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Supporting Information

Biocompatible Off-stoichiometric Copper Indium Sulfide Quantum Dots with Tunable Near-Infrared Emission *via* Aqueous Based Synthesis

Mingxia Jiao[a], Xiaodan Huang[b], Linzheng Ma[a], Yun Li[a], Peisen Zhang[b], Xiaojun Wei[b], Lihong Jing[b,*], Xiliang Luo[a,*], Andrey L. Rogach[c], Mingyuan Gao[b]

[a] *Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Zhengzhou Road 53, Qingdao 266042, China*

[b] *Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Bei Yi Jie 2, Zhong Guan Cun, Beijing 100190, China*

[c] *Department of Materials Science and Engineering, and Centre for Functional Photonics (CFP), City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong SAR*

Experimental Section

Chemicals. $CuCl_2 \cdot 2H_2O$ (459097), $InCl_3 \cdot 4H_2O$ (334073), $Na_2S \cdot 9H_2O$ (431648), L-glutathione reduced (GSH, V900456), Sodium citrate dihydrate (S4641), $ZnCl_2$ (456845) were purchased from Sigma-Aldrich and used as received. Analytical grade chemicals such as NaOH and ethanol were purchased from Sinopharm Chemical Reagent Beijing, Co., Ltd and used as received. 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT, 98%), dimethyl sulfoxide (DMSO), Dulbecco's Modified Eagle Medium (DMEM, high glucose), and fetal bovine serum (FBS) were bought from Biodee Biotechnology Co., Ltd., Beijing, China. Other solvents and chemicals were used without further purification.

Synthesis of Cu-In-S QDs. For synthesizing Cu-In-S (CIS) QDs with Cu/In molar ratio of 0.025, $CuCl_2 \cdot 2H_2O$ (0.001 mmol), $InCl_3 \cdot 4H_2O$ (0.04 mmol), $Na_2S \cdot 9H_2O$ (0.052 mmol), Sodium citrate dihydrate (0.16 mmol), and GSH (0.01 mmol) were dissolved into 20 mL ultrapure water in a 50-mL flask under magnetic stirring, to form a homogeneous solution with the pH value kept at about 6. The resultant solution was then heated to the boiling point and kept for 1 h. Afterwards, the solution was cooled to room temperature. The resultant QDs were precipitated by ethanol, collected by centrifugation, washed with ethanol three times, and finally redispersed in water for further experiments. For preparing Cu-In-S QDs with different Cu/In molar ratio, the molar ratio of $CuCl_2$ and $InCl_3$ was adjusted accordingly, while their total amount was kept constant. The molar ratios of Cu/L-GSH and In/Sodium citrate were kept at 1/10 and 1/4 respectively for all syntheses.

Synthesis of Cu-In-S/ZnS QDs. Following the aforementioned procedures for synthesizing Cu-In-S seeds, the reaction solution was cooled to 80°C after heated for 1 h. Without applying the purification procedures, a stock solution containing 0.05 mmol $ZnCl_2$ and 0.05 mmol GSH was introduced into the reaction system, followed by addition of 0.05 mmol Na_2S. The solution was kept at 80°C for certain time to accomplish the ZnS coating, and a series of aliquots was extracted at 80°C for monitoring the particle growth. The purification procedures for the collected particles were the same as those described above.

Spectroscopic Characterization. Steady-state UV−Vis absorption and PL spectra were recorded at room temperature on a Shimadzu UV-2600 UV−Vis spectrophotometer and an Edinburgh Instruments FLS980 spectrometer, respectively. The excitation wavelength for all steady-state PL measurements was set to 360 nm. The PL QY of the QDs was estimated by using Rhodamine 6G as a fluorescence standard according to literature methods.[1] Temperature-dependent steady-state PL spectra and time-resolved PL decay curves were measured on Edinburgh Instruments FLS980 spectrometer equipped with a picosecond pulsed diode laser (EPL-360) as a single wavelength excitation source (360 nm) for time-correlated single-photon counting (TCSPC) measurements.

