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Microwave-assisted particle size-controlled synthesis of ZnO nanoparticles and its application in fabrication of PLED device

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ZnO nanoparticles were synthesised in diethylene glycol (DEG) with different ZnO molar precursor concentration (1 mmol, 2 mmol, 4 mmol and 8 mmol) in a microwave reactor for 15 minutes up to 250 °C. Zinc acetate dihydrate was used as the precursor for ZnO nanoparticles and oleic acid as a capping agent. It was found that different mmol precursor concentration yielded in different nanoparticle sizes. The crystallinity and particle size was analysed by XRD and the optical properties of the nanoparticles were studied by UV-Vis and PL. Oleic acid forms a layer around the ZnO nanoparticle surface. This layer helps in preparing nanocomposite solution by dispersing the ZnO nanoparticles in MEH-PPV solution. Further, the nanocomposite solution is deposited as a thin-film by spin-coating and this forms the emissive layer of the fabricated PLED device. The diode characteristics were analysed by studying the I-V and EL graphs.

1. Introduction

ZnO semiconductor nanoparticle has been widely researched over the past few decades due to its wide direct band gap (3.37 eV) and high exciton binding energy (60 meV) at room temperature. Further, the versatile nature of ZnO nanoparticles has led to the many applications as catalysts [1], pieozoelectric device [2], gas sensors [3], optoelectronic devices [4] [5] etc. Moreover, several wet chemical techniques to synthesise ZnO nanoparticles have been reported in the literature- co-precipitation, sol- gel, solvothermal, hydrothermal etc.

In this study, different Zn(CH3COO)2.2H2O molar concentrations (1 mmol, 2 mmol, 4 mmol and 8mmol) were used to synthesise ZnO nanoparticles by polyol method. And, due to oleic acid surfactant, stable dispersions of ZnO nanoparticles in toluene were prepared. In polyol-mediated synthesis the high-boiling point polyol has function as solvent and stabilizing agent preventing particle agglomeration [6]. Further, nanocomposite solutions were prepared by mixing the colloidal solution with a conductive polymer MEH-PPV. The solution is then deposited as thin film by spin coating process for the fabrication of PLED diodes.

2. Experimental

2.1. Material

Zinc acetate dihydrate (Zn(OAc)2.2H2O, p.a., Mw = 219.51 g mol-1) and MEH-PPV Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (Mw = 40000–70000 g mol-1) were purchased from Sigma-Aldrich, diethylene glycol (p.a., DEG), oleic acid (p.a. Mw = 282.46 g mol-1), toluene (p.a.), methanol (p.a.) were purchased from PENTA Czech Republic, and PEDOT:PSS (poly(3,4-ethylenedioxythiophene)polystyrene sulfonate) supplied from Heraeus (CleviosTM P AI 4083).

2.2. Synthesis

ZnO nanoparticles were prepared from different molar concentrations of $Zn(OAc)_2.2H_2O$ (1 mmol, 2 mmol, 4 mmol and 8 mmol). The $Zn(OAc)_2.2H_2O$ (0.225 g, 1.03 mmol, ZnO-1) was mixed with 50 ml diethylene glycol (DEG) and oleic acid (0.768 g) in a Teflon-lined container. Further, the reaction mixture was then put in a microwave reactor, turned on and the power applied was 100% for 15 minutes up to 250 °C. Later, when the reaction was completed, the white suspension was centrifuged and washed with methanol and dried at 80 °C. In addition, some part of the precipitates from the Teflon container was dispersed in 50 cm^3 of toluene to form a colloidal dispersion. Correspondingly, the other samples with different precursor concentration were prepared similarly. The labelling of the samples ZnO-1, ZnO-2, ZnO-3 and ZnO-4 are as follows for I mmol, 2 mmol, 4 mmol and 8 mmol respectively.

The nanocomposite dispersion was prepared by dispersing 10 mg of MEH-PPV in 3.5 ml of ZnO nanodispersion containing 10 mg of nanoparticle powder. And the PLED device was prepared by depositing a hole transporting layer PEDOT:PSS on an ITO-coated glass substrates. Then, the polymer nanocomposite material was cast as an active layer by spin coating at 1000 rpm and annealed at 100 °C for two hours. Later, Mg electrode was sputtered on the active layer using sputter coater Q300TT Quorum Technologies. The schematic diagram of the PLED diode is illustrated in figure 1. The labeling of the nanocomposite samples were continued from the previous notations by adding letters ME (e.g. Fe-1 ZME). Also, pure MEH-PPV and ZnO/MEH-PPV thin films were prepared for comparison purpose.

