General Method for the Synthesis of Ultrastable Core/Shell Quantum Dots by Aluminum Doping

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S *Supporting Information*

ABSTRACT: Semiconductor quantum dots (QDs) have attracted extensive attention in various applications because of their unique optical and electronic properties. However, long-term photostability remains a challenge for their practical application. Here, we present a simple method to enhance the photostability of QDs against oxidation by doping aluminum into the shell of core/shell QDs. We demonstrate that Al in the coating shell can be oxidized to Al_2O_3, which can serve as a self-passivation layer on the surface of the core/shell QDs and effectively stop further photodegradation during long-term light irradiation. The prepared CdSe/CdS:Al QDs survived 24 h without significant degradation when they were subjected to intense illumination under LED light (450 nm, 0.35 W/cm^2), whereas conventional CdSe/CdS QDs were bleached within 3 h.

Semiconductor quantum dots (QDs), which exhibit excellent photoluminescence (PL) quantum yields (QYs), size-tunable emission color, and solution processability, are highly favorable for many applications such as in light-emitting diodes (LEDs), solar cells, sensors, and biomedical labeling.[1−6] However, QDs suffer from poor chemical-/photo-stability against air and moisture, which hinders their actual application and commercialization. Over the past few decades, various approaches have been developed to improve the stability of these QDs. Coating a second semiconductor layer onto QDs was demonstrated to be a powerful method to improve the photostability and QYs of QDs. Hines reported that coating a few monolayers (MLs) of ZnS improved the QYs of CdSe from a few percent to 50%,[7] and dramatically enhanced the stability of PL. However, the originally high QYs of these conventional core/shell QDs are substantially reduced after repeated cycles of purification or ligand exchange of the QDs. Some researchers developed a type of ultrastable QDs known as "giant dots" by coating a CdSe core with multiple MLs (11−20) of CdS.[8,9] These giant dots exhibit excellent chemical and photostabilities and can survive several days under continuous laser irradiation. However, giant dots are intrinsically a sulfide and supposedly have the same issue as conventional sulfide phosphors, which are easily hydrolyzed in the presence of moisture and usually require further protection. Silica coatings have been used to stop the penetration of water and oxygen and to consequently improve the photostability of QDs and phosphors.[10,11] However, silica coatings via Stöber process generally reduce the QYs of QDs.[12] In addition, silica-coated QDs are usually large (up to 20−100 nm) and not well suited for bioimaging applications because they tend to become trapped in vesicles.[13] Thus, the stability of QDs must be improved by coating a thin layer with robust barrier properties against moisture and air (oxygen); that is, the QDs must be smaller but more stable.

Self-passivation was observed in several metals hundreds of years ago. When exposed to air, many metals, including aluminum,[14] chromium,[15] zinc,[16] titanium,[17] and silicon (metalloid),[18] naturally form a hard, relatively inert surface, that can notably slow corrosion of the metal in ambient air. This phenomenon has been widely used in metallurgy to make stainless steel and other alloy metals to avoid corrosion and oxidation. Recently, this phenomenon was also found on some nanoscale materials. It was reported that graphene QDs and silicon QDs could be stabilized by a self-passivation layer of their corresponding oxides.[19,20] However, almost no reports have been found to use self-passivation for improving the stability of conventional II−VI and III−V QDs.

In this communication, a convenient method was developed to improve the photostability of CdSe/CdS QDs by simply doping Al into the shell of the QDs. The doping of Al was observed to not alter the optical properties of the QDs, which maintained their unique properties such as their small size, high QYs, and narrow emission width. More impressively, "small" CdSe/CdS:Al QDs (6.2 ± 0.6 nm) with a coating of 4 MLs of Al-doped CdS are even more stable than 14 ± 1.2 nm giant dots, which are coated with approximately 17 MLs of CdS (Supporting Information Figure S1).

