

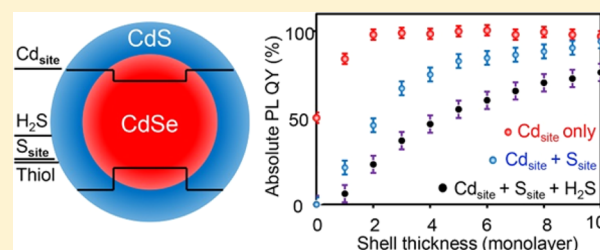
To Battle Surface Traps on CdSe/CdS Core/Shell Nanocrystals: Shell Isolation versus Surface Treatment

Chaodan Pu and Xiaogang Peng*

Center for Chemistry of Novel & High-Performance Materials, Department of Chemistry, Zhejiang University, Hangzhou, 310027, P. R. China

S Supporting Information

ABSTRACT: Electronic traps at the inorganic–organic interface of colloidal quantum dots (QDs) are detrimental to their luminescent properties. Several types of interface traps were identified for single-crystalline CdSe/CdS core/shell QDs, which were all found to be extrinsic to either the core/shell structure or their optical performance. The electron traps—presumably excess or unpassivated Cd surface sites—are shallow ones and could be readily isolated from the electron wave function of the excitons with more than ~ 2 monolayers of CdS shell. There were two identifiable deep hole traps within the bandgap of the QDs, i.e., the surface adsorbed H_2S and unpassivated surface S sites. The surface adsorbed H_2S could be removed by either degassing processes or photochemical decomposition of H_2S without damaging the QDs. The unpassivated surface S sites could be removed by surface treatment with cadmium carboxylates. Understanding of the surface traps enabled establishment of new phosphine-free synthetic schemes for either single-precursor or successive-ion-layer-adsorption-and-reaction approach, which yielded CdSe/CdS core/shell QDs with near-unity photoluminescence quantum yield and monoexponential photoluminescence decay dynamics with 2–10 monolayers of CdS shell.



INTRODUCTION

Colloidal quantum dots (QDs) have been pursued as versatile luminescent and optoelectronic materials because of their size- and composition-tunable electronic structure and solution processability.^{1–4} As promising luminescent materials, QDs are likely in the form of core/shell nanocrystals with a certain thickness of wide-bandgap shells to isolate a narrow-bandgap core from the outer environment. Highly luminescent CdSe/ZnS core/shell QDs were demonstrated ~ 20 years ago.^{5,6} Because of the substantial lattice mismatch between CdSe and ZnS,^{7–9} CdSe/CdS core/shell QDs have gradually attracted more attention.^{10–18} Unfortunately, there exists limited knowledge on how the shells function as electronic barriers even for most studied CdSe/CdS core/shell QDs. This work aims to identify different types of surface traps at the inorganic–organic interface and their shell-thickness dependence for CdSe/CdS core/shell QDs. Furthermore, we seek means to battle these traps during synthesis as well as postsynthesis.

A recent report revealed that it was feasible to synthesize CdSe plain core QDs—either zinc blende or wurtzite—with near-unity photoluminescence (PL) quantum yield (QY) and monoexponential PL decay.¹⁹ In fact, highly luminescent plain core CdSe QDs have been reported widely in the literature.^{20–23} These facts indicate that the additional wide-bandgap shells should not be considered as a prerequisite for highly luminescent QDs. However, high quality plain core QDs often lack durability and stability for most technical applications and some fundamental research.^{11,24,25} For example, CdSe QDs

might lose their PL brightness substantially upon purification and/or ligand exchange needed for nearly all applications.¹⁹

Ideally, wide-bandgap shells can ensure inertness of the QDs to the outer environment by complete isolation of the wave function of an exciton—photo- or electro-generated electron and hole pair bonded together through electrostatic interaction in a QD. However, wave function communication with the outer environment is sometimes necessary. For instance, QD light-emitting diodes with $\sim 100\%$ internal electroluminescence QY would require efficient charge injection into the QDs.^{26–28} Therefore, ideal core/shell QDs for optoelectronic applications should be sensitive to external electronic changes with a certain level of thermodynamic drive but not possess intrinsic deep traps. In this sense, CdSe/CdS core/shell QDs might be a better system than CdSe/ZnS ones.¹⁰

Growth of ideal core/shell QDs without detrimental traps should include two complementary tasks. First, the shell materials should be epitaxially grown onto a single crystalline core in high quality to remove internal electronic traps, including those at the core–shell interface. Second, all inorganic–organic interface traps should be either excluded by practical surface treatments or isolated by the shells with reasonable thickness. To fulfill the second task, the electronic traps at the inorganic–organic interface must be extrinsic to the structural integrity and function of the core/shell QDs. In

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addition, knowledge on shell-thickness dependence of trapping efficiency of those traps is much needed.

