Electronic Supplementary Information

Synthesis and electroluminescence of novel white fluorescence quantum dots based on Zn-Ga-S host

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Materials. Silver acetate (AgOAc, 99.99%), manganese acetate ($Mn(OAc)_2$, 98%), gallium acetylacetonate ($Ga(acac)_3$, 99.99%), zinc acetate dihydrate ($Zn(OAc)_2{\cdot}2H_2O$, 99%), sulfur powder (99.99%), 1-dodecanethiol (DDT, 98%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%) and 11-mercaptoundecanoic acid (MUA, 95%) were obtained from Sigma-Aldrich and used as received without further purification.

Synthesis of Ag, Mn: Zn-Ga-S and Ag, Mn: Zn-Ga-S/ZnS QDs. Core QDs were synthesized via a typically facile one-pot non-injection approach, mixing Ag^+ (0.01 M) precursor and Mn^{2+} (0.01 M) precursor need to be synthesized firstly, via loading 16.7 mg of AgOAc and 17.3 mg of $Mn(OAc)_2$ separately with 1mL of OAm and 9 mL of ODE in two three-necked flasks. And then both of the two mixture solutions were heated up to 70 °C for 10 min in nitrogen atmosphere. For preparation of Ag, Mn: Zn-Ga-S QDs, 2 mL of Ag^+ precursor, 0.2 mL of Mn^{2+} precursor, $Zn(OAc)_2{\cdot}2H_2O$ (8.8 mg, 0.04 mmol), $Ga(acac)_3$ (132.1 mg, 0.36 mmol), sulfur powder (25.6 mg, 0.8 mmol), 2.0 mL of DDT, 6.0 mL of OA, and 20.0 mL of ODE were loaded in a 100 mL three-flask at room

temperature and heated up to 100 °C with degassing. After that, the mixture solution was heated to 220 °C under nitrogen atmosphere, annealing for 40 min for the growth of Ag, Mn: Zn-Ga-S QDs. To monitor the optical properties of the resultant QDs, aliquots of the sample were taken at different time intervals during the reaction process. Finally, the mixture solution was cooled down to 60 °C and dispersed into toluene. The as-prepared QDs were precipitated by using methanol and acetone under centrifugation and decantation.

Before synthesis of Ag, Mn: Zn-Ga-S/ZnS QDs, Zn precursor was prepared firstly by dissolving 4.0 mmol ZnSt2 into 5.0 mL ODE at 160 °C. Then, Ag, Mn: Zn-Ga-S/ZnS QDs were synthesized by adding 4.0 mmol Zn precursor into the Ag, Mn: Zn-Ga-S QDs core solution at 100 °C, following with heating at 220 °C for 50 min under nitrogen flow for preparation of Ag, Mn: Zn-Ga-S/ZnS QDs. Similarly, the resultant core/shell QDs were precipitated by adding methanol and acetone to the mixture QDs solution. Besides, hydrophilic Ag, Mn: Zn-Ga-S/ZnS QDs were obtained through a ligand exchange strategy on the basis of the reported literature approaches. [1]

White QD-LEDs fabrication. White QD-LEDs were fabricated by layer-layer spin-coating procedure on indium tin oxide (ITO)-coated glass substrates. Glass substrates were sequentially cleaned by deionized water, acetone and ethanol, and then dried with nitrogen and treated with O_2-plasma for 10 min. The ZnO nanoparticles dispersed in ethanol were deposited by spin-coating on top of the ITO glasses at 2000 rpm for 40 s and baked at 150 ^{o}C for 30 min. After that, Ag, Mn: Zn-Ga-S/ZnS QDs with a concentration of 10 mg/L were spin-coated at 2000 rpm for 40 s and baked at 90 ^{o}C for 20 min. The polyethylenimine ethoxylated (PEIE) was spin coated at 5000 rpm for 40 s and annealed at 110 ^{o}C for 10 min. Afterwards, the poly [N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine] (Poly-TPD, 10 mg mL^{-1} in chlorobenzene) and phosphomolybdic acid hydrate (PMAH, 10 mg mL–1 in ethanol) were spin coated sequentially at 3000 rpm for 40 s and baked at 120 °C for 15 min. In the end, the glass substrates samples were loaded into an evaporation chamber to deposit Al anode at a speed of 0.5 nm s^{-1} under 2 $\times 10^{-4}$ Pa.

