

CHAPTER XI

HYBRID ORGANIC-INORGANIC OF ZNS EMBEDDED PVP NANOCOMPOSITE FILM FOR PHOTOLUMINESCENT APPLICATION

11.1 Abstract

ZnS nanoparticle was successfully synthesized by wet chemical synthetic route. Hybrid organic-inorganic ZnS embedded PVP film was consequently deposited by desktop inkjet printer in order to enhance the properties for use. This hybrid material exhibited blue fluorescence at the cluster of ZnS nanoparticle embedded PVP. The photoluminescence peak located at 428 nm in the spectra excited 310 nm wavelengths. The hybrid film can be used as emitter layer in organic light emitting diodes (OLEDs).

11.2 Introduction

The advance in research is dependent on the possibility to have different properties in the same material, ranging from optimized processing step, excellent micro- or nano-scale structure along with the functionalities required for the specific desired application. In the recent years, many groups of researcher have successfully prepared nanocomposite systems by incorporating inorganic nanoparticle into organic matrix [2, 232-234]. These hybrid nanocomposite provides a path for a novel class of material which inherent in properties of both inorganic nanoparticles and organic matrix in order to tailor the excellence in chemical and physical properties. These include mechanical strength, chemical resistance, thermal stability as well as optical properties [235].

In particular, a typical hybrid material was contained as organic phase bound with inorganic nanoparticle. Polyvinylpyrrolidone (PVP) is a class of organic compounds that has a well-defined structure with N-vinylpyrrolidone monomer connected as long chain. The incorporation of inorganic nanoparticle into a polymer matrix can result in significant improvements in a variety of chemical and physical properties [203, 236].

On the other hand, ZnS, fluorescent and piezoelectric material, has been widely used as transparent electrodes in solar cell [237, 238], thin film transistor [239] as well as blue light emitter [240-242]. The most important point of this aspect is exciton binding energy of ZnS. Chen et al reported that the exciton binding energy of ZnS is 39 meV. Due to this energy band gap, the exciton is stable at ambient temperature even in bulk particle. Owing to these properties, ZnS is an excellent candidate for optoelectronic device such as light emitting diodes.

In our previous work, ZnS and related metal (Mn, Cu)-substituted ZnS were successfully synthesized by wet chemical synthetic route at room temperature [243]. The reaction of zinc acetate and sodium sulphide was conducted in water. The advantages of this synthetic route are a high yield of product and relatively low energy costs. Nevertheless, ZnS and related metal (Mn, Cu)-substituted ZnS colloid exhibited agglomeration among of each particle due to the existence of water. Bulk particle of ZnS and metal (Mn, Cu)-substituted can generate PL intensity, however, the use of this particle is limited due to device fabrication process. The use of inkjet printing technique, commercially available method of light emitting device, has been widely employed in market [244, 245]. The use of printed nanoparticle has limitation of particle size less than 200 nm, suggested by supplier. To quantify ZnS nanoparticle growth (less than 200 nm), size measurement of quantum dots is necessary. A potential protective material is the use organic matrix that includes polyvinylpyrrolidone (PVP) in order to control the effective size and size distribution but maintain the photoluminescent properties.

In this research work, we wish to extent our previous experiment. Bacterial cellulose nanocomposite was successfully prepared [246]. The hybrid organic-inorganic ZnS embedded PVP was investigated the possibility to be used as emissive layer on OLED devices.

11.3 Experimental

11.3.1 Chemical Reagents

Sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from Caledon Chemical Company, Canada and J. T. Baker Chemical

Company, Canada, respectively. Polyvinylpyrrolidone (PVP) ($M_w \sim 10000$) was purchased from Sigma Aldrich Company, Canada. Analytical grade of methanol was purchased from Bioshop, Canada. Distilled water and analytical grade of methanol were used as solvent. All the chemical reagents were used without further purification.