Electronic traps in/on QDs are obvious because most PL QYs of QDs reported in the literature are significantly below 100% and their PL decay dynamics is complex. However, identification of those detrimental electronic traps and their shell-thickness dependence of trapping efficiency remains elusive. One challenge is the entanglement of epitaxial growth of the shell and chemical/electronic structure of the inorganic–organic interface. The Scholes group reported that both core–shell and inorganic–organic interfaces might carry electronic traps for typical CdSe/CdS/ZnS core/shell/shell QDs.²⁹ Several groups attempted to decouple these two difficult synthetic tasks. For example, the Viswanatha and Rosenthal groups demonstrated that interfacial defects between core and shell could be crucial for high PL QY.^{30,31} Other groups found that the chemical nature of the inorganic–organic interface played a significant role in determining the PL QY of CdSe/CdS core/shell QDs, with a cadmium-rich surface for relatively high PL QY and a sulfur-rich surface for very low PL QY.^{11,32} Consistently, the Greytak group recently demonstrated that passivation of the surface anion sites by cadmium carboxylate and organophosphines could greatly enhance the PL intensity of CdSe/CdS core/shell QDs.³³

Applying CdSe/CdS core/shell QDs with high structural perfection of both crystallinity and morphology as the model system, we here report identification of electronic traps—including both electron and hole traps—on their inorganic–organic interface. Results revealed that common detrimental traps are extrinsic and can be removed either during or after synthesis as long as the CdS shell is thicker than ~ 2 monolayers. For either successive-ion-layer-adsorption-and-reaction (SILAR)¹¹ or single-precursor³⁴ approach, these understandings readily enabled synthesis of CdSe/CdS core/shell QDs with near-unity PL QY and monoexponential PL decay. Importantly, the new synthetic schemes could be phosphine-free, i.e., without involvement of any organophosphine for either SILAR or the single-precursor approach.

RESULTS AND DISCUSSION

Identification of H₂S as Detrimental Hole Traps on CdSe/CdS Core/Shell QDs. For simplicity, surface traps of QDs in this report specifically refer to the traps at their inorganic–organic interface, given no detectable traps at the core–shell interface (see below). CdSe/CdS core/shell QDs with X monolayers of CdS shell would be denoted as CdSe/XCdS. For identification of surface traps, CdSe/CdS core/shell QDs with 1–10 monolayers of CdS shell were synthesized using a single-precursor approach for epitaxy of the CdS shell.³⁵ If shell-thickness dependence was not involved, CdSe/5CdS QDs would be applied as the default sample. These QDs were single crystalline in zinc-blende structure, nearly monodisperse, and nearly spherical in shape (Figure S1, [Supporting Information](#)).

The CdSe core dots were synthesized using the Se-suspension approach, which only included carboxylic acid, cadmium carboxylate, Se powder, and octadecene (ODE).³⁶ For epitaxy of the shell, amine was used as the sole ligand, cadmium diethyldithiocarbamate (Cd(DDTC)₂) was applied as the single precursor, and ODE was the solvent. For 8–10 monolayers of the CdS shell, a small amount of cadmium oleate (~ 10 – 20% equivalent of the amount of Cd(DDTC)₂ used for each targeted monolayer) was added as additional cadmium

precursors. In this new epitaxy scheme, organophosphine was excluded for two purposes, namely, identification of the role of organophosphine during growth of the core/shell QDs and development of phosphine-free synthesis of high quality core/shell QDs. FTIR and NMR measurements only detected fatty amine as the ligands for the resulting core/shell QDs (Figure S1, [Supporting Information](#)).