Characterization. UV- PL emission and UV-vis absorption spectra were recorded by using a fluorescence spectrophotometer (Cary Eclipse Varian) and a UV-visible spectrophotometer (Shimadzu UV-3101 PC), respectively. Transmission electron microscopy (TEM) was taken with a JEOL JEM-2100 microscope. The chemical compositions of the QDs samples were characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Elemental IRIS 1000). X-ray diffraction (XRD) patterns were obtained on a Siemens D5005 X-ray Powder diffractometer. The transient PL decay curves were obtained with an Edinburgh FL 900 single-photon counting system fitted out with a hydrogen lamp. Electroluminescent (EL) spectrum, voltage-luminance-current density characteristics as well as color rendering index (CRI) of the as-prepared devices were carried out by using a SpectraScan® Spectroradiometer PR-670.

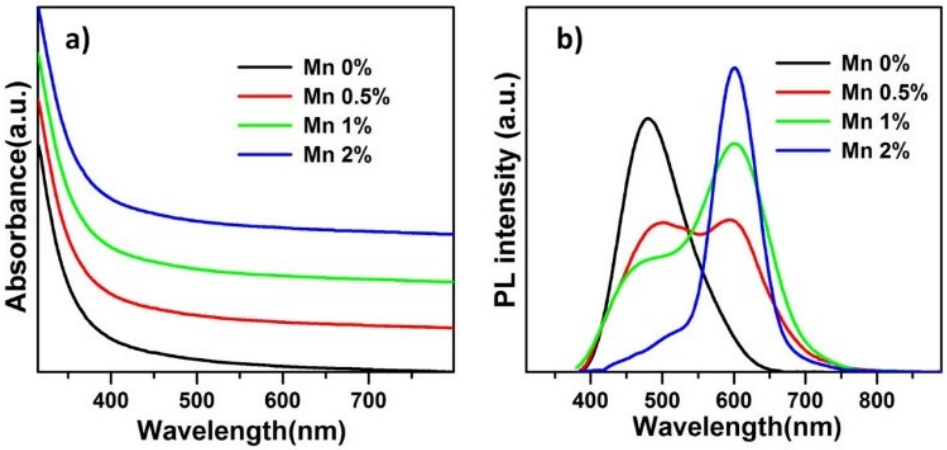

Fig. S1 (a) UV-vis absorption and (b) PL emission spectra of Ag, Mn: Zn-Ga-S QDs with different Mn2+ dopant concentration from 0.5% to 5% at the fixable a 5% Ag+ concentration and a 9/1ratio of Ga/Zn.

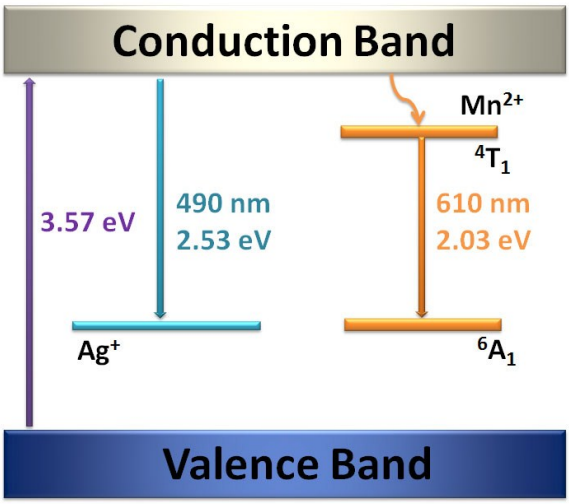

Fig. S2 Proposed correlated energy level diagram of the Ag, Mn: Zn-Ga-S QDs.

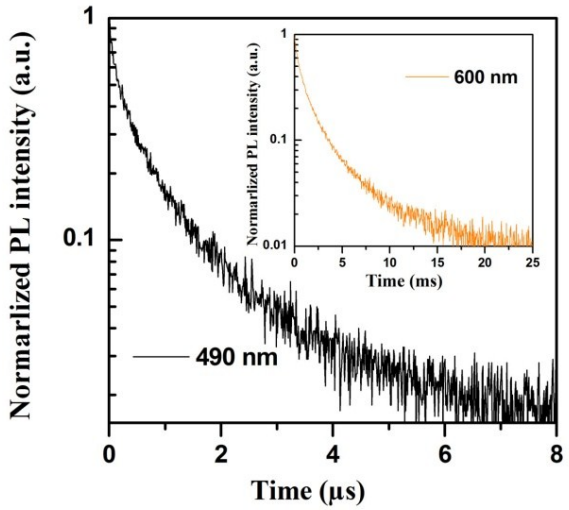

Fig. S3 Time-resolved PL decay curves of Ag,Mn:Zn-Ga-S/ZnS QDs at the monitored emission wavelength of 490 nm and 600 nm (inset)