11.3.2 Instruments

- Fourier transform infrared spectroscopy (FTIR)

FTIR was performed on a Bruker Vector 22 mid-IR spectroscopy (Bruker, Germany), All FTIR absorption spectra were recorded over $4500\text{-}500\text{ cm}^{-1}$ wavenumbers region at a resolution of 8 cm^{-1} with 1024 scans using a deuterated triglycine sulfate (DTGS) detector. A straight line between two lowest points in the respective spectra region was chosen as a baseline. Potassium bromide (KBr) acting as a non-absorbing medium was mixed with a solid sample (0.3-0.5 wt %) by an agate mortar and pestle to prepare a pellet specimen.

- X-ray Diffraction (XRD)

The synthesized ceramic powders were stored in an oven above 150°C overnight for water absorption prevention. The crystal structure of the powders was analyzed by XRD (Phillips P.W. 1830 diffractometer) using nickel-filtered $\text{CuK}\alpha$ radiation. Diffraction patterns were recorded over a range of $25\text{-}80^\circ$. The consistency result was compared with literature.

- Scanning electron microscope (SEM) and energy dispersive analysis (EDX)

The powders were investigated by SEM (a JOEL JSM-6301F scanning microscope). The machine was operated at an acceleration voltage of 20 keV at a working distance of 15 mm to identify the morphological properties of powders. Before investigation, the samples were sputter-coated with Au to enhance the electrical conductivity.

- Laser confocal microscope and photoluminescence spectroscopy

Laser confocal microscope and luminescence experiments were performed using an Olympus BX41 fibre-coupled confocal microscope. Excitation of the dopant ions is performed using a continuous argon laser. The excitation beam was focused

on the sample surface by means of an 100 achromatic microscope objective (NA0.9) down to approximately 0.3 mm spotsize. To separate the excitation beam and the sample luminescence, an interferential filter that removes the excitation wavelength (notch filter) was used. The fluorescence was focused into a fibre-coupled high-resolution spectrometer (SPEX500M) and then detected using a CCD camera.

- Transmission electron microscope (TEM)

The particle size of ZnS was investigated by TEM, Hitachi H-7000. The ZnS solution was suspended in methanol and dropped on a molybdenum grid. After that, the grid was dried at 50°C for methanol evaporation and kept into the TEM chamber. The image thus obtained was processed with computer for identification of the domains in which certain lattice fringes appear. For this propose, TEM image was captured under 40000X magnification. The acceleration voltage of electron beam was set at 75 keV.

- Desktop inkjet printer

The Dimatix DMP-2800 inkjet printer (Fujifilm Dimatix, Inc., Santa Clara, CA, USA) was used to deposit conductive solution on 50x50 mm² substrate with a disposable piezo inkjet cartridge. The cartridge reservoir contained 2 ml of ZnS/PVP solution. The temperature of vacuum plate, which secured the substrate in place, was adjusted to 60 °C. ZnS/PVP solution was filtered by nano-size filter (200 nm) and before usage in order to prevent agglomeration among silver particle and control the ink particle size (<200 nm), suggesting by desktop inkjet supplier.

11.3.3) Methods

- Preparation of ZnS nanoparticle

The ZnS nanoparticle was prepared as follow: 10 g of Na₂S. 9H₂O was added to 50 ml of distilled water. The mixture was stirred for 1 hour. In parallel, 10 g of ZnSO₄. 7H₂O was also dissolved into 50 ml of distilled water. Na₂S. 9H₂O solution was then poured into ZnSO₄. 7H₂O solution.

The stoichiometric of chemical reaction was below;



After that, PVP 10 g was subsequently added into ZnS precursor solution. The reaction was continuously stirred for 3 hours at room temperature. After that, the

solution was centrifuged at 500 rpm for 30 min in order to remove solvent. The obtained ZnS nanoparticle would precipitate.

- Preparation of ZnS embedded PVP as hybrid nanocomposite film

The ZnS/PVP solution was dissolved in 3 ml of water and loaded into the cartridge reservoir of desktop inkjet printer. Each of 3 ink formulations was sonicated for 3 hours prior to printing in order to prevent the agglomeration among ink particles. Then, the amount of solution and plate temperature was controlled at 3 ml and 50°C. After that, deposited-silver film was dried at 180°C over night.

