

Synthesis and Structural Investigations of ZnO/PVP nanocomposites

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Abstract- Zinc oxide (ZnO)– Polyvinylpyrrolidone (PVP) nanocomposite films were prepared by using pre-synthesized ZnO nanoparticles of 3- 5nm size. Various films with varying concentrations of ZnO nanoparticles in PVP matrix were prepared. The Structural and Optical properties of the samples were also studied in this work. The freshly prepared ZnO nanoparticles and ZnO-PVP nanocomposites were thoroughly characterized by XRD, SEM, UV-visible and Fourier Transform Infrared Spectroscopy (FTIR). The crystallite size was calculated using the Scherrer's formula. The FTIR spectra confirm the presences of ZnO and ZnO/PVP peaks.

Index Terms-ZnO nanoparticles, PVP, XRD, SEM, FTIR, Structural and Optical properties.

1. INTRODUCTION

Nanocomposite materials have attracted large attention [1-5] these days as they are novel materials which combine the advantages of different constituting materials. Novel properties of nanocomposites can be obtained from successful coupled characteristics of parent constituents in a single material. These materials are different, as both materials like pure polymers, inorganic nanoparticles with some physical and chemical properties. Considerable research efforts in the past years have been devoted to the design, preparation and characterization of inorganic particle-polymer based composite materials. In these kinds of materials, specially, the nanomaterials with their host Polymer are often synthesized by embedding nanoparticles of metal or semiconductors in polymers [6, 7]. Polymers are able to provide required control of nanoparticles avoiding their coalescence; thus protecting the novel size dependent properties of nanomaterials. However depending upon the polymer as well as concentration of nanoparticles, properties of resulting nanocomposites may change. ZnO is an important wide-band-gap semiconductor that has a direct band-gap (3.37 eV) with a high exciton binding energy (60 meV), good piezoelectric properties, high chemical stability, and bio-compatibility. It is a promising material used for various applications such as solar cells, light emitting diodes, gas sensors, biosensors, surface acoustic wave devices, ultraviolet nano-optoelectronic devices, varistors, antireflection coatings, degradation of pollutants and random lasers [8-11]. Many people have studied the hybrid inorganic polymeric

nanocomposite based on ZnO clusters and polymeric matrix. Abdullah *et al.*: [12] described an *in-situ* method for preparing nanocomposite polymer electrolytes with very high luminescence intensity. ZnO nanoparticles directly grew in the PEG (poly(ethylene glycol)) polymer matrix and precursor materials containing alkali ions, which did or did not participate in the formation of nanoparticles. The size distribution, microstructure and the optical properties of the nanocomposite powders were investigated in detail by Guo *et al.*[13,14]. They have virtually investigated the synthesis of polymer-stabilized ZnO nanoparticles. PVP (poly(vinylpyrrolidone)) was used to stabilize ZnO nanoparticles. Xiong *et al.*: [15] prepared a series of hybrid PEO (poly(ethylene oxide)) thin films containing different concentration of ZnO nanoparticles. They claimed that the acetate groups on the surface of the ZnO nanoparticles are believed to play an active role in affecting crystallinity and conductivity of the composites. In Particular, ZnO/PVP nanocomposites has attracted considerable attention due to its unique individual and cooperative electrophysical, optical, physicochemical and magnetic properties which have been found to strongly depend on their morphology [16-18] Usually, Poly vinylpyrrolidone (PVP) is chosen as a matrix for the composites because it is a potential material with very high dielectric strength. It has good film-forming and adhesive behavior on many solid substrates. Furthermore, it has a good charge storage capacity, mechanical strength and dopant-dependant electrical and optical properties. Another is that the pyrrolidone group of PVP prefers to complex with many inorganic salts resulting in fine dispersion and surface passivation of them [19,20]. Furthermore, the amorphous structure of PVP also provides a low scattering loss, which make it an ideal polymer for

composite materials for optical application [21]. Due to these remarkable characteristic features it has drawn a special attention among the conjugated polymers. Here, we have synthesized Zinc oxide (ZnO)–Polyvinylpyrrolidone (PVP) nanocomposites with different amount of nanoparticles fillings. The Structural and Optical properties of the samples were also analyzed in this work. The freshly prepared ZnO nanoparticles and ZnO-PVP nanocomposites were thoroughly characterized by XRD, SEM, UV-visible and Fourier Transform Infrared Spectroscopy (FTIR) to determine the surface morphology, the chemical composition and the nanoparticle size in these films.

