Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Cd–Cu–Fe–S Quaternary Nanocrystals Exhibiting Excellent Optical/Optoelectronic Properties

Chao Wang, [†§] *Lucheng Peng,* [†] *Xiaotian Yang,* [†§] *Renguo Xie,* [†*] *and Shouhua Feng*[†*]

[†]*State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry Jilin University, Changchun 130012, China*

[§]*Jilin Provincial Key Laboratory of Architectural Electricity&Comprehensive Energy Saving, School of Electrical Engineering and computer, Jilin Jianzhu University, Changchun 130118, China*

Corresponding Author: renguoxie@jlu.edu.cn; shfeng@jlu.edu.cn

Experimental part:

Materials and Methods:

Materials. Technical-grade (90%) ODE, iron chloride ($Fe(Cl)_3$, 99.99%), copper(II) acetate (99.99%), oleic acid (90%), and cadmium acetate (99.99%) were purchased from Alfa. Oleylamine (97%), dodecylthiol (99.9%), and sulfur powder (S, 9.999%) were purchased from Aldrich.

Methods: In a typical synthesis of Cd–Cu–Fe–S NCs, cadmium acetate (0.5 mmol), copper acetate (0.5 mmol), iron chloride (0.1 mmol), DDT (1.5 mL), and oleic acid (1.5 mL) were mixed with ODE (2 mL) in a three-necked flask. The reaction mixture was degassed under vacuum for 1 min and purged with argon. The flask was heated to 120 °C, 150 °C, 180 °C, and 210 °C until a clear solution was formed, and then sulfur solution (0.9 mmol) dissolved in 0.9 mL oleylamine was quickly injected into the reaction solution. Afterward, the mixture was maintained at a definite temperature (120 °C, 150 °C, 180 °C, or 210 °C) for 3 min and then cooled to room temperature. For purification, 10 mL of hexane was added, and by-products were removed by successive methanol extraction until the methanol phase was clear. For syntheses of the Cd–Cu–Fe–S NCs with various compositions, only the ratio of precursors used was varied, while the other reaction conditions were kept constant.

Characterizations: TEM observations were conducted on a JEOL 100CX transmission electron microscope with an acceleration voltage of 100 kV. Carbon-coated copper grids were dipped in hexane solutions to deposit the NCs onto films. XRD patterns were obtained by using a Philips PW1830 X-ray diffractometer. The elemental compositions of the NCs were determined by EDS. UV–visible spectra were recorded on an HP8453 UV–visible spectrophotometer. PL spectra and PL dynamics were obtained through an FS900 steady-state fluorescence spectrometer and a Spex Fluorolog 112 spectrofluorometer, respectively. The time-resolved PL spectra were attained by an FL920 fluorescence lifetime spectrometer (Edinburgh Instruments). The excitation source was a hydrogen flash lamp (nF900) with a pulse width of 1.5 ns. The emission was monitored at the wavelength of the PL peak maximum for each sample during the PL decay measurements. The instrument response function (t) was measured using a Ludox scattering solution in water, and the decay curves were fitted using a multiexponential function in the proprietary software Data Station 2.3. Mean fluorescence lifetimes <τ> for multiexponential iterative fitting were calculated from the decay time and the pre-exponential factors. PL QYs of the samples were determined using organic dyes (IR-125, emission at 826 nm, QY=13.2%) as standards. The PL QY of the NCs with emission at 840 nm was ~57%.