11.4 Result and Discussion

ZnS nanoparticle was successfully synthesized by wet chemical synthetic route. The ZnS solution exhibited milk-like character, white color. The viscosity measured by Ubbelohde type canon was 14 cgs. It was acceptable for usage of desktop inkjet printer. The range of viscosity should be in 10-20 cgs at room temperature, suggested by supplier. In addition, this technique of synthesis offered high yield of product and excellent colloidal stability. In this synthetic procedure, polyvinylpyrrolidone (PVP) was chosen as the stabilizer for forming the precursor of ZnS and PVP. The result ZnS nanoparticle expose to carboxylic functionality of PVP to the outer environment leading to very hydrophilic surface which makes ZnS stable in water.

However, the limitation of as-synthesized ZnS is agglomeration among nanoparticle, the preferable use of this particle must be less than 200 nm. In order to prevent this phenomenon, the other role of ZnS is used to control and stabilize the particle size of ZnS. Therefore, we developed an analogous procedure for making the as-synthesized ZnS as hybrid nanocomposite film.

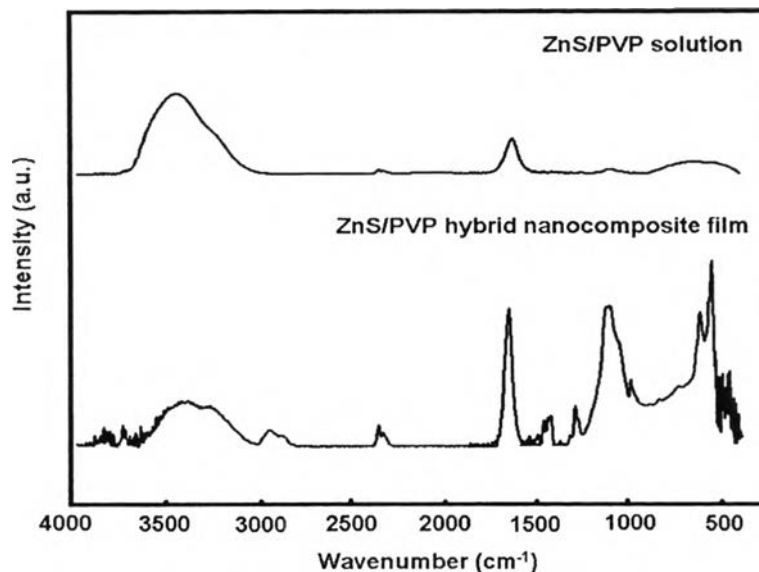


Figure 11.1 FTIR spectra of ZnS/PVP solution and ZnS/PVP hybrid nanocomposite film

FTIR spectra of the ZnS/PVP solution and ZnS/PVP hybrid nanocomposite film were recorded in the range of 4000-500 cm^{-1} and are exhibited in Figure 11.1. In case of ZnS/PVP hybrid nanocomposite film, the peak appearing at 1200 and 620 cm^{-1} are due to Zn-S vibration and 2920, 2360 and 1640 cm^{-1} are due to microstructure formation of the sample. On the other hand, this is in contrast to ZnS/PVP solution, the peak appearing from 1200-500 cm^{-1} was featureless. This is due to the small amount of ZnS nanoparticle in solution. However, the broad absorption peak in the range of 3410-3465 cm^{-1} corresponding to -OH group indicated the existence of water absorbed in the surface of nanoparticle. The presence of this band can be clearly attributed to the adsorption of some atmospheric water during measurement. The bands at 1600 and 2370 cm^{-1} are due to the C-O stretching modes arising from the absorption of atmospheric CO_2 on the surface. All of the appearing peak values are in good agreement with the previous literature [88, 247].