2. METHODOLOGY

Zinc oxide nanoparticles were synthesized by the chemical route. Basically, the nanoparticles are prepared by hydrolyzing zinc chloride in NaOH/methanol solution. ZnO nanoparticles were prepared using simple chemical route. Zinc oxide (ZnO) NPs about ~3-5 nm sizes were synthesized by dissolving 20 ml of zinc chloride (0.1M), 100 ml of sodium hydroxide (0.1 M NaOH) and thioglycerol (0.1 M TG) in methanol.[22]. The precipitate was washed in methanol and methanol was allowed to evaporate at room temperature to obtain ZnO nanoparticles in white powder form. By changing the thioglycerol concentration we could vary the particle size from ~2 nm to ~4 nm. Water was added to increase the size further up to 5.0 nm. The synthesized ZnO-TG NPs were dried in oven, suspended in water and then used for treatment. ZnO/PVP nanocomposite films were deposited as follows. PVP was first dissolved in dimethyl formamid and stirred for 40 minutes at room temperature to obtain a homogenous solution. To this solution the dispersion of zinc oxide nanoparticles was added rapidly with continuous stirring at room temperature for 90 minutes to make the composition of 1:1, 2:1, 5:1 ZnO/PVP. Finally the films were fabricated by dip coating method. Silicon wafers were used as substrates. Prior to dip-coating, silicon wafer were etched by dilute HF acid and ultrasonically cleaned in an acetone bath. The films were then dried in an oven at 90° C for 15 minutes after each coating. For reference, neat PVP film was prepared by casting PVP/ dimethyl formamide solution into a dish, followed by solvent evaporation. The freshly prepared ZnO nanoparticles and ZnO-PVP nanocomposites were thoroughly characterized by XRD, SEM, UV-visible and Fourier Transform Infrared Spectroscopy (FTIR).

3. RESULTS

The size and morphology of the ZnO nanoparticles were investigated using TEM. Fig.1 shows an TEM image of the nanoparticle sample.

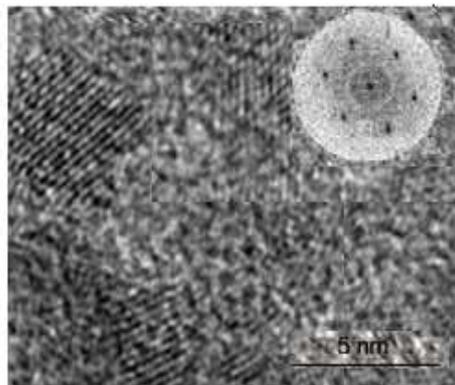
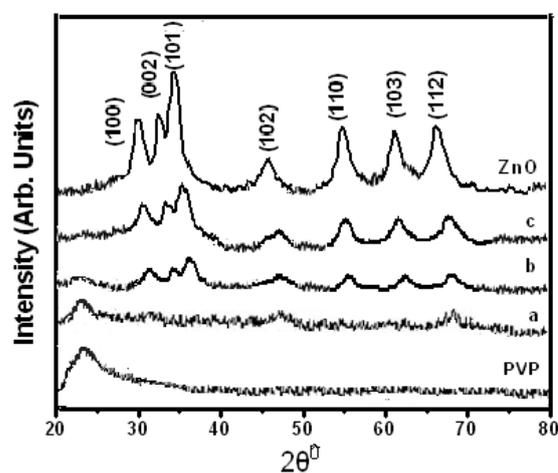


Fig. 1 High resolution transmission electron micrograph of ZnO nanoparticles



It shows the presence of spherical monodispersed particles and the lattice of ZnO is clearly seen. Particles with ~3 to 5 nm size can be seen. The optical properties of ZnO nanoparticles reacted with polyvinyl pyrrolidone have been studied. Fig.2 shows the optical absorption spectra for pure ZnO nanoparticles and zinc oxide-PVP nanocomposites respectively. The ZnO particle spectrum exhibits an obvious blue-shift excitation band at around 306 nm compared with that of bulk ZnO (373 nm) [23]. Also it was seen from the figure that for different concentration ratios of ZnO-PVP nanocomposites, the absorption peaks shifts from 306 nm to 337 nm with increasing ZnO content. It shows redshifting of the wavelength (λ_{onset}) as the ZnO concentration in PVP increases, which suggests the formation of larger size in the nanocomposite film containing more ZnO quantum dots. The spectral redshifting due to ZnO aggregates has also been seen in PEO/ZnO films reported by Xiong et al. [18]. Using Effective Mass Approximation formula (EMA) the average sizes of the resulting ZnO nanoparticles and ZnO/PVP nanocomposites was estimated to be about ~4 nm and ~4.8 to 6 nm respectively from the UV-Vis absorption

spectrum and EMA formula. XRD pattern of bare zinc oxide nanoparticles also confirms this result.