To synthesize CdSe/CdS:Al QDs, cadmium oleate and aluminum isopropoxide mixed with 1-dodecanethiol, which was diluted in 1-octadecene, were separately injected into presynthesized CdSe QDs solution under nitrogen bubbling.[21,22] The low-boiling byproducts, such as isopropyl alcohol, were purged. The nominal Al doping concentration in the resultant QDs was controlled via the dosage of the Al precursor (Al/Cd molar ratio). Figure 1 panels A and B (Figure S2) show TEM images of the undoped and doped CdSe/CdS QDs prepared using a coating time of 10 h and various nominal doping concentrations. All QDs exhibit a similar size of approximately 8.0 nm. The Al doping did not significantly alter the growth kinetics of the CdSe/CdS QDs (Figures S2 and S3). Notably, no byproducts such as Al_2O_3 crystals were observed in the HRTEM images of any of the doped samples. To clarify how much Al was incorporated into the CdS shell, we performed elemental analysis using energy-dispersive X-ray
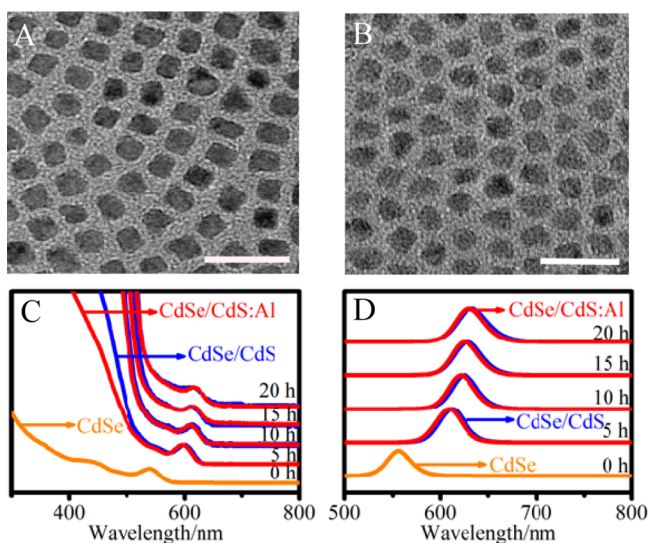
Figure 1. TEM images of (A) CdSe/CdS QDs and (B) CdSe/CdS:Al QDs (scale bars = 20 nm) with a coating time of 10 h. The normalized absorption (C) and PL spectra (D) are shown for CdSe/CdS QDs and CdSe/CdS:Al QDs that were synthesized at different coating times.

spectroscopy (EDX) and inductive coupled plasma emission spectrometry (ICP) (Table S1). When the Al nominal doping concentrations (Al/Cd) were 0, 0.5, 1, and 2, the Al/Cd molar ratios in the samples prepared using a coating time of 10 h were 0, 0.082, 0.11, and 0.16, respectively. These doping levels were achieved in the Al-doped CdS shell because of the formation of the alloy $Cd_{1-x}Al_xS$ ($x \approx 0-18\%$).[23] This result strongly indicates that only a small quantity of the Al atoms in the reaction solution was incorporated into the CdS lattice. To exclude the effects from the unreacted precursors and byproducts, we washed the samples with pyridine several times to remove the precursors and byproducts adsorbed onto the QDs' surface, and tested them again (Tables S2 and S3), which indicated that most of the Al remained in the resultant QDs. In addition, an etching experiment following ICP tests was done to further prove that Al atoms were really incorporated into the lattice of CdS. As shown in Figure S4, the absorption spectra of the CdSe/CdS:Al QDs blueshifted to shorter wavelength with the etching of HCl, where the surface CdS:Al were peeled off layer by layer (Figure S4). The ICP results (Table S4) showed that the Al/Cd ratio of the supernatants for the etched samples at different etching times kept constant within little deviation, which is strong evidence of the even distribution of Al atoms into the CdS shell.

