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Preparation and characterization of transparent ZnO/epoxy nanocomposites with high-UV shielding efficiency

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Abstract

Transparent ZnO/epoxy nanocomposites with high-UV shielding efficiency were reported in this paper. First, zinc oxide (ZnO) precursor was synthesized via the homogeneous precipitation method and ZnO nanoparticles were then made by calcination of the precursor at different temperature. The structural properties of the as-prepared ZnO nanoparticles were studied in detail using thermogravimetry (TGA), differential thermal analysis (DTA), X-ray diffractometer (XRD), Fourier transform infrared spectrometer (FT-IR) and transmission electron microscopy (TEM), respectively. Transparent ZnO/epoxy nanocomposites were subsequently prepared from transparent epoxy (EP-400) and as-prepared ZnO nanoparticles via in situ polymerization. Optical properties of ZnO/epoxy nanocomposites, namely visible light transparency and UV light shielding efficiency, were studied using an ultraviolet–visible (UV–vis) spectrophotometer. The optical properties of the as-obtained nanocomposites were shown to depend on ZnO particle size and content. The nanocomposite containing a very low content (0.07% in weight) of ZnO nanoparticles with an average particle size of 26.7 nm after calcination at 350 °C possessed the most optimal optical properties, namely high-visible light transparency and high-UV light shielding efficiency, that are desirable for many important applications.

Keywords: ZnO; Epoxy; Nanocomposite

1. Introduction

Since the first demonstration of the high-brightness blue light-emitting diode (LED) and subsequently the white LED, interest in using solid-state light sources for general illumination has been rapidly growing [1–3]. Transparent epoxy resins have been most frequently employed in standard LED technology as packaging materials because of their excellent transparency, high-glass transition temperature, low-water absorption and standard processability [4–6]. Recently, ultraviolet light-based white light-emitting dioxides (UV-WLED) have been under development for generation of white light [7,8]. Packaging materials for UV-WLED are required to possess high-visible light (>400 nm) transparency and yet high-ultraviolet (UV) light (<400 nm) resistance. High-UV light resistance of packaging materials may be achieved via structural design of transparent epoxies [9,10], and addition of organic [11,12] and inorganic [13,14] UV light absorbents. Structural design of transparent epoxies might lead to significant changes in physical and mechanical properties, causing great inconvenience in handling of packaging materials using standard process techniques. Moreover, this method is relatively difficult and costly to obtain UV light resistant transparent epoxies. Organic UV absorbents have long been employed for stabilization of polymers. However, organic UV absorbents themselves can be consumed and migrate within polymers [15]. Furthermore, organic ultraviolet light absorbents may pose a safety problem when used at high concentrations. Conversely, some notable inorganic particles also absorb UV light to stabilize polymers [16,17]. Inorganic UV absorbents, such as ZnO, TiO_2 and CeO_2, virtually do not migrate in a polymeric matrix, and their photo- and thermal-stability is not problematic even over decades [15].

Though the incorporation of inorganic UV absorbents to transparent epoxies can enhance significantly UV light resistance via UV light shielding, composites prepared by

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mixing of organic and inorganic components are generally opaque unless the refractive index of the filler is approximately equal to that of the transparent polymer matrix [18–20]. Fortunately, the transparency can be highly maintained when particle fillers are in nanometer scale and their content is low. Optically transparent composites have been obtained by incorporation of a low content of fillers with dimensions far below the wavelength of light [21,22]. Zinc oxide (ZnO) is a notable inorganic material closely related with ultraviolet light. The electrical conductivity of ZnO is extremely sensitive to ultraviolet light exposure and hence it has been assumed that ZnO nanowires would serve as highly sensitive UV-light detectors and optically switching devices [23]. In addition, ZnO is an extremely high-UV-shielding material with low-refractive index having been applied to polymers as UV-light filters [14–16,24]. It has been shown that ZnO/poly(styrene butylacrylate) latex nanocomposites exhibit high-UV-shielding efficiency [24]. However, as ZnO content increases, the visible light transparency decreases dramatically [24,25]. It was reported that the refractive index of ZnO (1.9–2.0) was somewhat higher than that of transparent epoxies (1.55) [15,24]. Thus, it seems that addition of a very low content of fine ZnO nanoparticles to a transparent epoxy matrix would maintain high-visible light transparency. However, if ZnO nanoparticles are too small they would bring about blue-shift, and hence reduce UV-shielding efficiency [26]. Consequently, a proper fine size of ZnO nanoparticles is critical to obtain high-UV-shielding efficiency. To obtain ZnO nanoparticles with fine particle size, many synthesis methods have been used, including precipitation, hydrothermal method, sol–gel and microemulsion [27–32]. Of these, the precipitation method makes possible the production of large quantities of ZnO nanoparticles in a reproducible way. Moreover, this is a relatively cheap synthesis method.

