

Supplementary Information

Sacrificial Oxidizing of Self-Metal Source for the Rapid Growth of Metal Oxides on Quantum Dots towards Improving Photostability

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Experimental Section

Materials. 1-dodecanethiol (DDT, 98%, Aladdin), 1-octadecene (ODE, 90%, Aladdin), cadmium oxide (CdO, 99.5%, Aldrich), oleic acid (OA, 90%, Aldrich), n-butylamine (99%, Aldrich), oleylamine (OLA, 90%, Aldrich), trioctylphosphine (TOP, 90%, Aladdin), selenium (Se, 99%, Aldrich), aluminum isopropoxide (99.99%, Aladdin), chromium acetate (Cr(Ac)₃, 99%, Aldrich), n-propyl zirconate (80 wt. %, Aladdin), copper iodide (CuI, 99.95%, Aladdin), indium acetate (In(Ac)₃, 99.99%, Alfa Aesar), zinc acetate (Zn(Ac)₂, 99%, Aladdin), benzoyl peroxide (BPO, 98%, Aladdin), ferrocene (99%, Aldrich), hydrofluoric acid (HF, 40%, Aladdin), toluene (98%, Aladdin), acetone (99.5%, Sinopharm Chemical Reagent Co. Ltd, China). All the chemicals were used without further purification.

Synthesis of CdSe core QDs. CdO (16 mmol), ODE (40 mL), and OA (16 mL) were mixed in a three-neck flask (250 mL) equipped with a reflux condenser and a thermocouple probe. The reaction system was degassed at 120 °C for 1 h, and then further heated to 270 °C under nitrogen flow to form an optically clear solution, following which a mixture of 8 mmol of TOP–Se was quickly injected into the solution. After the injection, the temperature was set at 240 °C for the growth of the nanocrystals. After three minutes, the solution was cooled down to room temperature, and then CdSe QDs were washed three times with acetone and toluene, and stored in toluene as stock solution.

Preparation of Cd(OA)₂ precursors. CdO (175 mmol), ODE (175 mL), and OA (175 mL) were mixed in a three-neck flask (500 mL) under magnetic stirring. The reaction system was evacuated at 120 °C for 1 h, and then further heated to 250 °C under nitrogen flow to form an optically clear solution. Then, the solution was cooled down to room temperature, and stored as stock solution.

Synthesis of Al doped CdSe/CdS core–shell QDs. Briefly, the washed CdSe core solution (0.8 mmol, cadmium atomic concentration) was dispersed into 40mL ODE in a three-neck flask (250 mL), and pumped down for 1 h to remove the toluene at 120 °C. The reaction temperature was raised to 280 °C under a nitrogen atmosphere. Starting at 230 °C, precursor solutions of Cd(OA)₂ (0.5 mmol/mL) and aluminum isopropoxide mixed DDT (0.6 mmol/mL) diluted in ODE were injected from separate syringes pump at a rate of 3.2 mL/h.

Preparation of Cr(OA)₃ precursors. Cr(Ac)₃ (175 mmol) was added into a three-neck flask containing OA (175 mL), and ODE (175 mL). The reaction system was evacuated at 120 °C for 1 h, and then further heated to 250 °C under nitrogen flow to form an optically transparent solution, then stored as a stock solution after cooling down to room temperature.

Synthesis of Cr doped CdSe/CdS core–shell QDs. The washed CdSe core solution (0.8 mmol, diluted to 40mL with ODE) was added into a three-neck flask (250 mL), and evacuated for 1 h at 120 °C under magnetic stirring. The reaction temperature was raised to 280 °C under a nitrogen atmosphere. Starting at 230 °C, precursor solutions of Cd(OA)₂ (0.5 mmol/mL) and Cr(OA)₃ mixed DDT (0.6 mmol/mL) diluted in ODE were injected from separate syringes pump at a rate of 3.2 mL/h.

Synthesis of Zr doped CdSe/CdS core–shell QDs. The washed CdSe core solution (0.8 mmol, diluted to 40mL with ODE) was added into a three-neck flask (250 mL), and evacuated for 1 h at 120 °C under magnetic stirring. The reaction temperature was raised to 280 °C under a nitrogen atmosphere. Starting at 230 °C, precursor solutions of Cd(OA)₂ (0.5 mmol/mL) and n-propyl zirconate mixed DDT (0.6 mmol/mL) diluted in ODE were injected from separate syringes pump at a rate of 3.2 mL/h.

Synthesis of CuInS₂ (CIS) core QDs. A 500 mL three-neck flask equipped with a reflux condenser and a thermocouple probe was charged with CuI (2.8 g), In(Ac)₃ (4.5 g), OLA (15 mL), DDT (145 mL), and ODE (145 mL) under magnetic stirring. The mixture was degassed at 120 °C for 1 h, then further heated to 230 °C under a nitrogen atmosphere. After 40 minutes, the solution was cooled down to room temperature, and then CIS QDs were washed three times with acetone and toluene, and stored in toluene as stock solution.

Preparation of Zn(OA)₂ precursors. Zn(Ac)₂ (32.11 g), ODE (210 mL), OA (105 mL), and n-butylamine (35 mL) were mixed in a three-neck flask (500 mL) under magnetic stirring. The reaction system was heated to 120 °C and refluxed for 1 h to form an optically clear solution. Then, the solution was cooled down to room temperature, and stored as stock solution.

Synthesis of Al doped CIS/ZnS core–shell QDs. The washed CIS core solution (0.8 mmol) was

dispersed into 40 mL ODE in a three-neck flask, and evacuated for 1 h at 120 °C. The reaction temperature was raised and maintained at 230 °C under a nitrogen atmosphere to allow the growth of shell. Precursor solutions of Zn(OA)₂ (0.5 mmol/mL) and aluminum isopropoxide mixed DDT (0.6 mmol/mL) diluted in ODE were injected from separate syringes pump at a rate of 3.2 mL/h.

Benzoyl peroxide (BPO) treatment. BPO was firstly dissolved into toluene (0.01 mmol/mL). The diluted BPO solution was slowly added into CdSe/CdS:Al QDs solution (15 mg/mL, Abs_{600 nm} = 2) at room temperature. The mixture was then incubated in water bath at 60 °C. After 2 h, the solution was cooled down to room temperature, and then washed three times with acetone and toluene, and stored in toluene. Treatment with other QDs systems was similar.