The PL QY of all core/shell QDs with 1–10 monolayers of CdS shell in their fresh aliquots synthesized using the new scheme outlined above was significantly below unity. For instance, the PL QY—measured by an integration sphere—was 55% for fresh aliquots of CdSe/5CdS core/shell QDs, which would be as low as 10–20% if the aliquots were taken right after completion of the epitaxy at ~ 120 – 130 °C. Previous studies on CdSe core QDs revealed two routes to create electron traps for CdSe core QDs, i.e., either excess cadmium carboxylate or removal of fatty amine ligands.¹⁹ Since there were no cadmium carboxylates on the surface of QDs and a large excess of amines in the solution for epitaxy, such electron traps should not be a major concern (see more detail later). Thus, one could conclude that the relatively low PL QY of CdSe/5CdS core/shell QDs ($\sim 50\%$) was caused by the detrimental hole traps related to anionic species. This hypothesis was considered to be consistent with nonexistence of organophosphines in the current system, which are commonly known as quenchers for hole traps.^{17,35} In fact, similar synthetic schemes with organophosphines did yield CdSe/CdS core/shell QDs with significantly high PL QY.^{34,37}

One source of hole traps on the core/shell QDs could be the side products from the decomposition of Cd(DDTC)₂ for this simple reaction system. According to the literature, 1 mol of Cd(DDTC)₂ would decompose into 1 mol of CdS monomer, 1 mol of H₂S, and 2 mol of thiourea in the presence of fatty amines.³⁸ Further reactions of the sulfur-containing side products in the system might generate small amounts of elemental sulfur and polysulfides (S_n⁻).^{39,40} In the literature, these sulfur-containing side products were all reported to quench the PL of the CdSe core or CdSe/CdS core/shell QDs.^{41–44} Although H₂S is a gas under the reaction temperatures (60–150 °C), fatty amine in the reaction solution might help to retain it by formation of alkylammonium sulfide.⁴⁰ Indeed, we found that liquid oleylamine could collect H₂S gas up to ~ 0.1 mmol/mL at room temperature.

Addition of stoichiometric amounts of H₂S in the form of the saturated H₂S-amine solution (equivalent to half a monolayer of S atoms per dot) into the fresh aliquots of CdSe/5CdS core/shell QDs immediately quenched PL substantially (Figure 1a). Conversely, addition of thiourea, elemental S, or polysulfide solutions in large excess could barely vary the brightness and contour of the PL (Figures 1a and S2 ([Supporting Information](#))). Consistent with the change trends of PL QY, addition of the H₂S-amine solution substantially shortened the average lifetime of PL decay dynamics of the QDs, while neither of the other sulfur-containing side products varied the biexponential PL decay dynamics of the QDs in the fresh aliquots (Figure 1b).

While the results related to surface treatments using the H₂S-amine solution were convenient and reproducible, amine would convert H₂S to a mixture of H₂S and alkylammonium hydrosulfide. Surface treatments without amine in both QD solution and H₂S source were carried out. To do so, oleylamine in the QD solution was removed by purification, and gaseous H₂S was generated separately and directly purged into the

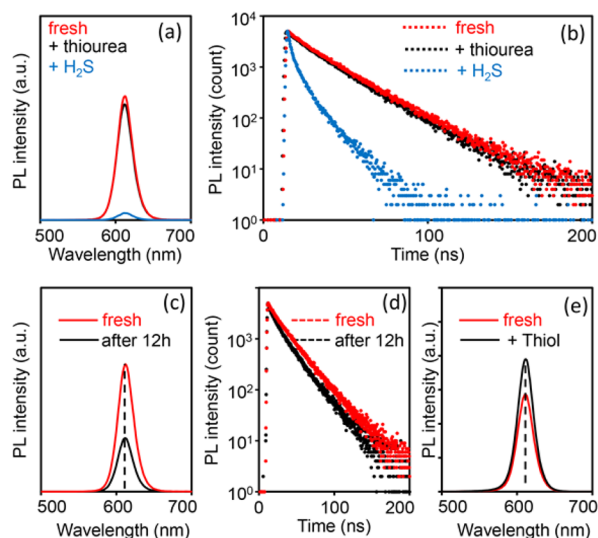


Figure 1. Steady state (a) and transient (b) PL spectra of fresh CdSe/5CdS core/shell QDs (red) and upon addition of thiourea (black) and H₂S (blue). Steady-state (c) and transient (d) PL of fresh CdSe/5CdS core/shell QDs (red) and the QDs stored in crude solution for 12 h (black). (e) PL spectra of fresh CdSe/5CdS core/shell QDs (red) and upon addition of thiol (black).