In this paper, the precipitation method was used to prepare ZnO nanoparticles with variable fine particle sizes. Investigation of the effects of calcination temperature on particle size and structural properties of ZnO nanoparticles was carried out using TGA, DTA, XRD, FTIR and SEM. Transparent ZnO/epoxy nanocomposites were prepared by incorporating ZnO nanoparticles with various particle sizes into a transparent epoxy matrix (EP-400) and the optical properties of the nanocomposites were characterized by an ultraviolet–visible (UV–vis) spectrophotometer. The effects of ZnO particle size and content on the optical properties of the nanocomposites were studied. It is interesting to note that the nancomposite containing an extremely low content (0.07 wt%) of ZnO nanoparticles with an average particle size of 26.7 nm after calcination at 350 °C possesses optimal optical properties, namely high-visible light transparency and high-UV light shielding efficiency. Incorporation of an extremely low content of ZnO nanoparticles has the advantage that there is no effect on processability of the packaging materials using standard processing techniques. Moreover, it should be emphasized that whilst this transparent epoxy nanocomposite is initially proposed as packaging materials for UV-WLED, it is also an excellent candidate for a variety of practical applications, such as components for precision optical devices, and windows for automobiles, trains and ships, etc. where high-visible light transparency and high-UV light shielding efficiency are desired [21].

2. Experimental work

2.1. Preparation of ZnO nanoparticles

ZnO nanoparticles were prepared by a precipitation method similar to that described by Wang et al. [30]. Chemicals of analytical purity and distilled water were used. Two solutions were prepared as follows: solution A −0.1 mol $Zn(NO_3)_2 6\text{-}H_2O$ dissolved in 0.2 dm^3 distilled water; and solution B −0.12 mol Na_2CO_3 dissolved in 0.24 dm^3 distilled water. Solution A was added to solution B drop by drop under vigorous stirring. The resulting white precipitates were filtered and washed with distilled water three times. The solids were then washed with ethanol and dried at 100 °C for 6 h in a vacuum system to remove the solvent. Finally, ZnO nanoparticles were obtained after calcination of the solids in air at 200, 250, 300, 350, 400, 500 and 600 °C for 2 h, respectively.

2.2. Preparation of ZnO/epoxy nanocomposites

Transparent epoxy (EP-400, A and B) used for LED packaging was purchased from Bao and Lin Optoelectronic Co. Ltd of China. As-prepared ZnO nanoparticles were dispersed in curing agent (EP-400B) using the ultrasonic technique for 10 min, the resulting mixture was then mixed with epoxy (EP-400A). The epoxy and curing agent were well stirred until a homogeneous mixture was obtained. The mixture was poured into a stainless steel mould and heated in an oven for 1 h at 130 °C and 6 h at 100 °C. After this curing process, the samples were removed from the mould.

2.3. Characterization

ZnO powder X-ray diffraction patterns were recorded on a Bruker D8 ADVANCE X-ray Diffractometer with graphite monochromatized Cu Kα radiation. Thermal analysis was performed using a Universal V2.6D TA Instrument in a

Table 1
Preparation of ZnO nanoparticles by calcination of precursor at different temperature for 2 h

Sample code	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8
Calcination temperature (°C)	Precursor	200	250	300	350	400	500	600

nitrogen atmosphere in the temperature range of 30–1000 °C and a heating rate of 10 °C/min. Fourier transform infrared spectra (FT-IR) were recorded at ambient temperature using a Bio-Rad spectrometer (Model Win-IR). Transmission electron microscopy (TEM) of ZnO samples was performed with a transmission electron microscope (Model H-800, Hitachi) and the particle sizes from TEM were estimated with a software (SemAfore 4.0). The optical properties of the transparent epoxy/ZnO nanocomposites were studied by using a UV–vis spectrophotometer (Model Lambda 900). The absorbance and transmittance spectra were scanned in the range of 250–900 nm with a 1-nm interval.