Structural and Compositional Characterization. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images of the QDs were taken on a JEM-2100F electron microscope at an acceleration voltage of 200 kV. The particle size was determined by averaging at least 300 particles per sample. The metal composition and QD concentration were determined by the Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) method using a Thermo Fisher IRIS Intrepid II XSP. Powder X-ray diffraction (XRD) pattern of the particle sample was recorded on a Regaku D/Max-2500 diffractometer under Cu $K\alpha_1$ radiation (λ = 1.54056 Å). X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Thermo-VG Scientific ESCALAB 250Xi spectrometer with a monochromatic Al Kα X-ray source. Dynamic light scattering (DLS) measurements were carried out at 25°C with a Nano ZS (Malvern) equipped with a solid-state He-Ne laser (λ = 633 nm) for measuring the hydrodynamic size of the resultant QDs.

Cytotoxicity assay of Cu-In-S/ZnS QDs. The colorimetric MTT assay was performed to assess the cytotoxicity of Cu-In-S/ZnS QDs. Specifically, HeLa cells were first seeded in 96-well plates at a density of 4000 cells per well and cultured for about 24 h in DMEM supplemented with 10% FBS. Then, the cells were washed with 1×PBS and incubated with Cu-In-S/ZnS QDs at different concentrations at 37°C for 24 h. Subsequently, the cells were washed twice with 1×PBS followed by further proliferating in the culture medium for 48 h. Afterwards, 20 μL of MTT with a concentration of 5 mg/mL was added and allowed to react with the cells for 4 h before the addition of 150 μL of DMSO for dissolving of the precipitation. Finally, the absorption of each solution was measured at 490 nm on a microplate reader (Thermo, Varioskan Flash).

Supplementary Results

Table S1 The elemental composition of CIS QDs with different Cu/In feeding molar ratios.

Cu/In feeding molar ratio	0.025	0.050	0.10	0.20	0.25	0.33
Cu/In from ICP-OES	0.023 ± 0.002	0.046 ± 0.003	0.093 ± 0.005	0.19 ± 0.011	0.26 ± 0.019	0.32 ± 0.009

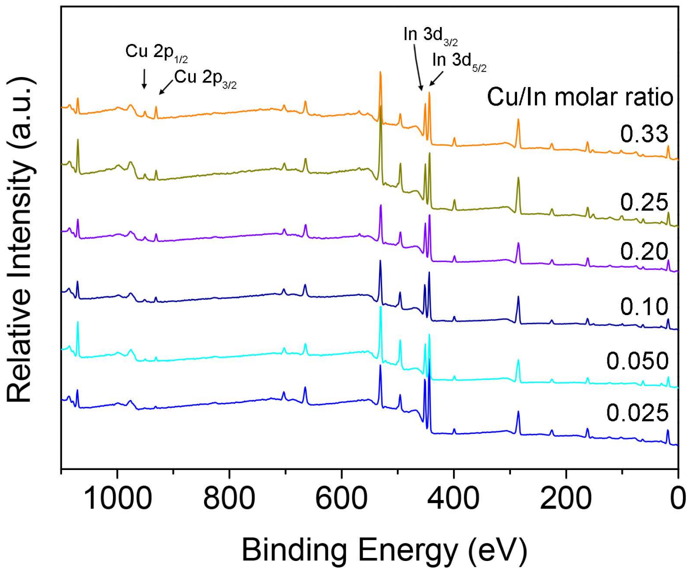

Fig. S1 XPS spectra of CIS QDs with different Cu/In molar ratios.

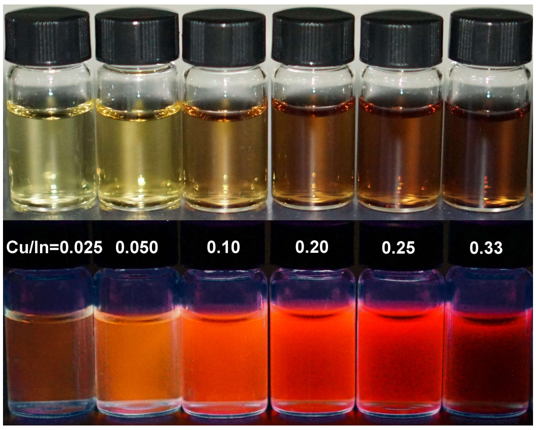

Fig. S2 Photographs of CIS QDs with different Cu/In ratio in water under room light (upper row) and 365 nm UV irradiation (bottom row).

Table S2 PL peak wavelength, FWHM, and PL QY of CIS QDs as a function of the Cu/In molar ratio.