Characterization. The high-resolution transmission electron microscope (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were characterized using the FEI Talos F200X TEM instruments operated at an accelerating voltage of 200 kV. X-ray powder diffraction (XRD) patterns of samples were performed on a Bruker D8 Advance X-ray Diffractometer at 40 kV and 40 mA using Cu K_α radiation ($\lambda=1.5406 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) analysis was collected by a Kratos Axis Ultra-DLD spectrometer, and all the spectra were calibrated to the C 1s peak at 284.8 eV. UV-vis absorption spectra were recorded on a Cary-60 UV-vis spectrophotometer. Photoluminescence (PL) spectra were measured by using an F-380 fluorescence spectrometer (Tianjin Gangdong Sci. & Tech. Development Co., Ltd., China). Photoluminescence quantum yield were obtained using an integrating sphere with a Hamamatsu Quantaury-QY Absolute PL quantum yield spectrometer (Model: C11347-11). Electron spin resonance (ESR) analysis was performed on a JEOL JES FA200 spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation. Nuclear magnetic resonance (NMR) measurements were performed using a Bruker Avance III 600 spectrometer.

Photostability test. The photostability measurements were analyzed using bottom-transparent airtight quartz colorimetric cuvettes containing 3 mL of the colloidal QD solutions with same absorbance (Abs_{450 nm} = 0.27). Every periodic interval, the PL and UV-vis absorption spectra of the colloidal QD solutions after illuminating with 450 nm LED light (175 mW/cm², Philips Fortimo)

were recorded.

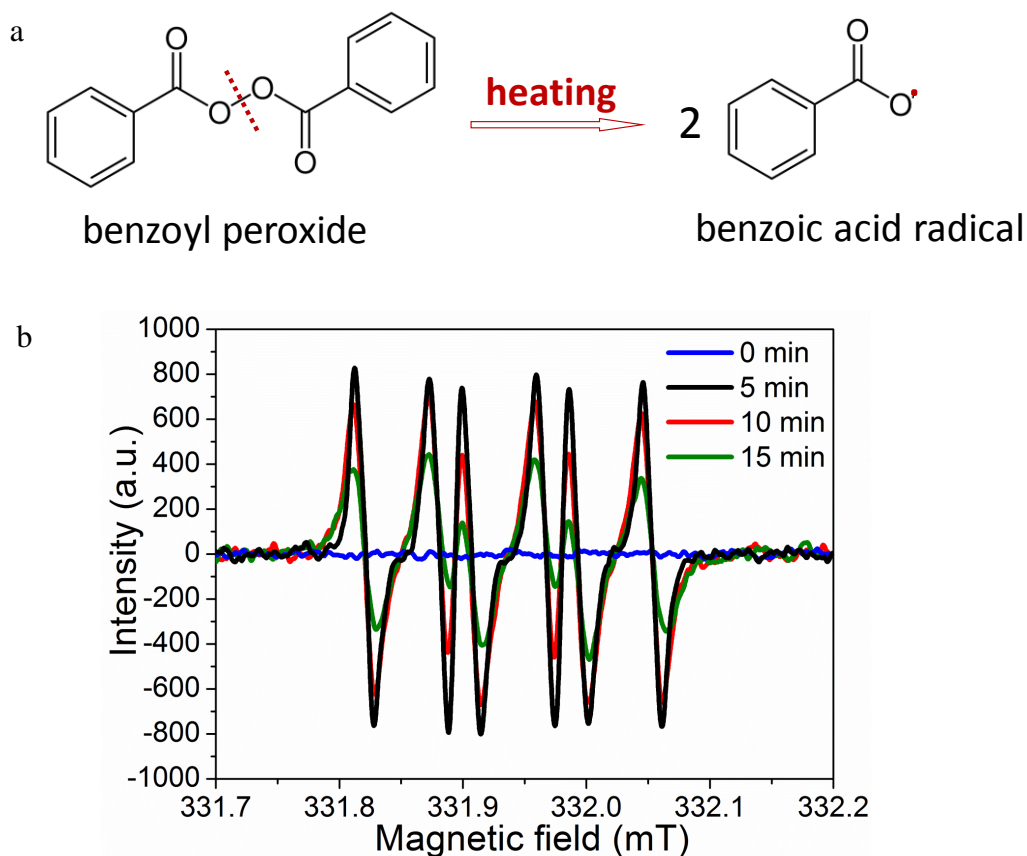


Figure S1. (a) Schematic of form benzoic acid radical. (b) The ESR signals of benzoic acid radical of BPO treated CdSe/CdS:Al QDs with DMPO (100 mM) at different BPO treated time.

Notes: ESR spectra were used to explore the radical formation mechanism. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used as trapping agent for benzoic acid radical.¹ When BPO, CdSe/CdS:Al QDs and DMPO were mixed together in toluene solution, the ESR signal attributed to benzoic acid radical adduct can be detected. As shown in Fig. S1b, the intensity of benzoic acid radical rapidly reaches the maximum at 5 min, and then gradually decreases with the increment of reaction time. The benzoic acid radical contains one unpaired electron, which are highly reactive. During this treatment process, it may combine with Cd^{2+} and Al^{3+} , and transform the Al doped CdS to CdO and Al_2O_3 .