Figure 1 panels C and D show the evolution of the absorption and PL spectra of CdSe/CdS QDs and CdSe/CdS:Al QDs (Al/Cd = 0.5) with the coating time. Both the PL and absorption peaks are red-shifted to longer wavelength because of the weak exciton confinement of the CdS shell.[22] No significant differences were observed in the absorption and PL spectra between the cases without and with doping of Al. The XRD pattern of CdSe/CdS and CdSe/CdS:Al QDs exhibited three preferential peaks assigned to (111), (220), and (311), which corresponded to the zinc-blende phase of CdS material (Figure S5). The position of the (111) peak slightly shifted to a larger angle with the increase of Al doping concentration in comparison to that of the CdSe/CdS QDs with similar sizes, possibly due to Al doped into the lattice of CdS.[24] The QYs of CdSe/CdS QDs and CdSe/CdS:Al QDs were measured using a

standard method (Figure S6).[25] Interestingly, the doping of Al into the CdS shell improved the QYs of the CdSe/CdS QDs, and the improvements varied with the nominal Al doping concentration.

For the application of QDs in practical devices such as LEDs, high photostability of the QDs under irradiation by a high-energy excitation source is critical. We performed photostability tests of CdSe/CdS:Al QDs on a blue LED module with 0.35 W/cm² light intensity (peak at 450 nm, Philips Fortimo). The CdSe/CdS:Al QDs with similar sizes (average diameter: 8.0 nm) (Figure S2) but different nominal doping concentrations were selected to avoid the effects from the shell thickness, and they were carefully prepared to achieve comparable optical densities in toluene (sealed vial). Figure 2A shows that the
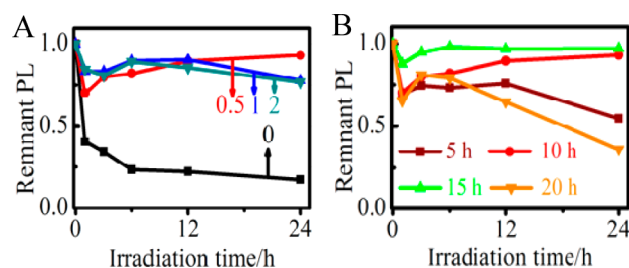

Figure 2. (A) Photostability of the CdSe/CdS:Al QDs with similar sizes of 8.0 nm but various nominal doping concentrations (Al/Cd = 0, 0.5, 1, 2); (B) photostability of the CdSe/CdS:Al QDs at identical nominal doping concentration (Al/Cd = 0.5), but different coating times.

photostability of the QDs was obviously improved when Al was doped into the CdS shell. The sample with a nominal doping concentration (Al/Cd ratio) of 0.5 was the most stable sample among those tested samples, and its emission was maintained at approximately 93% of the initial intensity for 24 h of operation; in contrast, the emission from the undoped CdSe/CdS QDs decreased to approximately 34% of the initial intensity in 3 h. But the further increasing of the Al/Cd molar ratio (1 and 2) did not further improve the photostability of CdSe/CdS:Al QDs. The possible reason was that too much of Al would worsen the intrinsic chemical stability of CdS:Al and subsequently decrease the photostability of CdSe/CdS:Al QDs due to the unstable Al–S bond. The PL intensity of all doped QDs sharply decreased in the first 1 h of irradiation, perhaps because the self-passivation layer did not form at this stage and could not provide good protection. With further irradiation, the PL intensity of the doped samples began to stabilize and even increased because of the photobrightening effect.[26,27] In contrast, the PL intensity of the undoped CdSe/CdS QDs continuously decreased to approximately 17% of the initial intensity within 24 h of operation. This relative instability is attributed to the photoinduced degradation (presumably photo-oxidative degradation) of the CdSe/CdS QDs. In addition to the nominal doping concentration, the thickness of the coating shell also plays an important role in determining the photostability. Figure 2B shows the photostability tests of the four samples that were synthesized with identical nominal doping concentrations but different thickness values (coating times) (Figure S3). To our surprise, the most stable sample was not the sample with the thickest shell, but the sample that was synthesized when the coating time was 15 h; the size of this sample was approximately 11.4 ± 0.8 nm, and its emission was almost constant during 24 h of blue-light irradiation. When the

