

Material design and synthesis of ZnO-polymer nanocomposites (ZnO-PNCs) for photonic applications

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INTRODUCTION

Polymer nanocomposites (PNCs) are hybrid materials which consist of nanoparticles dispersed in a polymer matrix. Compared to stand-alone bulk materials, PNCs offer substantial property enhancement and improved performance in terms of processability, flexibility, mechanical strength, thermal stability, and chemical resistance. Zinc oxide (ZnO), a potential constituent material of PNCs, has attractive properties such as non-toxicity, biocompatibility, high surface-to-volume ratio, UV absorption, visible transparency, and affordability. Hence, ZnO-PNCs are promising luminescent materials for various photonic applications such as phosphors, scintillators, sensors, and LEDs.

In this study, the structural and optical properties of ZnO-polyvinylpyrrolidone (ZnO-PVP) composite are investigated. PVP is a water-soluble, nonionic polymer and it is used in this study because it exhibits strong interaction with the ZnO surface. The stability of the ZnO-PVP composite in terms of morphology, crystallinity, and photoluminescence is evaluated after it has been subjected to a heated environment. Based on the observed properties of the ZnO-PVP composite, a potential application of this material is proposed.

EXPERIMENTAL

The fabrication of the ZnO-PVP composite involved two steps: 1) hydrothermal growth of ZnO and 2) dip-coating of the ZnO rods in PVP. For the hydrothermal growth, zinc acetate dihydrate [99.5%, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] and hexamethylenetetramine [99.0%, $(\text{CH}_2)_6\text{N}_4$] were used as precursors and Si (100) wafer as the substrate. Aqueous 8-mM solutions of the precursors were mixed to produce the growth solution wherein the Si substrates were submerged. The growth solution was heated at 90 °C for 2 h, after which the substrates were removed, washed with deionized water, and were left to dry in ambient air. For the dip-coating in PVP, the Si substrate with the deposited ZnO rods was submerged in an aqueous PVP solution (10,000 MW) for

1 h while being heated at 50 °C. After dip-coating, the composite was harvested from the solution, washed with deionized water, and dried in air.

Different structural and optical characterization techniques were implemented to investigate the ZnO-PVP composite. The structural properties of the composites were studied using scanning electron microscopy (SEM) and x-ray diffraction (XRD) measurement. The optical properties of the composites were also characterized using time-integrated photoluminescence (TIPL) and time-resolved photoluminescence (TRPL) spectroscopies. The surface interactions between ZnO and PVP were investigated using Fourier transform infrared (FTIR) spectroscopy. The material characterizations were performed before and after subjecting the ZnO-PVP composite to a heated environment at 300 °C for 2 h in order to evaluate the stability of the composite against heat.

RESULTS

Figure 1 shows the SEM image of the ZnO-PVP composite. The ZnO rods of the composite are randomly oriented and distributed on the Si substrate. The average length and width of the rods are $7.4 \pm 1.7 \mu\text{m}$ and $1.9 \pm 0.4 \mu\text{m}$, respectively.

Figure 2 shows the XRD patterns of the ZnO-PVP composite before and after heating at 300 °C for 2 h. The diffraction peaks are indexed to the reflections of hexagonal wurtzite ZnO and the lattice constants are calculated to be $a = 3.24 \text{ \AA}$ and $c = 5.20 \text{ \AA}$. No peaks associated to impurities or other phases can be observed. Based on the similar XRD spectra, heating at 300 °C has no apparent effect on the degree of crystallinity of the composite.

Figure 3 shows the TIPL spectra of the ZnO-PVP composite before and after heating. The composite exhibits an intense UV emission centered at 392 nm and a broad visible emission between 470-700 nm. After heating, the visible emission is reduced and shifted in center wavelength from 557 nm to 574 nm while the intense UV emission is retained. Hence, it can be inferred that the UV emission of the composite is stable against heat at 300 °C.

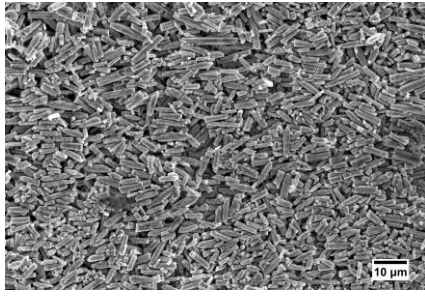


Fig. 1. SEM image of the ZnO-PVP composite.

