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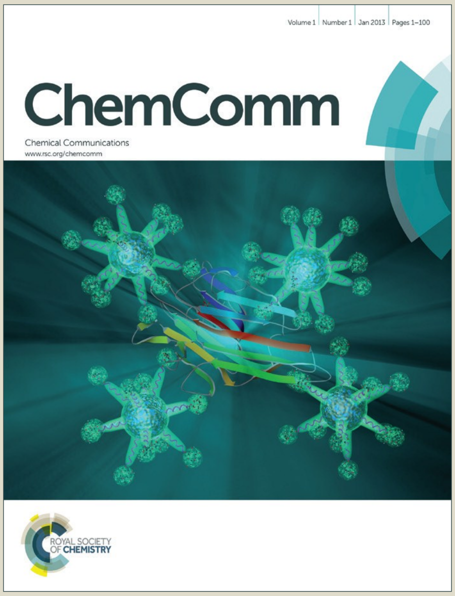

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Highly stable $CuInS_2$@ZnS:Al core@shell quantum dots: role of aluminium self-passivation

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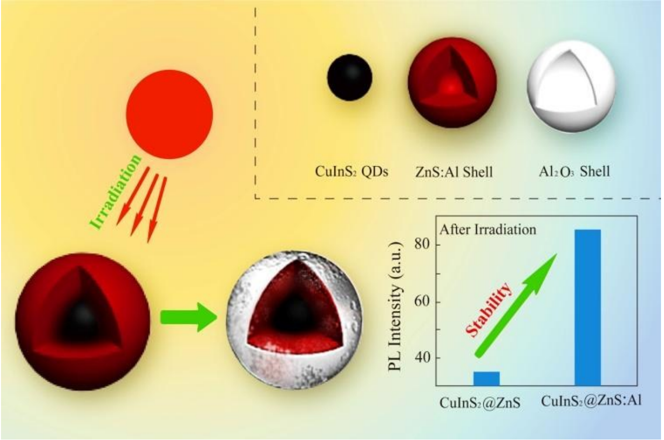
A simple approach was introduced to enhance the photostability of $CuInS_2$@ZnS core@shell quantum dots (QDs) by doping aluminium into ZnS shell. Aluminium in the as-prepared QDs was oxidized to Al_2O_3, which formed a passivation oxide layer that effectively prevents photo-degradation of QDs during long-term light irradiation.

Quantum dots (QDs) with electrical and optical properties are of great interest for fundamental studies[1,2] and technology applications such as light emitting diodes (LEDs),[3,4] solar cells,[5,6] sensors,[7,8] and biomedical labeling.[9,10] During the past decades, inorganic metal chalcogenide QDs including CdS, CdTe, PbS and CdSe have been intensively studied. However, the applications of these QDs in practical devices are limited because of the intrinsic toxicity of cadmium and lead.

$CuInS_2$ (CIS) QDs with a band gap of 1.5 eV, which are cadmium-free and lead-free, have been considered as an emerging alternative for those toxic conventional QDs.[11-13] However, CIS QDs tend to be unstable in air and provide poor fluorescence quantum yield (QY).[14,15] Various methods were developed to enhance the stability of CIS QDs. Kruszynska *et al.* indicated that the organic ligand had an important effect on the stability of CIS QDs.[16] Zhang *et al.* found that Cu/In molar ratio affected the stability of the CIS QDs.[17] Another common method to enhance the stability of CIS QDs is by growing a shell of a higher band gap material to form core@shell structured QDs.[18] ZnS is typically chosen as a shell material for CIS QDs passivation. However, similar to other types of core@shell QDs, CIS@ZnS QDs are also susceptible to the photo-induced degradation. Besides, CIS@ZnS QDs are easily to be hydrolyzed in moisture, which is a general issue for nano-scale and micro-scale sulfides. It was reported that silica-embedded CIS@ZnS QDs could stop the penetration of moisture and air, and thus enhanced the stability of CIS@ZnS QDs,[19] but such an approach usually results in the decrease of QY of QDs. Song *et al.* found that CIS@ZnS QDs overcoated with $ZnGa_2O_4$ showed a strong resistance against photo-stimulated degradation.[20] However, the preparation process was very complicated. Therefore, it is important to find a simple and efficient method to enhance the stability of CIS QDs without altering their optical properties and their sizes related characters.

