

Supporting Information

Doped quantum dot@silica nanocomposites for white light-emitting diodes

Bingxia Zhao, Yulian Yao, Mengyu Gao, Kang Sun*, Wanwan Li*

State Key Lab of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China
E-mail: wwli@sjtu.edu.cn (Wanwan Li); ksun@sjtu.edu.cn (Kang Sun)

Experimental

Chemicals

Zinc stearate (ZnSt₂, technical grade), stearic acid (SA, 95%), tetramethylammonium hydroxide pentahydrate (TMAH, ≥97%), 1-dodecanethiol (DDT, ≥98%), oleylamine (OAm, >90%), tetraethylorthosilicate (TEOS, 99%), poly(5)-oxyethylene-4-nonylphenyl-ether (NP-5), and mono-methylamine (40 wt.% in H₂O) were purchased from Sigma Aldrich. Selenium powder (Se, 99.99%), manganese chloride (MnCl₂•4H₂O, 99.9%), copper chloride (CuCl₂•4H₂O, ≥99%), liquid paraffin (chemical pure), methanol (analytical reagent), chloroform (analytical reagent), n-butanol (analytical reagent), acetone (analytical reagent), and ethanol (analytical reagent) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Transparent epoxy (EP-400 A and B) used for LED packaging was purchased from SWANCOR (Shanghai) Fine Chemical Co., Ltd.

Precursors preparation

(1) Synthesis of manganese/copper stearate (MnSt₂/CuSt₂): In general, 20 mmol of stearic acid (SA) was dissolved in 39 mL methanol at 50 °C. The solution was then cooled to room temperature after turning clear. TMAH solution was prepared by dissolving 20 mmol of TMAH in 13 mL methanol. The SA and TMAH solutions were then mixed and stirred for 15 min. At this time, 10 mmol of MnCl₂/CuCl₂ in 13 mL methanol was added dropwise to the reaction while stirring vigorously, allowing for the precipitation of MnSt₂/CuSt₂. The precipitates were washed with methanol 3 times and dried under vacuum.

(2) Preparation of stock solutions

Zn-precursor I: Zinc precursor I was prepared by dissolving 0.72 g of ZnSt₂ and 0.08 g of SA in 6 mL of paraffin liquid. The resultant solution was degassed at 110 °C for 30 min by bubbling with N₂.

Zn-precursor II: Zinc precursor II was prepared by dissolving 1.26 g of ZnSt₂ in 10 mL of paraffin liquid. The resultant solution was degassed at 110 °C for 30 min by bubbling with N₂.

Se-precursor: Se-precursor was prepared by dissolving 2 mmol of Se powder in 20 mL of paraffin liquid. The resultant solution was degassed at 110 °C for 30 min by bubbling with N₂ and then heated to 220 °C for 3h.

Mn-precursor: Manganese precursor was prepared by dissolving 0.05 g of MnSt_2 in 6.5 mL of liquid paraffin. The resultant solution was degassed at 110 °C for 30 min by bubbling with N_2 .

Cu-precursor: Copper precursor was prepared by dissolving 0.01 mmol of CuSt_2 in 10 mL of liquid paraffin. The resultant solution was degassed at 110 °C for 30 min by bubbling with N_2 .

All precursors were freshly made prior to each synthesis.

Samples preparation

(1) Synthesis of Mn:ZnSe QDs: In general, 0.3 mmol of Se powder and 0.12 mL of OAm in 6 mL of liquid paraffin were added to a flask. The solution was degassed at 110 °C for 30 min by bubbling with N_2 . The temperature was then raised to 280 °C. After the Se powder was completely dissolved, 1 mL Mn-precursor was injected into the flask. The reaction was then cooled to 260 °C and held at this temperature for 4 min to allow for the nucleation of the MnSe clusters. The reaction mixture was then further cooled to 220 °C, at which time 1.2 mL Zn-precursor I and 0.25 mL OAm were added dropwise. After 15 min, Zn-precursor I and OAm were added a second time.