Optoelectronic Device Fabrication and Current−Voltage Measurement. ITO-coated glass was cleaned by rinsing in acetone and methanol with sonication for 20 min in each solvent. The pre-treated ITO-coated glass was dried and exposed to UV light for 1 h before further use. To purify the NCs, the mother solution (2.0 mL) was dispersed in hexane (5.0 mL), and acetone (0.3 mL) was then added. The mixture was then centrifuged at 3000 rpm for 10 min. After centrifugation, the excessive salt was precipitated as a white powder. It was found that the removal of the byproduct was critical to obtaining optically clear solutions. The supernatant was then isolated, chloroform (1.0 mL), methanol (5.0 mL), and acetone (2.0 mL) were added, and then the dispersion was centrifuged at 4000 rpm for 10 min to precipitate the NCs. The semi-pure plug could then be purified by several precipitation/dispersion cycles using chloroform/methanol/acetone (1:1:2 v/v). The ligand on the surface of NCs is crucial factor on control the performance of device. As purified NCs in chloroform were ligand exchanged with pyridine as reported in literature. Films were spun on ITO substrates (1000 rpm, 30 s). The films were then placed on a hot plate at 200 °C for 10 min inside a N_2 filled glove box to ensure complete remove residual organic solvents. To provide a metal back contact, Au film with the thickness of 80 nm was deposited through a mask using an electron beam evaporator after a standard photolithography process, and the sputtering power and time were 80 W and 4 min, respectively.

Current−voltage (I−V) characteristics were recorded using Keithley 2601 Source Meter in the dark and under simulated AM1.5 illumination (100 mW/cm^2). The scan voltage tuned from -5.0 to 5.0 V. All the tests of the devices were processed in ambient condition. Photocurrent and dark current of standard vertical structure (ITO-NCs-Au) devices were measured using a Labview-controlled voltage/source meter (Keithley 2400) in the dark and under AM1.5 G condition (100 mW/cm^2), respectively. The scan voltage tuned from -5.0 to 5.0 V. All the tests of the devices were processed in ambient condition.

