Highly luminescent and transparent ZnO quantum dots/epoxy composite used for white light emitting diodes

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1. Materials and methods

1.1. Reagents and materials

Zinc acetate dihydrate (99.99 %), tetramethylammonium hydroxide pentahydrate (TMAH, 97 %), tetrabutyl ammonium bromide (TBAB, AR) and γ-(2,3-epoxypropoxy)propytrimethoxysilane (KH560, 97 %) were supplied by Aldrich. D.E.R. 332 epoxy resin with an average epoxide equivalent weight of 185 and methylhexahydrophthalic anhydride (MHHPA) were purchased from Dow Chemical. Other chemicals were purchased from Guangzhou Chemical Reagent Factory, China.

1.2. Preparation of ZnO QDs

Zn(OAc)₂·2H₂O (6 mmol) was dissolved in ethanol (120 mL) by sonication (600 W/cm², 40 kHz). KH560 (6 mmol) was then added and the solution was heated to 75 °C under atmospheric pressure with stirring. Afterwards, TMAH (9 mmol) dissolved in ethanol (9 ml) was rapidly mixed with the above solution. Having been agitated for 5 min, the reaction was stopped by adding hexamethylene (50 ml) and the system was cooled down in an ice bath. After centrifugation at 7000 rmp, the resultant KH560-stabilized ZnO QDs (denoted by ZnO_{KH560}) were washed with the mixture of ethanol and hexamethylene for three times, dried at 80 °C under vacuum or...
redispersed in acetone. Control experiment was carried out in the absence of KH560 and the produced ZnO QDs are denoted by ZnO<sub>bare</sub>.

Reaction temperature had obvious effect on PL characteristics of the ZnO quantum dots. As shown in Fig. S1, although the ZnO quantum dots prepared at 45 °C had the strongest PL intensity, low temperature was found to be adverse to the reaction between ZnO quantum dots and KH560. Dispersibility and compatibility of ZnO quantum dots prepared at lower temperatures in epoxy resin were rather poor, according to the feedback of application results, we considered 75 °C as the optimized reaction temperature.

1.3. Preparation of ZnO QDs/epoxy nanocomposites

ZnO<sub>KH560</sub> dispersed in acetone was mixed with D.E.R. 332 epoxy and then the mixture was continuously sonicated for 30 min. When the solvent was removed by rotary evaporation under vacuum at 50 °C, MHHPA with equal epoxide equivalent weight and TBAB (0.3 wt%) were added into the system. After thorough compounding, the mixture was poured into a preheated mold, cured at 120 °C for 2 h, and cooled down naturally to room temperature.

1.4. Characterization

HRTEM and STEM images were taken by FEI Tecnai G2 F30 transmission electron microscope. UV-visible absorption spectra were collected using PE-Lambda 750 UV-vis-NIR spectrophotometer. PL spectra were obtained by a FLS920 combined with time resolved & steady state fluorescence spectrometer (Edinburgh Instruments) using the 350 nm line of an Xe lamp as the excitation source and R1527 photomultiplier tube as the detector. Absolute PL QYs of ZnO QDs and ZnO QDs/epoxy resin nanocomposites were obtained using an integrating sphere connected by the FLSP920. XPS measurements were performed on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with AlKα X-ray radiation as the X-ray source for excitation. FTIR spectra were recorded by an EQUINOX55 Fourier transformation infrared spectrometer (Bruker). XRD patterns were obtained by a D8 Focus diffractometer (Bruker) equipped with graphite
monochromatized Cu Kα (λ = 0.15405 nm) radiation source operating at 30 kV and 30 mA. TGA was performed on a TA Q50 analyzer (TA Instruments) under nitrogen atmosphere at a heating rate of 20 °C/min. DMA was conducted on a Mettler Toledo DMA/SDTA861 using single cantilever mode under 1 Hz at a heating rate of 2 °C/min in nitrogen.

2. Supporting Table and Figures

<table>
<thead>
<tr>
<th>Specimen</th>
<th>ZnObare (in acetone)</th>
<th>ZnObare (in dry state)</th>
<th>ZnOKH560 0 wt%</th>
<th>ZnOKH560 1 wt%</th>
<th>ZnOKH560 3 wt%</th>
<th>ZnOKH560/epoxy nanocomposites 5 wt%</th>
<th>ZnOKH560/epoxy nanocomposites 8 wt%</th>
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<tr>
<td>Ex (nm)</td>
<td>364</td>
<td>345</td>
<td>383</td>
<td>364</td>
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<td>Em² (nm)</td>
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<td>585</td>
<td>549</td>
<td>435</td>
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<td>564</td>
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<tr>
<td>Absolute QYb (%)</td>
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<td>1</td>
<td>11</td>
<td>5</td>
<td>27</td>
<td>21</td>
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</table>

*aExcited at the correspondent excitation peak. **Excited at 350 nm.

**Fig. S1** Effect of reaction temperature on PL characteristics of ZnOKH560.
**Fig. S2** UV-vis absorption spectra of ZnO_{bare} and ZnO_{KH560} in acetone (0.5 mg/ml). For nanoparticles’ diameter $D$ within the range of 2.5 ~ 6.5 nm, there is an empirical equation (see E. A. Meulenkamp, *J. Phys. Chem. B* 1998, 102, 5566): \[ \frac{1240}{\lambda_{1/2}} = a + \frac{b}{D^2} - \frac{c}{D} \] where $\lambda_{1/2}$ denotes the wavelength at which the absorption is 50 % of that at the excitonic peak (or shoulder), and $a$, $b$ and $c$ are fitting constants. By using this equation and Fig. S1, the size of ZnO_{bare} is estimated to be about 4.21 nm, while that of ZnO_{KH560} is about 2.89 nm, which well agree with the evaluation based on TEM observation.

**Fig. S3** XRD patterns of ZnO_{bare} and ZnO_{KH560}.
**Fig. S4** TEM images of ZnO$_\text{bare}$ (a) and ZnO$_{\text{KH560}}$ (b).

**Fig. S5** Fourier transformation of Fig. 3a.
Fig. S6 Photographs of (a, b) ZnO$_{\text{bare}}$ and (c, d) ZnO$_{\text{KH560}}$ taken under (a, c) room light and (b, d) 365 nm irradiation.

Fig. S7 Thickness of ZnO QDs/epoxy nanocomposites with different ZnO$_{\text{KH560}}$ contents.
**Fig. S8** Drift corrected spectrum image scanning of the ultrathin section of nanocomposites with 8 wt% ZnO\textsubscript{KH560} (~40 nm thick). Insert: the corresponding EDX elemental maps of Zn obtained in STEM mode.

**Fig. S9** Temperature dependence of loss factor, tan $\delta$, of ZnO QDs/epoxy nanocomposites with different ZnO\textsubscript{KH560} contents measured by dynamic mechanical analysis (DMA).