The PL peak wavelength of the prepared Mn:ZnSe QDs was about 580 nm and did not change significantly with reaction time or elemental ratios. To obtain Mn:ZnSe QDs with longer PL peak wavelengths, a thiol modification was introduced. In general, after the Mn:ZnSe QDs were formed at 220 °C, the temperature was raised to 260 °C, at which time 0.7 g of 1-dodecanethiol (DDT) was injected. The reaction temperature was held at 260 °C, during which aliquots were taken at different time intervals and injected into n-hexane. The reaction solution was then cooled to room temperature once the doped QDs with the desired PL peak wavelength were obtained.

Acetone was added in order to purify the prepared doped QDs, which were then redispersed in chloroform for further use.

(2) Synthesis of Cu:ZnSe QDs: In general, 3 mL of Se-precursor was mixed with 5 mL of liquid paraffin in a flask. The resultant solution was then heated to 300 °C under N_2 , and 2 mL of Zn-precursor II was injected into the flask. The mixture was then cooled to 280 °C and 0.2 mL of OAm was added. Aliquots were taken at different time intervals and injected into n-hexane. Once the desired PL peak wavelength was obtained, the temperature was cooled to 60 °C and 5 mL of Se-precursor was then injected into the flask. The solution temperature was subsequently increased to 180 °C, and 0.5 mL of Cu-precursor was added dropwise. The temperature of the solution was then raised to 240 °C, at which time 4 mL of Zn-precursor II and 0.2 mL of OAm were added again. Aliquots were taken at different time intervals and injected into n-hexane. Once the doped QDs with the desired PL peak wavelength were obtained, the reaction was cooled to room temperature. Acetone was added in order to purify the prepared doped QDs, which were then redispersed finally in chloroform for further use.

(3) Synthesis of doped ZnSe QD@SiO₂ nanocomposites: The silica coating was formed via a water-in-cyclohexane reverse microemulsion as described in previous literature. Briefly, 0.1 mL of TEOS and 10 mL of doped ZnSe QDs (1 mM) in a cyclohexane solution were mixed together. The mixture was then stirred for 10 min before adding 1 mL of surfactant dropwise. The solution was then stirred for 30 min to form the microemulsion system. Afterwards, 0.1 mL of catalyst was introduced dropwise to initiate polymerization. After stirring for 24h at room temperature, the silica growth was stopped by the addition of acetone. The resultant nanoparticles were collected by centrifugation, washed with ethanol three times, and then redispersed in chloroform.

(4) Preparation of doped ZnSe QD@SiO₂/epoxy composites: A specific quantity of doped ZnSe QD@SiO₂ nanocomposites in chloroform (ca. 0.8 mL) were added to a mixture of epoxy resin (EP400A, 1 g) and anhydride curing agent (EP400B, 1 g) while stirring vigorously. The homogeneous mixture was then poured into a stainless steel mold and solidified in an oven at 40 °C for 60 min, followed by another 60 min at 80 °C and a final 60 min at 120 °C.

(5) Fabrication of d-dot@SiO₂ based white LEDs: The Cu:ZnSe QDs with PL peak wavelengths of 470 nm and 550 nm and the Mn:ZnSe d-dots with a peak wavelength of 605 nm were used to fabricate white LEDs. The three kinds of doped ZnSe QD@SiO₂ (molar ratio of Cu:ZnSe(470nm): Cu:ZnSe(550nm): Mn:ZnSe(605nm)=3:1:1) were mixed together with epoxy resin and anhydride curing agent while stirring vigorously. The doped ZnSe QD@SiO₂/epoxy composite was prepared as described above. The obtained solution (ca. 65μL) was then coated onto near-UV LED chips ($\lambda_{em} = 365$ nm) and thermally cured in a vacuum oven at 120 °C for 45 min.