3. Results and discussion

We started with preparation of the zinc oxide (ZnO) precursor by using the homogeneous precipitation method. ZnO nanoparticles were then obtained after calcination of the precursor in air at 200, 250, 300, 350, 400, 500 and 600 °C for 2 h, respectively (Table 1). Fig. 1 shows the TGA/DTA curves in nitrogen for the precursor (sample Z1). Small exothermic signals are recorded near 75 °C (see DTA curve), which is attributed to the evaporation of absorbed water in the precursor. It is also observed that the endothermic peak occurs at 253.85 °C, indicating the transformation of the precursor to ZnO. TGA curve shows that the weight loss proceeds in successive stages with increasing temperature. It can be seen that most significant weight loss occurs in the temperature range 190–260 °C. Also, it is clearly shown from the TGA curve that the precursor can be completely decomposed to ZnO after calcination at ∼350 °C or above.

Fig. 2 displays the XRD patterns of ZnO nanoparticles calcined in air at different temperature. They show that ZnO is formed after calcination of the precursor at ∼200 °C or above, since the precursor is a complex of $ZnCO_3$ and $Zn(OH)_2$, and $Zn(OH)_2$ can be easily transformed to ZnO at 200 °C or above. This is confirmed by FT-IR results (Fig. 3), namely the broad band in the range of 3200–3500 cm^{-1} has become a broad peak centered at 3450 cm^{-1}, indicating at least the partial disappearance of the OH group [33]. The ZnO crystallite sizes are calculated using Scherrer's formula and the results are given in Table 2. Clearly, an increase in calcination temperature brings about a corresponding increase on crystallite size, leading to sharper diffraction peaks.

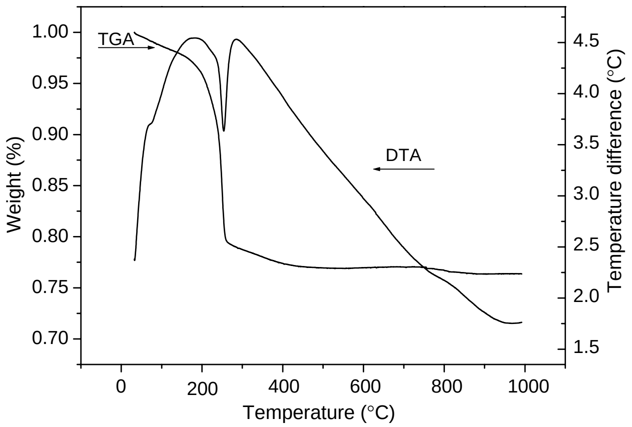

Fig. 1. TGA/DTA curves recorded for sample Z1.

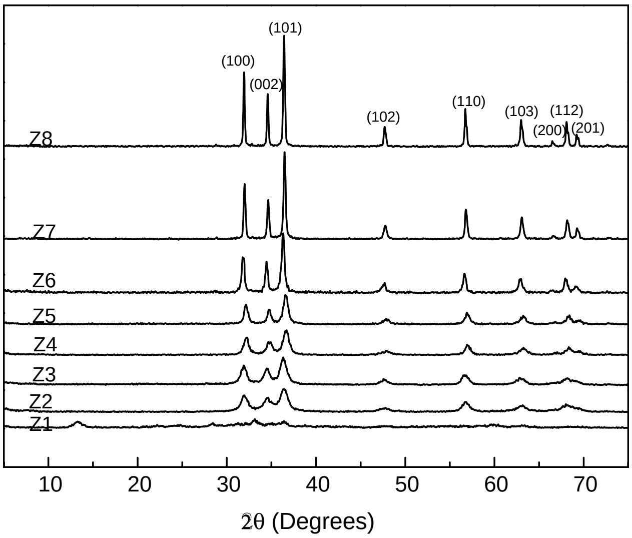

Fig. 2. XRD patterns of ZnO nanoparticles calcined at different temperatures.