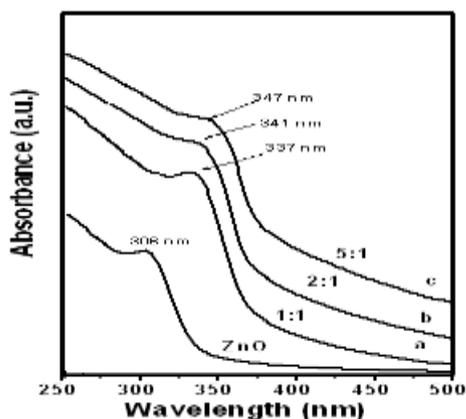


Fig. 2 UV- vis of ZnO nanoparticles and ZnO-PVP nanocomposite films with different concentration ratios (a) 1:1 (b) 2:1 (c) 5:1

The phase structures of the obtained ZnO/PVP nanocomposites were characterized by XRD analysis as shown in Fig. 3

Fig. 3 X-ray diffraction pattern for ZnO nanoparticles, PVP, ZnO-PVP nanocomposite films with different concentration ratios (a) 1:1 (b) 2:1 (c) 5:1

X-ray diffraction pattern for ZnO-PVP nanocomposites film shown along with the diffraction pattern for pure ZnO nanoparticles for comparison. All diffraction peaks corresponding to (100), (002) (101) (102), (110) (103) and (112) planes are present and are in agreement with the typical wurtzite structure of bulk ZnO and the lattice constants c_0 and a_0 are 5.21 and 3.25 Å respectively. The broadening of the ZnO peaks is due to the small particle size. However these diffraction peaks for sample 'a' were not clearly observed in the XRD patterns of zinc oxide-polymer nanocomposites due to the lower ZnO content. In this sample the diffraction peak of the amorphous polymer matrix is very strong ($\sim 21.2^\circ$) but those of the ZnO in the polymer matrix are very weak. As the concentration of ZnO increases (sample b and c) the ZnO peaks were clearly observed. The average particle size (D) calculated from the half-peak width using the Scherrer equation is ~ 3.7 nm for ZnO nanoparticles, and the crystal size varies from 4.5 nm to 5 nm for ZnO-PVP nanocomposites as the nano ZnO content increased in the composites. The crystal sizes of all the nanocomposite samples obtained from XRD are consistent with our UV-Vis spectral observations (Fig.1). It was observed that the peak positions and their relative intensities changed slightly with changing the concentration of ZnO. We further

used FTIR measurements to study the interaction of ZnO with PVP. FTIR was recorded at room temperature on Shimadzu FTIR spectrometer.

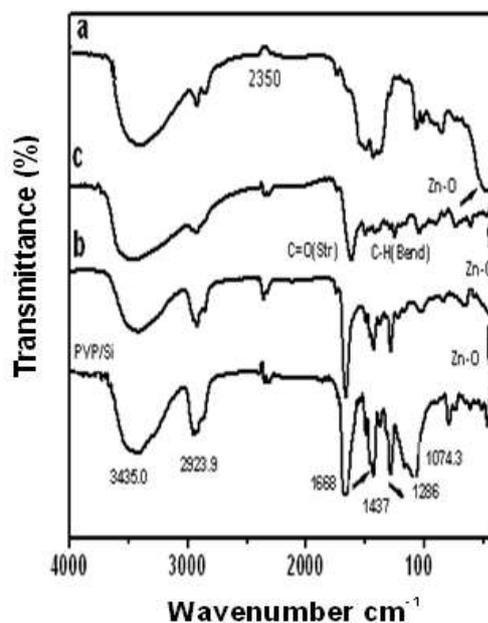


Fig. 4 FT-IR spectra for PVP/ Si, ZnO nanoparticles (a), ZnO-PVP nanocomposite films with different concentration ratios (b) 1:1 (c) 5:1

