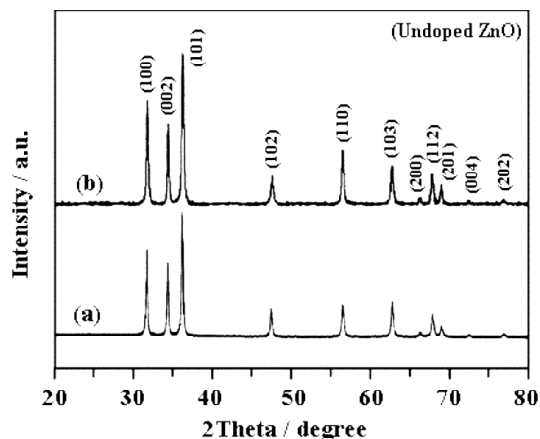


Fig. 1. XRD patterns of ZnO samples calcined at : (a) 650 and (b) 750 °C temperatures for 3 h.

were polycrystalline. The results also show that with increasing the annealing temperature, the intensity of the major diffraction peaks increased indicating that the crystallization of ZnO nanoparticle was improved at higher temperatures. Notably, this result was similar to that of vanadium doped ZnO nanoparticles (Fig. 2). The particles sizes can be calculated using Scherrer's equation : $D = 0.9 \lambda / (\beta \cos \theta)$ where λ is the X-ray wavelength (1.54 Å), β is the full-width at half-maximum intensity of the diffraction line and θ is the diffraction angle. The crystallites sizes are estimated to be around 24.3–32.6 nm. Also the surface area of 358 m²/g was obtained for ZnO catalyst calcined at 750 °C temperature.

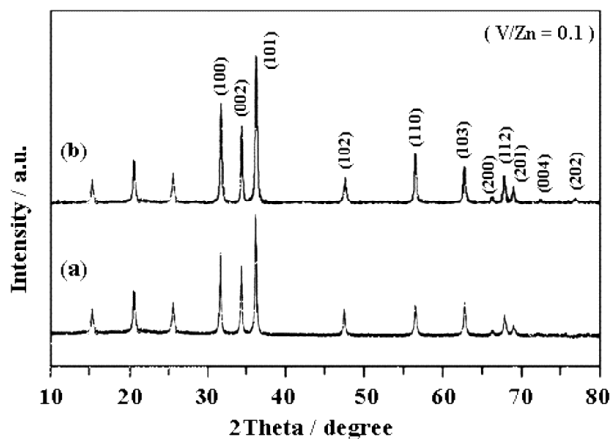


Fig. 2. XRD patterns of V_2O_5 -doped ZnO samples using ZnO calcined at : (a) 650 and (b) 750 °C temperatures for 3 h.

Fig. 3 shows the XRD patterns of vanadium doped ZnO samples. In Fig. 3 (V/Zn= 0.05) three weak new

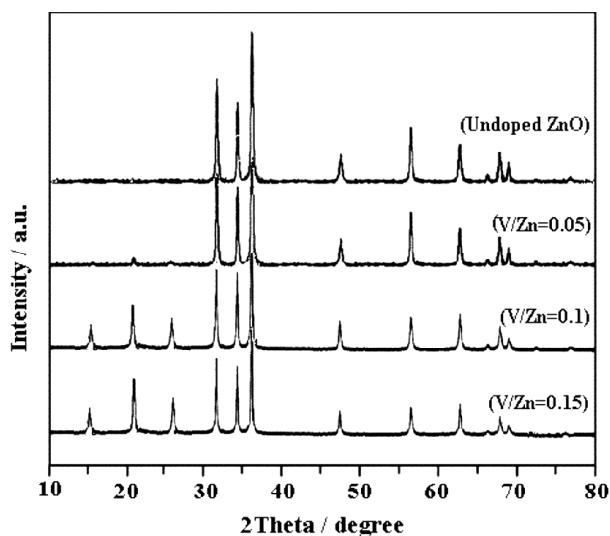


Fig. 3. XRD patterns of V_2O_5 -doped ZnO samples using ZnO calcined at 750 °C temperature for 3 h.