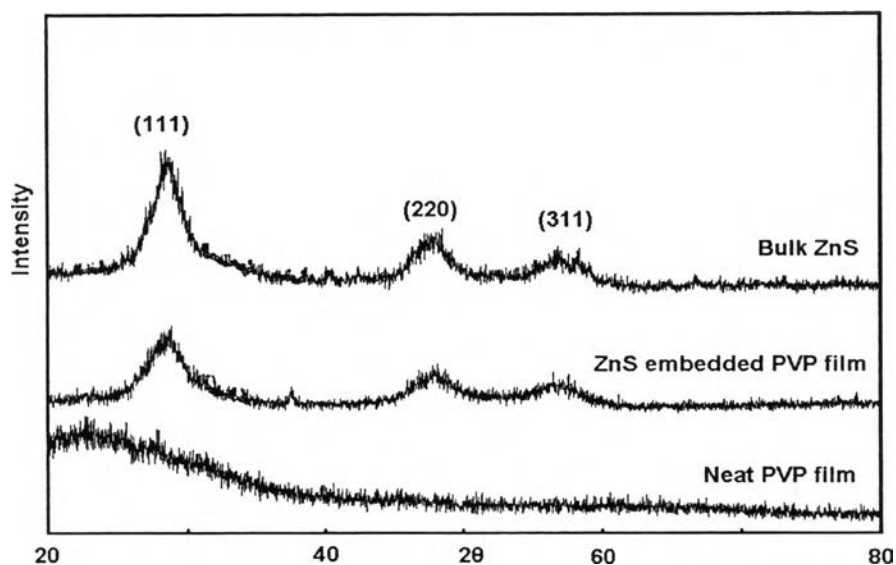


Figure 11.2 XRD spectra of neat PVP film, ZnS embedded PVP film and bulk ZnS particle

The XRD patterns of the neat PVP film, ZnS embedded PVP film and bulk ZnS are exhibited in Figure 11.2. X-ray diffraction technique was used to investigate the crystalline structure of film materials. No diffraction peak was detected for the neat PVP film, suggesting that it did not contain any crystallite structure. However, more diffraction peaks appeared in the case of ZnS embedded PVP film. Three positions can be remarkably correspond to the lattice planes of (111), (220) and (311), are very well matched with the cubic ZnS structure (JCPDS No. 05-0566). This result is consistent with bulk ZnS [248].

According to the Debye-Scherrer formula, the mean crystallite sizes calculated from the full-width at half maximum (FWHM) by this equation below,

$$D = k\lambda/(\beta\cos\theta)$$

Where D is the mean grain size, k is constant (shape factor, approximately 1), λ is the X-ray wavelength (1.54056 \AA for Cu-K α), β is the full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg angle.

According to the FWHM of the most intense peak (111) plane, the average crystallite sizes of ZnS was 50 \AA . This is close to the value deduced from SEM and TEM image.

