

Supporting Information

Highly stable CuInS₂@ZnS:Al core@shell quantum dots: role of aluminium self-passivation

Pinhua Rao^{§a}, Wei Yao^{§a}, Zhichun Li^b, Long Kong^b, Wenqi Zhang^a and Liang Li^{*b}

^a School of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, P. R. China,

^b School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai, P. R. China.

[§] These authors contributed equally to this work.

Email: liangli117@sjtu.edu.cn

Reagents

Dodecanethiol (DDT, 98%), 1-octadecene (ODE, 90%), n-butylamine (99%), copper iodide (CuI, 99.9%), zinc acetate (Zn(Ac)₂, 99%), aluminium isopropoxide (Al(IPA)₃, 99.9%), oleylamine (90%), toluene (99.5%), methanol (99.5%) and acetone (99.5%) were purchased from Aladdin. Indium acetate (In(Ac)₃, 99.9%) and oleic acid (OA, 90%) were purchased from Alfa Aesar and Sigma-Aldrich, respectively. All the chemicals were used without further purification.

Preparation of CuInS₂ (CIS) quantum dots (QDs)

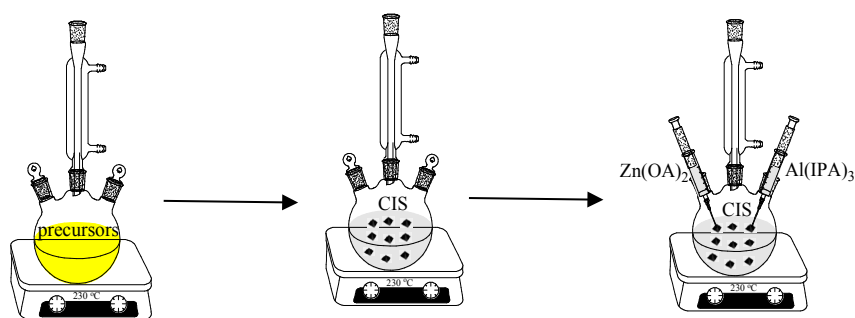
2.8 g of CuI and 4.5 g of In(Ac)₃ were added into a three-neck flask containing 15 ml of oleylamine, 145 ml of DDT and 145 ml of ODE. The mixture was heated to 120 °C under a primary vacuum and magnetic stirring for 1h, backfilled with N₂ and then heated to the reaction temperature of 230 °C with a rate of 15 °C/min. After keeping the mixture at 230 °C for 30 min, the mixture was cooled to the room temperature. The formed CIS QDs were isolated by adding methanol and centrifuging. Then, the QDs were re-dispersed in toluene. The precipitation/dispersion cycle was repeated at least three times to remove the byproducts, unreacted precursors and ODE.

Preparation of Zn(OA)₂ precursors

32.11 g of Zn(Ac)₂ was added into a three-neck flask containing 105 ml of OA, 210 ml of ODE and 35 ml of n-Butylamine. Under a vacuum condition, the mixture was heated to 120 °C and refluxed for half an hour until the solution became clear, which indicated that the Zn(OA)₂ had been prepared successfully.

Preparation of CIS@ZnS QDs and Al doped CIS@ZnS (CIS@ZnS:Al) QDs

The CIS@ZnS QDs were prepared by dropwise adding Zn(OA)₂ solution and DDT into a three-neck flask containing CIS QDs of 0.5mmol (Cu atomic concentration) under N₂ atmosphere. The mixture was reacted at 230 °C for a desired time. The addition rate of Zn(OA)₂ solution and DDT was designed at 2 ml/h. Preparation procedures of the CIS@ZnS:Al QDs were basically the same as that of CIS@ZnS QDs. Differently, the Al precursor, i.e. Al(IPA)₃, firstly was dissolved in the DDT.



Scheme S1 Synthesis process of Al-doped CIS@ZnS (CIS@ZnS:Al) QDs

Characterization of QDs

PL and UV-vis absorption spectra of QDs were recorded on a Hitachi F-4500 spectrofluorometer and a HP 8452A spectrometer, respectively. Values of the absolute fluorescence QY were determined by comparison of the integrated fluorescence intensity of a QDs' dispersion with that of a standard of known QY (Rhoamine 6G in ethanol, QY=95%). The absorbance of the QDs' dispersion was below 0.1 at the higher-energy shoulder close to the absorption onset. The absorbance of the standard solution was adjusted to be identical to that of the QDs' dispersion at the excitation wavelength (450nm). The QY of each sample was determined for at least five different concentrations.

