Electronic Supplementary Information

Bright violet-to-aqua-emitting cadmium-free Ag-doped Zn−Ga−S quantum dots with high stability

Wen-Jin Zhang,[a] Chun-Yang Pan,*[a] Fan Cao,[b] Haoran Wang,[b] and Xuyong Yang*[b]

[a]School of Light Industry and Chemical Engineering, Guangdong University of Technology, Guangzhou 510006, China

[b]Key Laboratory of Advanced Display and System Applications, Education of Ministry, Shanghai University, 149 Yanchang Road, 200072, P. R. China

Email: panchuny@gdut.edu.cn; Tel /Fax: +86 20 39322231

Materials. Silveracetate (AgOAc, 99.99%), indium acetate ($In(OAc)_3$, 99.99%), 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 without further purification.

Synthesis of Ag: Zn-Ga-S and Ag: Zn-Ga-S/ZnS QDs. Core QDs were synthesized via a typically facile one-pot non-injection approach, mixing AgOAc (3.3mg, 0.02mmol), $Zn(OAc)_2{\cdot}2H_2O$ (44.0 mg, 0.2 mmol), $Ga(acac)_3$ (73.4 mg, 0.2mmol), and sulfur powder (25.6 mg, 0.8 mmol) together with 2.0 mL of DDT, 6.0 mL of OA and 12.0 mL of ODE in a 100 mL three-flask at room temperature. Then the mixture was heated up to 100 °C with degrassing, followed by annealing at 240 °C for 30 min to obtain the Ag: Zn-Ga-S core QDs. Aliquots of the sample were taken at different time intervals and injected into toluene solvent to record their optical spectra. Whereafter, the reaction mixture was cooled to 60 °C and dispersed into toluene, and methanol was added thereafter for purification via repeated centrifugation and decantation. Other Ag: Zn-Ga-S core QDs were prepared simply by varying other experimental variables.

For the preparation of Ag: Zn-Ga-S/ZnS core/shell QDs with injection of the Zn precursor once (4 mmol), the as-prepared Zn precursor solution consisting of 88.0 mg of $Zn(OAc)_2 \cdot 2H_2O$ (0.4 mmol), 0.3 mL of OA and 0.7 mL of ODE dissolved at 280 °C was further injected into the core crude solution when it cooled to 100 °C, followed by annealing at 240 °C for 20 min to grow the ZnS shell upon the Ag: Zn-Ga-S core QDs. For the preparation of Ag: Zn-Ga-S/ZnS QDs with injection of the Zn precursor twice (8 mmol), another 4 mmol of Zn precursor was injected into the previous core/shell QDs solution when the mixture solution was cooled to 100 °C and then grew at 240 °C for 20 min. Further purification of Ag: Zn-Ga-S/ZnS QDs was analogous to that of Ag: Zn-Ga-S QDs as aforementioned. Water solubilization of the initially oil-soluble Ag:Zn-Ga-S/ZnS QDs was performed by ligand exchange, replacing their initial hydrophobic surfactants with hydrophilous ligand MUA according to the previous literature methods.[1]

Characterization. UV-vis spectra were obtained on a UV-visible spectrophotometer (Shimadzu UV-3101 PC). PL spectra were recorded on a fluorescence spectrophotometer (Cary Eclipse Varian). The PL QY of the as-obtained QDs were assessed by the integrated emission of the QDs samples in solution in comparison to that of standard organic dye (9,10-diphenylanthrancene) with a PL QY of 91% in ethanol with identical optical density.[2] Transmission electron microscopy (TEM) pictures were achieved on a JEOL JEM-2100 transmission electron microscope by using wide-angle X-ray diffraction. X-ray diffraction (XRD) spectra were measured on a Siemens D5005 X-ray Powder diffractometer using a graphite monochromatized Cu K_α as the radiation source. The composition of the QDs samples were performed through Thermo Fisher Scientific ESCALAB 250Xi XPS System.