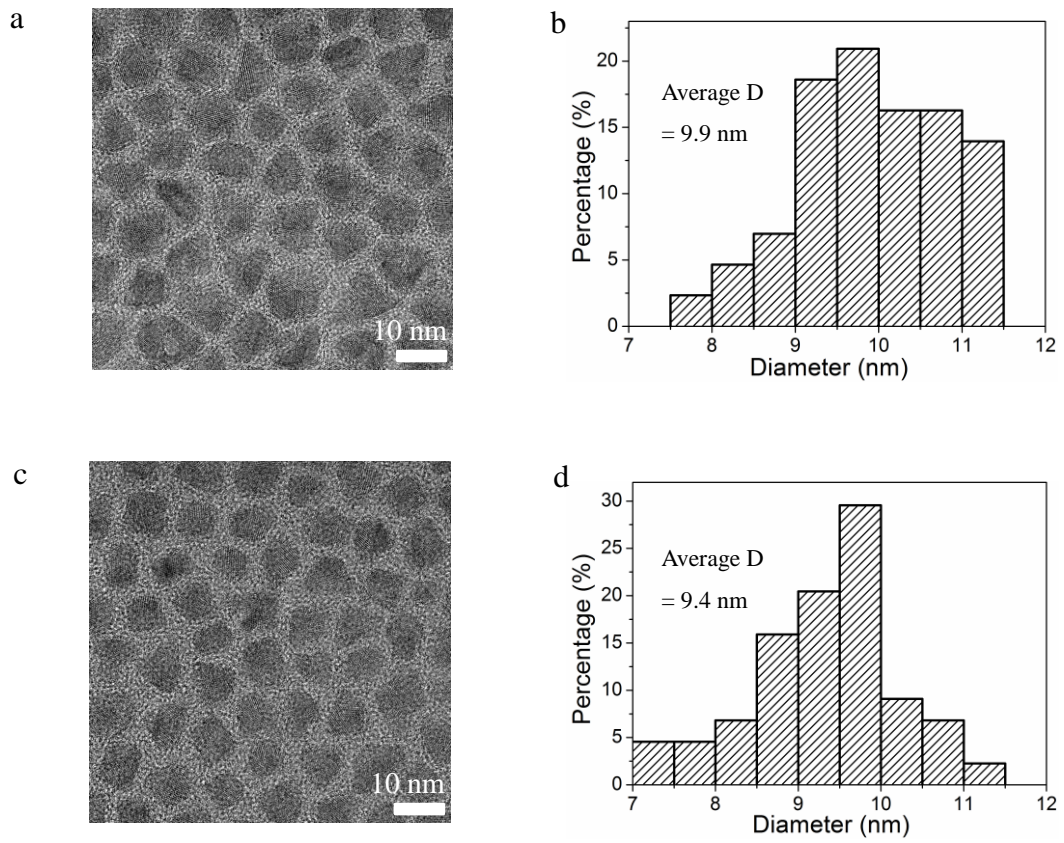


Figure S2. TEM images and corresponding size distributions of (a, b) untreated and (c, d) BPO treated CdSe/CdS QDs.

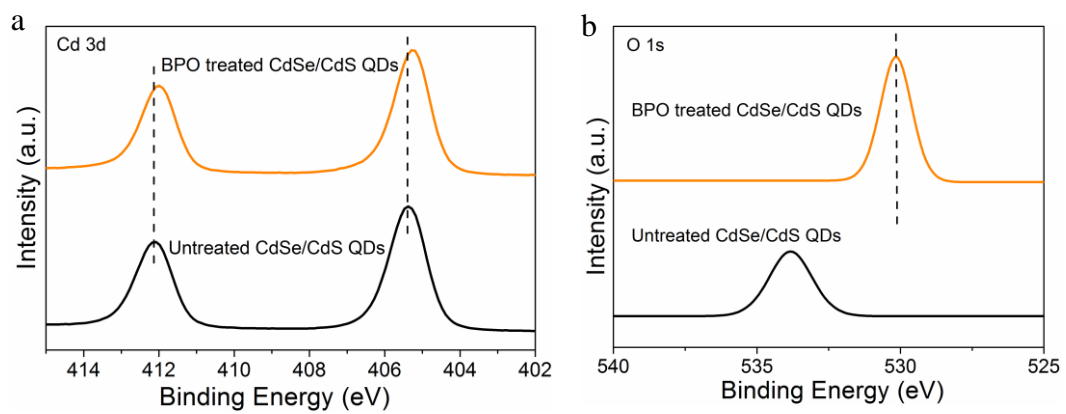


Figure S3. XPS spectra of (a) Cd 3d and (b) O 1s of CdSe/CdS QDs before and after BPO treatment.

Table S1. The O/Cd molar ratios of the CdSe/CdS QDs before and after BPO treatment from XPS analysis.

Samples	molar ratios
Untreated CdSe/CdS QDs	O : Cd = 0.050 : 1
BPO treated CdSe/CdS QDs	O : Cd = 0.095 : 1

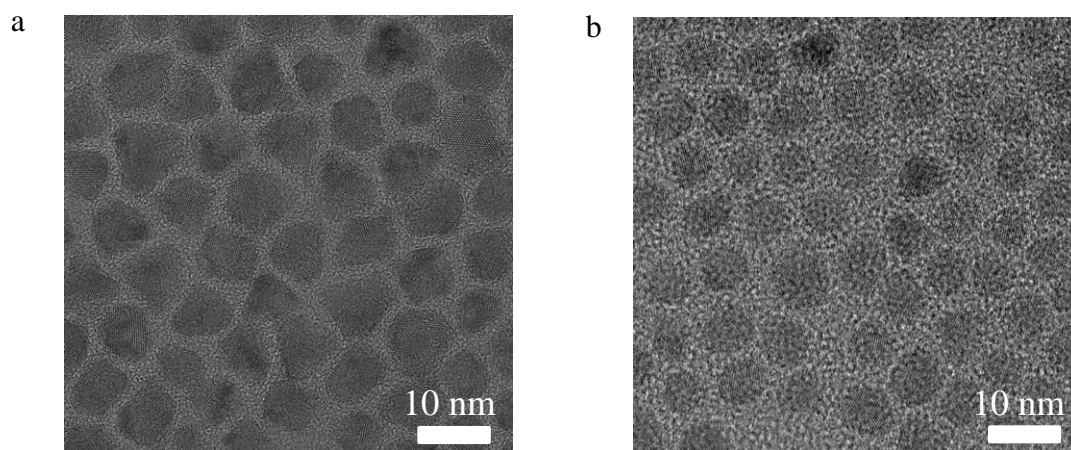


Figure S4. TEM images of (a) CdSe/CdS QDs and (b) Al doped CdSe/CdS (CdSe/CdS:Al) QDs.

