Synthesis and characterization of the ZnO nanoparticles and the polyvinyl pyrrolidone (PVP) encapsulated ZnO nanoparticles

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Abstract ZnO and Polyvinyl pyrrolidone (PVP) capped ZnO nanoparticles were synthesised using the sol-gel method at low temperature with ethanol as a solvent, zinc acetate as a precursor and methanol as the cleaning agent. The influence of the PVP on the morphology, structure and the optical properties of the ZnO nanoparticles were investigated. The effect of the addition of different masses of the PVP during the synthesis on the ZnO emission peaks was systematically monitored. PVP is utilized to cap the ZnO nanorods from a zinc acetate precursor at low temperature, since the PVP can be easily removed by burning the solid products. The photoluminescence characterization of the ZnO nanostructures exhibited a broad emission in the visible range with maximum intensity peaks at 449 and/or 530 nm, this was influenced by the addition of different molar masses of the PVP. The scanning electron microscopy images of ZnO and PVP capped ZnO has showed the presence of the agglomerated ZnO particles which could be due to the agglomeration of smaller particles. The x-ray diffraction spectra for ZnO nanoparticles show the entire peaks corresponding to the various planes of wurtzite ZnO, indicating a single phase. The absorption edges of these PVP encapsulated ZnO did not show any shifting. The absorption spectra of the ZnO showed slight shifts with reference to the various masses of PVP.

1. Introduction

As a semiconductor material, zinc oxide spans a wide range of applications from solar cells and chemical sensors to electrical, acoustic and luminescent devices [1]. ZnO is also a versatile direct-band gap semiconductor with a wide band gap of 3.37 eV, and its large exciton binding energy (60 meV) makes the exciton state stable even at room temperature. Furthermore, it is an environmentally friendly material and shows a broad luminescence emission spectrum in the blue yellow region [2]. ZnO appears to be a major candidate for room temperature optoelectronic applications such as efficient short-wavelength ultraviolet light-emitting diodes and laser diodes [3]. Various processes have been employed to synthesize the ZnO nanostructures, such as electrochemical deposition [4], hydrothermal [5], sputter deposition technique [6], and vapour method [7]. From all these methods, we have chosen to use the sol-gel method because of its reliability, inexpensiveness and most of all simplicity. The crystalline quality of ZnO films is determined not only by the growth processes, but also by the do-pants, impurities, surfactants and the surface modifiers such as polymer matrices used. The nanoparticles which are produced by this route show good optical properties, but this can be achieved only by good control of the size and the morphology of the particles [8]. Several workers have used capping agents such as poly vinyl pyridine (PVP), poly ethylene glycol (PEG) etc to stop particle agglomeration and obtained nanoparticles of size less than 5 nm and these polymers produce spherical nanoparticles in shape because of the property of surface tension [9]. PVP is utilized to make ZnO nanorods from a zinc acetate precursor at a low temperature, since the PVP can easily be removed by burning the solid products [10]. In this investigation we concentrating on the encapsulated ZnO nanoparticles and the effect that PVP have on the optical properties and the morphology and structure of the ZnO powders.

1. Experimental

The solutions of ZnO were prepared by dissolving 5.508g of zinc acetate in 300 mls of ethanol with different masses of PVP. This was repeated six times with the following different molar masses; 0.5, 0.75, 1.0, 1.5, 2.0 and 2.5g. The mixtures were magnetically stirred for about 24 hrs at a temperature of 80 °C, this was to let the mixture mix thoroughly. The mixtures where let on the stirrer until the gel-like of the zinc acetate and PVP was obtained. It was then washed using methanol to remove the impurities. Then the gel was calcined in a furnace at 150 °C for 2 hrs. These powders have been characterized under different techniques such as X-ray diffraction (XRD), Photoluminescence (PL), Scanning electron microscopy (SEM) and Energy dispersive spectroscopy (EDS) and the UV-VIS absorption (UV).

1. Results and Discussion
   1. *Structure*

In this part, we studied the role of PVP molar masses in controlling the size and shape of the PVP encapsulated ZnO nanoparticles. Figure 1(a) represents the SEM image of the PVP encapsulated ZnO nanoparticles. The figure shows the chunk of particles which probable consist out of agglomerated smaller particles in the PVP matrix Fig. 1(b) is the EDS for the encapsulated ZnO nanoparticles. It gives out the elements that exist in the sample. Figure 2 (a) and (b) are the powder x-ray diffraction pattern (XRD) of the ZnO nanoparticles and the 0.5 g PVP encapsulated ZnO nanoparticles. The ZnO nanoparticles pattern showed the standard diffraction pattern of wurtzite hexagonal ZnO. Fig. 2(b) shows that the XRD peak positions shifted as well as the peaks have broadened. This confirms that the PVP has an effect on the structure of the ZnO nanoparticles. The crystallite size was calculated from the peaks width using the Debye-Scherer formula

D = (0.9λ) / (β1/2 cosθ),

Where λ is the x-ray wavelength (1.5406Å), θ is the Bragg diffraction angle, D is the diameter of the crystallites, and β is the peak width at half maximum (FWHM). The particle sizes of the encapsulated PVP ZnO and ZnO nanoparticles were calculated were found to be 13 nm and 42 nm. The XRD peaks in Fig. 2(a) gave lattice parameters a = 3.25 Å and c = 5.20 Å and that of Fig. 2(b) are a = 3.25 Å and c = 4.88 Å.

**C:\Users\Amy\Documents\MY RESULTS\Amelia SEM and EDS 2011\MAT_0-75-ga-_003.tif**

(b)

(a)

**Figure 1**: (a) SEM image of the ZnO (b) EDS spectra for the ZnO nanoparticles capsulated in PVP which confirms the presence of the different elements.

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**Figure 2**: XRD patterns of (a) ZnO nanoparticles and (b) PVP encapsulated ZnO nanoparticles.

* 1. *Optical properties*

The photoluminescence spectra of the seven different concentrations of PVP samples, which were recorded with the excitation wavelength set at 325 nm, as shown in Figure 3. The two emission peaks, one a blue emission peak around 448 nm and another green emission peak around 532 nm, were observed for all samples except for the sample with no PVP. The sample without PVP shows only one violet emission peak around 403 nm. Comparing the maximum intensity and peak shape of the six samples with the one without PVP, it is observed that PVP has a clear effect on the ZnO nanoparticles. The relative intensities of these two emission band vary drastically with the molar ratio of Zn:PVP. The addition of the PVP has brought an increase in the intensity with various molar masses.



**Figure 3**: (a) PL emission spectra of the ZnO with different masses of PVP (b) PL emission intensity versus various masses of the PVP encapsulated ZnO nanoparticles.

Fig. 3(b) shows the intensity versus the concentration or different masses of PVP which shows that the 0.75g of PVP has the highest intensity followed by the 2.0 g of PVP. The absorption spectra of the PVP encapsulated ZnO nanoparticles with different masses of PVP are shown in Fig. 4. The absorption peaks of PVP encapsulated ZnO are obtained at the wavelength of 272 nm and the other one at around 358 nm.



**Figure 4**: UV-visible absorbance various spectra of the PVP encapsulated ZnO nanoparticles.

1. Conclusion

In this investigation, the synthesis of PVP encapsulated ZnO nanoparticles with different molar mass of PVP was reported. This was done with the sol-gel method. The characterization was done using XRD, SEM, PL, and UV-VIS absorption. The PL covered the wavelength range of 350-750nm.

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