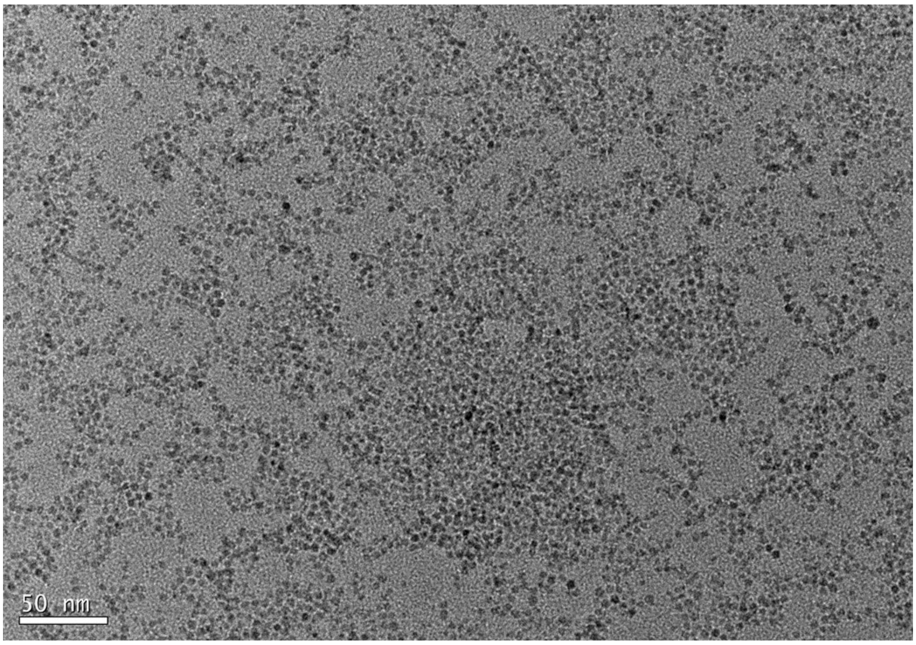

Figure S1. Low magnification TEM images of Cd–Cu–Fe–S NCs with a size of 4.5 nm

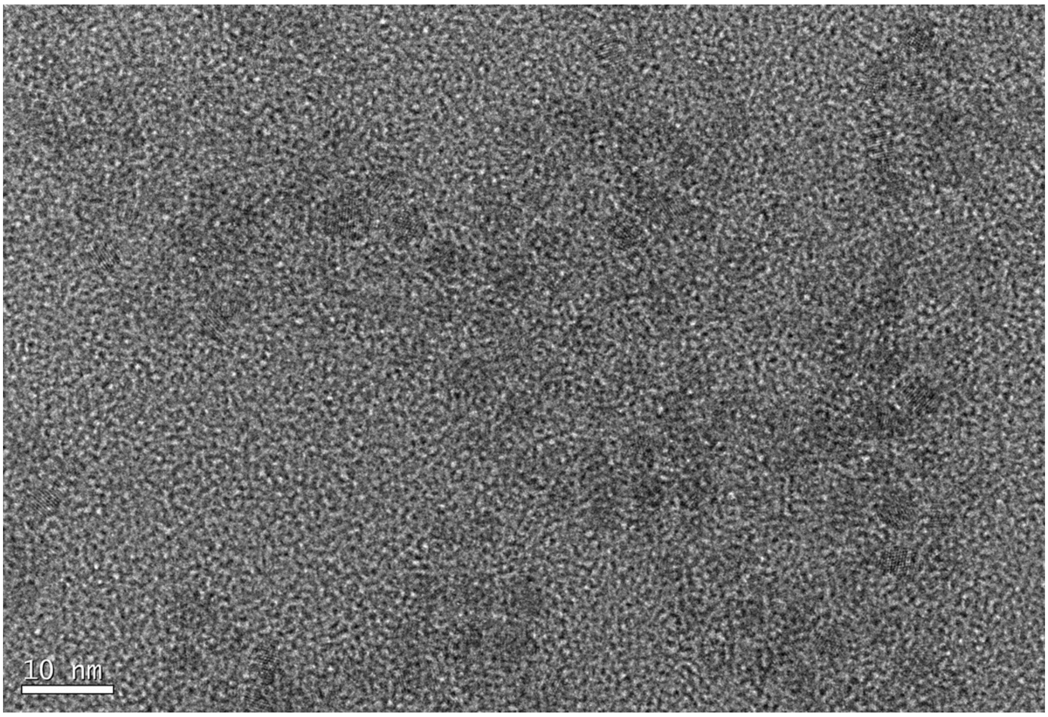

Figure S2. High resolution TEM images of Cd–Cu–Fe–S NCs with a size of 4.5 nm.