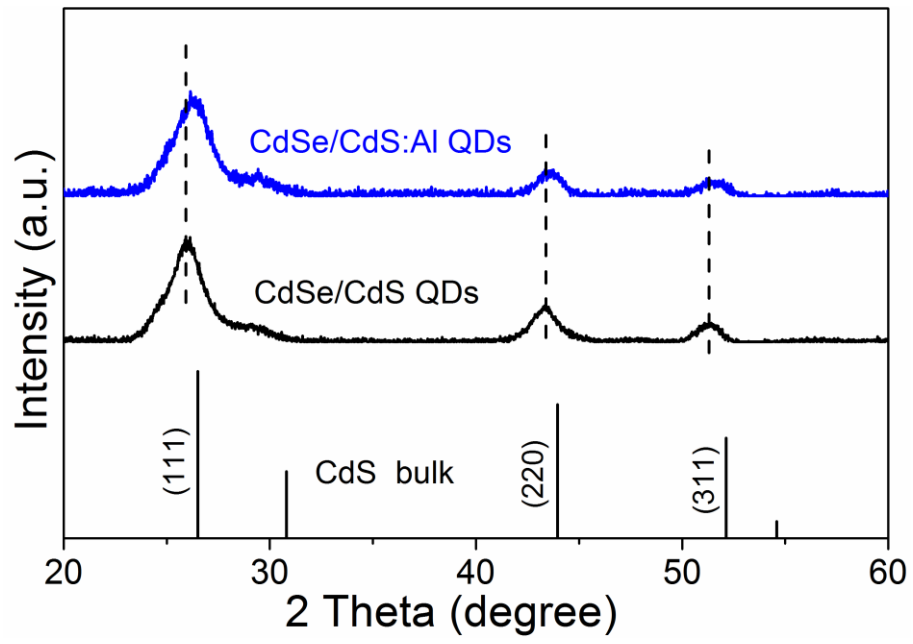


Figure S5. XRD of the CdSe/CdS QDs and CdSe/CdS:Al QDs.

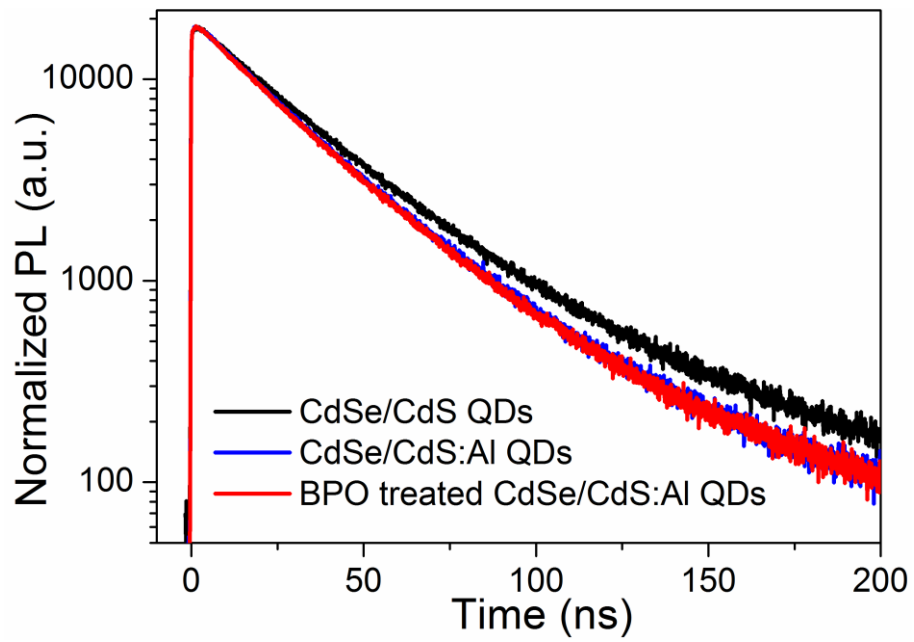


Figure S6. Time-resolved PL decays spectra of CdSe/CdS QDs, CdSe/CdS:Al QDs, and BPO treated CdSe/CdS:Al QDs (excitation at 405 nm, the same collection time).

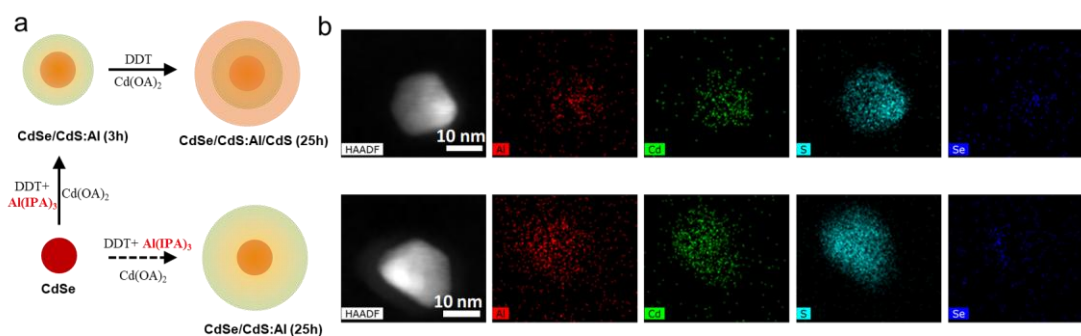


Figure S7. (a) Schematic of the synthesis process, (b) HAADF-STEM images and elemental maps of the Al, Cd, S, and Se of the CdSe/CdS:Al/CdS and CdSe/CdS:Al QDs (coating for 25 h).

Notes: We purposely synthesized a new structure CdSe/CdS:Al/CdS QDs, in which Al precursors were injected in the first 3 h of coating, and then continue coated CdS shell without Al doping for 22 h. According to our assumption, if the Al atoms in QDs are just on the surface, the anchored Al atoms will easily spread over the entire QDs region during the continue coating process of CdS shell. As shown in Fig. S7, there are big differences between the location of Al atoms in CdSe/CdS:Al/CdS QDs and CdSe/CdS:Al QDs (coating for 25 h), which clearly shows that the Al is located in the center of CdSe/CdS:Al/CdS QDs, but in the sample of CdSe/CdS:Al QDs, the Al signals are located over the whole particle. Obviously, the above results strongly suggest that the Al atoms can really doped into CdS shell of the CdSe/CdS:Al QDs.