Self-passivation of material surface is a common phenomenon and generally employed to protect the exposed surface of metals against oxidation and other chemical reactions.[21] For example, Aluminium (Al) is an active metal but very stable in ambient conditions because it usually forms a compact Al_2O_3 protective layer covering the bulk material by self-passivation process. Similar self-passivation was observed on copper alloy and metal Zn in air.[22,23] This phenomenon is also existing on nano-scale materials. It was reported that Al nanoparticles could be stabilized by forming passivation Al_2O_3 layer.[24]

However, rare reports have been found to use the self-passivation technology for improving the photostability of QDs. In this communication, we reported a simple and efficient method to enhance the photostability of QDs by using the self-passivation behavior of Al. Al element was introduced into the shell of ZnS on CIS core, which was oxidized to Al oxides and then formed a passivation layer against further oxidation when the surface ZnS was degraded in ambient conditions or under irradiation (Scheme 1).



Scheme 1 Schematic illustration for enhancing photostability of CIS@ZnS QDs by doping aluminium

Preparation processes of CIS, CIS@ZnS and Al doped CIS@ZnS (CIS@ZnS:Al) QDs as well as characterization methods of as-prepared QDs were given in supporting information. Figure 1 shows the corresponding evolution of the photoluminescence (PL) and UV-vis absorption spectra of the CIS QDs with the overcoating process of Al doped ZnS (ZnS:Al) shell. The PL and UV-vis absorption spectra both blue shift to short wavelength with overcoating, resulting from the diffusion of Zn into CIS core.[14] No significant differences of PL and UV-vis absorption spectra were observed between the QDs with/without doping of Al (Fig. 1 and Fig. S1, ESI†). Figure 2a-d shows TEM images of CIS@ZnS:Al QDs synthesized at the same overcoating time (10h) but with different Al/Zn molar ratios. The four samples show similar sizes around 3.0 nm, which indicates that Al doping had no significant effect on the sizes of CIS@ZnS:Al QDs. Elemental analysis results showed that the Al/Zn molar ratios of three doped samples were 0.075, 0.188 and 0.218 (Tab. S1, ESI†), respectively, lower than nominal Al/Zn molar ratios (0.5, 1, 2). With the increase of the overcoating time, however, the crystal size tended to increase (Fig. S2, ESI†) and (Cu+In)/(Al+Zn) molar ratio of QDs decreased (Tab. S2, ESI†), resulting from the increase of ZnS:Al shell thickness. When the overcoating time was set at 20h, the crystal size was about 4.0 nm.

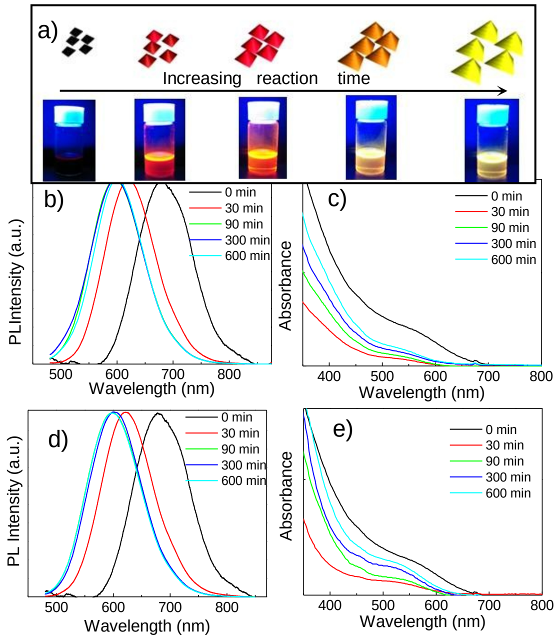


Fig. 1 a) Crystal growth process and color change of CIS@ZnS:Al QDs; b) Photoluminescence (PL) and c) UV-vis absorption spectra of CIS@ZnS QDs; d) PL and e) UV-vis absorption spectra and CIS@ZnS:Al QDs with a Al/Zn molar ratio of 0.5