purified QD solution. Results in Figure S3 (Supporting Information) revealed that, without free amines, PL of CdSe/5CdS core/shell QDs was rapidly and completely quenched. Interestingly, using H₂S gas, we observed much more mild PL quenching for the QDs in the directly diluted solution of the QDs (containing ~ 0.075 mol/L oleylamine), i.e., from 100% quenching without amines to $\sim 30\%$ quenching with amines (Figure S3, Supporting Information). In addition to supporting PL quenching by H₂S, the reduced PL quenching by the addition of amines implies a few hints to the quenching mechanism. First, high coverage of amine ligands on the QDs likely prevented H₂S from approaching the surface of the QDs. Second, S²⁻, SH⁻, and H₂S should be weakly adsorbed onto the QDs because they could not compete with fatty amines in the nonpolar solution. In comparison, thiols (or thiolates) could completely replace the amine ligands under similar conditions.⁴⁵ Third, without a large excess of amines in the epitaxy solution, the PL QY of the fresh aliquots of CdSe/5CdS core/shell QDs would be much lower than the value mentioned above ($\sim 50\%$).

After the reaction mixture containing CdSe/5CdS core/shell QDs was stored under dark at room temperature overnight, the PL QY of the QDs dropped to 23% without varying the PL contour (Figure 1c). Simultaneously, the fast component in the PL decay dynamics observed for the corresponding fresh aliquots became further apparent (Figure 1d). Presumably, H₂S collected by the amines in the reaction mixture could slowly adsorb onto the surface of the QDs at reduced temperatures and quench the PL as efficient hole traps. A control experiment excluded PL quenching induced by ligand dissociation. The corresponding fresh aliquot (diluted for ~ 100 times in pure hexane) was also stored under the same conditions overnight. Opposite to PL quenching shown in Figure 1c, the PL brightness of the diluted solution after storage increased significantly (Figure S4, Supporting Information).

Bubbling Ar through the reaction mixture, prolonged heating of the reaction mixture, vacuum pumping the reaction mixture,

and other means to assist evaporation of a gas could all brighten the PL of the core/shell QDs (see examples later). By using lead acetate testing paper,^{40,46} we followed the H₂S concentration in the gaseous mixture above the epitaxy solution under constant Ar bubbling. Figure S5 (Supporting Information) illustrates the H₂S concentration in the gas phase along with the relative PL QY of CdSe/5CdS core/shell QDs in the corresponding solution. As expected, the H₂S concentration in the gas phase anticorrelated with the PL QY of the QDs in the solution.

UV-vis absorption measurements further revealed that, without degassing by any means, addition of cadmium carboxylates into the original reaction mixture would result in formation of CdS nanocrystals even at room temperatures (Figure S6, Supporting Information). This indicated existence of an active and gas-phase sulfur-containing compound—H₂S—in the reaction solution. The same experiment also suggested adsorption of H₂S on the surface of core/shell QDs because a noticeable PL red-shift of the core/shell QDs was observed upon addition of cadmium carboxylates (Figure S6, Supporting Information). Conversely, after complete degassing (see detail below), formation of CdS nanocrystals was no longer observed and the PL red-shift was much reduced to a level expected for adsorption of cadmium ions onto the QDs.

It should be pointed out that all results related to the CdSe/5CdS core/shell QDs described in this subsection were only qualitatively reproducible for different batches of QDs and/or QDs with different shell thickness. This is so because, as a gas, the concentration of H₂S would be very difficult to be quantitatively controlled under the experimental conditions. These qualitatively reproducible phenomena should be the main reasons for irreproducibility of the synthesis for CdSe/5CdS core/shell QDs. Furthermore, quantifiable results could be obtained by applying the QDs from the optimized synthetic schemes to be discussed below.

Verification of H₂S as Detrimental Hole Traps by Ligand Exchange and Photochemical Treatments. The results above suggested that H₂S generated by decomposition of Cd(DDTC)₂ could adsorb onto the surface of CdSe/5CdS core/shell QDs and act as efficient traps of the photogenerated excitons. Presumably, H₂S either in the solution or on the surface of QDs could interact with fatty amines in the epitaxial solutions, which would make the adsorbed H₂S behave similarly to HS⁻ and S²⁻. In the literature, the oxidation potential of H₂S (or S²⁻)—potential for H₂S (or S²⁻) to lose one electron—was suggested to be significantly higher than the top of the CdSe valence band, indicating H₂S (or S²⁻) as efficient hole traps.⁴⁴ In comparison, the oxidation potential of thiol (or thiolate) was lower than that of H₂S (or S²⁻).⁴⁷ This means that H₂S should be more efficient than thiols as the traps for the photogenerated holes. In other words, though thiol ligands are well-known quenchers of CdSe based quantum dots, they might brighten the PL of the CdSe/5CdS core/shell QDs by replacing the adsorbed H₂S.