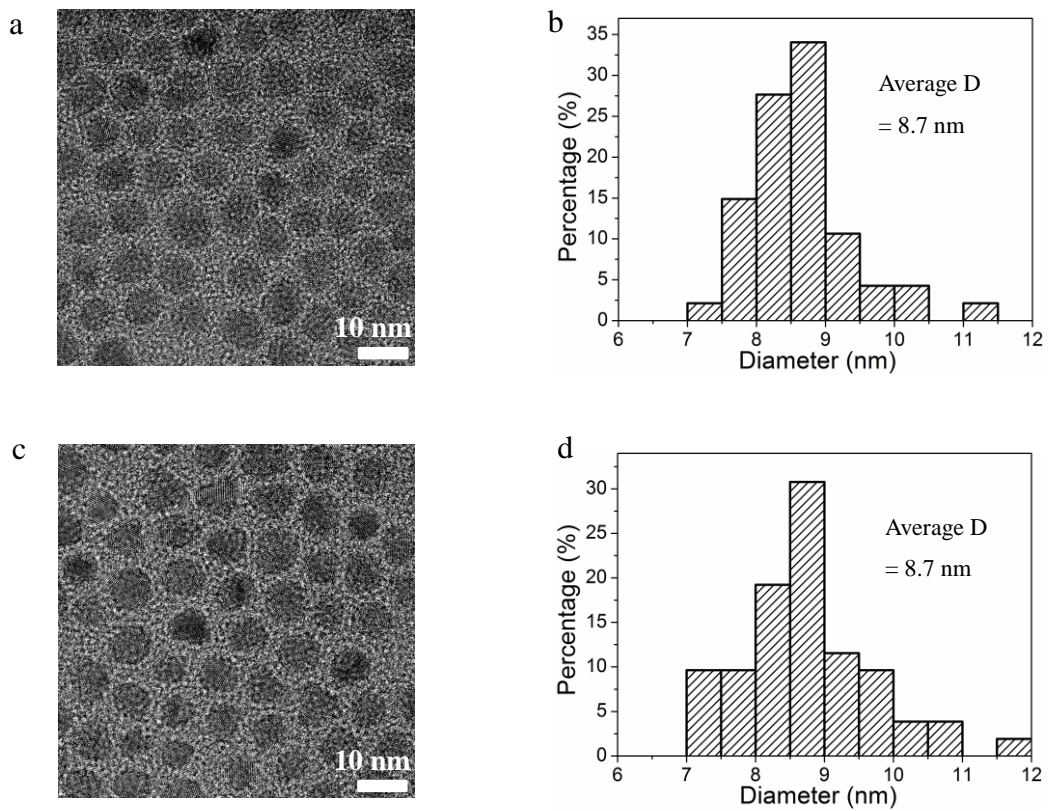


Figure S8. TEM images and corresponding size distributions of (a, b) untreated and (c, d) BPO treated CdSe/CdS:Al QDs.

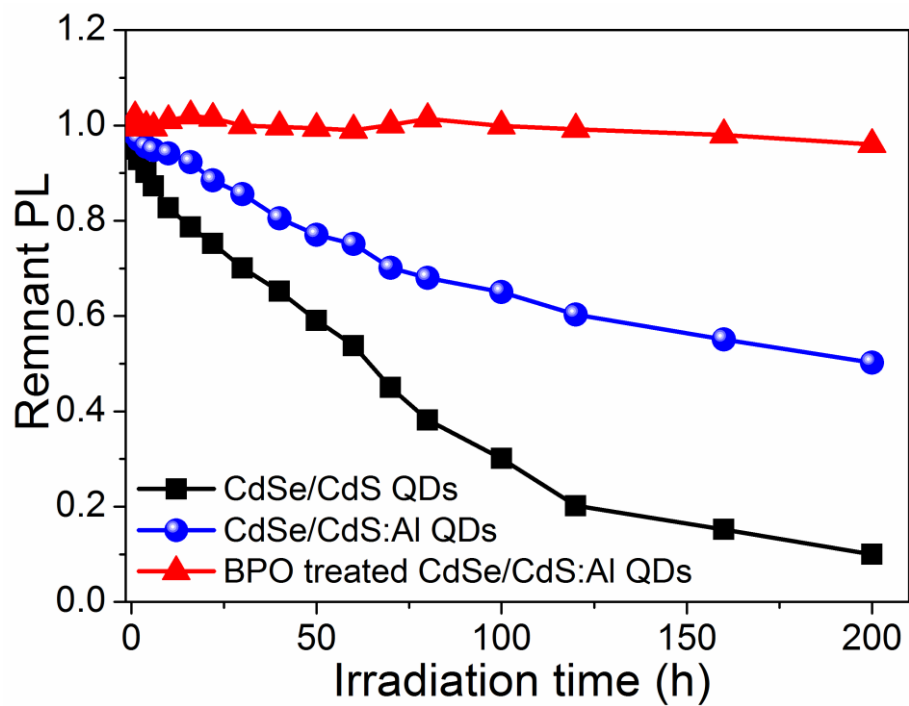


Figure S9. Photostability of CdSe/CdS, CdSe/CdS:Al, and BPO treated CdSe/CdS:Al QDs films (85 °C, 85% RH).