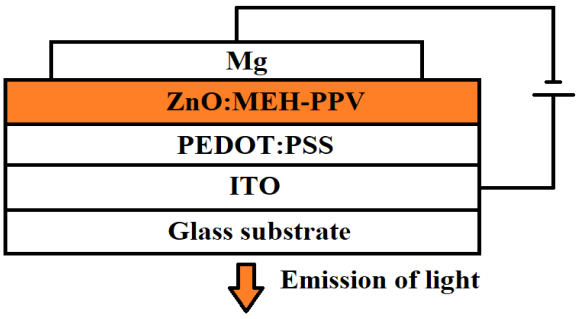


Figure 1. Schematic diagram of a PLED device.

3. Results and discussions

The XRD analysis of ZnO nanoparticles is shown in Figure 2. The crystal structure of the different ZnO nanoparticles is unchanged with wutrzite hexagonal crystal structure which is in good agreement with standard JCPDS file for ZnO (JCPDS 36-1451). Also, the average sizes of nanocrystallite structure was determined by using Scherrer's formula:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta}$$

where λ is the wavelength of the incident X-ray, $Co_{K\alpha}$ (λ = 1.7903 Å), and β is the line broadening at the half maximum intensity of the XRD peak corrected for the instrumental function. The average size of the nanoparticles is between 4-14 nm.

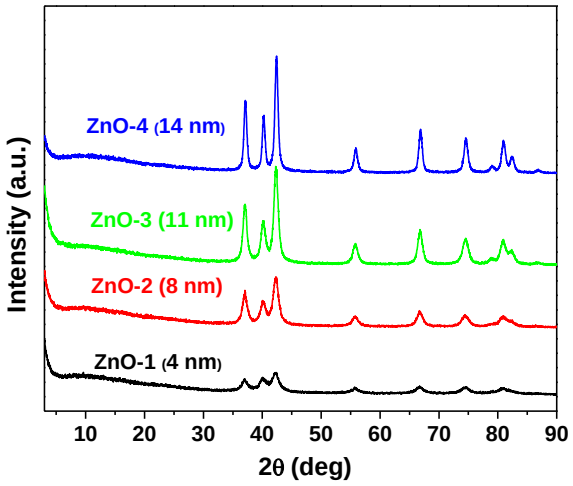


Figure 2. XRD patterns of ZnO nanoparticles (ZnO-1, ZnO-2, ZnO-3 and ZnO-4).

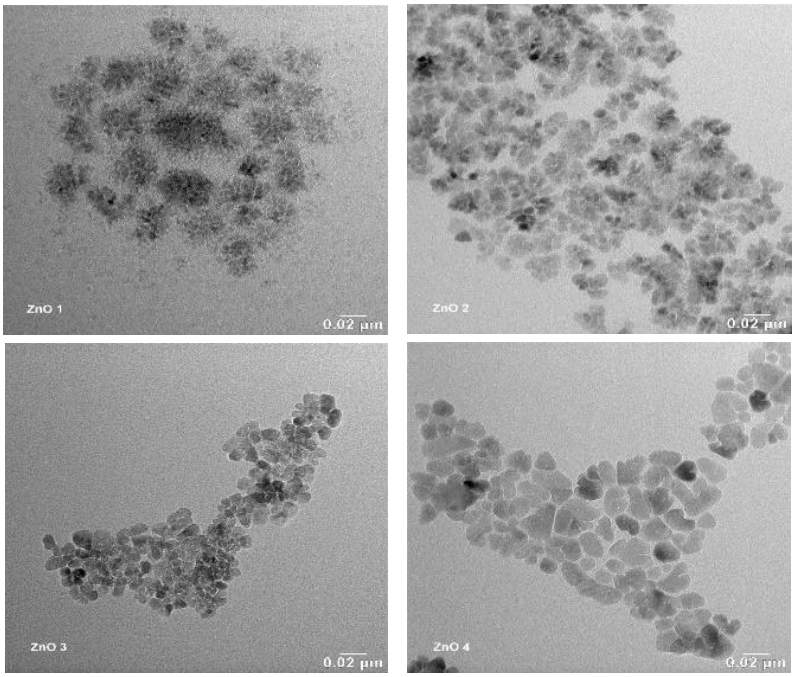
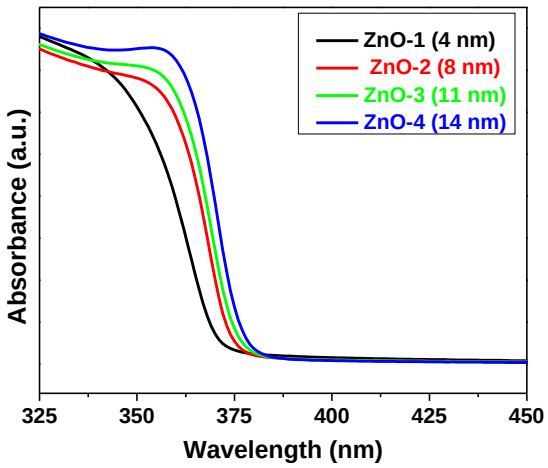