Ligand exchange with aliphatic thiols was performed, and the results were consistent with the adsorbed H₂S as deep hole traps. Results revealed that, upon addition of thiols, the PL QY of a fresh aliquot of CdSe/5CdS core/shell QDs substantially increased (Figure 1e). Noticeably, the final PL QY of the thiol-coated CdSe/5CdS QDs reached $\sim 78\%$, which was slightly lower than that by the UV irradiation treatments to be discussed below. These results and those in Figure S3 (Supporting Information) implied that, though ~ 6 monolayers

of CdS shell would be sufficient to isolate the hole traps related to thiols as the surface ligands,⁴⁵ it would be insufficient for isolation of the hole traps associated with the species removed by thiols, presumably the adsorbed H₂S.

It has been well established that thiol ligands on II–VI QDs could be photo-oxidized to disulfides.^{48,49} If it was the adsorbed H₂S that acted as efficient hole traps to quench PL of the as-synthesized CdSe/CdS core/shell QDs in the current system, H₂S might go through a similar photochemical reaction to become elemental sulfur,^{49,50} which would be an inert substance for the photogenerated excitons as discussed above. Consequently, the PL QY of the QDs should gradually recover upon destruction of the adsorbed H₂S. Results in Figure 2a

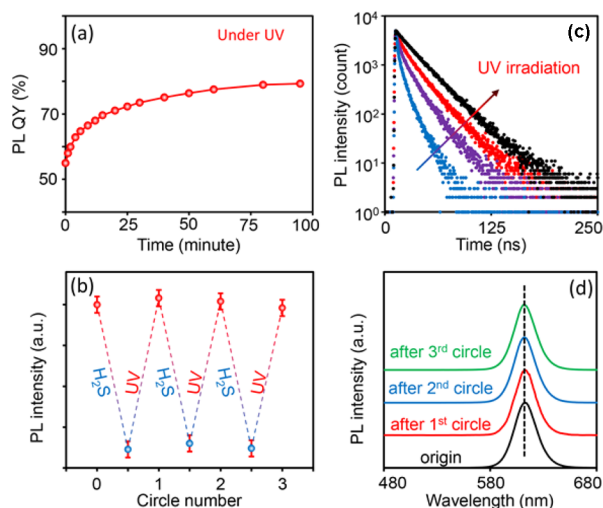


Figure 2. (a) Evolution of PL QY of fresh CdSe/5CdS core/shell QDs upon UV irradiation. (b) Reversible changes of PL intensity of CdSe/5CdS core/shell QDs after addition of H₂S (blue) and UV irradiation (red). (c) PL spectra of CdSe/5CdS core/shell QDs after every quenching/brightening circle. (d) Evolution of PL decay curves of CdSe/5CdS core/shell QDs upon UV irradiation. The CdSe/5CdS core/shell QDs were pretreated with H₂S.

confirmed that the PL QY of CdSe/5CdS core/shell QDs directly from the reaction mixture increased steadily upon UV irradiation and reached a plateau of ~82%. A control experiment showed no noticeable PL brightening within the given time period by placing one portion of the same solution under dark. Unfortunately, we did not directly detect the photochemical products related to H₂S. However, additional experimental results, such as photochemical treatments using a long wavelength light source (518 nm, slightly below the bandgap of the CdS shell) and without oxygen (Figure S7, Supporting Information), were found to be consistent with the mechanism of photochemical degradation.

Addition of the H₂S-amine solution into the solution with the photobrightened QDs would immediately reduce the PL QY down to ~18%, which could again be photobrightened to ~82% of the PL QY. Along with the photobrightening, the long-lifetime component in the transient PL spectra—presumably the intrinsic PL decay channel (see below)—became more and more dominating (Figure 2b). Figure 2c shows three cycles of the reversible “UV irradiation–H₂S addition” processes. During the “UV irradiation–H₂S addition” cycles, spectra of the QDs remained identical (Figure 2d), consistent with photochemical and chemical processes on the

surface of the QDs without photo-oxidation (or photo-annealing) of the QDs.

