## Electronic Supplementary Information

# Low-Cost and Gram-Scale Synthesis of Water-Soluble Cu-In-S/ZnS Core/Shell Quantum Dots in an Electric Pressure Cooker

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## Experimental Section

### I. Chemicals

Zinc chloride ($ZnCl_2$, 98.0%), copper chloride ($CuCl_2·2H_2O$, 99.0%), indium chloride ($InCl_3$, 99.9%), sodium citrate ($C_6H_3Na_3O_7·2H_2O$, A.R.), thiourea (99.0%), dimethyl sulfoxide (DMSO, 99%) and thioglycolic acid ($C_2H_4O_2S$, 98%) were purchased from Aladdin. Sodium sulfide ($Na_2S·9H_2O$, 98%), sodium hydroxide (NaOH, 99.99%), ethanol ($C_2H_6O$, 99.7%), hydrogen chloride (HCl, 36%) and isopropyl alcohol ($C_3H_8O$, 99.7%) were purchased from Beijing Chemical works. All chemicals were used as recieved without further purification. The 5-L electric pressure cooker was bought from www.taobao.com.

### II. Synthesis of Cu-In-S core QDs

In a typical procedure for the synthesis of Cu-In-S core QDs with a Cu/In ratio of 1:4, 0.426 g (2.5 mmol) of $CuCl_2$, 2.212 g (10 mmol) of $InCl_3$, 11.76 g (40 mmol) of sodium citrate, 0.552 g (6 mmol) of thioglycolic acid, and 4.0 L de-ionized water

were loaded in a 5-L electric pressure cooker. Afterwards, 3.900 g (16.25 mmol) of $Na_2S$ dissolved in 0.1 L of de-ionized water was added into the mixture solution under magnetic stirring. Subsequently, the cooker was heated up and kept up the pressure for 60 min. Cu-In-S core QDs with different Cu/In ratios were synthesized by changing the mole ratio of $CuCl_2$ and $InCl_3$. Note that the molar ratio of sodium citrate to $In^{3+}$ was 4:1.

**III. Synthesis of Cu-In-S/ZnS Core/shell QDs**

After 60 min, the cooker was cooled and opened. The appropriate amount of $ZnCl_2$, thiourea, and thioglycolic acid dissolved in 0.1 L of deionized water were added into the crude solution to deposite ZnS shell around the Cu-In-S cores and the reaction would be lasted for another 60 min under the pressure. The pH value of the mixture solution was adjusted to 5.80 by adding NaOH solution (1.0 M). The mole ratio of $ZnCl_2$, thiourea, and thioglycolic acid is 1:1:2. Finally, the Cu-In-S/ZnS core/shell nanocrystal solution was cooled naturally. The thickness of the ZnS shell was controlled by repeating injection of ZnS shell stock solution. Note that the thickness of one monolayer of ZnS is around 0.31 nm.

**IV. Cell Culture.**

Human liver cancer cells (HepG2) cells were cultured in 25 $cm^2$ flasks in Dulbecco's Modified Eagle's Medium (DMEM) (Gibco) containing 10% (v/v) fetal bovine serum (Gibco) at 37 °C in an atmosphere of 5% (v/v) $CO_2$ in air. The media were changed every 48 h, and the cells were passaged by trypsinization before confluence.

**V. Cytotoxicity Assay.**

MTT assays were used to probe cellular viability. Briefly, HepG2 cells were seeded at a density of 5000 cells/well (100 μL total volume/well) in 96-well assay plates. After 24 h, drugs at the indicated concentrations were added and cells were further incubated for 48 h. To determine toxicity, 10 μl of MTT solution (BBI) was added to each well of the microtiter plate and the plate was incubated in the $CO_2$ incubator for an additional 4 h. The cells then were lysed by the addition of 100 μl of DMSO. Absorbance values of formazan were determined with Bio-Rad model-680 microplate reader at 490 nm (corrected for background absorbance at 630 nm). Six replicates were done for each treatment group.

**VI. Cellular Imaging**.

HepG2 cells were seeded in a 24-well plate and cultured for 24 h. The cell medium was removed, and then cells were incubated with 0.5 mL of fresh cell medium containing 20 μg of Cu-In-S/ZnS core/shell quantum dots for 4 h. After that, cells were washed three times with PBS, and then stained by DAPI. Cells were viewed and counted using an Olympus BX-51 optical system microscopy. Pictures were taken with an Olympus digital camera.