The as-prepared QDs with and without Al doping were re-dispersed in toluene respectively (for the comparison, the concentration of QDs was set the same). 5-ml toluene solution with re-

dispersed QDs was moved to the 10-ml glass vials under open environment at 25 °C, which were rapidly sealed using screw caps containing rubber septa. Then, glass vials with toluene solution were continuously irradiated with lamp (450nm; irradiation power at the sample surface, approximately 1W/cm²). The PL spectra were measured at certain time intervals to monitor the PL intensity evolution. It can be seen obviously that the toluene solution with CIS@ZnS QDs became turbid after 5-h irradiation, while the toluene solution with CIS@ZnS:Al QDs still kept clear.

Transmission electron microscopy (TEM) images and energy dispersive x-ray spectroscopy (EDXs) of CIS@ZnS QDs and CIS@ZnS:Al QDs were obtained with a TEM-2100F microscope which operated at 200 kV. The QDs were drop-cast from a diluted dispersion in the solution of toluene and n-hexane onto a thin holey carbon film supported by a molybdenum grid. Powder x-ray diffraction (XRD) was performed by a Philips X'PERT diffractometer with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) was performed on a PHI5600 photoemission spectrometer using Al K α (1486.6 eV) x-rays. FTIR spectra of CIS@ZnS:Al QDs were performed on AVATAR380 with 2 cm⁻¹ spectral resolution.

Figure S1 shows photoluminescence (PL) and UV-vis absorption spectra of the CIS@ZnS:Al QDs with different Al/Zn molar ratios. As observed, the PL and UV-vis absorption spectra both had blue shifts with the overcoating of ZnS:Al shell, resulting from the diffusion of Zn into CIS core.

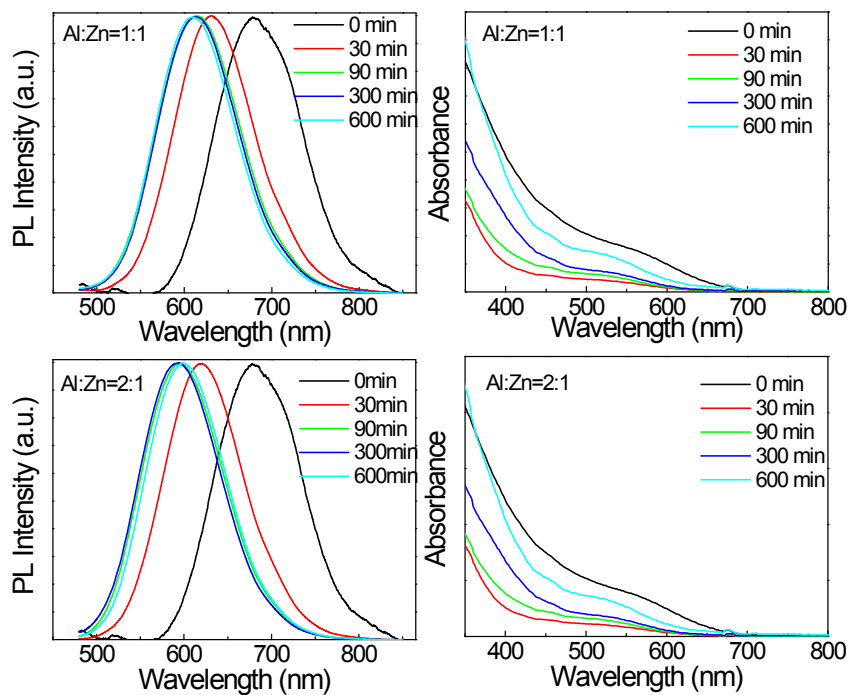


Figure S1 PL and UV-vis absorption spectra of CIS@ZnS:Al QDs with different Al/Zn molar ratios

According to Table S1, measured Al/Zn molar ratio in CIS@ZnS:Al QDs increased with the increase of nominal Al/Zn molar ratio. However, the increase gradient of measured Al/Zn molar ratio tended to reduce with the increase of the nominal Al/Zn molar ratio, indicating that doping of Al in CIS@ZnS QDs had a limit value. It should be mentioned that the nominal Al/Zn molar ratios were used in the figures and discussion in this article unless otherwise specified.

