SUPPLEMENTAL MATERIAL

Intrinsic quantum dots based white-light-emitting diodes with layered coating structure for reduced reabsorption of multiphase phosphors

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EXPERIMENTAL SECTION

Reactants

Cadmium oxide (CdO, 99.5%), oleic acid (OA, ＞90%) were purchased from Sigma-Aldrich. Selenium powder (Se, 99.99%), S powder (99.99%), zinc oxide (ZnO, 99.99%), paraffin liquid (chemical pure), *n*-hexane (analytical reagent), methanol (analytical reagent), chloroform (analytical reagent) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Odium sulfide nonahydrate ($Na_2S·9H_2O$, analytical reagent), oleylamine (OAm, ＞90%) were purchased from Aladdin Reagent. Transparent epoxy (EP-400 A and B) used for LED packaging was purchased from SWANCOR (SHANGHAI) FINE CHEMICAL CO., LTD.

Preparation of precursors

Cd-precursor I: CdO (2 mmol) was dissolved in the mixture of oleic acid (OA, 2 mL) and paraffin liquid (8 mL) in a three-neck flask at 180℃, yielding a transparent solution for CdSeS core QDs.

Cd-precursor II: CdO (1 mmol) was dissolved in the mixture of oleic acid (OA, 2 mL) and paraffin liquid (6 mL) in a three-neck flask at 180℃, yielding a transparent solution for CdS shell growth.

Zn-precursor: ZnO (1mmol) was dissolved in the mixture of oleic acid (OA, 2 mL) and paraffin liquid (8 mL) in a three-neck flask at 280℃ under nitrogen with vigorous stirring, yielding a transparent solution for ZnS Shell growth.

S-precursor: S powder (1mmol) was dissolved in liquid paraffin (10 mL) in a three neck flask at 120℃ with vigorous stirring, yielding a colorless transparent solution for ZnS Shell growth.

All the precursors are freshly made before the synthesis.

Synthesis of CdSeS/CdS/ZnS core/multi-shell QDs

Typically, Se powder (0.2 mmol) and S powder (0.3 mmol) were dissolved in liquid paraffin (20 mL) at 220℃ under vigorous stirring. 4 mL Cd-precursor I was rapidly injected into the solution. Aliquots were taken at different time intervals and immediately injected into n-hexane to stop further growth for the wavelength test. The reaction was stopped once the desired wavelength was reached.

7.5 mL CdSeS crude solution was taken mixed with 0.25 mmol $Na_2S{\cdot}9H_2O$ in 2.5 mL paraffin liquid in a three-neck flask. The temperature was then raised up to 180℃ where 4 mL Cd-precursor II was added dropwisely. The temperature maintain at 180℃ for 20 min before the reaction was stopped and CdSeS/CdS core/shell QDs solution were gotten.

7 mL CdSeS/CdS core/shell QDs solution was taken and 2 mL oleylamine (OAm) was added. The mixture was heated to 120℃. Then the prepared Zn (2 mL) and S (4mL) precursor solutions were separately injected into the reaction flask, with 5 minutes time interval between the injection. The temperature was then increased to 220℃ immediately and kept there for 15 min, then the solution was cooled and kept at 100℃ for 30 min and CdSeS/CdS/ZnS core/multi-shell QDs solution were gotten.

Preparation of CdSeS/CdS/ZnS QDs/epoxy composite

CdSeS/CdS/ZnS QDs were dispersed in chloroform (5 wt%) after wash by methanol. Certain amount of the solution were added into the mixture of epoxy resin (EP400A) and anhydride curing agent (EP400B) with vigorous stirring. The weight of EP400A and EP400B were both 1 g. The homogeneous mixture was poured into a glass mold and heated in an oven at 40℃ for 60min followed by another 60min at 80℃ and finally at 120℃ for 60 min.

Fabrication of CdSeS/CdS/ZnS layered coating white LED

The green-emitting and red emitting CdSeS/CdS/ZnS QDs/epoxy composite were separately prepared as described but maintain at 80℃. Then the red-emitting QDs/epoxy composite (*ca.* 35 μL) was dispersed on LED chips and thermally cured

at 120℃ for 45 min. then green-emitting QDs/epoxy composite (*ca.* 25 μL) was dispersed on it and thermally cured at 120℃ for another 45 min.

