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

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A simple approach was introduced to enhance the photostability of CuInS₂@ZnS core@shell quantum dots (QDs) by doping aluminium into the ZnS shell. Aluminium in the as-prepared QDs was oxidized to Al₂O₃, 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 few 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.

CuInS₂ (CIS) QDs with a band gap of 1.5 eV, which are cadmium-free and lead-free, have been considered as emerging alternatives for the toxic conventional QDs.¹¹⁻¹⁴ However, CIS core-only QDs tend to be unstable in air and provide poor fluorescence quantum yield (QY).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 the 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 QD passivation. However, similar to other types of core@shell QDs, CIS@ZnS QDs are also susceptible to photo-induced degradation. Besides, CIS@ZnS QDs are easily 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 ZnGa₂O₄ showed 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 size 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 (AI) is an active metal but very stable under ambient conditions because it usually forms a compact Al_2O_3 protective layer covering the bulk material by the self-passivation process. Similar self-passivation was observed for 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 an Al_2O_3 passivation 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. The Al element was introduced into the shell of ZnS on the CIS core, which was oxidized to Al oxides and then formed a passivation layer against further oxidation when the surface ZnS was degraded under ambient conditions or under irradiation (Scheme 1).

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 the ESI.† Fig. 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 a short wavelength with overcoating, resulting from the diffusion of Zn into the CIS core.¹⁴ No significant differences in PL and UV-vis absorption spectra were observed between the QDs with/without doping of Al (Fig. 1 and Fig. S1, ESI†). Fig. 2a–d shows TEM images of CIS@ZnS:Al QDs synthesized at the same overcoating time (10 h) but with

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



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.

different Al/Zn molar ratios. The four samples show similar sizes at 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 (Table 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 the (Cu + In)/(Al + Zn) molar ratio of QDs decreased (Table S2, ESI[†]), resulting from the increase of ZnS:Al shell thickness. When the overcoating time was set at 20 h, the crystal size was about 4.0 nm.

The photostability of CIS@ZnS:Al QDs with different Al/Zn molar ratios is shown in Fig. 2e. A bare CIS QD sample was also



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

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 strong irradiation of blue light, and the bare CIS QDs show 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. The possible reason is that too much of 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 the photostability of CIS@ZnS:Al QDs can also be reflected from the change in the fluorescence peak with irradiation time (Table 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 (~ 2 nm), 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 Al₂O₃ which prevented the photo-corrosion of ZnS.

The effects of overcoating time, *i.e.*, the thickness of the ZnS:Al shell, on the photostability of CIS@ZnS:Al QDs were also studied,

and the results indicated that the thickness of the ZnS:Al shell significantly affected the photostability of CIS@ZnS:Al QDs (Fig. S5, ESI[†]). The highest photostability of CIS@ZnS:Al QDs was found when the overcoating time was designed at 10 h. Longer overcoating time did not cause further improvement of the photostability of 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 10 h (Fig. S7, ESI†), and longer overcoating often worsens 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 a smaller angle with the increase of Al doping concentration compared to the undoped QDs even though they are of 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 did not self-nucleate and formed some Al related crystals such as Al₂O₃ crystals.

In order to investigate the mechanism of photostability improvement of CIS@ZnS QDs by Al doping, the changes in the chemical states of the elements (Al, Cu, In, S, and 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 b, 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 or Al₂O₃).²⁵ During irradiation, CIS@ZnS:Al QD solutions were heated to 60-70 °C because of the high temperature of the LED module, which may accelerate the formation of Al oxides on the surface of CIS@ZnS:Al QDs. Nascent Al₂O₃ 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 d), In (Fig. 3e and f) 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 the 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 Al₂O₃ 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 did not change (Fig. 3h), indicating that the anti-oxidation of S was greatly enhanced, resulting from the protection of the Al₂O₃ passivation layer on the CIS@ZnS:Al QDs.

The FTIR spectra of CIS@ZnS and CIS@ZnS:Al QDs were recorded to further elucidate the mechanism of the photostability



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.



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.

improvement during irradiation of the as-prepared QDs. As shown in Fig. 4, typical SO_4^{2-} peaks at around 1115 cm⁻¹ and 1065 cm⁻¹ occurred, after CIS@ZnS QDs have been irradiated,²⁷ which indicated that CIS@ZnS QDs were 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 obtained from oxidation of sulfur were not observed in the irradiated sample. This further confirmed the stability

improvement of CIS@ZnS QDs by doping Al. The peak at about 1380 cm⁻¹ was reported to be assigned to both the vibration of Al– $O^{28,29}$ or the carboxyl group^{30,31} from little zinc oleate adsorbed on QDs while the peak of CIS@ZnS:Al QDs at about 1380 cm⁻¹ was broad compared to that of CIS@ZnS QDs, which was attributed to the overlapping of the vibrations of Al–O and the carboxyl group, and it became stronger after irradiation possibly because of the formation of more Al oxides. Unfortunately, no other direct evidence of Al₂O₃ formation was found on the FTIR spectrum of the doped sample after irradiation, so further investigations are needed to be done in the future.

In order to further investigate the applicability of Al doping in enhancing the photostability of QDs, we doped Al into the 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 the photostability of QDs by Al doping is not limited to the ZnS shell, and can be extended to other shell materials.

A simple approach was developed to enhance the photostability of CIS@ZnS core@shell QDs by doping Al into the 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. The Al/Zn molar ratio and thickness of the 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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