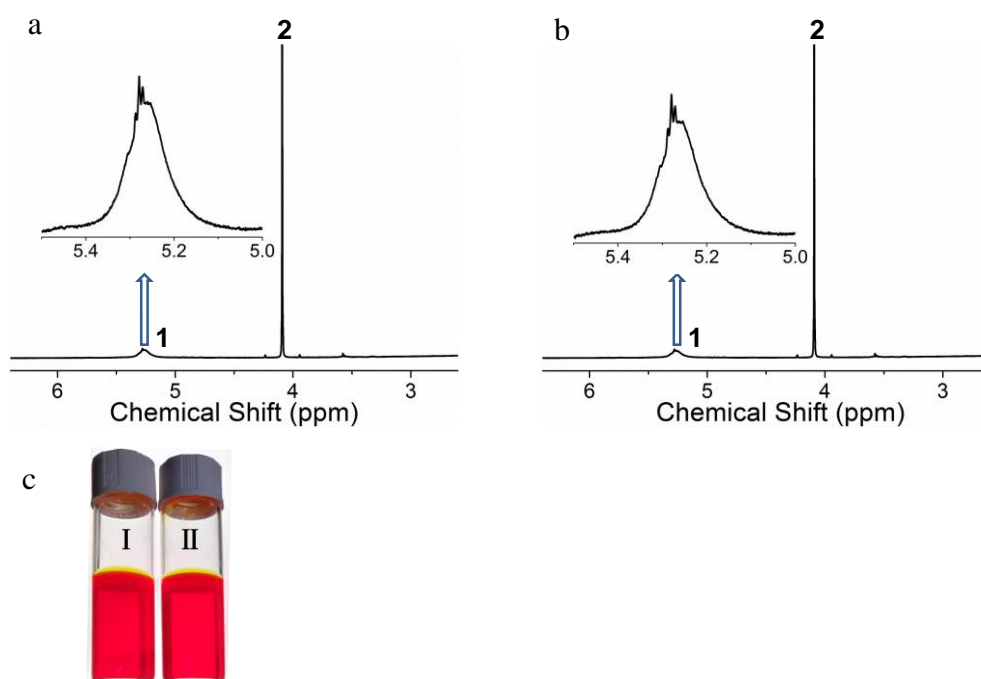


Figure S10. ^1H NMR spectra of (a) untreated and (b) BPO treated CdSe/CdS:Al QDs. Peaks labeled as 1 and 2 are the resonances from bound oleic acid (vinyl) and ferrocene, respectively. (c) The photographs of (I) a fresh BPO treated CdSe/CdS:Al QDs sample and (II) an aged BPO treated CdSe/CdS:Al QDs sample after two years of storage.

Notes: NMR spectroscopy analysis was carried out to see the effect of BPO treatment on ligand binding. We dispersed CdSe/CdS:Al QDs in 2 mM of ferrocene d -chloroform solution for ligand quantification. Ligand was quantified by comparing the integrated area of OA and ferrocene in NMR spectra. The vinyl peak of bound OA was integrated for quantification.² The integrated area of bound OA were estimated to 0.55 and 0.54, respectively, for untreated and BPO treated CdSe/CdS:Al QDs (Fig. S10). The total number of bound oleic acid ligands is slightly reduced by 1.8%. Therefore, the oleic acid ligands of CdSe/CdS:Al QDs remain almost unchanged after BPO treatment. The picture (Fig. S10c) is the comparison of a fresh BPO treated CdSe/CdS:Al sample with an aged BPO treated sample after two years of storage. We didn't see any precipitations on the bottom of the aged sample solution, and its optical properties are almost unchanged. This indicates the BPO treated sample has excellent colloidal stability, and BPO treatment won't significantly change the colloidal stability of QDs.

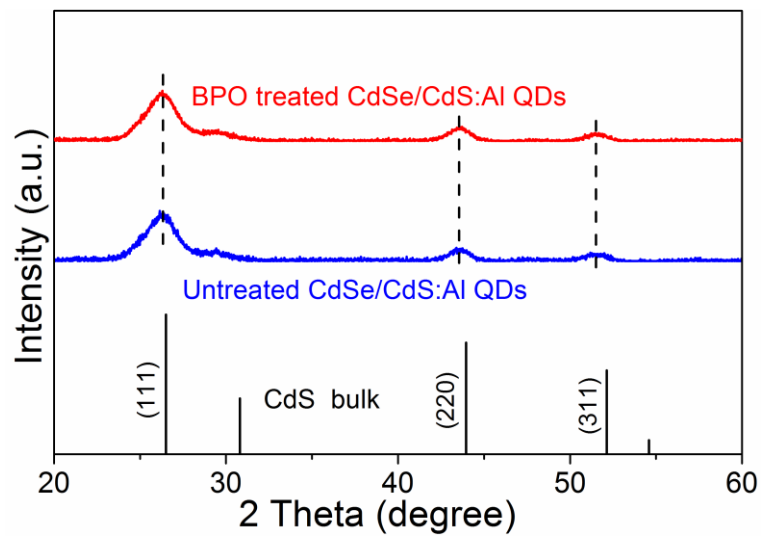


Figure S11. XRD patterns of the CdSe/CdS:Al QDs before and after BPO treatment.

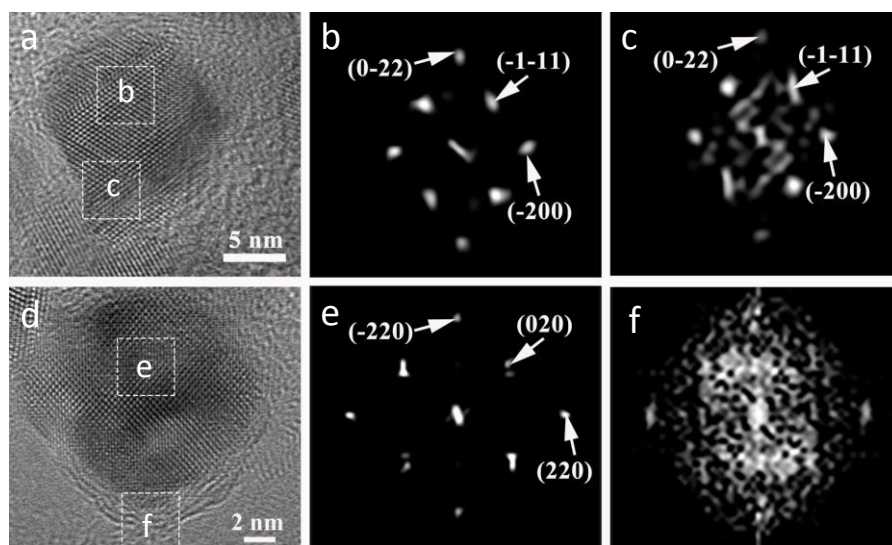


Figure S12. (a, d) High-resolution TEM (HRTEM) images and (b, c, e, f) the corresponding Fast-Fourier Transform (FFT) patterns of the white dotted box marked of (a-c) untreated and (d-f) BPO treated CdSe/CdS:Al QDs.