Characterization

UV–Vis absorbance and fluorescence data were acquired using UV–2550 Shimadzu UV–Vis spectrophotometer and RF-5301PC Shimadzu spectrofluorophotometer respectively at room temperature. All the aliquots were measured without any size sorting. Power X-ray diffraction (XRD) patterns were taken on a Bruker diffractometer using Cu Kα 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. Fluorescent decay curves were obtained by an FLS-920 Combined Steady State and Phosphorescence Lifetime Fluorimeter (Edinburgh Instruments). Optical characteristics of the QDs-LED were measured by a SPR-920F Spectral Radiation Analyzer with an integrating sphere (Instrument Systems) at room temperature. The temperature related tests were taken by firstly treated the samples for 60min under different temperature, and corresponding measurements were taken after the samples was cooled to room temperature in the air.

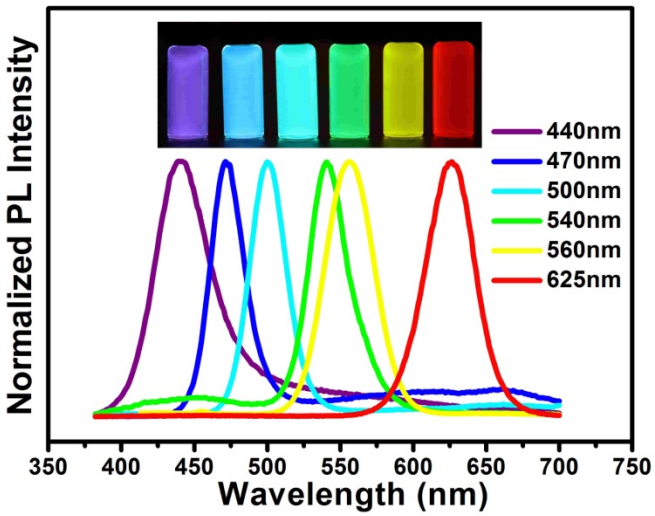

Fig. S1 PL spectra and photographs of the CdSeS/CdS/ZnS core/multi shell QDs with different emission peak wavelengths.

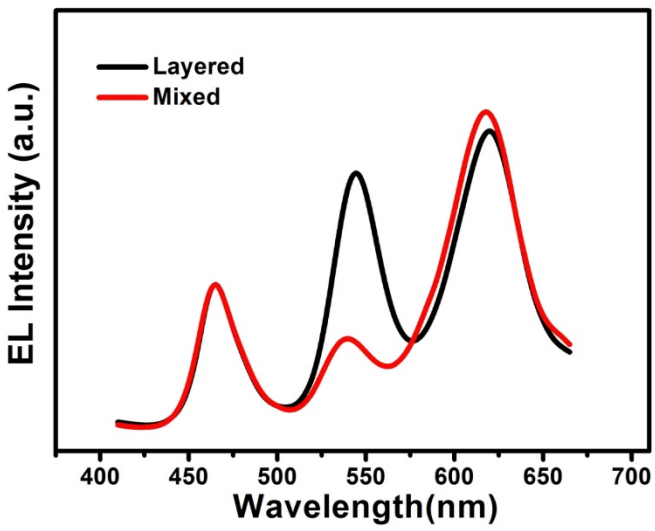

Fig. S2 EL spectra of the as-prepared QDs-WLED fabricated by layered coating method and mixing method at 140mA.