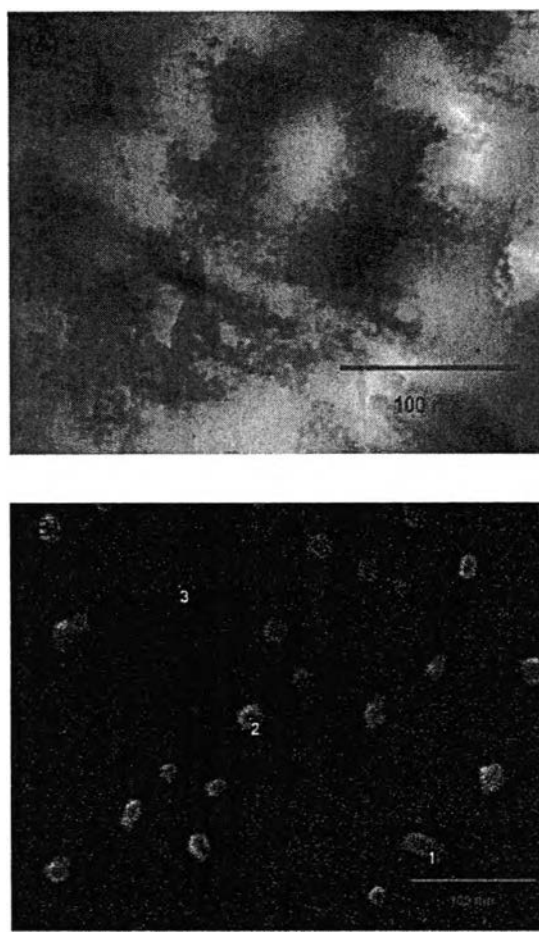


Figure 11.3 TEM and SEM image of ZnS nanoparticle

The TEM and SEM micrographs of the ZnS nanoparticles are given in Figure 11.3A and 11.3B, respectively. The particle size was estimated with the distribution histogram that exhibited the maximum frequency for the state particle range. The shape of nanoparticle exhibited spherical form, and the size was about 30-50 \AA . A comparison of particle sizes obtained XRD and TEM illustrates good agreement. On the other hand, while SEM image, it exhibited agglomeration character among each nanoparticle due to solvent removal. Three points on SEM image shows the position of EDX analysis. It revealed that the amount of zinc and sulfur atom can be detected.

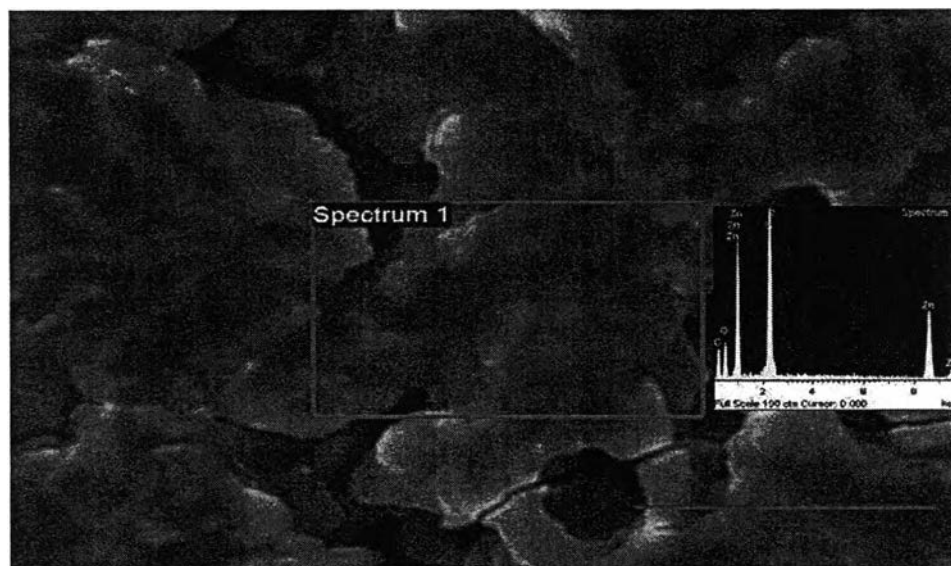


Figure 11.4 SEM image of printed hybrid organic-inorganic ZnS embedded PVP film

Figure 11.4 shows that ZnS embedded PVP was successfully deposited on our bacterial cellulose substrate. The detail of substrate preparation, characterization on scientific properties has been discussed elsewhere [246]. SEM image reveals that the morphology of deposited film has uniform surface. Inkjet printer offer printed film with high density on printed area. No space can be observed. The ZnS nanoparticle was successfully penetrated surrounding PVP matrix. The presence of white color represents the position of ZnS nanoparticle. The homogeneous distribution of ZnS was successfully controlled by the use of sonicator on ink solution prior to printing. However, the film was still exhibited crack-like character. Before SEM observation, the hybrid ZnS embedded PVP was deposited on flexible substrate. The optimization between mechanical properties and expected device efficiency need to be considered in order to prevent crack phenomena. On the other hand, the inset figure exhibits the EDX analysis. It shows that deposited film mainly composed of zinc and sulfur atom with the scan area (Pink color). The presence of carbon and oxygen was possibly due to the use of carbon tape and retained solvent after deposition step.