peaks are appeared at diffraction degrees 15.37°, 20.29° and 26.20°, which can be well indexed to V_2O_5 crystal-line structure (JCPDS, No. 41-1426). The results exhibit that while the amount of vanadium increased, the intensity of three new peaks was increased. Therefore it can be concluded that the V_2O_5 -loaded ZnO is carried out successfully. Also, the XRD patterns (Fig. 3) indicate that the major diffraction peaks are decrease with increasing of vanadium concentration, which shows V_2O_5 -doping resulted in a decrease in the crystalline quality. Comparing the crystallization of undoped ZnO with V_2O_5 -doped ZnO, a large amount of doped V_2O_5 resulted in lattice disorder, which is associated with the stress generated.

The FT-IR spectra of undoped ZnO and V_2O_5 -doped ZnO nanoparticles are shown in Fig. 4. The vibrational peaks in the range of 3600–3650 cm^{-1} and 1600–1650

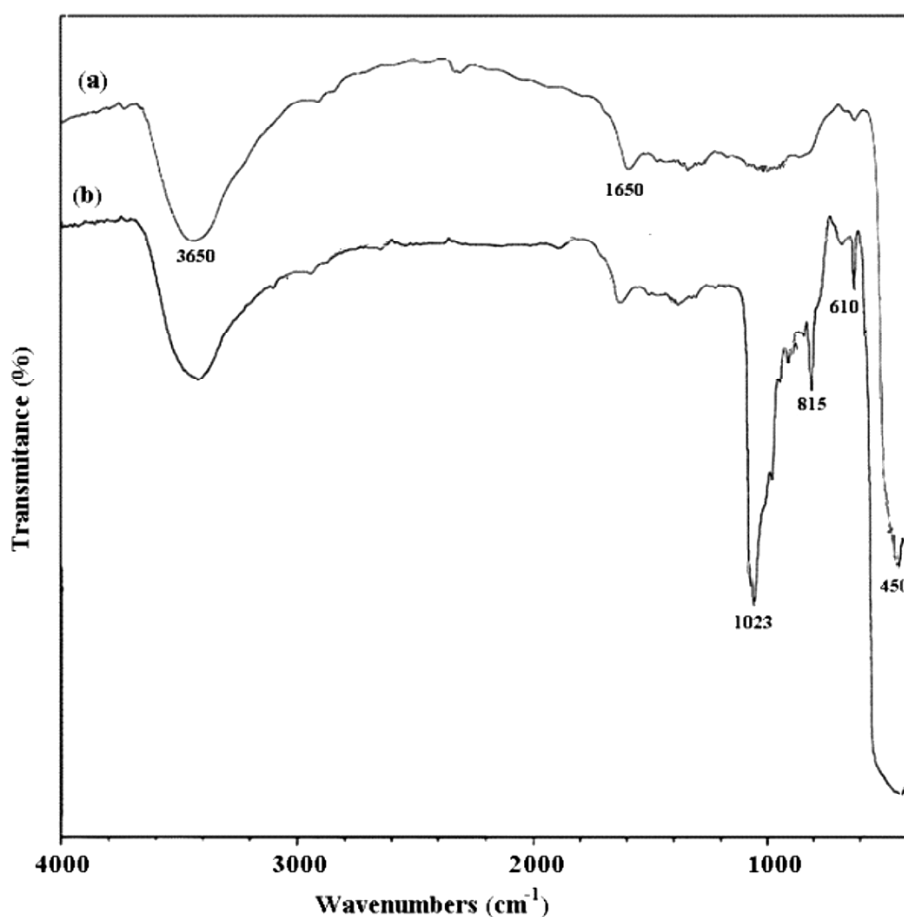


Fig. 4. FT-IR spectra of (a) undoped ZnO and (b) V_2O_5 -doped ZnO ($V/Zn = 0.1$) nanoparticles.