The FT-IR spectra of samples Z1 to Z8 are given in Fig. 3. The main features of the spectrum of the precursor (Z1) correspond to basic zinc carbonate. After calcination of the precursor, a peak is observed at ∼500 cm^{-1}, which can be identified as the stretching mode of ZnO [34]. The FT-IR spectra also show that the shoulders of ZnO stretching peaks in the range of 1200–500 cm^{-1} become steeper as the calcination temperature increases, suggesting that the purity of ZnO increases with increasing calcination temperature.

Fig. 4 shows TEM micrographs of the precursor and the ZnO nanoparticles prepared at different calcination temperatures. As shown in Fig. 4(a), the precursor consists of 30–40 nm spherical particles. After calcination of the precursor at different temperature, the ZnO nanoparticles with variable fine particle sizes are obtained and the particle size increases with calcination temperature. For the samples calcined at 300 °C (Fig. 4(b)) and 400 °C (Fig. 4(c)), the average particle

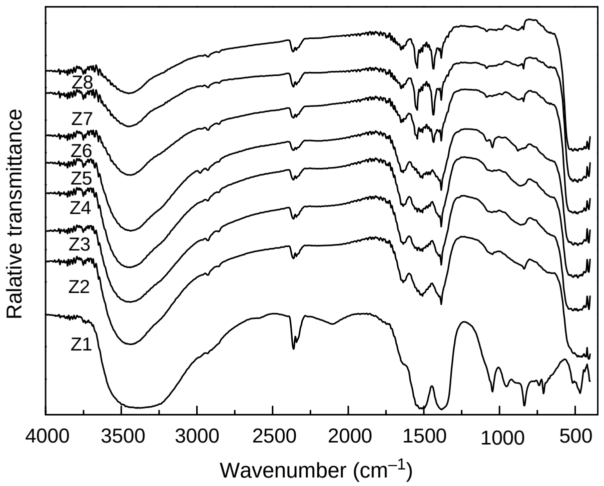

Fig. 3. FT-IR spectra of samples Z1–Z8.

Table 2
Crystallite size of ZnO nanoparticles estimated using the XRD technique and Scherrer's equation

Sample code	Z2	Z3	Z4	Z5	Z6	Z7	Z8
Mean particle size (nm)	15.9	18.6	22.1	26.7	45.9	63.6	71.9

sizes are, respectively, 21.6 and 48.3 nm. These results are in good agreement with the apparent crystallite sizes (of 22.1 and 45.9 nm, respectively, in Table 2) determined by the XRD technique. But, for samples calcined at 500 °C (Fig. 4(d)) and 600 °C (Fig. 4(e)), ZnO particles aggregated into clusters of several hundred nanometers in size, showing large differences from the XRD results (Fig. 2). The applicability of Scherer's formula is restricted to small particles (usually smaller than 100 nm) and the above observed large differences reflect the inapplicability of Scherer's equation to large ZnO crystallites.

Transparent ZnO/epoxy nanocomposites were prepared from transparent epoxy (EP-400) and as-prepared ZnO nanoparticles via in situ polymerization. The UV–vis transmittance spectra of epoxy and nanocomposites (0.07 wt%) are shown in Fig. 5(a). As the calcination temperature increases, the transmittance of UV light generally decreases. Though the samples calcined at 400 °C or above (Z6–Z8) exhibit almost perfect UV light shielding efficiency (Fig. 5(a)), their transparencies are quite poor (Fig. 6). However, it can be seen from Fig. 5(a) that the nanocomposite containing Z5 nanoparticles calcined at 350 °C shows not only high UV light shielding (∼96% at 320 nm and ∼91% at ∼370 nm, Fig. 5(a)) but also high-visible light transparency (Fig. 6).