**VII. Characterizations**

UV-*vis* absorption spectra were measured by Metash 5200 spectrophotometer. Photoluminescence (PL) spectra were taken using Shimadzu RF 5301PC. All the samples were measured in air. The PL QYs of the QDs at room temperature were determined by comparing the integrated emission of the QD samples in aqueous

solution with that of a fluorescence dye (coumarin 6 in ethanol, 78% QY). The luminescence decay curve was obtained from a Lecroy Wave Runner 6100 digital oscilloscope (1 GHz) using a tunable laser (pulse width=4 ns, gate=50 ns) as the excitation source (Continuum Sunlite OPO). The powder XRD patterns were recorded using a Bruker D8 FOCUS X-ray diffractometer. High-resolution transmission electron microscopy (HR-TEM) images were taken on a FEI Tecnai G2 F20 with an accelerating voltage of 200 kV. Energy Disperse Spectroscopy (EDS) spectra were recorded by using a scanning electron microscope (Hitachi S-4800) equipped with a Bruker AXS XFlash detector 4010.

***Table S1.*** EDS results of Cu-In-S cores and Cu-In-S/ZnS core/shell quantum dots.

| **Cu/In ratios of starting materials** | **Cores Cu/In/S** | **1 monolayer Cu/In/Zn/S** | **2 monolayers Cu/In//Zn/S** |
|---|---|---|---|
| 1:1.5 | 1/1.33/2.24 | 1/1.19/1.65/6.20 | 1/1.11/3.05/5.24 |
| 1:3 | 1/2.62/4.98 | 1/2.33/3.14/7.64 | 1/1.95/4.24/7.96 |
| 1:4 | 1/3.60/6.79 | 1/3.17/2.60/9.31 | 1/2.92/3.42/8.24 |
| 1:6 | 1/5.25/8.59 | 1/5.14/7.68/16.08 | 1/4.81/8.32/8.96 |
| 1:8 | 1/6.56/10.63 | 1/6.25/5.38/23.70 | 1/4.91/7.19/9.27 |

***Table S2.*** Calculated cost of Cu-In-S/ZnS core/shell quantum dots with an initial Cu/In ratio of 1:4 and 3 monolayers of ZnS shell. The price of reactants in Chinese Yuan (RMB) was taken from Aladdin Inc. except for DI-water. ~3 grams of quantum dots were obtained in a batch, leading to 14.54 RMB/g (~2.3 $/g) quantum dots.

| **Reactants** | **Purity** | **Price (RMB)** | **Usage** | **Cost/batch** |
|---|---|---|---|---|
| $CuCl_2 \cdot 2H_2O$ | 2N | 118.0/500g | 0.426 g | 0.10 |
| $InCl_3$ | 3N | 397.0/25g | 2.212 g | 35.13 |
| $ZnCl_2$ | AR | 69.0/500g | 6.646g | 0.92 |
| Sodium citrate | AR | 69.0/500g | 11.76 g | 1.62 |
| Thioglycolic acid | AR | 128.0/500g | 9.442g | 2.42 |
| $Na_2S \cdot 9H_2O$ | AR | 39.8/500g | 3.90 g | 0.31 |
| Thiourea | 2N | 89.0/500g | 3.705 g | 0.66 |
| De-ionized water | 18MΩ·cm | 14.0/25L | 4.4 L | 2.46 |
| | | | | 43.62 |