coating shell was too thick, the QDs generally deteriorated as a consequence of strain induced by the lattice mismatch of the core and shell materials, accompanied by the generation of defect states, and then reduced stability.[2] Considering the operating temperature in the real LED application, the thermal stability of CdSe/CdS:Al QDs and CdSe/CdS QDs in the solid state were also tested at 100 and 150 °C(Figure S7), and the CdSe/CdS:Al QDs exhibited much better performance compared with the undoped QDs; it was likely that the formed aluminum oxide layer partly insulated the thermal oxidation of QDs.

The degradation of QDs upon irradiation has been extensively studied[28,29] and has been hypothesized to be a consequence of direct surface oxidation by air. Figure 3 shows
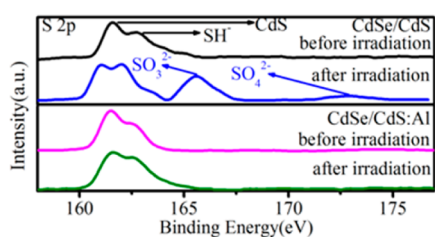

Figure 3. S 2p XPS spectra of the CdSe/CdS QDs and CdSe/CdS:Al QDs before and after light irradiation.

the X-ray photoelectron spectroscopy (XPS) spectra of the CdSe/CdS QDs samples before and after light irradiation. The peaks of S 2p at 161.6 and 162.8 eV were attributed to CdS and thiols adsorbed onto CdSe/CdS QDs, respectively.[30] After light irradiation, another two peaks emerged at higher energies: a strong peak at 165.6 eV,[31] which is associated with the SO_3^{2-} group, and a weak peak at 173.4 eV, which is usually assigned to SO_4^{2-} group.[32] These two peaks might originate from the oxidation of sulfur. In contrast, the XPS spectra of the CdSe/CdS:Al QDs showed almost no changes after light irradiation. These results strongly indicated that the doping of Al dramatically improved the photostability of CdSe/CdS QDs, as expected.

Figure 4A shows the obtained Al 2p XPS spectra. The Al 2p peak appeared at 74.6 eV, which may be associated with
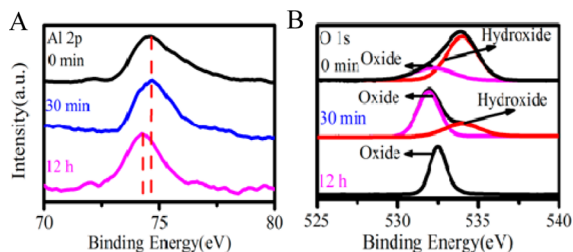

Figure 4. XPS spectra of the (A) Al 2p and (B) O 1s of CdSe/CdS:Al QDs (irradiation of 0 min, 30 min, and 12 h).

oxidized aluminum species such as Al−S or Al−O;[33,34] however, these species are difficult to distinguish on the basis of comparisons to results in the NIST XPS database. After irradiation, we observed that the peak shifted to a smaller binding energy (74.3 eV), which may be related to reactions such as the transformation from Al−S to Al−O or from Al−OH to Al−O.