Table S1 Comparison of nominal and measured Al/Zn molar ratio in CIS@ZnS:Al QDs

Nominal Al/Zn molar ratio	0	0.5	1	2
Measured Al/Zn molar ratio ^a	0	0.075	0.188	0.218

a) Ratios of Al and Zn in CIS@ZnS:Al QDs were obtained by TEM-EDXs

Figure S2 shows effects of reaction time on the size of CIS@ZnS:Al QDs. It can be seen that the crystal size tended to increasing with the increase of the reaction time. When the reaction time was set at 20 h, the crystal size was about 4.0 nm

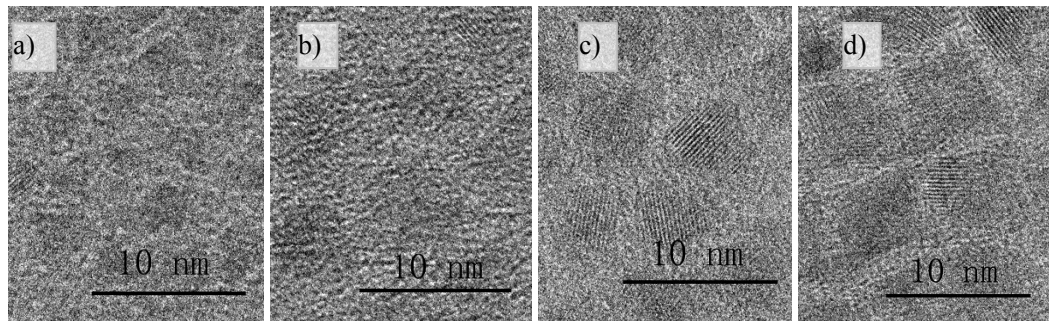


Figure S2 TEM images of CIS@ZnS:Al QDs with Al/Zn molar ratio of 0.5 at a reaction time of a) 3h, b) 5h, c) 10h, d) 20h.

According to Table S2, (Cu+In)/(Al+Zn) molar ratio in CIS@ZnS:Al QDs decreased with the increase of reaction time, resulting from the increase of QDs shell thickness which was echoed by TEM images in Figure S2.

Table S2 Molar ratio of (Cu+In)/(Al+Zn) in CIS@ZnS:Al QDs at different reaction times

Time	3 h	5 h	10 h	20 h
(Cu+In)/(Al+Zn) ^a	0.24	0.18	0.14	0.047

a) Ratios of Cu, In, Al and Zn in CIS@ZnS:Al QDs were obtained by TEM-EDXs

Table S3 shows effects of irradiation time on the fluorescence peak of CIS@ZnS QDs with/without Al doping. During the first 30 min, the fluorescence peaks of both CIS@ZnS QDs and CIS@ZnS:Al QDs showed a blue shift. After 30 min irradiation, the fluorescence peak of CIS@ZnS QDs showed a red shift with the increase of irradiation time. However, the fluorescence peak of CIS@ZnS QDs with Al doping, i.e., CIS@ZnS:Al QDs, maintained a stable value, possibly resulting from the formation of Al passivation layer which prevented the spalling of ZnS.

Table S3 Change of fluorescence peaks of CIS@ZnS QDs with/without Al doping during irradiation

Time (min) ^a	Fluorescence peaks of CIS@ZnS QDs	Fluorescence peaks of Al doped CIS@ZnS QDs ^b
0	609.0 nm	618.4 nm
30	607.0 nm	614.0 nm
60	607.0 nm	614.4 nm
120	609.0 nm	614.6 nm
180	612.2 nm	615.0 nm
300	612.2 nm	615.0 nm
420	615.8 nm	614.0 nm
540	617.0 nm	614.8 nm

a) Irradiation wavelength, 450 nm; b) Al/Zn molar ratio, 0.5.