Characterizations

UV–Vis absorbance and PL spectra were acquired at room temperature using a UV–2550 Shimadzu UV–Vis spectrophotometer and a RF-5301PC Shimadzu spectrofluorophotometer, respectively. Aliquots were all measured without any size sorting. Powder X-ray diffraction (XRD) patterns were taken on a Bruker diffractometer using Cu K α radiation. Transmission electron micrographs (TEM) were obtained on a JEOL-JEM 2100 electron microscope operating at an accelerating voltage of 200 kV. High-resolution TEM (HRTEM) images were obtained on a JEM-2100F. Optical characterization (EL spectra, CIE chromaticity coordinates, CRI values, and luminous efficiencies) of the LEDs was done by a SPR-920F Spectral Radiation Analyzer (Sensing Instruments Co., Ltd.) with an integrating sphere (Instrument Systems) at room temperature.

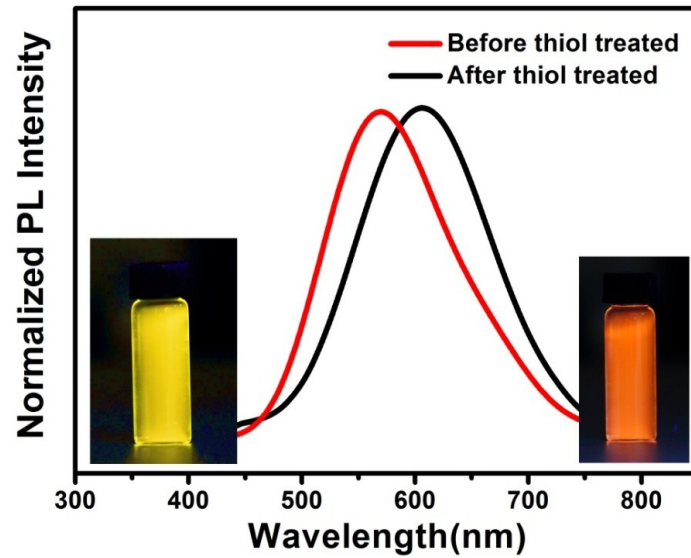


Fig. S1 PL spectra and fluorescent pictures of Mn:ZnSe doped QDs before and after 1-dodecanethiol treated.

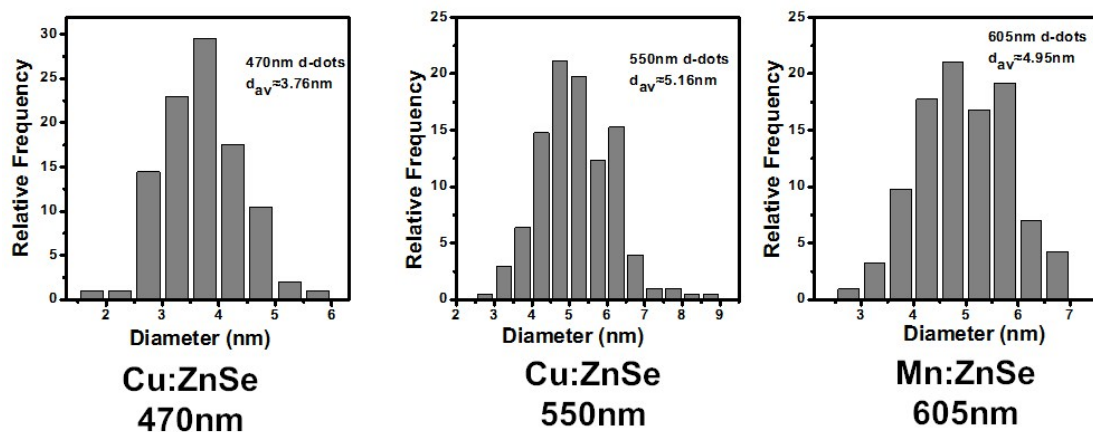
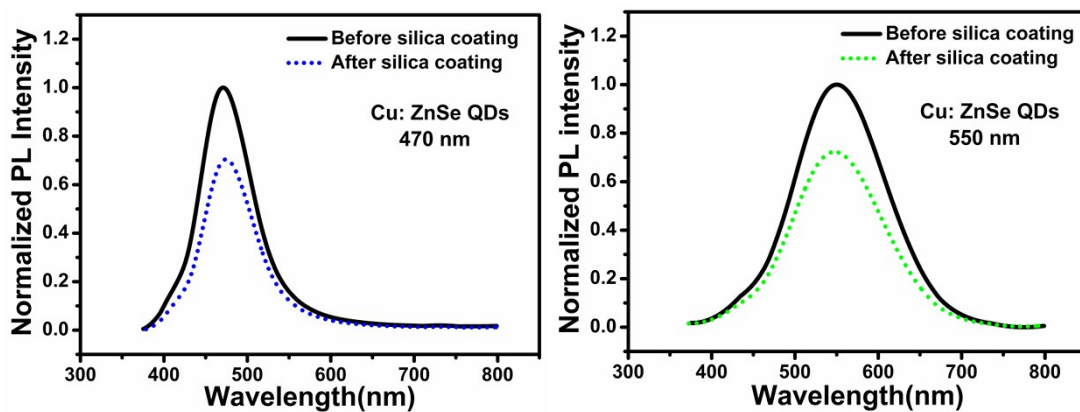