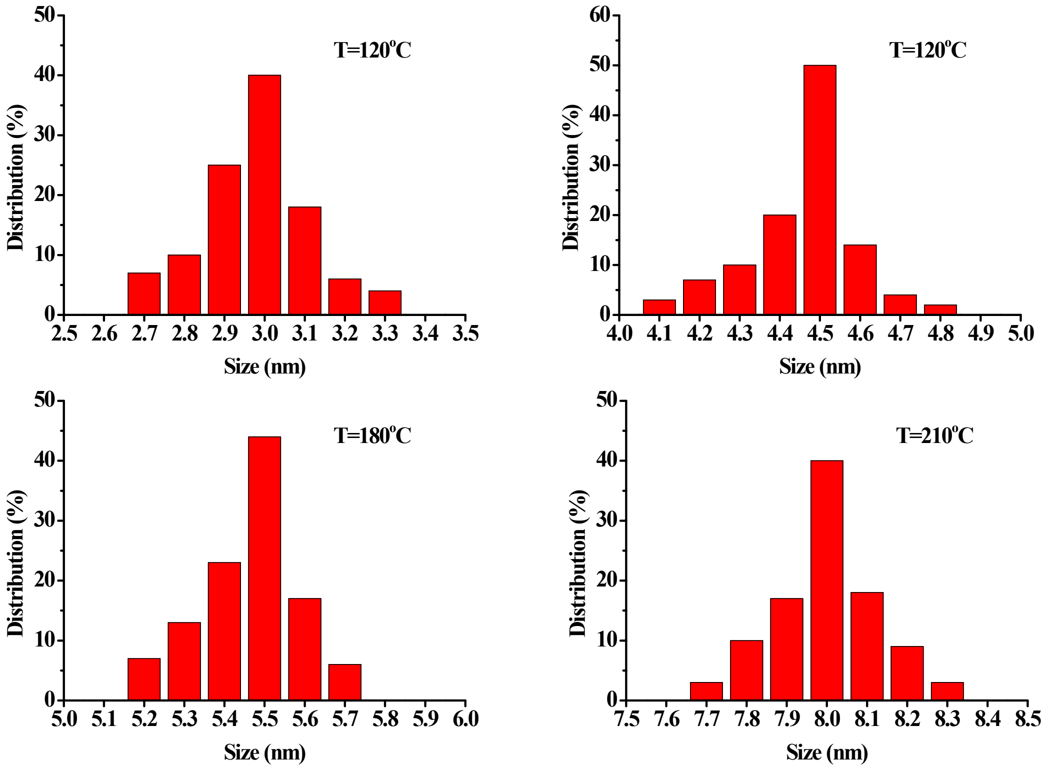

Figure S3. The size distribution histograms of as prepared samples synthesized at different reaction temperatures shown in Figure 1.

Table S1 Relevant parameters for syntheses of as prepared NCs.

T (^{o}C)	*Size (nm)*	**Cd:Cu:Fe:S (atomic ratio)**	*PL peak position (nm)*	*PLQY (%)*
120	*3*	*0.6:0.9:0.1:1.2*	*640*	*13*
150	*4.5*	*0.6:0.8:0.1:1.2*	*740*	*25*
180	*5.5*	*0.6:0.9:0.1:1.2*	*830*	*57*
210	*8*	*0.5:0.5:0.1:0.9*	*980*	*8*

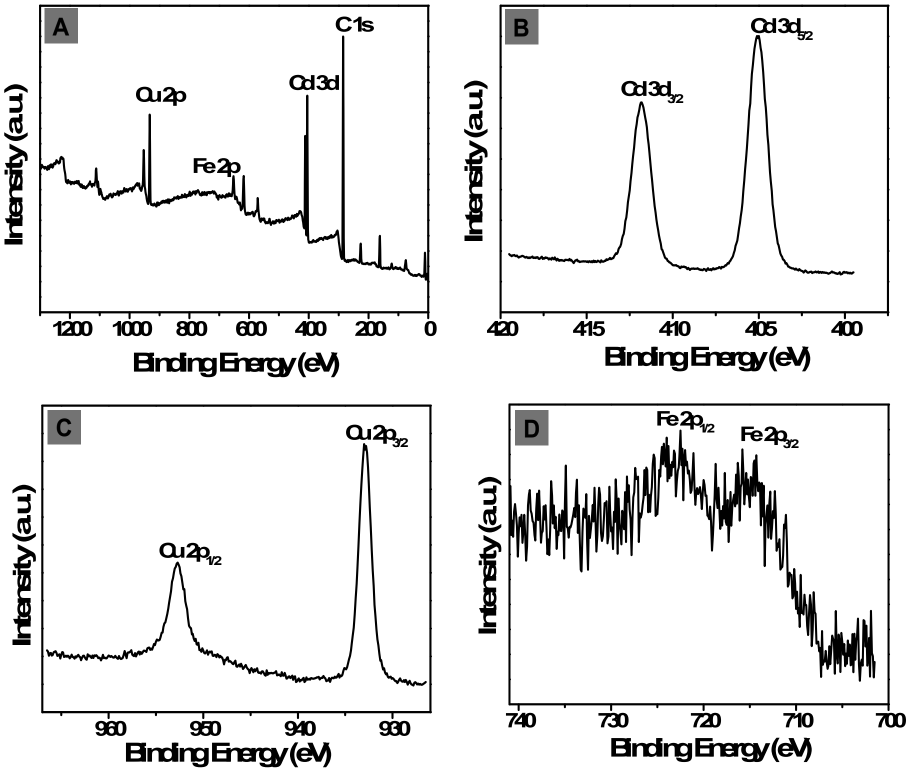

***Figure S4**. Comparison of XPS (A) survey scans and high resolution scans of Cd 3d (B), Cu 2p (C) and Fe 2p (D) photoelectron of as prepared sample with a size of 5.5 nm selected for XPS measurement.*