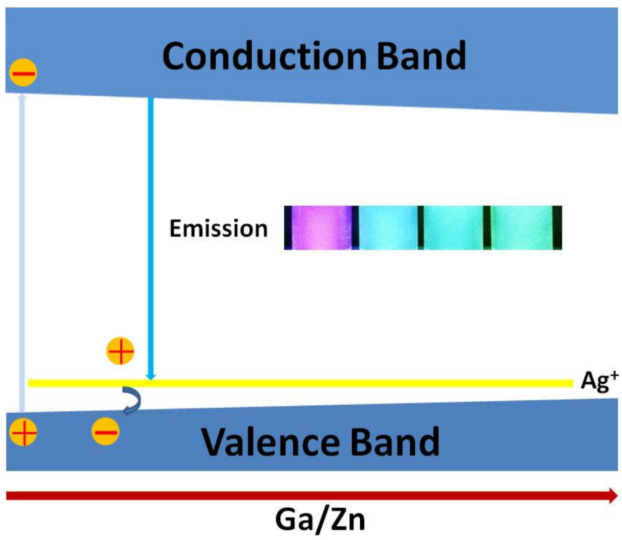

Fig. S1 The mechanism schematic of Ag^+ energy state in the composition variable alloyed QDs and the recombination mechanism.

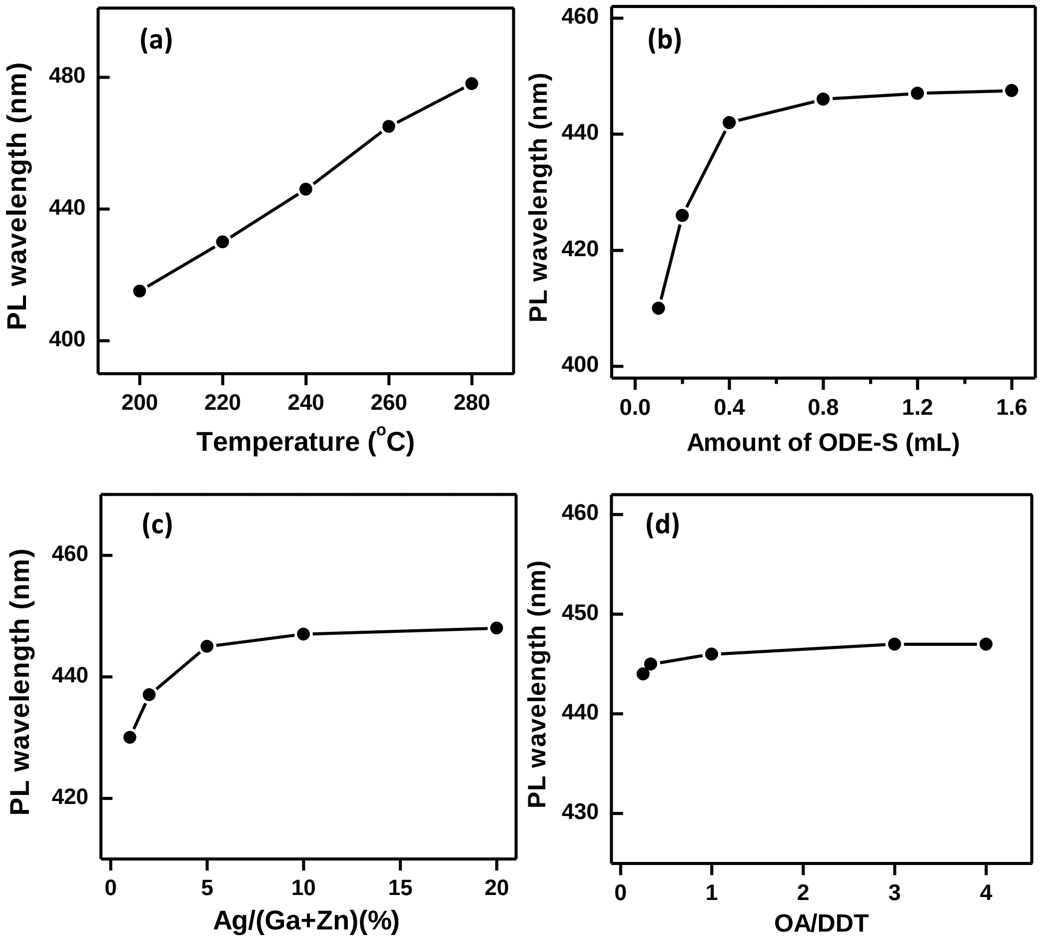

Fig. S2 Summarization of the dependence of PL peak position on the (a) reaction temperature (b) amounts of elementary sulfur (c) Ag dopant concentrations (d) OA/DDT ratios.