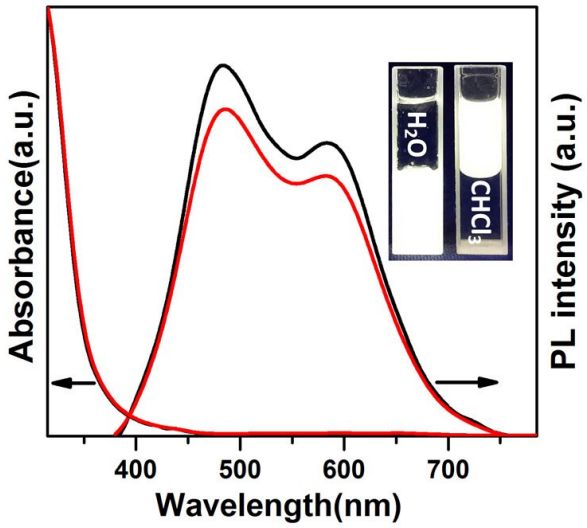

Fig. S4 UV-vis absorption and PL emission spectra of Ag, Mn: Zn-Ga-S/ZnS QDs before ($CHCl_3$ solvent, black curves) and after (H_2O aqueous, red curves) phase transfer using MUA. Inset: photographs of Ag, Mn: Zn-Ga-S/ZnS QDs dispersed in H_2O and $CHCl_3$ media under UV irradiation.

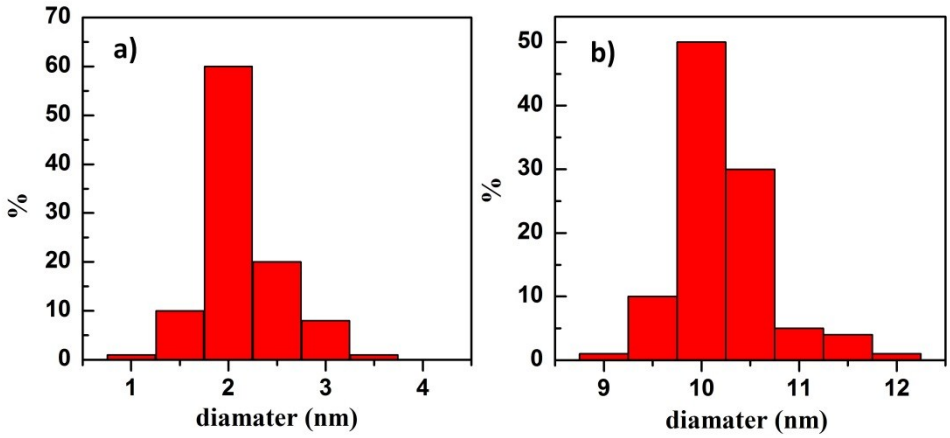

Fig. S5 Particle size histograms of Ag, Mn: Zn-Ga-S and Ag, Mn: Zn-Ga-S/ZnS QDs.

Tab. S1 Atomic% of the elements in QDs core and core/shell samples determined by ICP characterization (average value of 5 independent measurements per sample)

QDs samples	Ag	Mn	Zn	Ga	S
Core	4.51	0.41	9.46	85.62	100
Core/shell	4.25	0.33	85.21	10.21	100

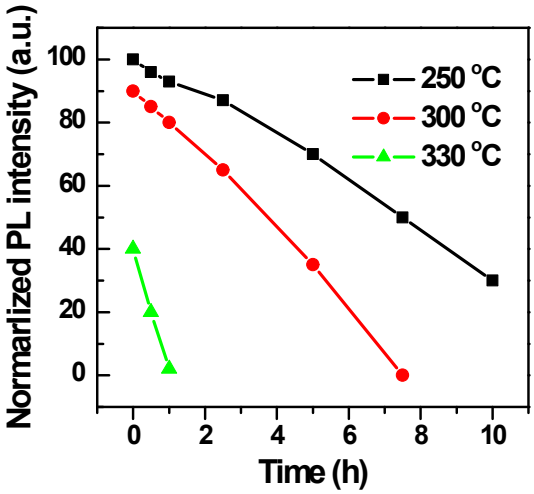

Fig. S6 The time depending stability of the Ag, Mn: Zn-Ga-S/ZnS QDs solution at different high temperature.