The photostability of CIS@ZnS:Al QDs with different Al/Zn molar ratios is shown in Fig. 2e. A bare CIS QDs sample was also measured for comparison purposes. The four samples were synthesized by overcoating of ZnS:Al for 10 h, and they have similar sizes that can avoid the effects from shell thickness on photostability. As seen in Fig. 2e, the PL intensities of all samples decrease with the strong irradiation of blue light, and the bare CIS QDs shows the worst photostability among them. It is obvious that the photostability of CIS@ZnS QDs is dramatically enhanced by Al doping, and the sample synthesized with the Al/Zn molar ratio of 0.5 has the best photostability. Possible reason is that too much Al would worsen the intrinsic chemical stability of ZnS:Al and subsequently decrease the photostability of CIS@ZnS:Al QDs due to the unstable Al-S bond. The improvement of photostability of CIS@ZnS:Al QDs also can be reflected from the change of fluorescence peak with irradiation time (Tab. S3, ESI†). During the first 30 min of irradiation, the fluorescence peaks of both CIS@ZnS QDs and CIS@ZnS:Al QDs showed a blue shift (~2nm), which could result from the quenching of the big QDs with more red emission during irradiation (Fig. S3, ESI†). After 30 min irradiation, the fluorescence peak of CIS@ZnS QDs showed a red shift with the increase of irradiation time, possibly due to the further corrosion of the gradient alloyed buffer layer between ZnS and CIS after the spalling of ZnS, which can be confirmed by the red-shift of UV-vis absorption spectra (band gap becomes smaller) of the CIS@ZnS QDs during irradiation (Fig. S4 and Scheme S2, ESI†). 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_2O_3 which prevented the photo-corrosion of ZnS.

Effects of overcoating time, i.e., the thickness of ZnS:Al shell, on the photostability of CIS@ZnS:Al QDs were also studied, and results indicated that the thickness of ZnS:Al shell significantly affected the photostability of CIS@ZnS:Al QDs (Fig. S5, ESI†). A highest photostability of CIS@ZnS:Al QDs was found when the overcoating time was designed at 10 h. Longer overcoating time didn't cause further improvement of the photostability of QDs.

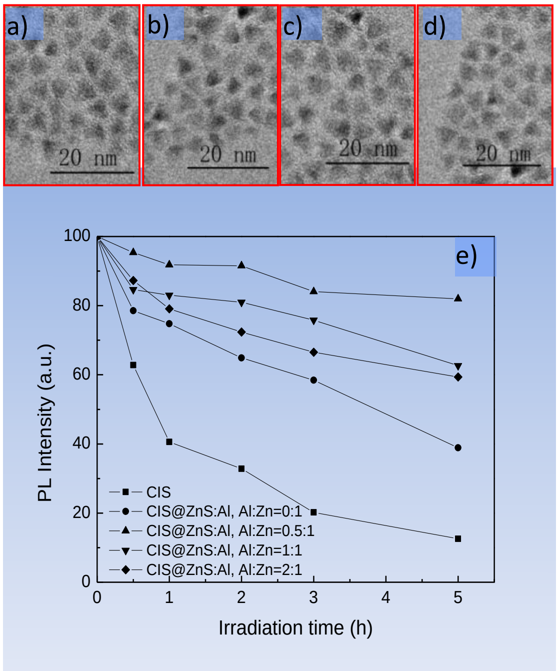


Fig. 2 TEM images of CIS@ZnS:Al QDs with the Al/Zn molar ratios of a) 0, b) 0.5, c) 1, d) 2; e) Effects of Al/Zn molar ratio on the photostability of CIS@ZnS:Al QDs.