Figure S3 show the PL and UV-vis absorption spectra of CIS@ZnS and CIS@ZnS:Al QDs before and after irradiation, During the first 30 min of irradiation, the fluorescence peaks of both CIS@ZnS QDs and CIS@ZnS:Al QDs showed a blue shift (~ 2 nm), which could result from the quenching of the big QDs with more red emission during irradiation

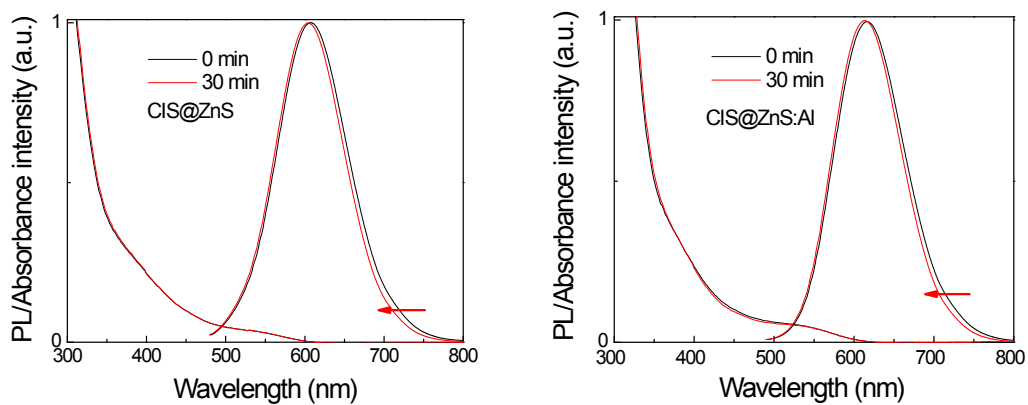


Figure S3 PL and UV-vis absorption spectra of CIS@ZnS and CIS@ZnS:Al QDs before and after irradiation

Figure S4 shows the UV-vis absorption spectra of CIS@ZnS and CIS@ZnS:Al QDs during the irradiation. The UV-vis absorption spectra of the CIS@ZnS QDs showed an obvious red-shift compared to that of CIS@ZnS:Al QDs. It is possibly due to the further corrosion of the gradient alloyed buffer layer (shown in Scheme S2) after the spalling of ZnS. The UV-vis spectra of CIS@ZnS QDs with Al doping, i.e., CIS@ZnS:Al QDs, showed few shift, possibly resulting from the protection of Al passivation layer.

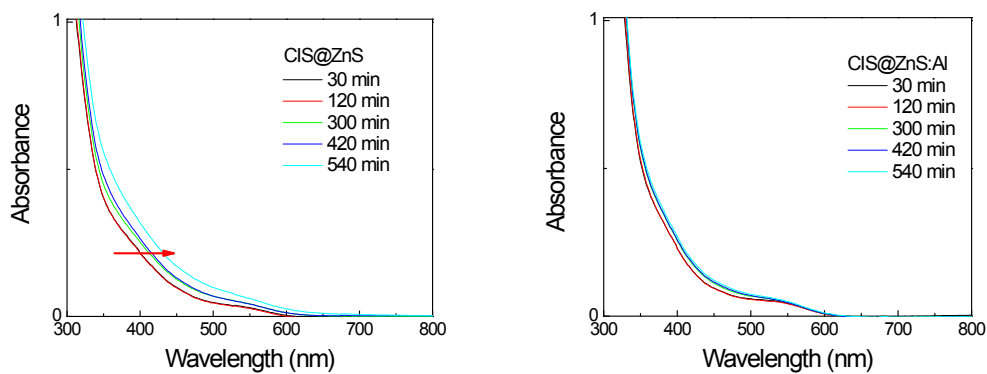
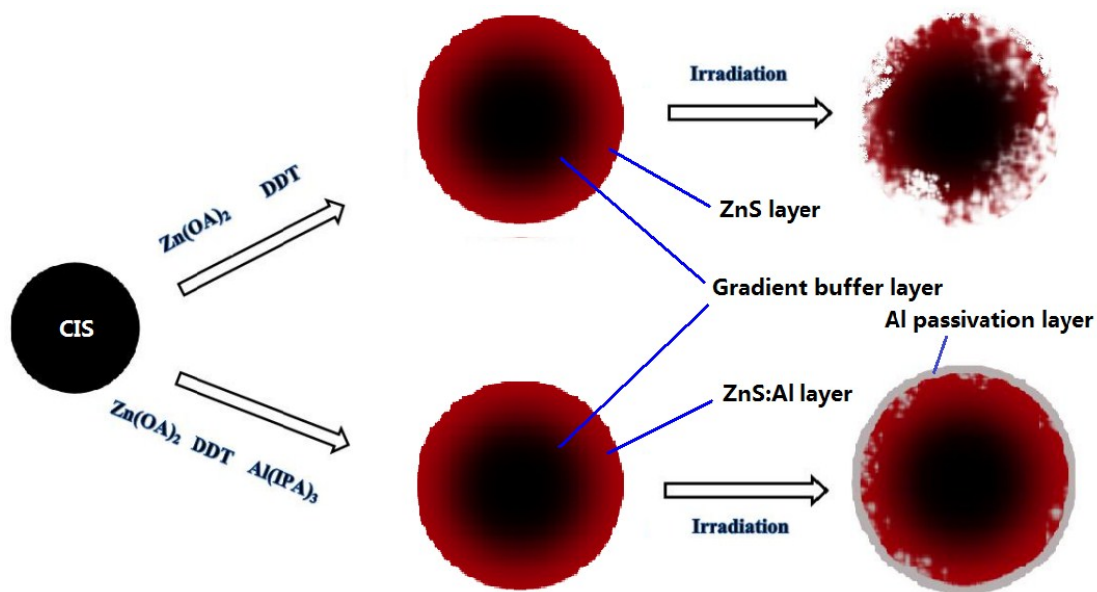