Fig. S2 Size distributions of doped ZnSe QDs with emission peaks at 470 nm (Cu: ZnSe QDs), 550 nm (Cu: ZnSe QDs) and 605 nm (Mn: ZnSe QDs).



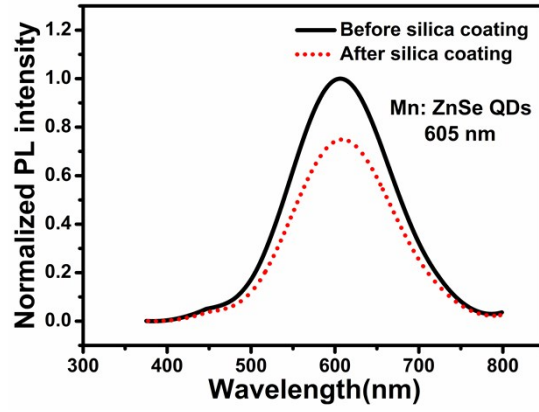
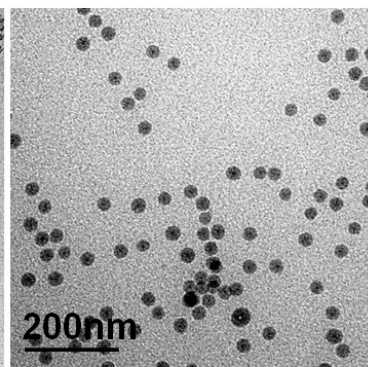
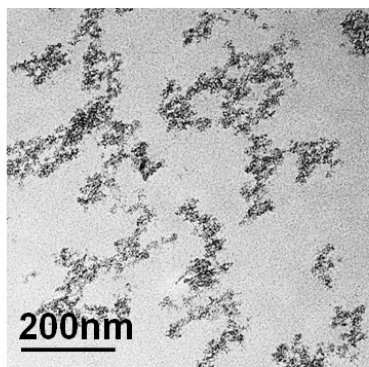
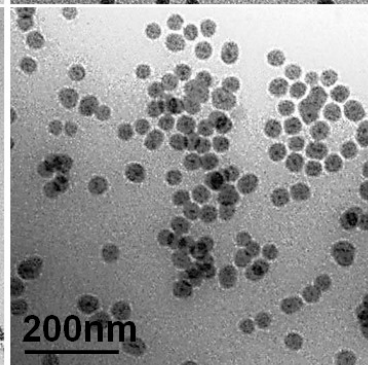
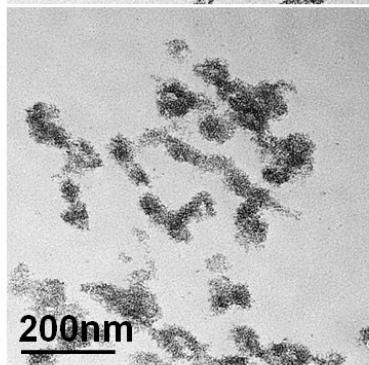


Fig. S3 PL spectra of the doped ZnSe QDs and the corresponding doped ZnSe QD@SiO₂ nanocomposites after silica coating.