Cu/In molar ratio	**PL peak wavelength (nm)**	**FWHM (nm)**	**PL QY (%)**
0.025	560 670	/	3.0
0.050	560 690	/	3.6
0.10	560 700	/	4.2
0.20	720	160	3.8
0.25	730	152	2.8
0.33	746	151	1.2

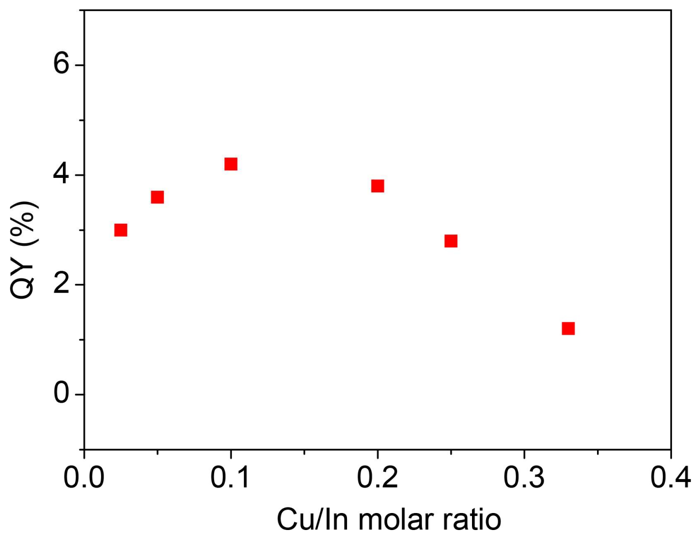

Fig. S3 PL QYs of CIS QDs with different Cu/In molar ratios.

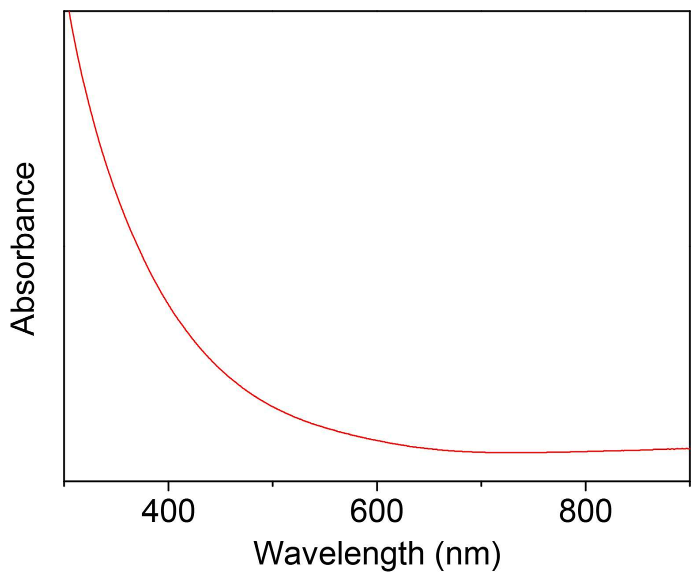

Fig. S4 UV-Vis absorption spectra of the $CuInS_2$ QDs.

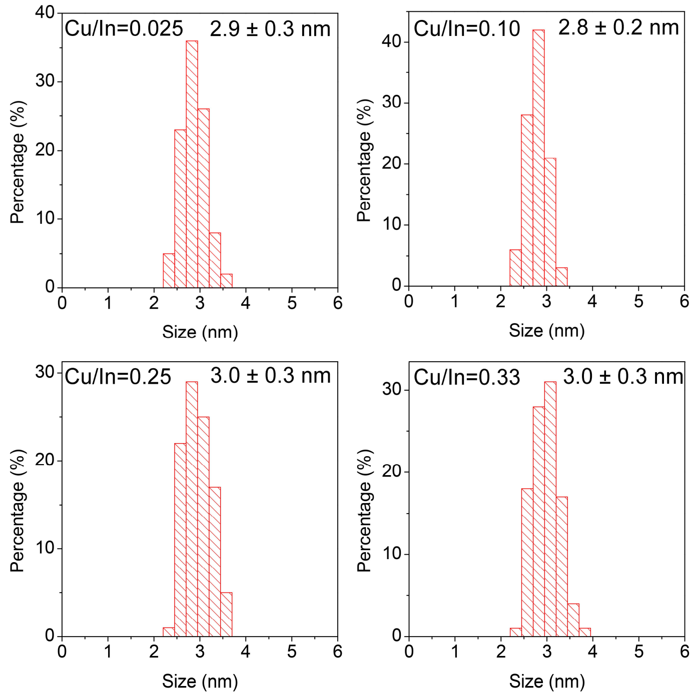

Fig. S5 Size histograms of CIS QDs with different Cu/In molar ratios.