Passivation of the Secondary Hole Traps for CdSe/CdS Core/Shell QDs. Proper degassing treatments would boost the PL QY of the CdSe/CdS core/shell QDs to a plateau (see Figure 2a as an example). The plateau increased with the shell thickness but was always below 100% for the QDs with less than 10 monolayers of CdS shells (see detail below). These reproducible results suggested that there were other traps in addition to the adsorbed H₂S.

Existence of secondary hole traps seems to be reasonable, given the special ligand system in the current synthesis. As mentioned above, the sole ligand for the CdSe/CdS core/shell QDs up to this point was fatty amine (Figure S1). Fatty amines are neutral ligands, which would result in two surface features for the resulting QDs. First, the surface of a QD should possess both Cd and S sites to maintain charge neutrality of the entire nanocrystal–ligands complex. Second, the anionic S sites would be unpassivated, given fatty amines being solely electron donating ligands. These facts suggested that the secondary traps should still be hole traps and likely the unpassivated anionic lattice sites on the surface of the QDs.^{19,51}

Organophosphines and metal carboxylates are commonly suggested as passivation reagents for the surface anionic sites on cadmium chalcogenide nanocrystals.^{19,25,33,51,52} However, efficiency of each type of these ligands is unclear, and either type seems to be insufficient for removal of the surface anionic defects. For example, we reported that, only with tributylphosphines, cadmium carboxylates, and fatty amines in a proper ratio, the excited state of CdSe core nanocrystals could be promoted to 100% of the PL QY with monoexponential PL decay dynamics.¹⁹

We studied the effects of organophosphines and metal carboxylates separately for passivating the remaining anionic sites on the CdSe/CdS core/shell QDs after removal of the surface adsorbed H₂S. Addition of tributylphosphine would immediately boost the PL QY of the degassed CdSe/CdS core/shell QDs to near-unity (>95%) and convert the PL decay dynamics of the QDs to be monoexponential (Figure S9, Supporting Information). Additionally, the PL peak position and contour of the QDs did not change upon the tributylphosphine treatment.

The results shown in the above paragraph suggested that organophosphines could efficiently passivate the surface anionic defects without the help of cadmium carboxylates. However, organophosphines are pyrophoric and unstable. In comparison, cadmium is an intrinsic component of the QDs and cadmium carboxylates are common yet stable ligands for the QDs.

Studies on using cadmium carboxylates as the sole passivation reagent for the anionic sites of the QDs revealed some similarities and differences between cadmium carboxylates and organophosphines. When the CdS shell was only one monolayer, tributylphosphine could promote the PL of the QDs to near-unity QY and with monoexponential decay (Figures S9, S10a, and S10b, Supporting Information). For the same batch of the CdSe/1CdS QDs, cadmium carboxylates could only boost the PL QY to ~85% and the PL decay dynamics was multiexponential with a long lifetime component (Figures S10a and b, Supporting Information). When the CdS shell was ≥ 2 monolayers, cadmium carboxylates worked well as the sole passivation reagent for the secondary hole traps, which yielded QDs with near-unit PL QY and monoexponential PL

decay dynamics (Figure S10c and d (Supporting Information) and Figure 3).

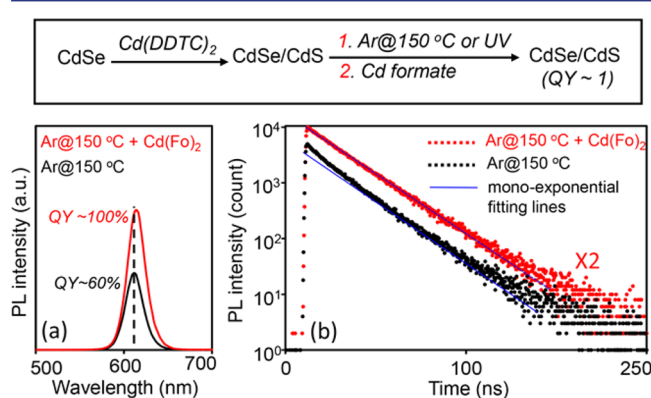


Figure 3. Top: A general scheme that coupled a single-precursor approach and surface treatments. Steady-state (a) and transient (b) PL spectra of the degassed CdSe/5CdS core/shell QDs before (black) and after (red) addition of cadmium formate ($\text{Cd}(\text{Fo})_2$).