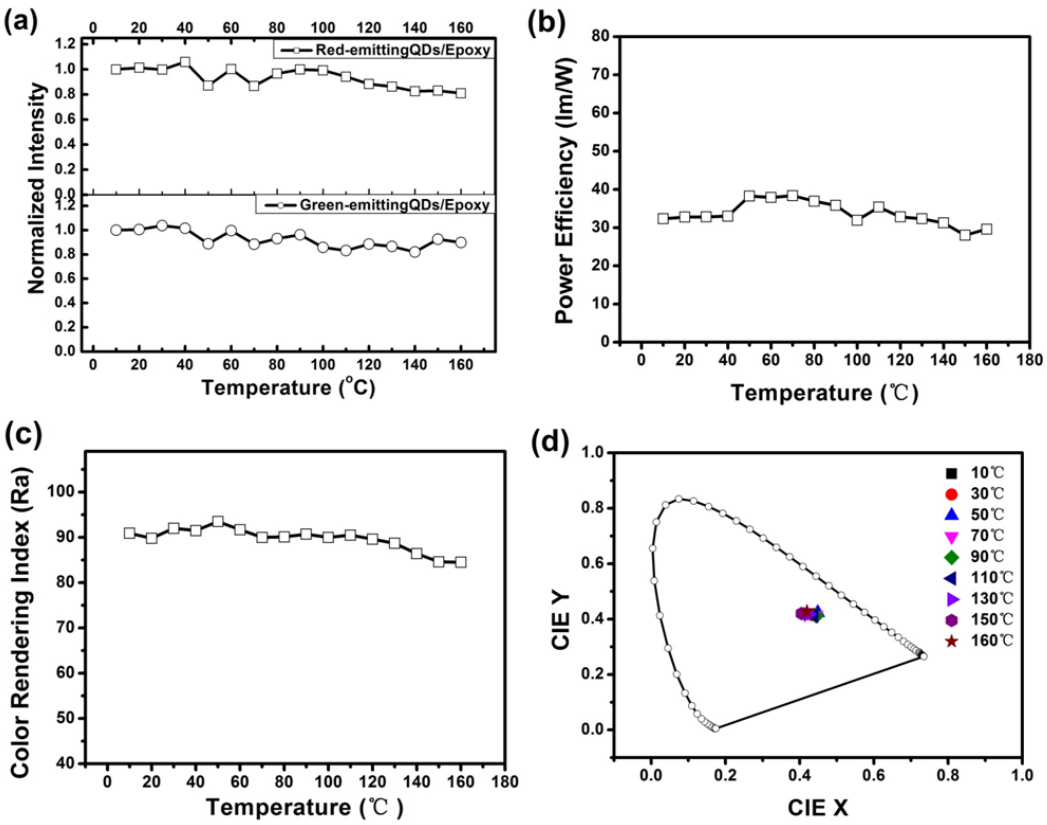

Fig. S3 (a) PL spectra evolution of the relative PL intensity of the QDs/epoxy composites at different temperature ranged from 10℃ to160℃. (b) power efficiency, (c) color rendering index (Ra) and (d) the CIE color coordinates of the as-prepared QDs-WLED fabricated by layered coating method at different temperature ranged from 10℃ to160℃ and the WLED was operated at 140mA.

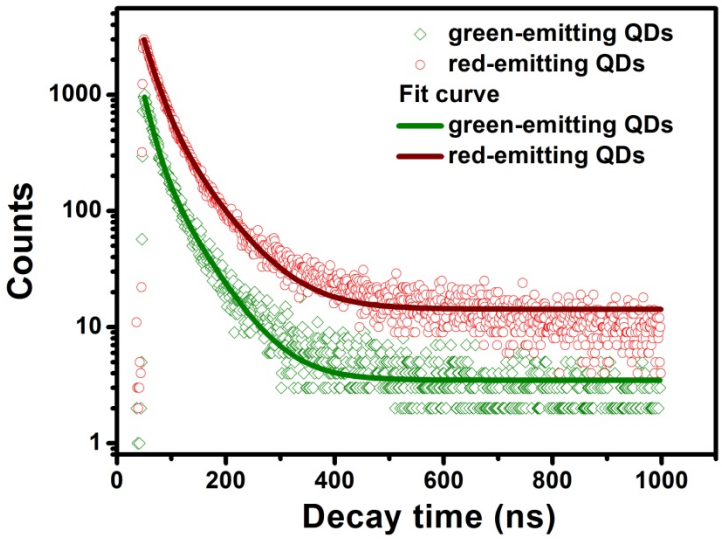

Fig. S4 Fluorescent lifetime decay curves of the green and red-emitting QDs.

Table S1 The exponential decay fitted results of the fluorescent lifetime decay curvess and the calculated average florescent lifetime of the green and red-emitting QD.

Quantum dots	τ_1 (ns)	a_1	τ_2(ns)	a_2	τ_{av}(ns)
Green-emitting QDs	17.32	12371.58	56.01	717.51	23.44
Red-emitting QDs	22.33	19790.73	65.13	1805.11	31.32