cm^{-1} can be attributed to the stretching and bending vibrations of structural hydroxyl groups of the adsorbed water. The peak in the range of $420\text{--}450\text{ cm}^{-1}$ can be associated to the stretching vibration mode of the Zn-O^{21-23} . Also, the peaks which are appeared at 610, 815 and 1023 cm^{-1} are due to the stretching vibration mode of V-O, the bending vibration mode of V-O-V and the stretching vibration mode of V=O , respectively, and are absent in Fig. 4a²⁴⁻²⁶. These results clearly show that V_2O_5 is successfully dope the ZnO nanoparticles. This is in agreement with the results of XRD patterns.

The morphology of the products was observed by SEM images. The SEM images of the undoped ZnO and V_2O_5 -doped ZnO ($\text{V/Zn} = 0.1$) are shown in Figs. 5(a-b), respectively.

The energy dispersive X-ray (EDX) analyses of prepared samples are shown in Figs. 6(a-b). The EDX analysis of the undoped ZnO sample confirms that the product consists of Zn and O (Fig. 6a). The elemental analysis of V_2O_5 -doped ZnO confirms the presence of V in the product (Fig. 6b). Also, these results are consistent with the XRD and FT-IR data.

The optical properties of ZnO nanoparticles :

Photoluminescence (PL) was used to investigate the optical quality and the effects of vanadium doping. The PL spectra of the undoped ZnO and V_2O_5 -doped ZnO nanoparticles (annealed at $750\text{ }^\circ\text{C}$) are shown in Fig. 7. In this spectrum, the ZnO nanoparticles contain a UV emission band at 373 and 386 nm (Fig. 7a). The near band emission of 373 nm was caused by the transition

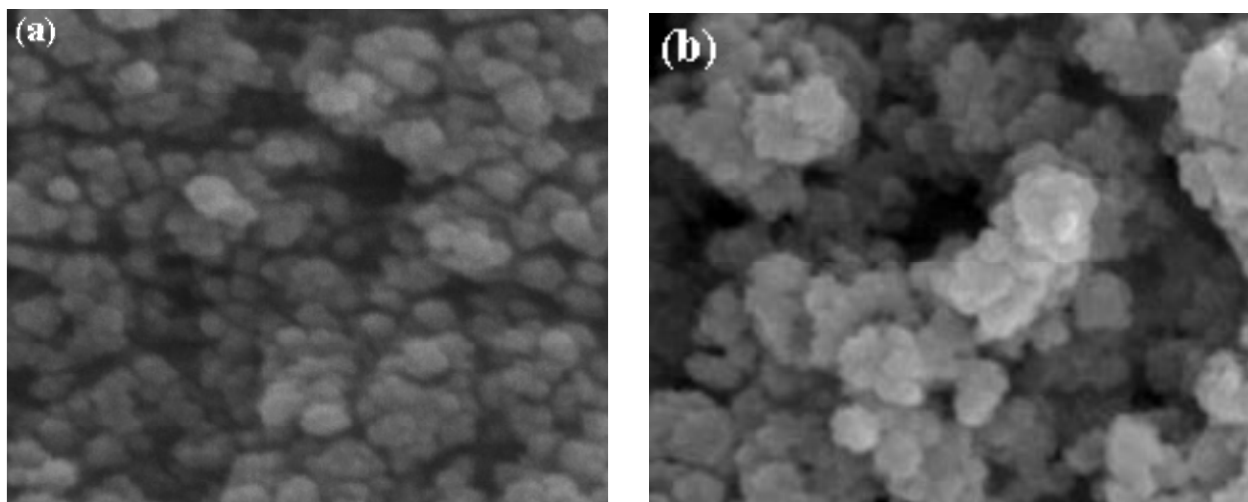


Fig. 5. SEM images of (a) undoped ZnO and (b) V_2O_5 -doped ZnO ($\text{V/Zn} = 0.1$) nanoparticles.