10% wt
doped ZnSe QDs



20% wt
doped ZnSe QDs



Doped QDs/Epoxy

Doped QD@SiO₂/Epoxy

Fig. S4 TEM images of Mn: ZnSe QDs in epoxy and Mn: ZnSe QD@SiO₂ nanocomposites in epoxy with different QDs contents.

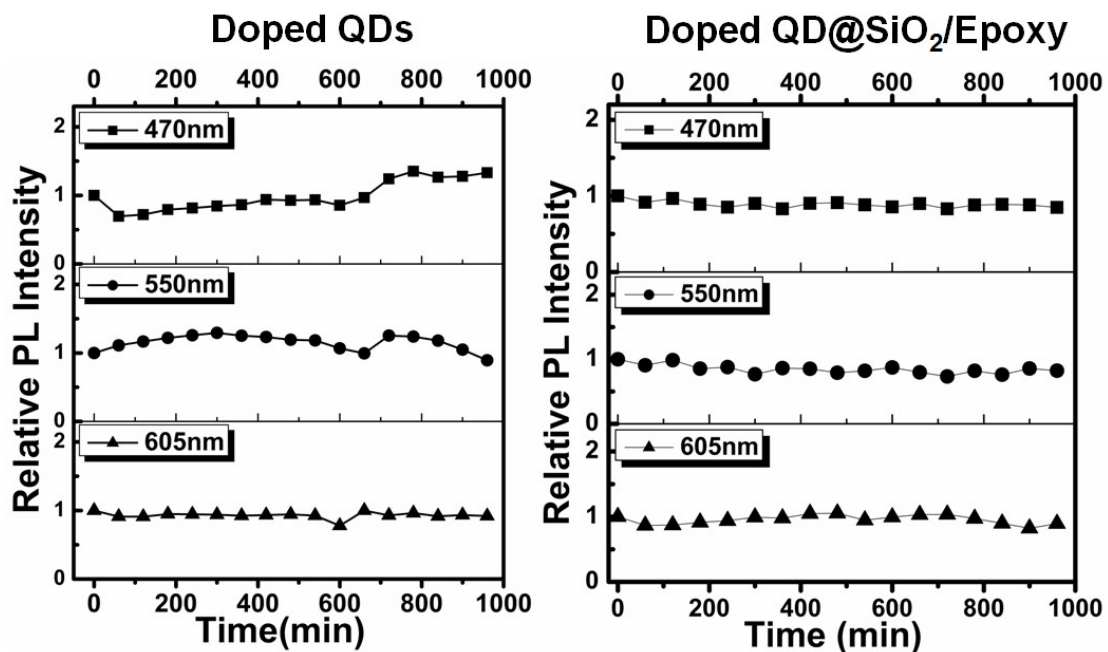


Fig. S5 Photostability of the doped ZnSe QDs and the corresponding doped ZnSe QD@SiO₂/ epoxy composites under 8 W 365 nm UV lamp illumination.