To clarify the transformation from hydroxides to oxides under light irradiation, we conducted a careful XPS study on the O 1s peaks (Figure 4B). The O 1s peak of CdSe/CdS:Al (0 min of irradiation) was located at 533.8 eV. We deconvoluted the spectra into two peaks with the binding energies of 532.2 and 534.0 eV. The peak at 532.3 eV is generally attributed to oxygen in the Al−O bonds of aluminum oxide, and the other at 534.0 eV is attributed to oxygen in the Al−OH bonds of aluminum hydroxide.[35,36] Before irradiation, aluminum hydroxides were the primary contributor to the O 1s peak; however, with increasing irradiation from 0 to 30 min, the Al−O peak curve contribution increased, which suggested that aluminum hydroxide gradually converted into aluminum oxide via dehydration with increasing irradiation time. After 12 h of irradiation, the O 1s peak of the Al−OH bonds of aluminum hydroxide almost completely disappeared, and the O 1s peak of Al−O was a narrow peak at 532.4 eV. This phenomenon is consistent with the aforementioned initial emission decrease in the first 1 h of irradiation and subsequent gradual stabilization.

A simple model is schematically proposed to explain the aforementioned phenomenon related to CdSe/CdS:Al QDs in Figure 5. The EDX, ICP, and XRD results demonstrated that

Figure 5. Schematic illustration for transformation process from aluminum hydroxide to aluminum oxide.

the Al was actually incorporated into the CdS shell during the coating process. After the synthesis, the prepared doped samples were purified by repeated washing and precipitation and finally dispersed into toluene. We speculated that the Al on the surface of the QDs was automatically transformed into aluminum oxidation products during these post-treatments in air and was most likely in hydroxide forms. When the doped samples were irradiated with strong blue light, the samples were heated to 60−70 °C by an LED module and the dehydration of aluminum hydroxides to oxides was accelerated. However, in the first 1 h, the compact oxide protecting layer had not formed; therefore, the PL sharply decreased during this term. The aluminum hydroxides were then almost completely transformed to aluminum oxides, which formed a compact layer on the surface of the QDs, and the PL peak and intensity were stabilized thereafter.

Figure 6 shows the FTIR spectra of the CdSe/CdS:Al QDs with different irradiation times. A new band at 800 cm⁻¹ was
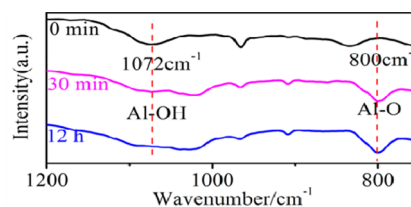

Figure 6. FTIR spectra of CdSe/CdS:Al QDs (0 min, 30 min, and 12 h of irradiation).

observed after irradiation; this band is related to the Al−O vibration in aluminum oxide.[37] Additionally, the band at 1072 cm^{-1} corresponds to Al−OH in the CdSe/CdS:Al QDs,[38] which became weaker with increasing irradiation time. This band may confirm that the aluminum oxide originated from the dehydration of Al−OH, which is consistent with the XPS results.

To test that our Al-doping strategy is a universal method to improve the photostability of QDs, we attempted to use this strategy to synthesize CdSe/ZnS:Al QDs and CdSe:Al QDs. In both cases, similar photostability improvement was observed when the QDs were exposed to high-intensity blue light in ambient air (Figures S8 and S9). In addition, an etching experiment following the ICP test further proved that the Al atoms were really incorporated into the CdSe QDs(Figure S10 and Table S5).

In conclusion, we have developed a simple approach to enhance the photostability of core/shell CdSe/CdS QDs by doping aluminum (Al) into the shell. The drastic improvement in photostability is attributed to the self-passivation characteristics of Al in the shell, which is possibly oxidized to aluminum oxide and acts as a protective layer to prevent the photo-degradation of the QDs. We also demonstrated that this strategy could be applied to other QD systems and even to core QDs. Because Al can be doped into numerous semiconductors, we believe that this strategy represents a universal approach to improve the photostability of QDs. Furthermore, our strategy enables the possible synthesis of smaller but more stable ideal QDs for in vivo imaging.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05462.

> Supporting figures, tables, and detailed experimental procedures, including the synthesis process; details related to the photostability of the CdSe/ZnS:Al QDs, CdSe:Al QDs; TEM, XRD, QYs, ICP, and EDX (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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