Figure 3. TEM images of ZnO nanoparticles (ZnO-1, ZnO-2, ZnO-3 and ZNO-4).

The morphology and size distribution was studied by taking the TEM image of ZnO nanoparticles, Figure 3. The nanoparticle sizes from the TEM images correspond with the obtained XRD values. The fine dispersion of the nanoparticles is also confirmed from TEM measurement.

The optical and optoelectronical properties of the synthesised nanoparticles were studied by using UV-Vis and PL spectrometric methods. We can observe a change in the absorption edges as the particle size is decreased, figure 4. A blue-shift is observed with the decrease in particle size. Further, decrease in band gap (as evident from Figure 5 Taucs plot) associated with particle growth and agglomeration, also confirmed by TEM images, are observed.



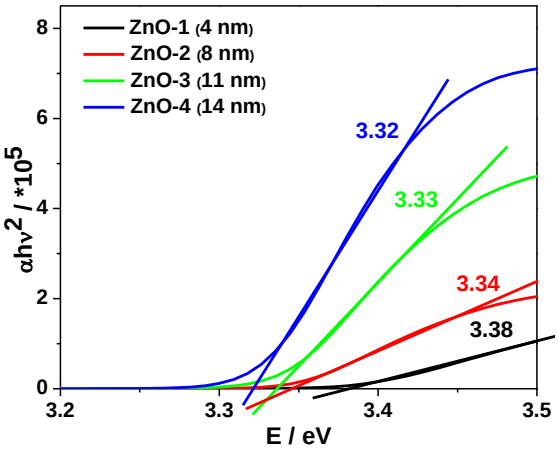


Figure 4. UV-Vis of ZnO nanoparticles. **Figure 5**. Band gap of ZnO nanparticles from Taucs plot.

The room temperature PL spectra of ZnO samples are shown in figure 6 (excited by laser with wavelength of 332 nm). The spectra observed at around 370-380 nm is attributed to UV near-band-edge emission due to excitonic recombination. And, the peaks also shift to higher wavelength (blue-shift) as the particle size is increased. In the spectra, it is clearly seen that smaller particle has higher PL intensity.

Figure 7 depicts the PL emission of ZnO/MEH-PPV observed at room temperature. Addition of n-type ZnO nanoparticles trap electrons and allow more holes to recombine through nanocomposite interphase. Then, the exciton formation in the active layer increases and enhances luminescent properties [7]. Additionally, the incorporation of nanoparticles also leads to the decrease in intensity of the luminescence. However, unlike the emission spectra of ZnO nanoparticles, similar trend is not observed in the quenching of ZnO/MEH-PPV with increasing particle size. Consequently, it is clearly seen from Figure 7 that smaller particle sizes of 4 nm (ZnO-1) and 8 nm (ZnO-2) resulted in luminescence quenching of the polymer. And this quenching is favourable in the fabrication of PLED device.

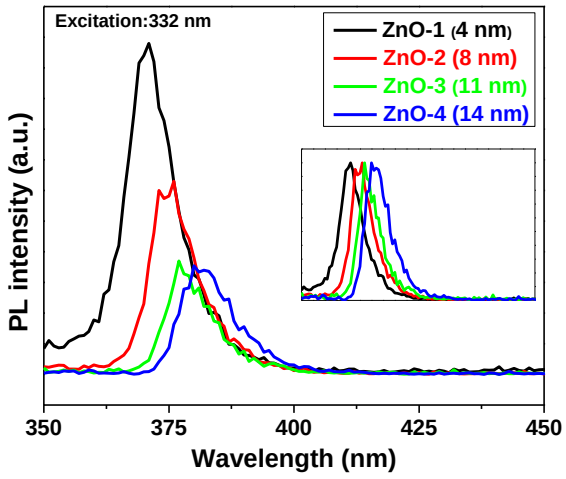


Figure 6. PL of ZnO nanoparticles.