Fig. 4 displays the Fourier Transform Infrared (FTIR) spectra of ZnO, PVP and zinc oxide-PVP nanocomposite films with varying ratios 1:1 and 5:1 respectively. Several characteristic IR vibrational bands at 1668 cm^{-1} (C=O stretching), 1371-1494 cm^{-1} (CH₂ bending and deformation), and 1286 cm^{-1} (C-N stretching) confirm organic groups of PVP, which indicates that the geometry of PVP is still preserved inside the hybrid film [24]. Compared with the infrared spectra of the pure PVP, each characteristic bond becomes stronger or weaker with a little shifts. The absorption C=O stretching peak of PVP is at ~ 1668 cm^{-1} . But After the addition of ZnO, the absorption peak shifted to ~ 1660 cm^{-1} for zinc oxide-PVP thin film having ratio 1:1. This band shifted to ~ 1652 cm^{-1} in sample having ratio 5:1 for increasing ZnO content, implying the existence of weak coordinative chemical bonding between O and Zn [25,26]. The peak at about 2358 cm^{-1} arises from the CO₂ atmosphere. It is confirmed from FTIR that the absorption bands of ZnO surface gradually increase in intensity with increasing ZnO nanoparticle content. Compared with the infrared spectra of the pure PVP, each characteristic bond becomes stronger or weaker with a little shift. The shifts of infrared bands for PVP in the hybrid film should be attributed to strong columbic interaction between ZnO and polymeric matrix. In order to realize the complete effects of nanoscale fillers on the nanocomposite properties, they must be dispersed well in the matrix. The surface

morphologies of the nanocomposite samples with different ZnO content are presented in Fig.4. All the ZnO nanoparticles are dispersed in the polymeric matrix homogeneously and randomly. The ZnO nanoparticles are clearly seen as white spheres dispersed through the entire area in the PVP polymer matrix. For the samples containing higher ZnO content, as seen in Figure 5 b and c, slightly different surface morphology was observed. The whole of the surface contains strongly connected spherical shape granular formation and the average grain size was found to be approximately 80 nm. The particle size of ZnO in the nanocomposite increases with increasing ZnO content.

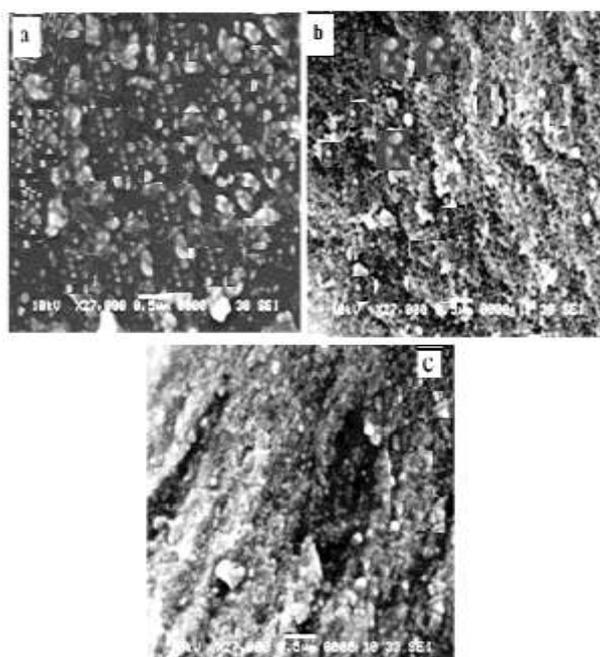


Fig.5 SEM images of ZnO-PVP nanocomposite films with different concentration ratios (a) 1:1 (b) 2:1 (c) 5:1

4. CONCLUSIONS

In this study we have presented the synthesis, characterization, and structural, optical properties of nanocrystalline ZnO and ZnO/PVP nanocomposite films. The ultraviolet-visible adsorption (UV-vis) showed distinct excitonic features. XRD and SEM results indicated that all the ZnO nanoparticles were dispersed in the polymeric matrix homogeneously and randomly. XRD results exhibited that diffraction peaks are in agreement with the typical wurtzite structure of bulk ZnO and the lattice constants c_0 and a_0 are 5.21 and 3.25 Å respectively. The broadening of the ZnO peaks is due to the small particle size. The crystallite size was calculated using the Scherrer's formula. The FTIR spectra confirm the presences of

ZnO and ZnO/PVP peaks. The shifts of infrared bands for PVP in the hybrid film should be attributed to strong coulombic interaction between ZnO and polymeric matrix. Thus, ZnO/ PVP nanocomposite films have been fabricated based on the stabilization of functional materials ZnO in the PVP matrix. Such nanocomposites can be used to make an efficient, low cost solid state solar cell.

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