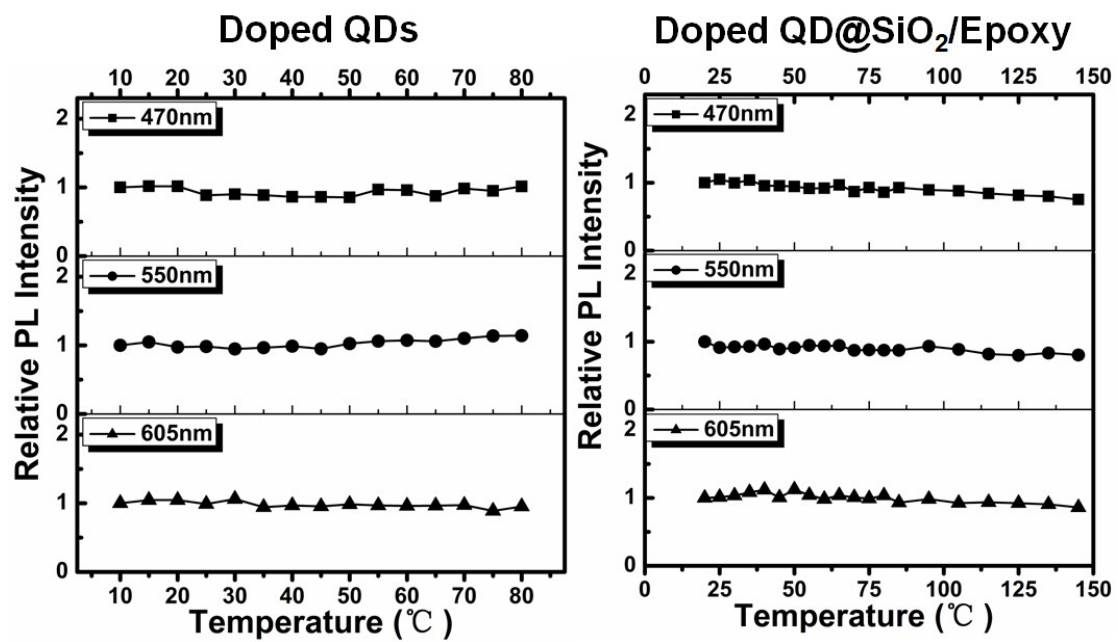


Fig. S6 Thermal stability of the doped ZnSe QDs and the corresponding doped ZnSe QD@SiO₂/epoxy composites.

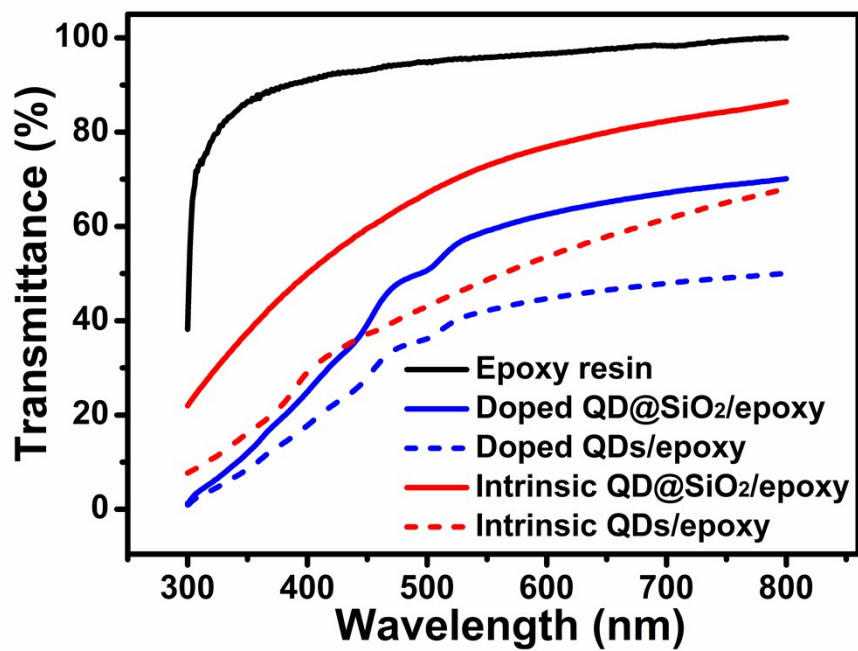


Fig. S7 UV-vis transmittance spectra of the epoxy matrix, Mn:ZnSe doped QDs /epoxy, Mn:ZnSe doped QD@SiO₂/epoxy, CdSe/CdS/ZnS QDs/epoxy and CdSe/CdS/ZnS QD@SiO₂/epoxy composite films (NPs content is 10%wt; the diameter and thickness of the samples are 10 mm and 1mm, respectively).