Moreover, Fig. 5(b) shows that UV light absorbance of the nanocomposites increases generally with increasing calcination temperature. This agrees with the transmittance result (Fig. 5(a)). The explanation is as follows. UV light absorption spectra consist of two contributions by ZnO:UV light absorption and light scattering. As the calcination temperature increases, more precursor is transformed to ZnO nanoparticles, which is beneficial to UV absorption. Also, as light transmits in an inhomogeneous medium (like composites) where the refractive index varies at different locations, light scattering will occur [35]; when calcined at 400 °C or above, particles

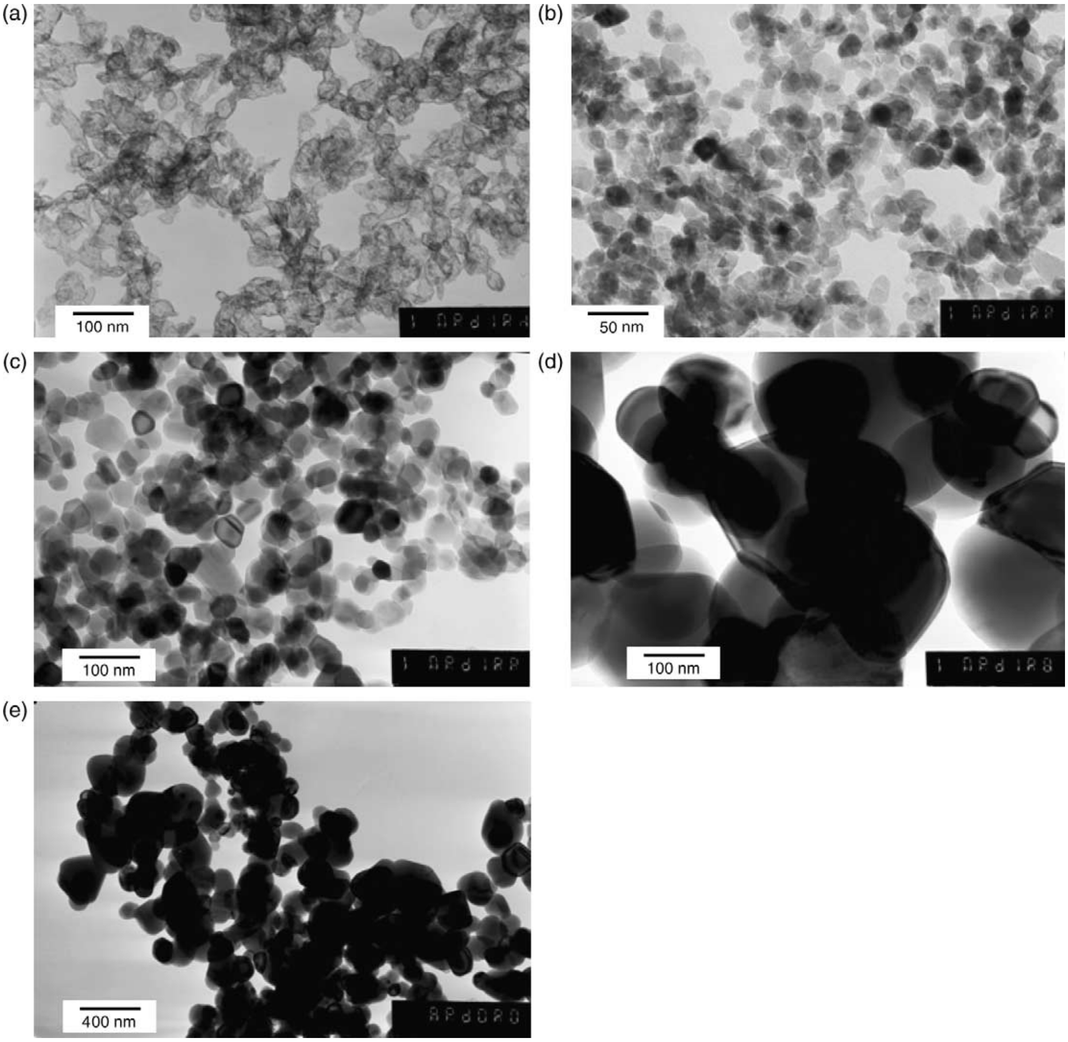

Fig. 4. TEM micrographs of ZnO nanoparticles prepared at different temperatures. (a) Precursor, (b) calcined at 300 °C, (c) 400 °C, (d) 500 °C, and (e) 600 °C.