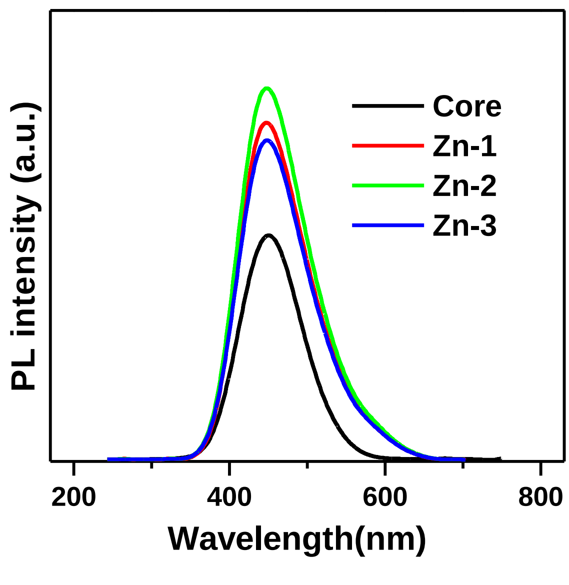

Fig. S3 PL emission spectra of Ag: Zn-Ga-S core QDs, Ag: Zn-Ga-S/ZnS core/shell QDs with injection of Zn precursor once, twice and thrice, respectively.

Tab. S1 atomic % of the elements determined from XPS analysis (mean values of 5 independent measurements per sample) for samples with different thickness of ZnS shell.

QDs Samples	S	Zn	Ag	Ga
Core	100	12.47	1.25	23.94
Core shell	100	68.49	1.14	20.18

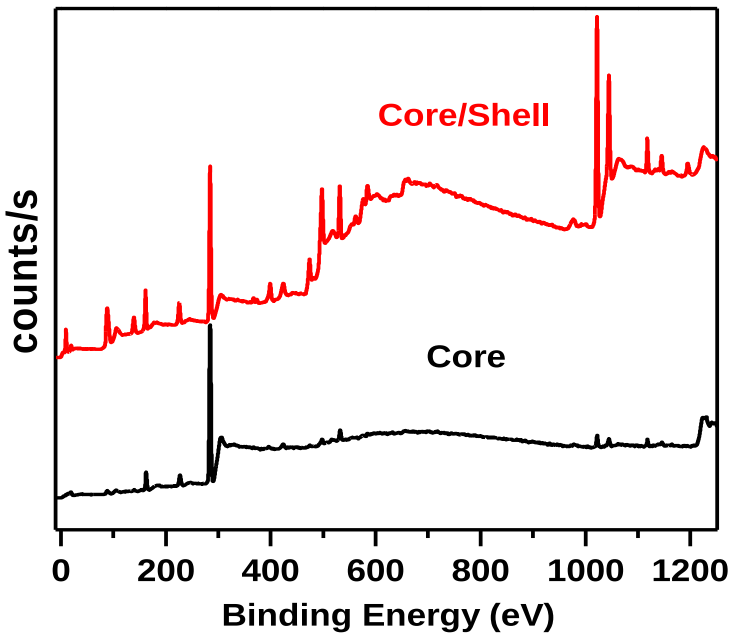

Fig. S4 XPS spectra of Ag: Zn-Ga-S core (black line) and Ag: Zn-Ga-S/ZnS core/shell QDs samples (red line).

