## **Electronic Supplementary Information**

## Synthesis of highly efficient azure-to-blueemitting Zn-Cu-Ga-S quantum dots

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## Synthesis of CGS/ZnS and ZCGS/ZnS QDs

For a typical synthesis of ternary Cu-deficient CGS core QDs with Cu/Ga precursor molar ratios of 1/4, 1/5, or 1/8, 0.125, 0.1, or 0.0625 mmol of CuI (99.999%), 0.5 mmol of GaI<sub>3</sub> (99.99%) and 1 mmol of sulfur (99.998%) were mixed in three-neck flask with 1.5 mL of 1-dodecanethiol (DDT,  $\geq$ 98%) and 5 mL of oleylamine (OLA, 70%). Then, the mixture was degassed in the course of heating to 120°C and further heated under N<sub>2</sub> purging to a growth temperature of 240°C. The reaction was maintained at that temperature for 5 min for growth of core QDs. Following the above synthetic procedure, a series of quaternary ZCGS QDs were synthesized by choosing a Cu/Ga ratio of 1/8 and additionally including different ZnCl<sub>2</sub> ( $\geq$ 98%) amounts of 0, 0.25, 0.5, 1.0, and 1.5 mmol, corresponding to Zn/Cu precursor molar ratios of 0, 4, 8, 16, and 24, respectively. All ternary and quaternary core QDs were then identically subjected to the following multiple-shelling reaction. The first ZnS stock solution, prepared by dissolving 8 mmol of Zn acetate (reagent grade) in 8 mL of oleic acid (OA, 90%) and 4 mL of 1-octadecene (ODE, 90%), was introduced slowly to the core growth solution at 240°C and the reaction was allowed for 1 h 15 min. Subsequently, the second ZnS stock solution, consisting of 4 mmol of Zn acetate, 4 mL of OA, 2 mL of DDT, and 2 mL of ODE, was slowly injected, followed by 30 min-reaction at the same temperature. After that, another ZnS solution containing 4 mmol of Zn stearate (10–12% Zn basis), 4 mL of ODE, and 2 mL of DDT was again injected and this final shelling reaction was retained at 250°C for 1 h. As-reacted QDs were then subjected to the conventional work-up processes of the precipitation with an excess of ethanol and repeated purification with a solvent combination of hexane/ethanol by centrifugation (9000 rpm, 10 min), and finally redispersed in hexane.

## Characterization

Absorption and photoluminescent (PL) spectra of QDs were recorded by using UV–visible absorption spectroscopy (Shimadzu, UV-2450) and a 500 W xenon lampequipped spectrophotometer (PSI Inc., Darsa Pro-5200), respectively. PL quantum yields (QYs) of QDs were evaluated by an absolute PL QY measurement system (C9920-02, Hamamatsu) in an integrating sphere. A powder X-ray diffraction (XRD, Rigaku, Ultima IV) with Cu K<sub>a</sub> radiation was employed to obtain information on crystallographic structure and signature of alloying of QDs. Actual chemical compositions of QDs were analyzed with an inductively coupled plasma optical emission spectrometry (ICP-OES, OPTIMA 8300, PerkinElmer). The particle transmission electron microscopy (TEM) image of QDs was collected using a Tecnai G2 F20 operating at 200 kV. For PL lifetime analysis, the QD dispersion was excited at 375 nm by 3 ps pulses from Ti:Sapphire laser at a repetition of 76 MHz and PL decay dynamics were resolved using a time-correlated single photon counting method.



**Fig. S1** As-recorded *versus* simulated PL, which can be resolved into two emission components, of azure-emitting CGS/ZnS QDs synthesized with a Cu/Ga=1/8.



**Fig. S2**  $(Ahv)^2 - hv$  plots converted from absorption spectra of a series of ZCGS core QDs synthesized with different Zn precursor amounts of 0, 0.25, 0.5, 1.0, and 1.5 mmol.



**Fig. S3** (a) Lower- and (b) higher-magnification TEM images of a representative ZCGS/ZnS core/shell QD sample with 1.5 mmol of Zn in core synthesis.



**Fig. S4** (a)  $(Ahv)^2 - hv$  plots of a series of ZCGS/ZnS QDs synthesized with different amounts of Zn precursor and (b) a plot showing the variations in band gap between ZCGS versus ZCGS/ZnS QDs.



**Fig. S5**. Time-resolved PL decay curves of three ZCGS/ZnS QDs with 0, 0.25, and 1.5 mmol of Zn precursor. The average PL lifetime ( $\tau_{avg}$ ) values were calculated by a triexponential function fitting.



**Fig. S6**. Temporal change in relative PL intensity of 1.5 mmol-based ZCGS/ZnS QD dispersion in hexane with UV (365 nm) irradiation.