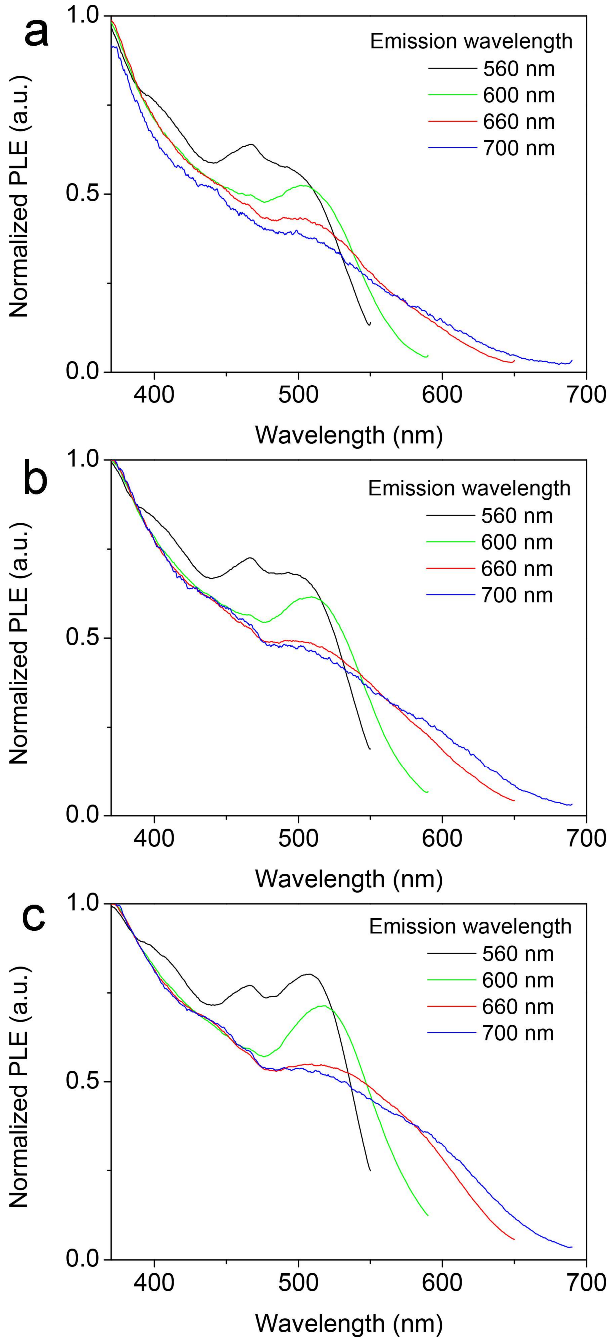

Fig. S6 PL excitation spectra of CIS QDs with Cu/In molar ratio of (a) 0.025, (b) 0.050, and (c) 0.10 recorded at different monitoring emission wavelength.

Time-resolved photoluminescence (TR PL) measurements

The PL decay curves were fitted using a multi-exponential function[2]:

$$I(t) = \sum_{i=1}^{n} B_i \exp\left(-t/\tau_i\right), \qquad \sum_{i=1}^{n} B_i = 1 \tag{S(1)}$$

In this expression, τ_i represent the decay time constants, and B_i represents the normalized amplitudes of each components, n is the number of decay times. Because the photoluminescence decays for all the QDs are best fitted using a three-exponential function (n = 3), the amplitude weighted average decay lifetime τ_{avg} of the entire fluorescence decay process was calculated with the form:

$$\tau_{\text{avg}} = \frac{\sum B_i \tau_i^2}{\sum B_i \tau_i} \qquad \text{S(2)}$$

The normalized lifetime-amplitude product is given as:

$$f_{\text{i}} = \frac{\tau_i B_i}{\sum \tau_i B_i} \qquad \text{S(3)}$$

In this expression, f_i represents the relative time-integrated contribution of each respective process to the overall number of emitted photons (i.e., the emission intensity measured in steady state PL spectra).

The PL decay-fitting data for all curves are summarized in **Table S3**.

Table S3 The parameters for multi-exponential fitting of the PL decay curves in **Fig. 3**, i.e., normalized amplitude *Bi*, time constant τ_i and their normalized products f_i, goodness-of-fit parameter χ^2, together with the emission peak wavelength at different temperature.