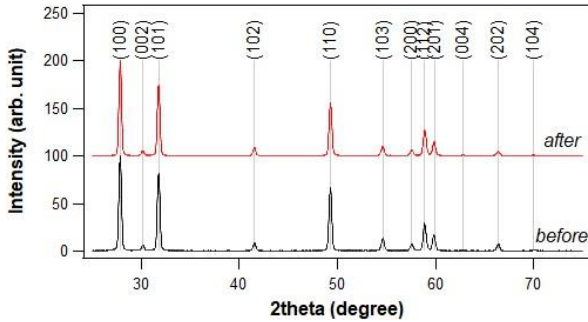


Fig. 2. XRD patterns of the ZnO-PVP composite before and after heating at 300 °C for 2 h.

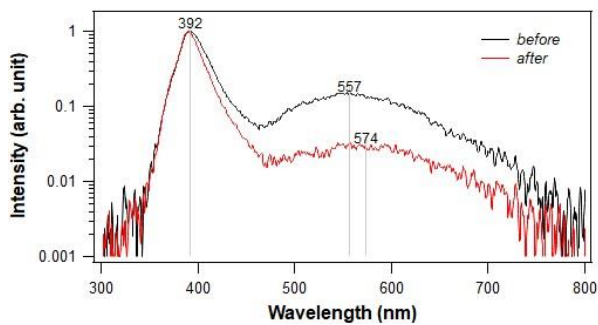


Fig. 3. TIPL spectra of the ZnO-PVP composite before and after heating at 300 °C for 2 h.

Figure 4 shows the UV emission profiles of the ZnO-PVP composite before and after heating. The decay profiles can each be fitted to a single exponential function with a time constant representing the emission lifetime. The UV emission lifetimes of the composite before and after heating are determined to be 28 ± 10 ps and 30 ± 10 ps, respectively. There is no significant difference in the lifetimes, hence, the UV emission lifetime is also stable.

Figure 5 shows the FTIR transmittance spectra of PVP and of the ZnO-PVP composite before and after heating. PVP exhibits an absorption band between 3100 and 3600 cm^{-1} , which corresponds to O–H stretching due to adsorbed water molecules, and four bands due to its functional group vibrations located around 2942, 1651, 1429, and 1276 cm^{-1} which are assigned to CH_2 asymmetrical stretching, C=O stretching, CH_2 bending, and C–N stretching, respectively. Before being subjected to heat, the ZnO-PVP composite exhibits the O–H stretching band as well and an absorption band around 870 cm^{-1} associated with the C–O vibration which can be attributed to hydrothermal reaction intermediates. After heating, the O–H stretching and C–O vibration bands are no longer present which can be due to the

removal of adsorbed water and reaction intermediates, respectively. The ZnO-PVP composite exhibits the C=O stretching band associated with PVP which confirms the successful adsorption of PVP to the ZnO surface. Even after heating at 300 °C, the C=O stretching band is still present indicating that there is no degradation of surface interaction between ZnO and PVP at this temperature.

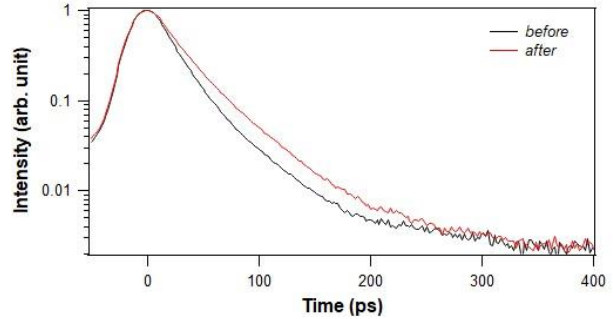


Fig. 4. UV emission profiles of the ZnO-PVP composite before and after heating at 300 °C for 2 h.

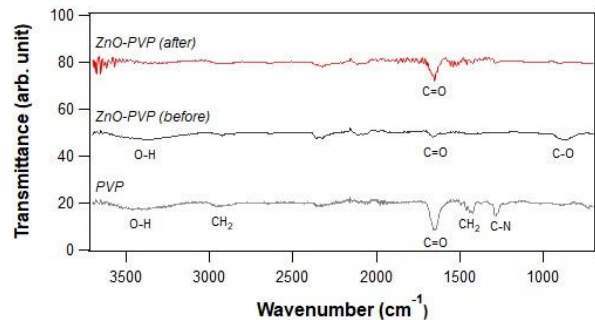


Fig. 5. FTIR transmittance spectra of the ZnO-PVP composite before and after heating at 300 °C for 2 h.

CONCLUSION

The structural and optical properties of ZnO-PVP composite are investigated. The crystal structure, UV emission, UV emission lifetime, and surface interactions of the composite are stable regardless of heating at 300 °C. With intense UV emission and ultrafast UV emission lifetime, the ZnO-PVP composite is a potential UV phosphor. Further evaluation of the composite properties under different conditions, such as at higher temperatures and aqueous environments, is anticipated in the future.

ACKNOWLEDGEMENTS

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