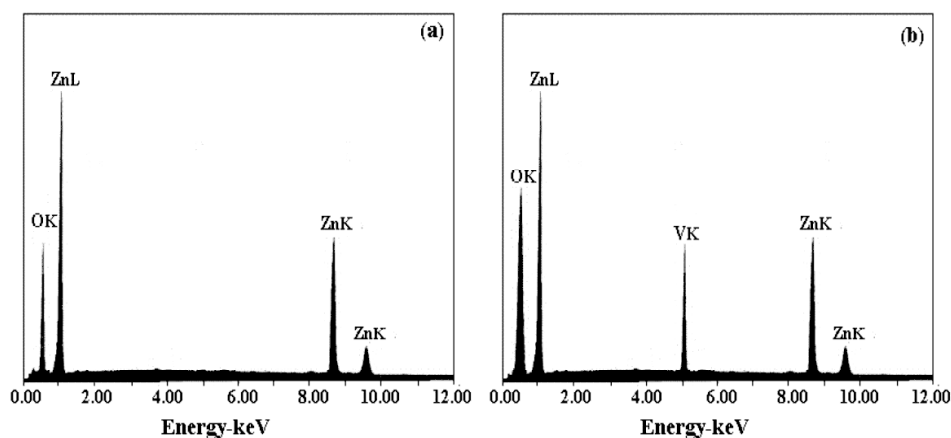


Fig. 6. EDX spectra of (a) undoped ZnO and (b) V_2O_5 -doped ZnO ($\text{V/Zn} = 0.1$) nanoparticles.

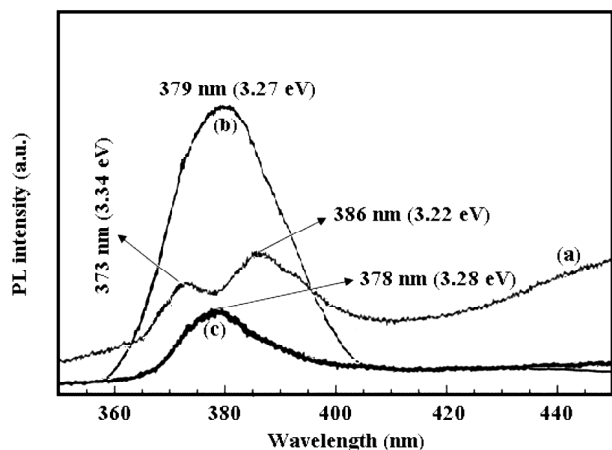


Fig. 7. PL spectra of (a) undoped ZnO, (b) V_2O_5 -doped ZnO ($V/Zn = 0.1$) and (c) V_2O_5 -doped ZnO ($V/Zn = 0.15$) nanoparticles.

from conduction band to valence band. Another UV emission of 386 nm was attributed to the free exciton recombination in ZnO^{27} . After vanadium loading, the UV emission peak position of nanoparticles indicated a slight blue-shift from 3.22 to 3.28 eV, and the intensity decreased with increasing the amount of vanadium, which is attributed to an increase in nonradiative recombination⁹. These results confirm that the V_2O_5 -doped ZnO nanoparticles ($V/Zn = 0.1$) had the best characteristics and optical properties in this study.

Conclusions

ZnO nanoparticles and vanadium doped ZnO were successfully synthesized by wet chemical and wet incipient method, respectively. The particle size increased with an increase in the heat treatment temperature. With increasing the amount of vanadium, the crystalline quality of ZnO deteriorated, which is associated with the stress generated which resulted in lattice disorder. The PL characteristics show that the optical quality deteriorated gradually with increasing the amount of vanadium. The V_2O_5 -doped ZnO nanoparticles ($V/Zn = 0.1$) had the best characteristics and optical properties in this study.

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