Notes: To get deeper insight of the QD surface, the high-resolution TEM (HRTEM) images of a single CdSe/CdS:Al QD were obtained. Compared to untreated crystalline QDs as shown in Figure S12a-c, amorphous structure is formed at the surface of BPO treated CdSe/CdS:Al QDs as confirmed by Figure S12d-f. At first, HRTEM manifest the distinct surface morphology: smooth and clean crystalline surface (Figure S12a) vs. rough and disordered shell-like amorphous surface (Figure S12d). Furthermore, the corresponding fast-fourier transform (FFT) patterns show the same crystalline structure in the center and at the edge of the untreated QD, as shown in Figure S12b and c. In contrast, FFT patterns of BPO treated CdSe/CdS:Al QDs (Figure S12e, f) indicate the crystal structure in the center but the existence of amorphous structure at the edge of the particle.

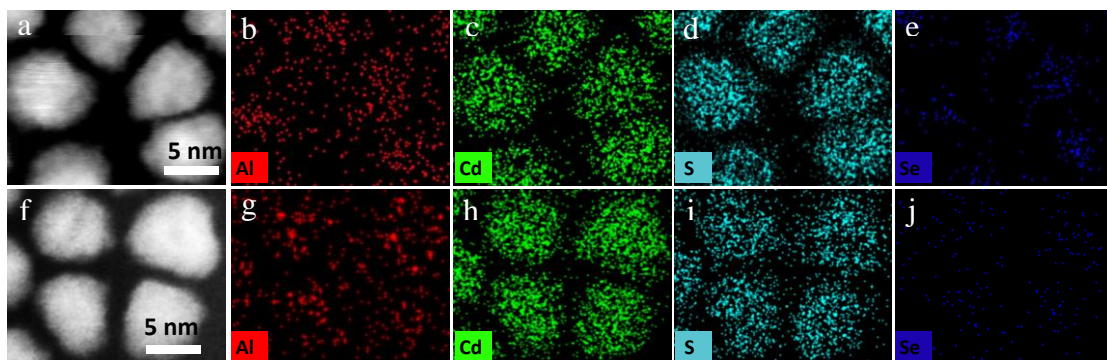


Figure S13. (a, f) HAADF-STEM images, the (b, g) Al, (c, h) Cd, (d, i) S, and (e, j) Se elemental maps of (a-e) untreated and (f-j) BPO treated CdSe/CdS:Al QDs.

Table S2. The O/Al/Cd molar ratios of the CdSe/CdS:Al QDs before and after BPO treatment from XPS analysis.

Samples	molar ratios
Untreated CdSe/CdS:Al QDs	O : Al : Cd = 0.075 : 0.085 : 1
BPO treated CdSe/CdS:Al QDs	O : Al : Cd = 0.240 : 0.119 : 1

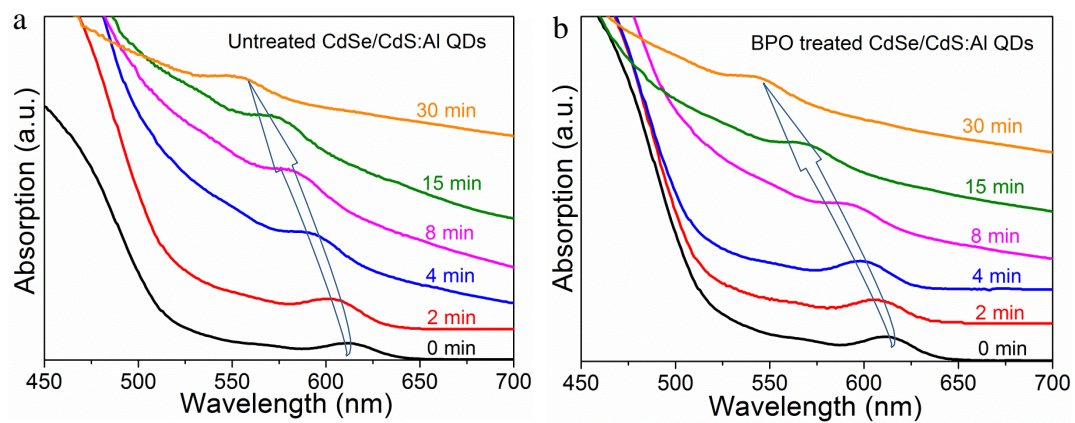


Figure S14. Evolution of the absorption spectra of (a) untreated and (b) BPO treated CdSe/CdS:Al QDs etched by HF solution at different time.

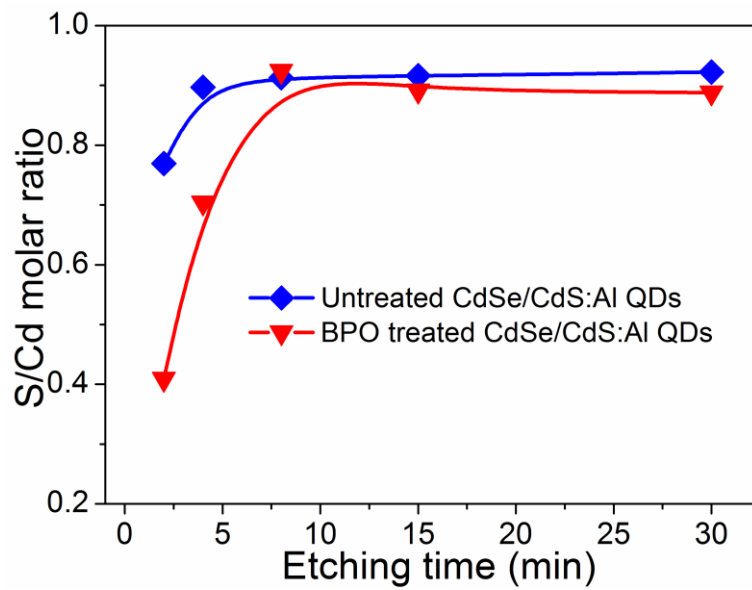


Figure S15. S/Cd molar ratio in the supernatants for the untreated and BPO treated CdSe/CdS:Al QDs taken at different etching time according to the ICP test.