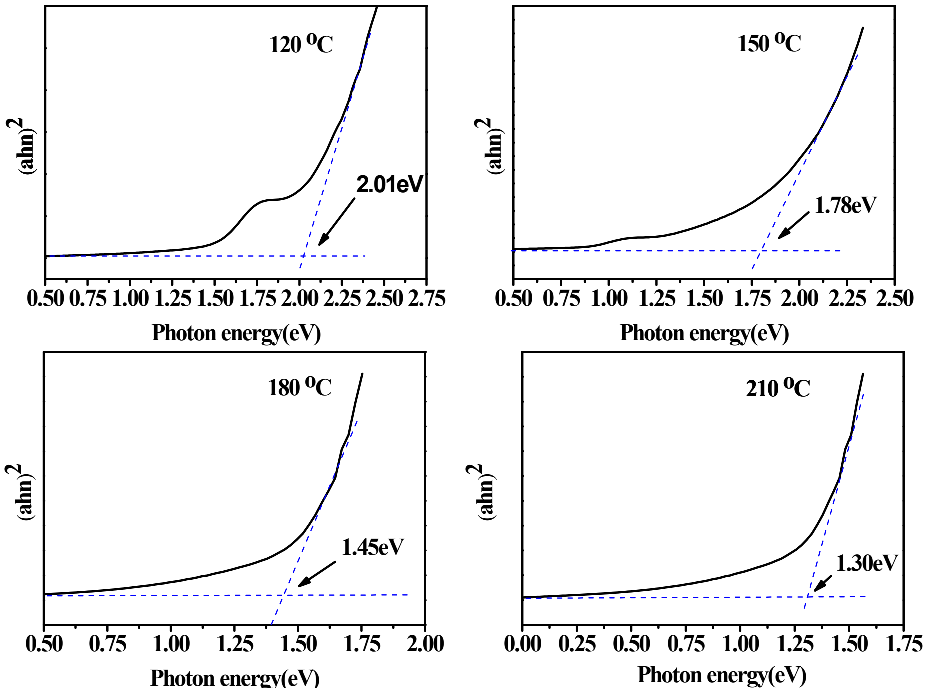

Figure S5. *Tauc Plots used to estimate band gap in figure 3b of the main text.*

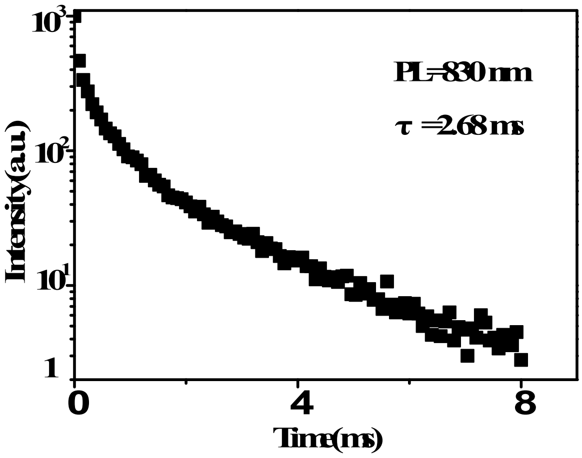

Figure S6. *The PL decay plot of Cd–Cu–Fe–S NCs with a size of 5.5 nm.*

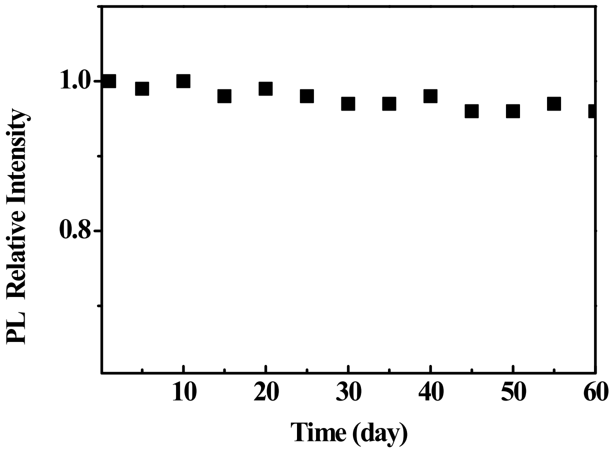

Figure S7. *Photoluminescence stability of Cd-Cu-Fe-S NCs in hexane at ambient condition.*