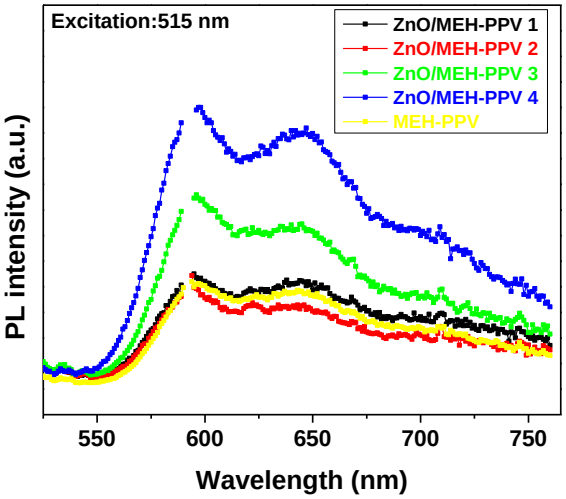


Figure 7. PL of ZnO/MEH: PPV nanocomposites.

In figure 8, the EL spectra were measured up to 10 V. The orange/red emission is from MEH-PPV, but incorporation of ZnO nanoparticles enhances the electroluminescence intensity. The EL spectra of ZnO/MEH-PPV show that emission peak maxima are around **586 nm** and for MEH-PPV is at **593 nm.**

The I-V characteristics measured up to 10 V of the nanocomposites are shown in Figure 9. The turn on voltages of the samples ZnO/MEH-PPV 1, ZnO/MEH-PPV 2, ZnO/MEH-PPV 3 and ZnO/MEH-PPV 4 were 4.9 V, 4.2 V, 5.0 V and 5.1 V respectively. In conclusion, the I-V characteristic is improved as smaller nanoparticles reduce the opening voltage of the PLED device.

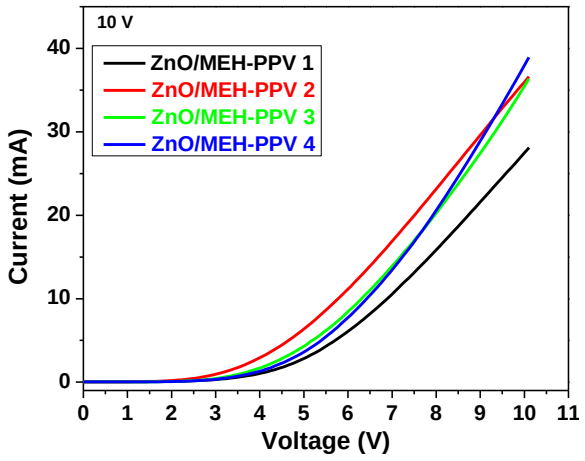


Figure 8 I-V characteristics of fabricated PLED devices.

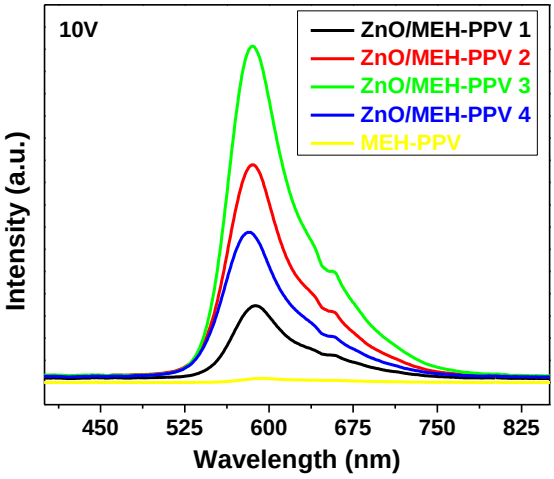


Figure 9. EL of fabricated PLED devices.

4. Conclusion:

To conclude, we were able to synthesis ZnO nanoparticles in a microwave reactor and dispersed the nanoparticles in a non-polar solvent toluene. This homogenous nanodispersion was then blended with MEH-PPV to get a nanocomposite solution. The nanocomposite was then successfully used in the fabrication of PLED diode. Upon application of potential difference, the diodes illuminated displayed both the I-V curve characteristics signifying the importance of using inorganic and organic materials. Equally, the size of ZnO nanoparticle also played a vital role in tuning the optical and optoelectronic properties. As evident from UV-Vis, we observed a blue shift as the size of the nanoparticles increased. Additionally, decrease in band gap, calculated by Tauc plot from DRUV-Vis spectra, was also observed with increasing particle size. Further, similar changes are evident in the emission spectra of both ZnO nanoparticles and ZnO/MEH-PPV nanocomposites.

5. Acknowledgement

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