The QY of CIS@ZnS:Al QDs was measured using a standard method.[18] It can be seen that the QY of CIS QDs is dramatically improved by the overcoating of ZnS, and the doping of Al into ZnS can further improve the QY of CIS@ZnS QDs (Fig. S6, ESI†). The best sample with the highest QY is that synthesized by overcoating ZnS:Al for 10h (Fig. S7, ESI†), and longer overcoating often worsen their QY. The XRD characterization of QDs with different Al doping levels was conducted and 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 (Fig. S8, ESI†). No mixture of different phases was observed, which indicated that Al precursors didn’t self-nucleate and formed some Al related crystals such as Al_2O_3 crystals.

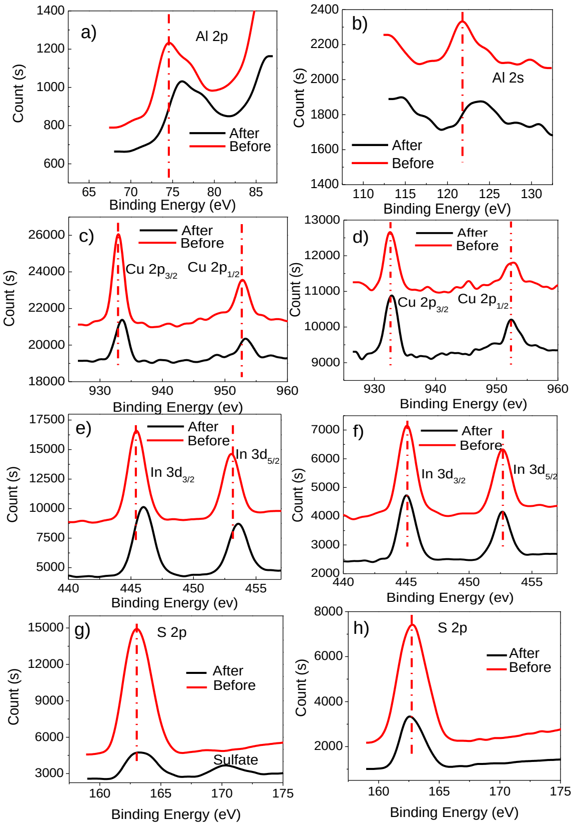


Fig. 3 XPS spectra of a) Al 2p, b) Al 2s, d) Cu 2p, f) In 3d and h) S 2p of CIS@ZnS:Al QDs (Al/Zn molar ratio is 0.5) before and after five-hour irradiation; XPS spectra of c) Cu 2p, e) In 3d and g) S 2p of CIS@ZnS QDs before and after five-hour irradiation.

In order to investigate the mechanism of photostability improvement of CIS@ZnS QDs by Al doping, the changes of the chemical states of the elements (Al, Cu, In, S, Zn) of CIS@ZnS QDs and/or CIS@ZnS:Al QDs before and after irradiation were measured by XPS. As shown in Fig. 3a and 3b, the peaks corresponding to Al 2p and Al 2s binding energy before irradiation are centered at 74.5 eV and 121.8 eV. After CIS@ZnS:Al QDs were irradiated, the peaks corresponding to Al 2p and Al 2s binding energy shifted towards to higher energy, which generally indicated that Al existed mainly in the form of Al-O (Al-OH, Al_2O_3).[25] During the irradiation, CIS@ZnS:Al QDs solutions were heated to 60-70 ℃ because of the high temperature of LED module, which may accelerate the formation of Al oxides on the surface of CIS@ZnS:Al QDs. Nascent Al_2O_3 could act as a passivation layer and inhibit the change of the chemical states of Cu, In, Zn in CIS@ZnS:Al QDs. This speculation was echoed by the XPS spectra of Cu (Fig. 3c and 3d), In (Fig. 3e and 3f) and Zn (Fig. S9 and S10, ESI†). After CIS@ZnS QDs had been irradiated, the chemical states of the elements Cu, In and Zn were changed and peaks corresponding to Cu 2p, In 3d and Zn 2p shifted towards higher energy compared to that before irradiation. However, when CIS@ZnS QDs were doped by Al, the irradiation to as-prepared QDs (i.e., CIS@ZnS:Al QDs) hardly changed the chemical states of the elements Cu, In and Zn, indicating stronger stability of CIS@ZnS:Al QDs which was confirmed by the results of photostability experiments (Fig. 2e). The XPS spectra of S further supported the mechanism of Al_2O_3 as the passivation layer. As observed in Fig. 3g, chemical states of S were changed after CIS@ZnS QDs has been irradiated. A new broad peak occurred near 170.4 eV, corresponding to S-O binding energy of sulfate.[26] However, chemical states of S in CIS@ZnS:Al QDs almost didn’t changed (Fig. 3h), indicating that the anti-oxidation of S was greatly enhanced, resulting from the protection of Al_2O_3 passivation layer on the CIS@ZnS:Al QDs.