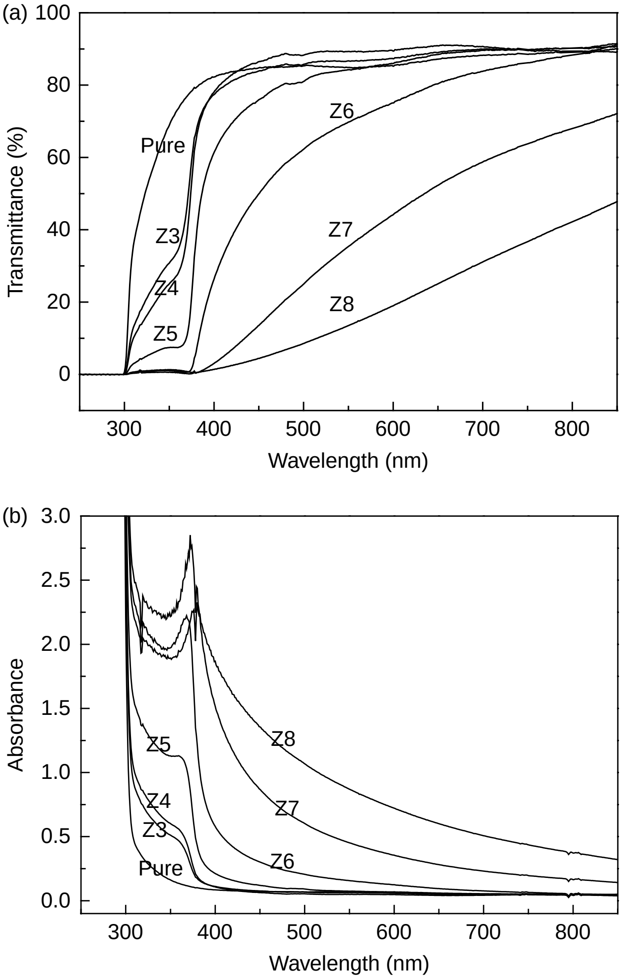

Fig. 5. UV–vis spectra of epoxy matrix and ZnO/T-epoxy nanocomposites containing 0.07 wt% ZnO nanoparticles. (a) Transmittance, and (b) absorbance.

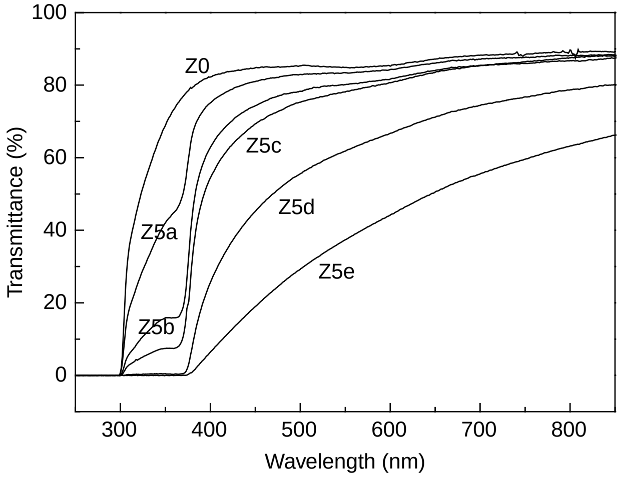

Fig. 7. Transmittance of ZnO/epoxy nanocomposites with different ZnO contents. Z0, Z5a, Z5b, Z5c, Z5d and Z5e denote 0, 0.03, 0.05, 0.07, 0.1, 0.15 wt% ZnO.

grow and agglomerate, UV light scattering will play a larger role in shielding. The nanocomposites containing ZnO nanoparticles calcined at 400 °C or above show high absorption of visible light, which is not desirable for transparent packaging materials. However, the nanocomposite containing ZnO nanoparticles with a mean particle size of 26.7 nm calcined at 350 °C exhibits high-UV light absorption and very low absorption of visible light, hence high-UV light shielding efficiency and high-visible light transparency, both of which are preferred properties for transparent packaging materials.