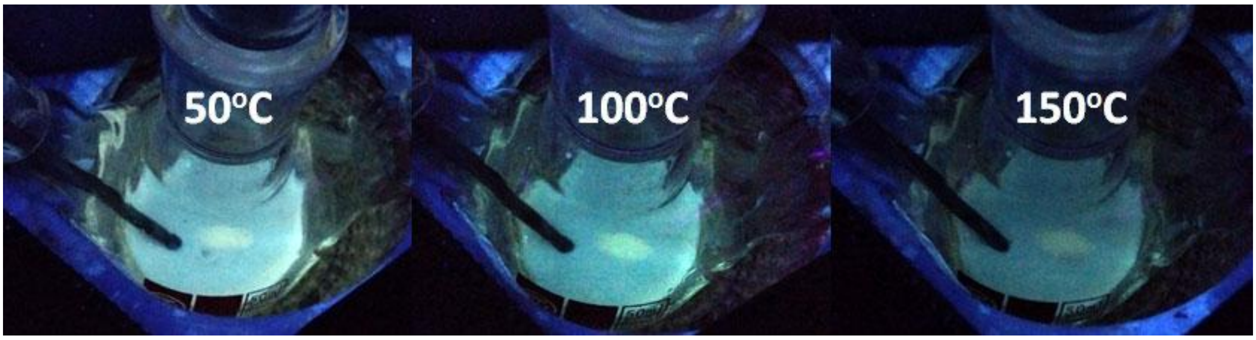

Fig. S5 Digital pictures of Ag: Zn-Ga-S QDs under different heating temperature from 50 to 150 °C under illumination of a UV lamp at 365 nm.

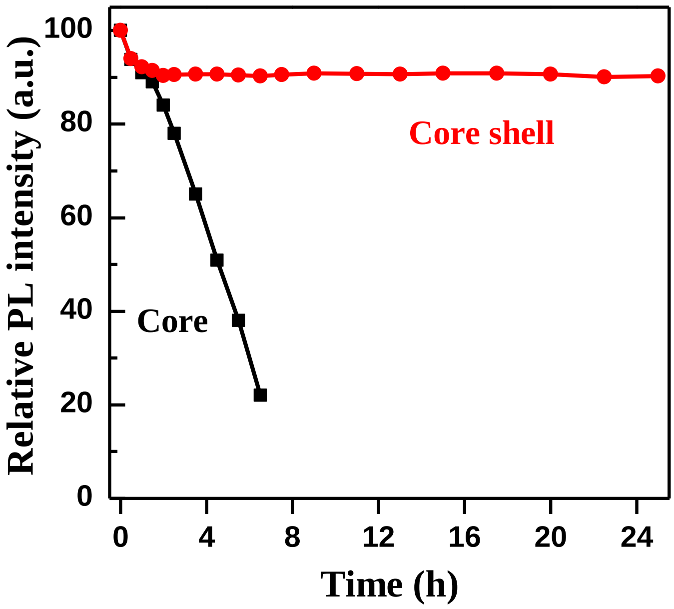

Fig. S6 Temporal evolution of the relative PL intensity of core Ag: Zn-Ga-S and core/shell Ag: Zn-Ga-S/ZnS QDs samples.

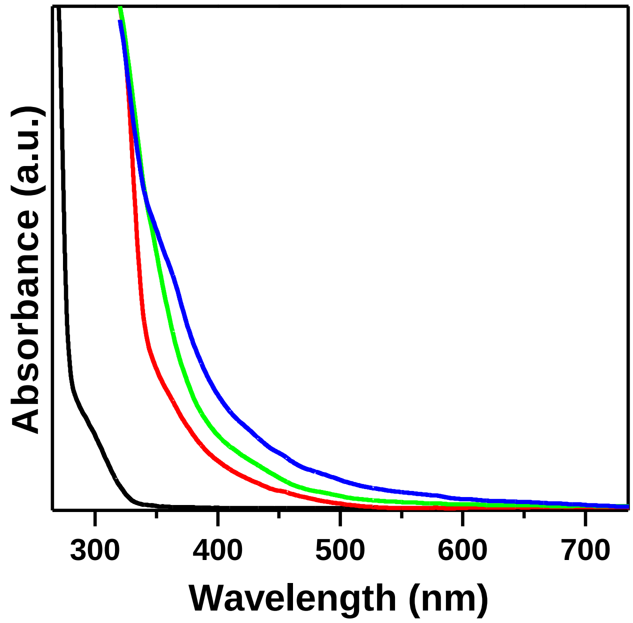

Fig. S7 UV-vis absorption spectrum of Ag: Zn-Ga-S/ZnS QDs under different Zn/Ga precursor ratios, Ag ion concentration and reaction temperature.

1 W. Zhang, Q. Lou, W. Ji, J. Zhao and X. Zhong, *Chem. Mater.*, 2014, **26**, 1204–1212.
2 J. Cho, Y. Jung, J.-K. Lee and H.-S. Jung, *Langmuir*, 2017, **33**, 3711–3719.