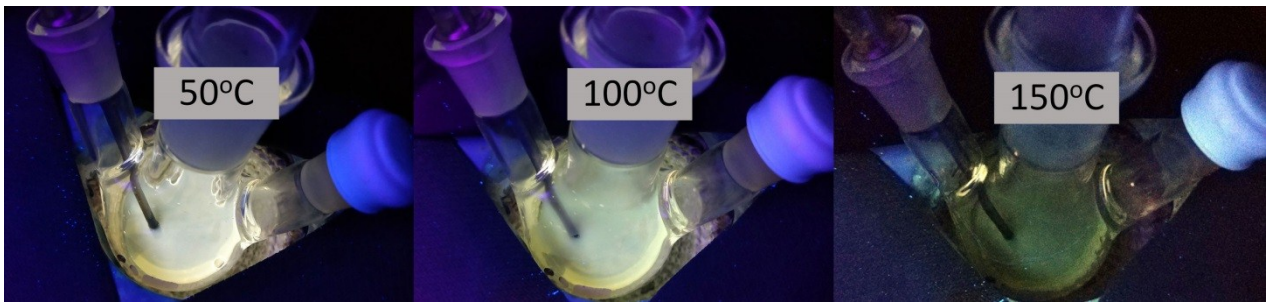

Fig. S7 Digital pictures of Ag, Mn: Zn-Ga-S QDs at different heating temperature from 50 °C to 150 °C with the illumination of a 365 nm UV lamp.

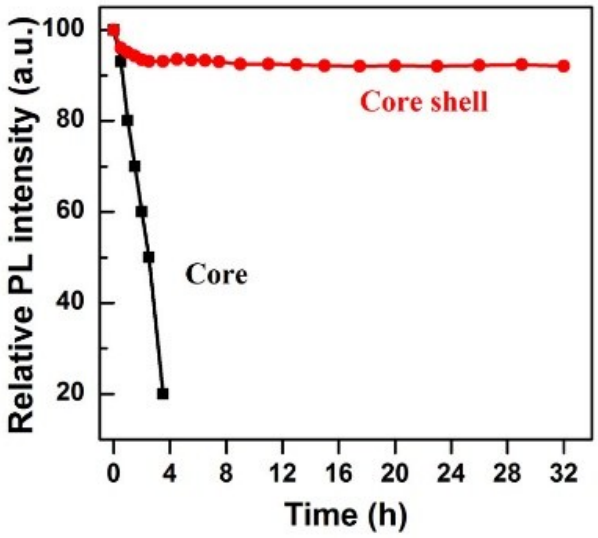

Fig. S8 Temporal evolution of the relative PL intensities of Ag, Mn: Zn-Ga-S QDs and Ag, Mn: Zn-Ga-S/ZnS QDs samples.

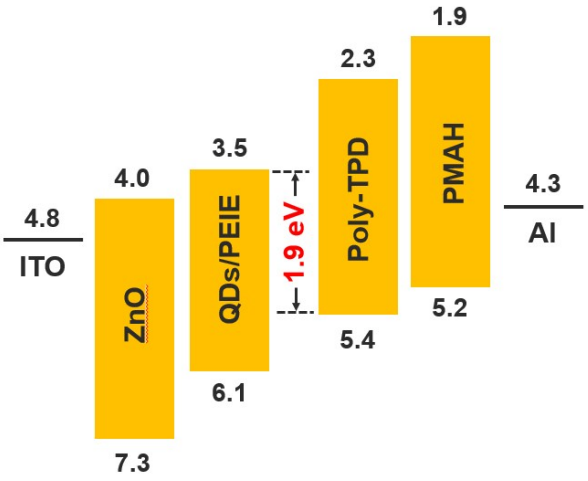

Fig. S9 Energy band diagram of QD-LEDs.

1 W. Zhang, Q. Lou, W. Ji, J. Zhao and X. Zhong, *Chem. Mater.*, 2014, **26**, 1204–1212.