Temperature/K	λ_{em}/nm	τ_1/ns	B_1/%	f_1/%	τ_2/ns	B_2/%	f_2/%	τ_3/ns	B_3/%	f_3/%	τ_{avg}/ns	χ^2
Cu/In=0.025 high-energy emission												
298	560	20.59	53.86	15.46	86.07	36.01	43.20	293.1	10.12	41.35	161.6	0.984
200	560	157.7	41.89	16.41	462.3	51.99	59.71	1568	6.126	23.87	676.3	1.189
150	560	258.5	56.19	26.07	747.7	40.67	54.58	3429	3.142	19.34	1139	1.089
100	560	484.1	71.42	39.83	1495	26.96	46.42	7373	1.619	13.75	1901	1.111
77	560	487.0	56.62	25.32	1547	40.58	57.67	6609	2.801	17.01	2140	1.178
Cu/In=0.025 low-energy emission												
298	670	123.0	66.39	33.97	408.8	32.24	54.84	1959	1.373	11.19	485.2	1.177
200	648	243.9	51.80	27.22	602.0	46.48	60.29	3377	1.716	12.49	851.2	1.185
150	646	349.2	57.81	33.36	793.1	40.43	52.99	4716	1.752	13.65	1181	1.194
100	643	557.4	71.20	45.14	1340	27.65	42.16	9724	1.149	12.70	2052	1.131
77	642	694.8	68.27	41.79	1725	30.62	46.55	11907	1.111	11.65	2482	1.063
Cu/In=0.33												
298	746	42.00	48.99	12.52	196.9	39.95	47.86	588.7	11.06	39.62	332.7	1.125
250	741	67.53	32.69	7.479	304.8	55.92	57.75	901.4	11.38	34.77	494.5	1.050
200	714	91.94	12.86	2.807	401.1	76.68	73.03	973.1	10.46	24.16	530.6	1.169
150	708	344.6	51.44	32.92	689.5	47.64	60.70	3569	0.9175	6.081	751.1	1.206
77	704	546.3	31.91	19.47	966.6	65.08	70.25	3057	3.011	10.28	1100	1.098

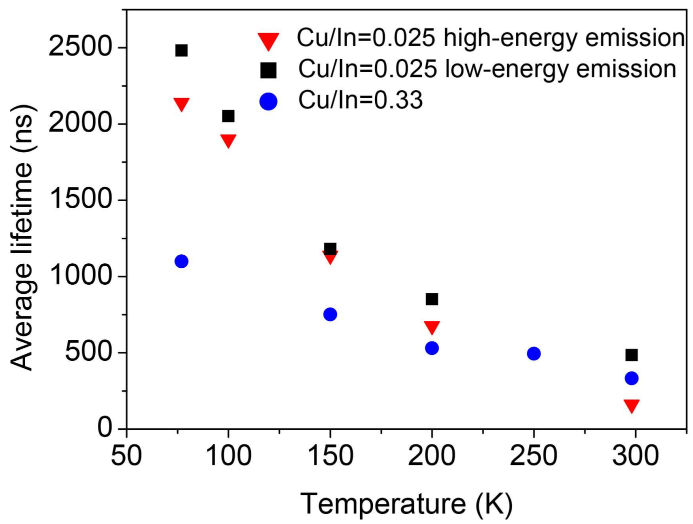

Fig. S7 Average lifetimes of CIS QDs with different Cu/In molar ratios against temperature.

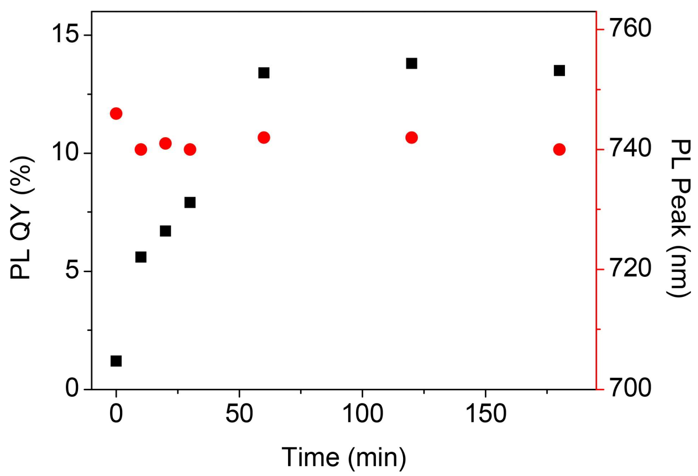

Fig. S8 Temporal evolutions of the PL QY and PL peak position of CIS/ZnS QDs.