Epoxy nanocomposites containing varying amount of ZnO nanoparticles have also been prepared and characterized. The results showed that only the nanocomposite (Z5c) containing 0.07 wt% ZnO nanoparticles corresponds to simultaneously high-visible light transparency and high-UV light shielding efficiency. For simplicity, only the transmittance results for the nanocomposites (Z5) with different loading of ZnO nanoparticles are presented in Fig. 7.

Since only an extremely low content (0.07 wt%) of ZnO nanoparticles was added to the transparent epoxy resin, the physical and mechanical properties were not changed. In addition, the processability of the packaging material would not change with this very low-ZnO content. Indeed, easy processing of these transparent ZnO/epoxy nanocomposites has been confirmed in practical encapsulation of UV-WLED, which is currently under investigation by the Chinese Academy of Sciences. Fig. 8 shows the standard UV-WLED lamps encapsulated with original transparent epoxy resin (A) and

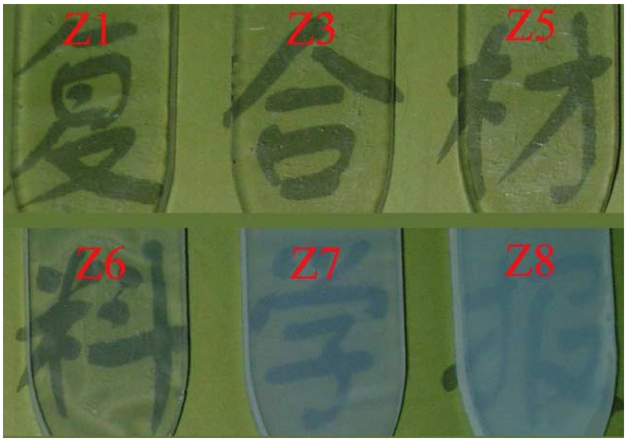

Fig. 6. Transparency of ZnO/T-epoxy nanocomposites with 0.07 wt% ZnO nanoparticle content prepared at different temperatures.

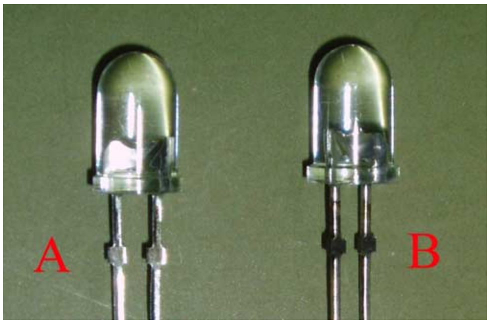

Fig. 8. UV-WLED lamps encapsulated with (A) pure transparent epoxy resin, and (B) ZnO/T-epoxy nanocomposite with 0.07 wt% ZnO loading (Z5c).

ZnO/epoxy nanocomposite resin (B). Except the processability, the appearance of the two lamps is also the same.

4. Conclusions

In summary, transparent ZnO/epoxy nanocomposites with high-visible light transparency and high-UV light shielding efficiency were reported in this paper. Different nanosized ZnO particles were obtained by calcination of the ZnO precursor derived from a homogenous precipitation method. The effects of calcination temperature on the particle size and structural properties of ZnO nanoparticles were studied. Transparent ZnO/epoxy nanocomposites were successfully prepared by incorporation of as-obtained ZnO nanoparticles in a transparent epoxy. The dependence of the optical properties of the nanocomposites on ZnO particle size and loading was investigated. The results showed that the nanocomposite containing an extremely low content (0.07 wt%) of ZnO nanoparticles with an average size of 26.7 nm after calcination at 350 °C would have the most optimal optical properties, viz. high-visible light transparency and high-UV light shielding efficiency, that are required qualities for transparent packaging materials for UV-WLED. This transparent ZnO/epoxy nanocomposite is also an excellent candidate for a range of engineering applications, such as parts for precision optical devices or windows for transportation vehicles etc.

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