Figure S4 UV-vis absorption spectra of CIS@ZnS and CIS@ZnS:Al QDs during the irradiation



Scheme S2 Schematic illustration for degradation process of CIS@ZnS and CIS@ZnS:Al QDs during irradiation

Figure S5 shows effects of reaction time, i.e., the thickness of ZnS:Al shell, on the photostability of CIS@ZnS:Al QDs. It can be seen that the thickness of ZnS:Al shell significantly affected the photostability of CIS@ZnS:Al QDs. A highest photostability of CIS@ZnS:Al QDs was found when the reaction time was designed at 10h.

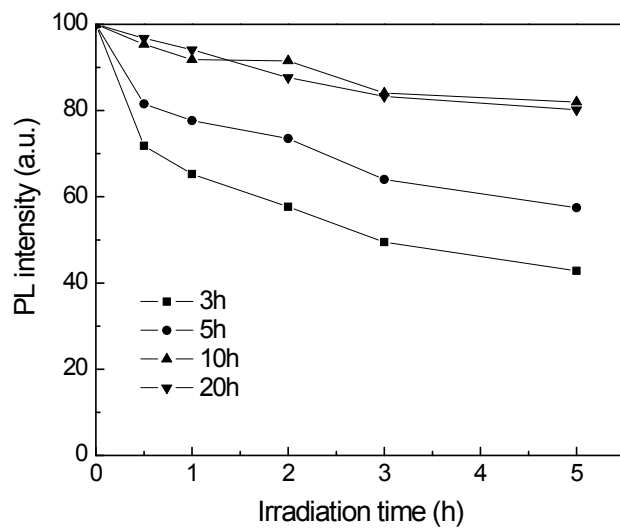


Figure S5 Effects of ZnS:Al overcoating time on the photostability of CIS@ZnS:Al QDs with Al/Zn molar ratio of 0.5

Figure S6 shows quantum yield (QY) of CIS@ZnS:Al QDs with different Al/Zn molar ratios. It can be seen that CIS@ZnS QDs have a higher QY than CIS QDs. The doping of Al had a slight improvement in the QY of CIS@ZnS QDs.

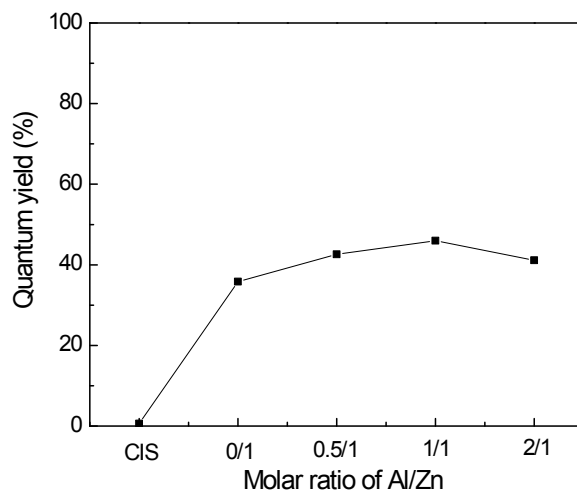


Figure S6 Quantum yield of CIS QDs and CIS@ZnS:Al QDs with the same sizes and different Al/Zn molar ratios

Figure S7 shows that reaction time had a significant effect on the QY of CIS@ZnS:Al QDs. A maximum QY was found when the reaction time was set at 10h.