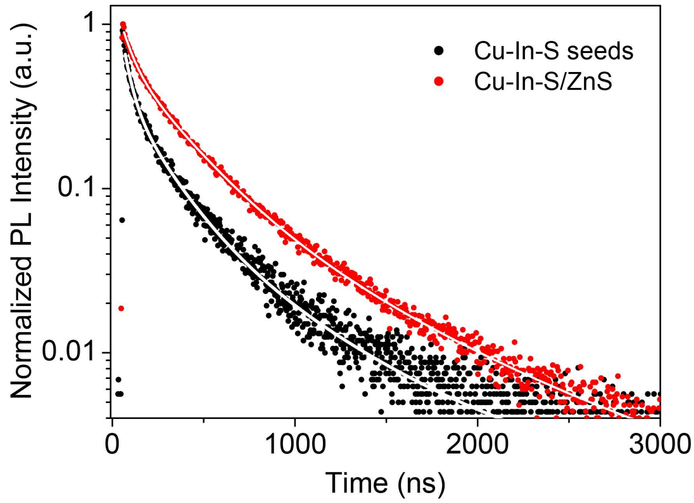

Fig. S9 Normalized time-resolved PL decay curves of CIS seeds and CIS/ZnS QDs measured at room temperature.

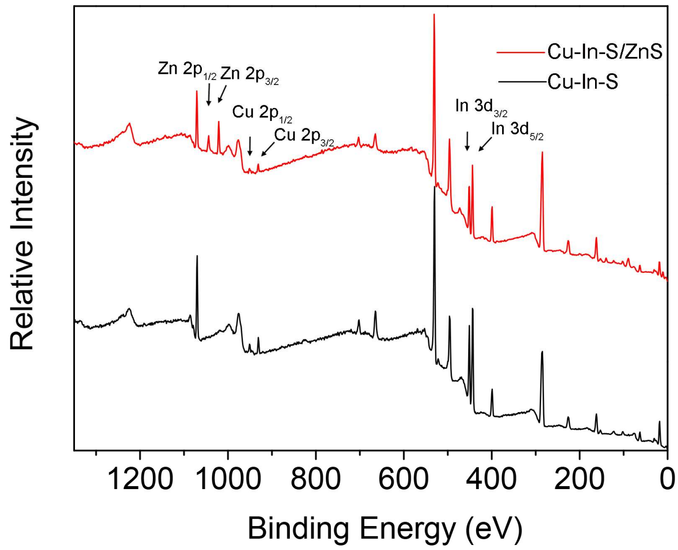

Fig. S10 XPS spectra of CIS seeds and CIS/ZnS QDs.

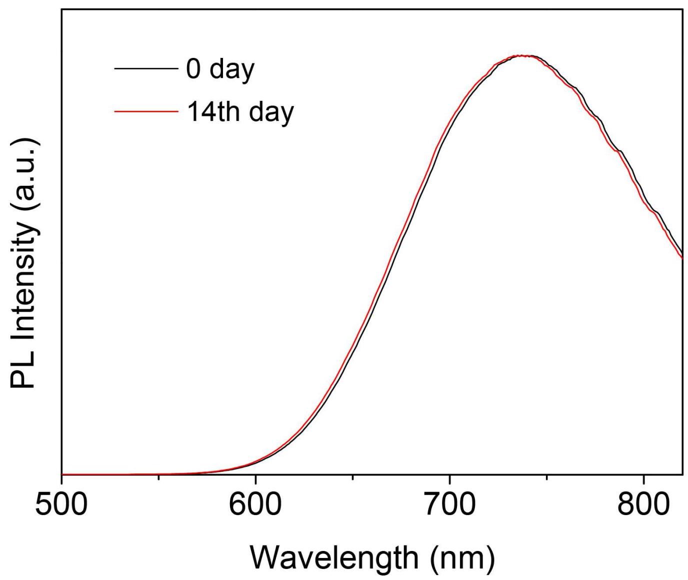

Fig. S11 PL spectra of the freshly prepared CIS/ZnS QDs and the same sample after being stored over 14 days.

References

1 Bao, H. B.; Gong, Y. J.; Li, Z.; Gao, M. Y. *Chem. Mater.*; 2004, 16, 3853.

2 Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Springer: New York, 2006.