It should be mentioned that degassing prior to addition of cadmium carboxylates was necessary because the H_2S trapped in the reaction mixture would cause formation of CdS particles (Figure S6, Supporting Information). Furthermore, without degassing, the PL QY of the cadmium carboxylate-treated QDs was always significantly below unity and PL decay dynamics was multiexponential. For the degassed samples, there would be a slight red-shift (~ 2 nm) upon the treatment by cadmium carboxylate (Figure S11 (Supporting Information) and Figure 3a), while the organophosphine treatment did not change the PL spectra of the same QDs (Figure S8, Supporting Information). Such a small red shift seems to be reasonable, given that the cadmium ions from cadmium carboxylates became an integral part of the resulting QDs. Consistent with this hypothesis, this red shift was preserved upon ligand exchange with thiols (Figure S11, Supporting Information).

Durability of the bright core/shell QDs from this phosphine-free approach was significantly better than the corresponding ones from the schemes with tributylphosphine.^{34,37} As shown in Figure S12 (Supporting Information), purification using the precipitation procedure with acetonitrile did not vary the PL properties of CdSe/5CdS core/shell QDs obtained from the phosphine-free approach.⁵³ In comparison, the same QDs treated with tributylphosphine—also with $\sim 100\%$ PL QY—lost their PL brightness significantly upon the same precipitation procedure.

At a single-dot level, PL blinking—PL intensity switching between different brightness states under constant excitation—of the QDs was largely suppressed by the combined treatment of degassing and addition of cadmium carboxylates (Figure S13, Supporting Information). Overall, the stability and durability at a single-dot level of the cadmium carboxylate-treated QDs was found to be comparable to that of the QDs from the standard organophosphine approach.³⁷

Isolation of Electron Traps for CdSe/CdS Core/Shell QDs by the CdS Shell. The results above revealed that the cadmium carboxylate treatment after the degassing process can boost the PL QY to near unity and promote the PL decay dynamics to being monoexponential for CdSe/CdS core/shell QDs with ≥ 2 monolayers of CdS shells (see Figure 3 for an example). In principle, to reach such luminescent quality for the

QDs, not only the anionic defects as hole traps should be passivated, but also there should be no electron traps. In the literature, electron traps for CdSe QDs were identified as excess cadmium ions on the surface and inefficient surface passivation of cadmium sites by proper ligands, namely, fatty amines.¹⁹

Results revealed that, for the tributylphosphine-treated CdSe/1CdS core/shell QDs, addition of excess cadmium carboxylates would still reduce the PL QY from near unity to $\sim 85\%$ and convert the PL decay dynamics from monoexponential to multiexponential with a long tail, similar to those treated solely by cadmium carboxylates in Figure S10a and b (Supporting Information). This means that the relatively poor PL properties of the cadmium carboxylate-treated CdSe/1CdS core/shell QDs were likely not associated with the secondary hole traps. Instead, an excess amount of cadmium carboxylates on the surface of the CdSe/1CdS core/shell QDs likely created electron traps by the cadmium ions.¹⁹ A long tail in the PL decay curves (see Figure S10b, Supporting Information) should be delayed fluorescence with the trapped electrons coming back to the QDs and restoring the luminescent states, which is common for shallow traps.^{29,54}

Removal of amine ligands by extraction of the CdSe QD solution was reported as the other route to create electron traps presumably by exposing unpassivated cadmium sites on the QDs.¹⁹ Despite there being no red shift of the PL peak, removal of the amines in the solution of tributylphosphine-treated CdSe/1CdS core/shell QDs reduced the PL QY to $\sim 81\%$ and converted the PL decay dynamics from monoexponential to multiexponential (Figure S10a and b, Supporting Information). These results along with those in the above paragraph revealed that one monolayer of CdS shell would be insufficient for isolation of both types of surface electron traps from the excitons.

For the QDs with 2 monolayers of CdS shell (Figure S10c and d, Supporting Information), however, addition of excess cadmium carboxylates and removal of amine ligands by extraction would barely vary either the PL QY or PL decay dynamics. Precipitation is known to be more efficient than extraction on removing free amines in the solution and amine ligands on the surface of the QDs, but results in Figure S12 (Supporting Information) revealed that, for the cadmium carboxylate-treated QDs with 5 monolayers of CdS shell, precipitation of the QDs by acetonitrile did not affect the PL properties.