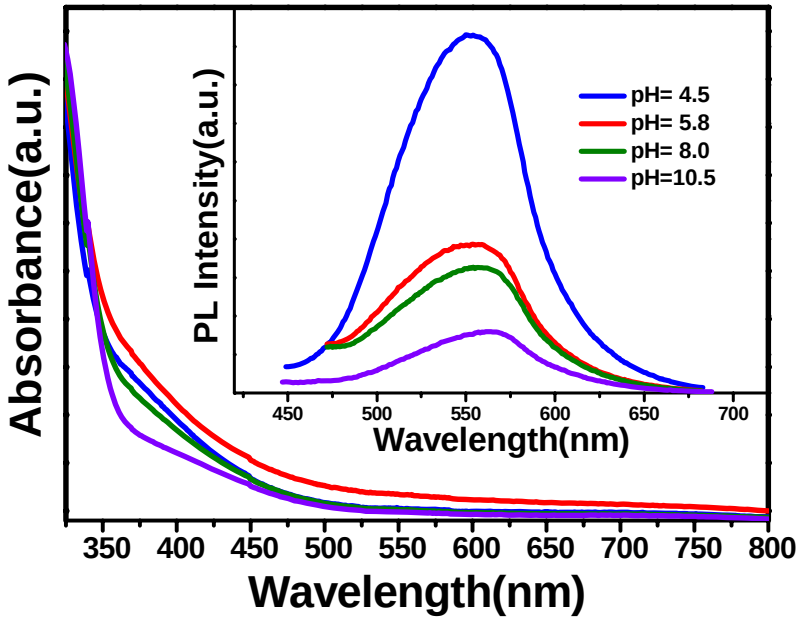


***Figure S1.*** UV-vis absorption and PL emission (inset) spectra of Cu-In-S/ZnS core/shell QDs with 1 monolayer of ZnS shell under different pH values.

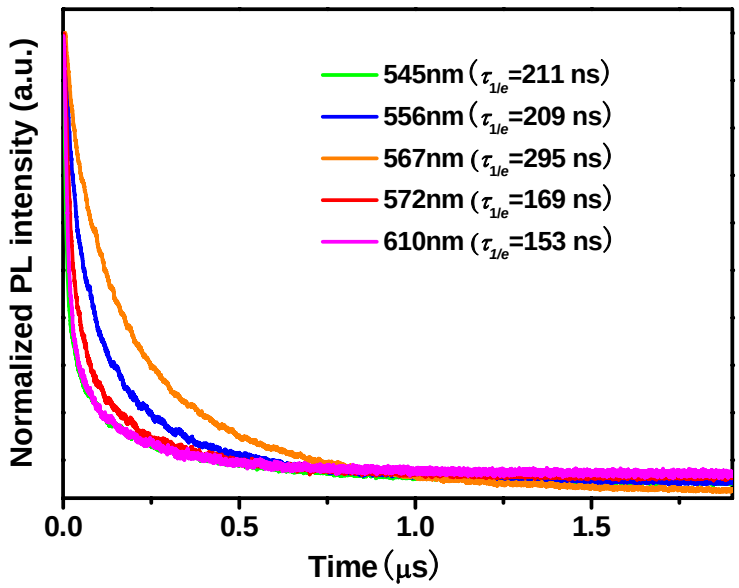


***Figure S2.*** Fluorescence decay curves and average lifetimes of Cu-In-S/ZnS core/shell quantum dots with different Cu/In ratios.

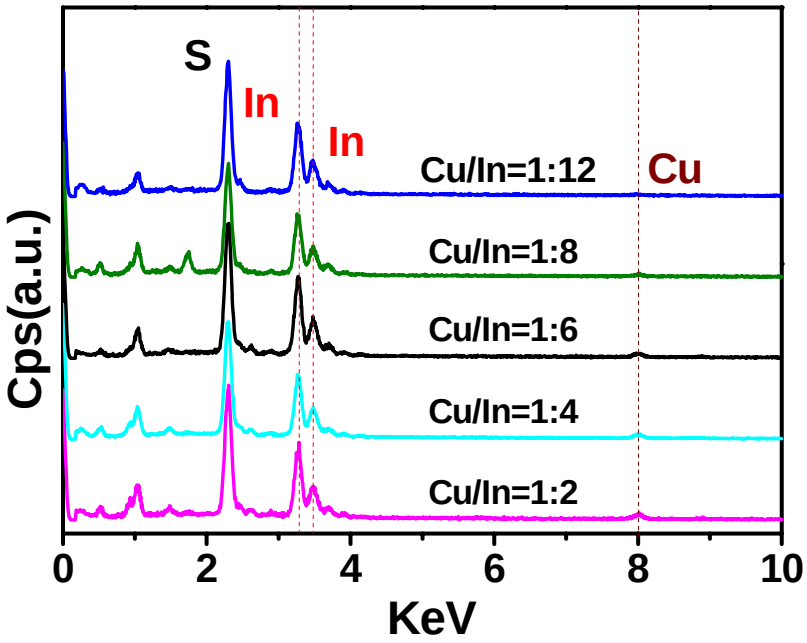


***Figure S3.*** EDS spectra of Cu-In-S core quantum dots with different Cu/In ratios.