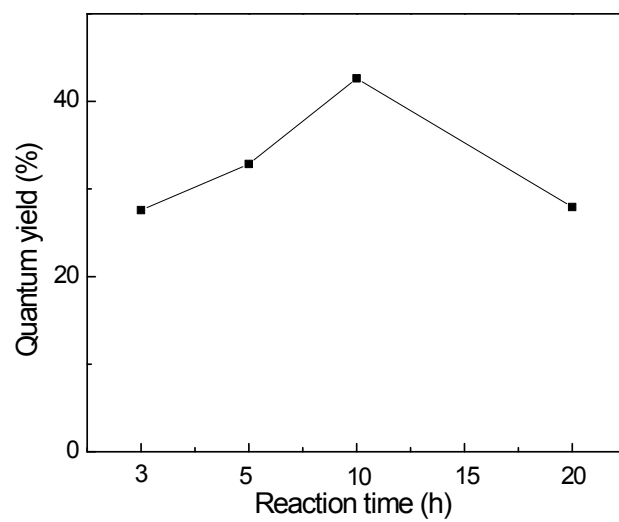


Figure S7 Effects of overcoating time on QY of CIS@ZnS:Al QDs with a Al/Zn molar ratio of 0.5

Figure S8 shows XRD patterns of CIS@ZnS QDs and a series of CIS@ZnS:Al QDs. The results indicated that the diffraction peaks of CIS@ZnS:Al QDs shifted to smaller angle with the increasing of Al doping concentration compared to the undoped QDs even they are in similar size, possibly due to Al alloyed into the lattice of CIS@ZnS QDs.

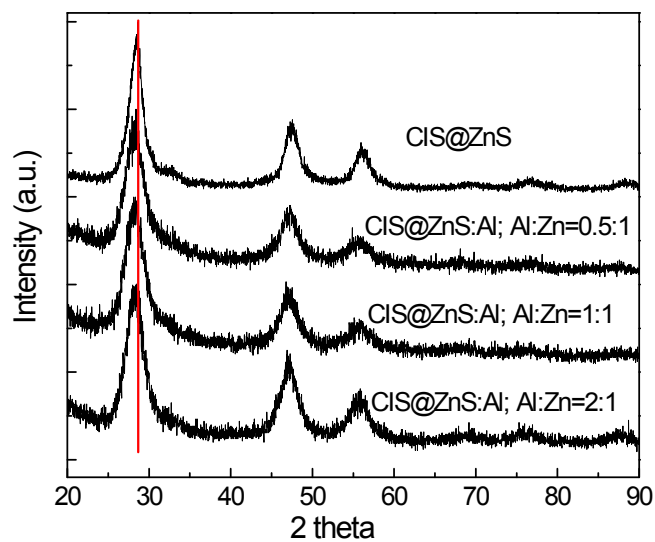


Figure S8 XRD patterns of CIS QDs and CIS@ZnS:Al QDs

XPS spectra of Zn in CIS@ZnS QDs and CIS@ZnS:Al QDs were showed in Figure S9 and Figure S10. It can be seen clearly that, after CIS@ZnS QDs has been irradiated for 5h, the peak corresponding to Zn 2p binding energy shifts towards the right, indicating that Zn mainly existed in the form of ZnO on the surface of CIS@ZnS QDs. However, when Al was doped into CIS@ZnS QDs, the peak corresponding to Zn 2p binding energy basically showed no shift before and after irradiation, indicating stronger photostability of CIS@ZnS:Al QDs and possibly resulting from the formation of Al₂O₃ on the CIS@ZnS:Al QDs due to self-passivation of Al.