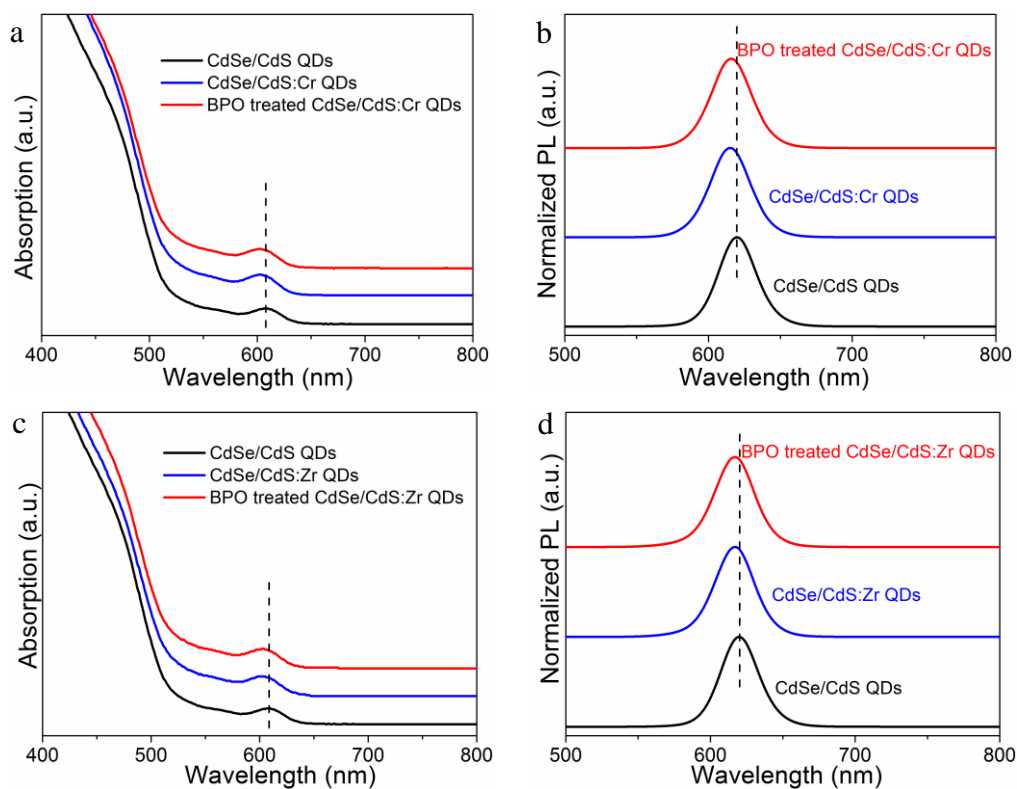


Figure S16. (a) Absorption and (b) PL spectra of the CdSe/CdS QDs, CdSe/CdS:Cr QDs, and BPO treated CdSe/CdS:Cr QDs. (c) Absorption and (d) PL spectra of the CdSe/CdS QDs, CdSe/CdS:Zr QDs, and BPO treated CdSe/CdS:Zr QDs.

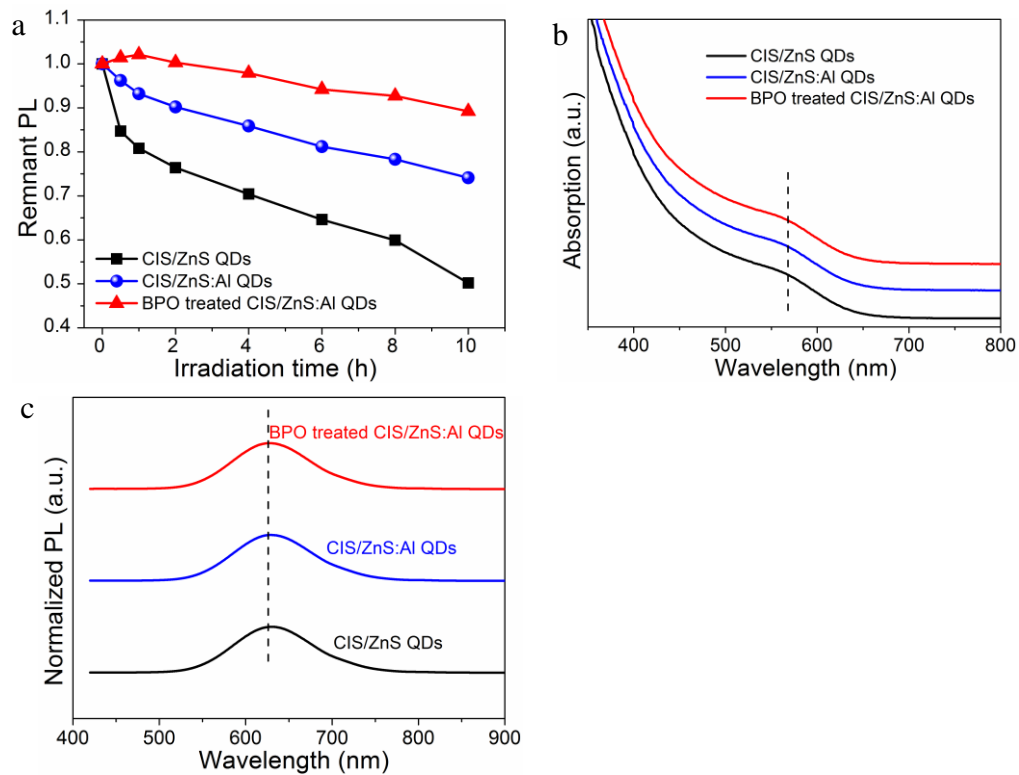


Figure S17. (a) Photostabilities (25 °C, 60% RH), (b) Absorption and (c) PL spectra of the CIS/ZnS QDs, CIS/ZnS:Al QDs, and BPO treated CIS/ZnS:Al QDs.

References

1. G. R. Buettner, *Free Radic. Biol. Med.*, 1987, **3**, 259-303.
2. J. Y. Woo, J. -H. Ko, J. H. Song, K. Kim, H. Choi, Y. -H. Kim, D. C. Lee and S. Jeong, *J. Am. Chem. Soc.*, 2014, **136**, 8883-8886.