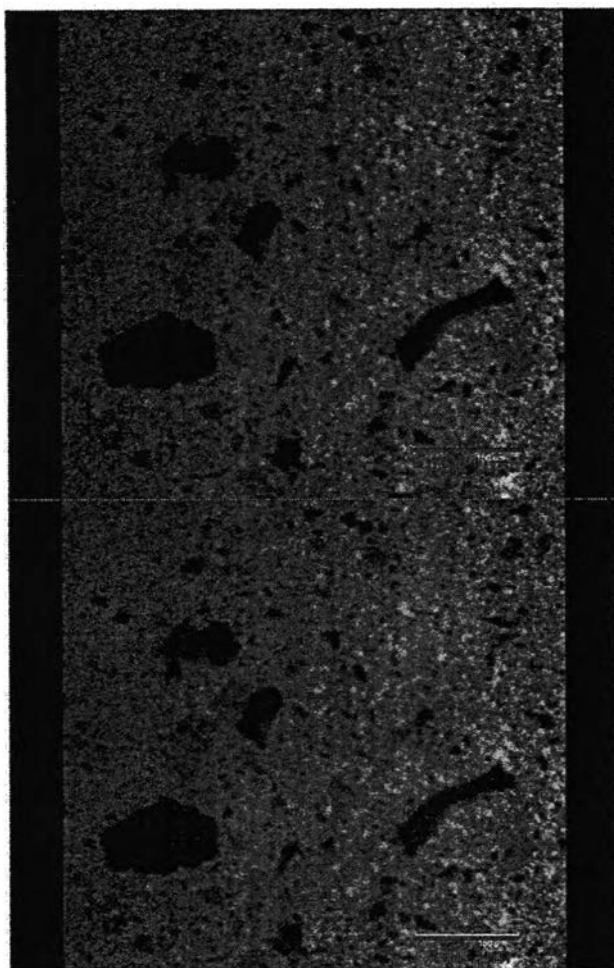


Figure 11.5 Photoluminescent image of ZnS embedded nanocomposite (A) without excitation (B) with excitation

After that, printed hybrid organic-inorganic ZnS embedded PVP was observed by laser confocal microscope. Figure 11.5A shows a fluorescence image of ZnS nanoparticle without excitation, where numerous ZnS clusters were aggregated by smaller particles. Under excitation of a UV light of 320 nm, they emit strong blue fluorescence light as exhibited in Figure 10.5B. The blue color corresponds to those clusters. On the other hand, the photoluminescence spectrum in Figure 10.6 exhibits a PL at 428 nm excited with 310 nm wavelength, completely coinciding with the blue fluorescence light. However, the intensity of PL spectrum is still low; no sharp peak can be detected. This is due to complete covering of ZnS in PVP matrix.

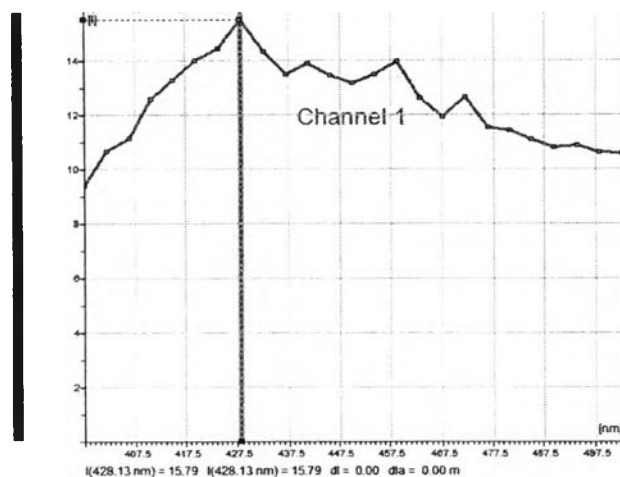


Figure 11.6 PL spectra of ZnS embedded PVP hybrid nanocomposite

11.5 Conclusion

ZnS nanoparticle was synthesized by wet chemical synthetic route. Hybrid organic-inorganic ZnS embedded PVP film was consequently deposited on bacterial cellulose nanocomposite substrate by desktop inkjet printer. The film emits blue fluorescence from ZnS cluster which penetrated among PVP matrix. This hybrid material can be used as emitter layer in organic light emitting diodes (OLEDs).

11.6 Acknowledgement

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