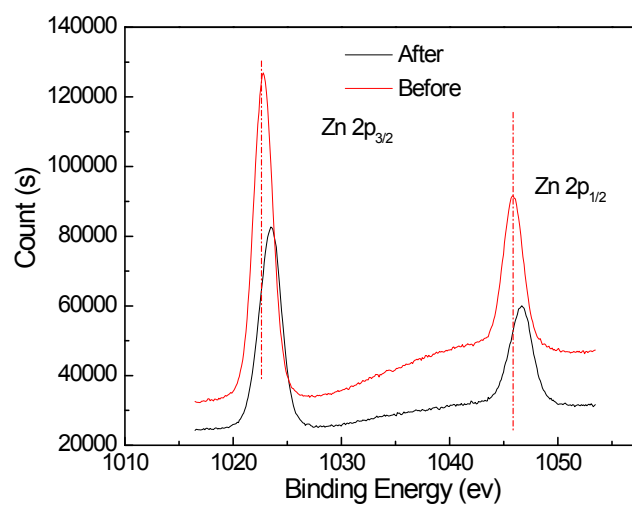


Figure S9 XPS spectra of Zn in CIS@ZnS QDs before and after irradiation

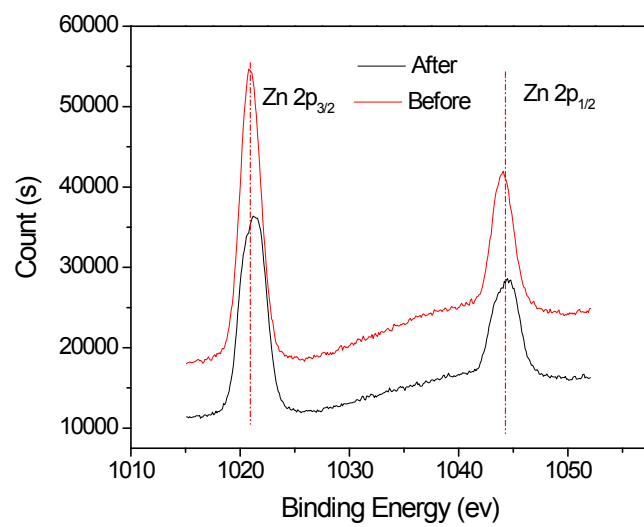


Figure S10 XPS spectra of Zn in CIS@ZnS:Al QDs before and after irradiation. The Al/Zn molar ratio is 0.5

In order to further investigate the applicability of Al doping in enhancing photostability of QDs, we compared the photostability of CIS@CdS QDs with/without Al doping. As shown in Figure S11, after nine-hour irradiation, the photostability of CIS@CdS QDs with Al doping can be improved compared to CIS@CdS QDs without Al doping, indicating that the approach to enhancing QDs photostability by Al doping is a very promising technology.

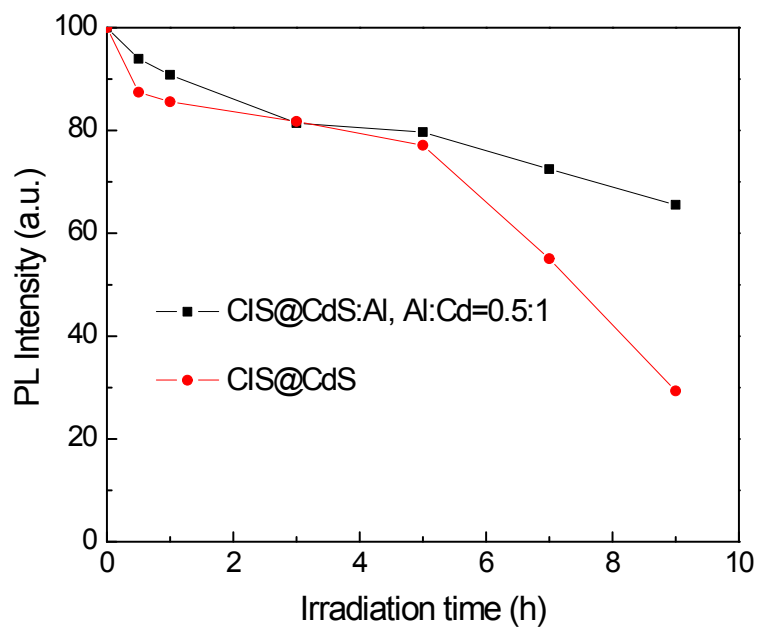


Figure S11 Effects of Al doping on the photostability of CIS@CdS QDs