FTIR spectra of CIS@ZnS and CIS@ZnS:Al QDs were operated to elucidate further the mechanism of the photostability improvement during irradiation of the as-prepared QDs. As shown in Fig. 4, typical SO_4^{2-} peaks around 1115 cm^{-1}, 1065 cm^{-1} occurred after CIS@ZnS QDs have been irradiated, [27] which indicated that CIS@ZnS QDs was unstable during irradiation. However, the FTIR spectra of CIS@ZnS:Al QDs before and after irradiation just caused a small change, and those two peaks from oxidation of sulfur were not observed in the irradiated sample. That further confirmed the stability improvement of CIS@ZnS QDs by doping Al. The peak about 1380 cm^{-1} was reported to be assigned to both the vibration of Al-O[28,29] or carboxyl group[30,31] from little $Zn(OA)_2$ adsorbed on QDs. While, the peak of CIS@ZnS:Al QDs about 1380 cm^{-1} was broaden compared to that of CIS@ZnS QDs, which was attributed to the overlapping of the vibrations of Al-O and carboxyl group, and it became stronger after irradiation possibly because of the formation of more Al oxides. Unfortunately, no other direct evidences of Al_2O_3 formation were found on the FTIR spectrum of the doped sample after irradiation, so further investigations are needed to be done in the future.

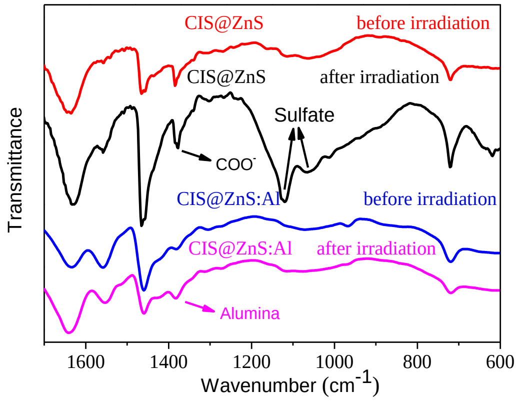


Fig. 4 Effects of five-hour irradiation on FTIR spectra of CIS@ZnS QDs and CIS@ZnS:Al QDs with a Al/Zn molar ratio of 0.5

In order to further investigate the applicability of Al doping in enhancing the photostability of QDs, we doped Al into CdS shell of CIS@CdS QDs using the same approach as above. The photostability test demonstrated that the photostability of CIS@CdS QDs with Al doping was enhanced significantly compared to CIS@CdS QDs without Al doping (Fig. S11, ESI†), indicating that the approach to enhancing QDs photostability by Al doping is not limited in ZnS shell, and can be extended to other shell materials.

Conclusions

A simple approach was developed to enhance the photostability of CIS@ZnS core@shell QDs by doping Al into ZnS shell. Compared to the undoped ones, the photostability of CIS@ZnS:Al QDs was drastically improved without significantly altering their optical properties. According to XPS results, the Al in the as-prepared QDs was confirmed to be oxidized to Al-O, which formed a passivation oxide layer that could effectively prevent photo-degradation of QDs during long-term light irradiation. Al/Zn molar ratio and thickness of doped ZnS shell had significant effects on the photostability of QDs. Such an approach was also confirmed to be applied in enhancing the stability of CIS@CdS QDs and thus would be a very promising technology.

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Notes and references

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