Overall, electron traps caused by either excess cadmium carboxylates or surface cadmium sites without amine passivation were significantly suppressed by one monolayer of CdS shell. Furthermore, for CdSe/1CdS core/shell QDs, passivation of the secondary hole traps solely by cadmium carboxylates could not be decoupled from bringing electron traps. For the QDs with ≥ 2 monolayers of CdS shell, these electron traps could be well isolated by the CdS shell and not affect the PL properties of the QDs.

Surface-Treatment Coupled Single-Precursor Synthesis of CdSe/CdS Core/Shell QDs. The surface treatments described above could be integrated with the single-precursor synthesis (Figure 3a, top). For the QDs with a targeted shell thickness, the CdSe core nanocrystals were synthesized using the Se-suspension approach³⁶ and epitaxy of the targeted CdS shell was performed using the single-precursor approach outlined above, both of which were performed in one pot and without organophosphines.

Prior to the surface treatments with cadmium carboxylates, degassing by UV irradiation at room temperatures would be suited for postsynthesis treatments of a diluted sample, such as aliquots of intermediate products taken from a reaction for thick-shell epitaxy. For concentrated reaction mixtures in a reaction flask, Ar bubbling at the reaction temperatures (140–150 °C) for ~15 min was identified as convenient degassing treatment. After the degassing process, addition of cadmium carboxylates into the solution with stirring for ~10 min would complete the entire synthesis. The temperature for addition of cadmium salts could be room temperature for small salts, such as cadmium formate. It is interesting to note that the surface treatments would be needed only once at the end of construction of the targeted core/shell QDs within 1–10 monolayers of CdS shells, which makes this phosphine-free scheme simple and efficient.

Surface-Treatment Coupled SILAR Synthesis of CdSe/CdS Core/Shell QDs. The results above revealed that both types of detrimental electronic traps for the CdSe/CdS core/shell QDs synthesized with the single-precursor approach were hole traps, which were extrinsic to the CdSe/CdS core/shell QDs. Both of them are associated with amendable surface structures. We thus suspected that, by coupling certain surface treatments, the conventional SILAR approach¹¹ might also yield CdSe/CdS core/shell QDs with “perfect” control of their excited states—100% of PL QY and monoexponential PL decay dynamics.

Simple extension of the “degassing followed by the treatment with cadmium carboxylates” procedure in Figure 3 (top) did not work for the SILAR system. A thorough anion treatment was found to be necessary (Figure 4, top), which might help adjusting the surface stoichiometry of the core/shell QDs. With fatty amines in the system, elemental S under elevated temperatures would generate H₂S *in situ*.^{40,46} Though there was no detectable spectral shift, sufficient adsorption of H₂S was confirmed by nearly zero luminescence (Figure 4a and b). After this surface anion treatment, the QDs were treated with

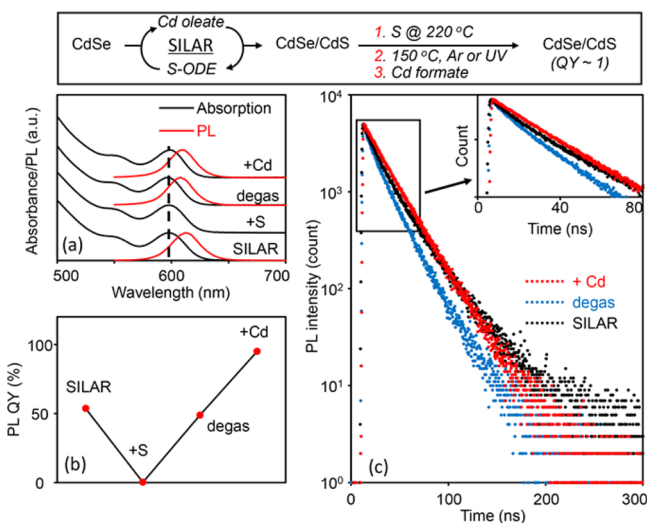


Figure 4. Top: Surface treatment coupled SILAR approach for CdSe/CdS core/shell QDs. (a) Evolution of absorption (black) and PL (red) spectra of CdSe/SCdS core/shell QDs during the surface treatment. (b) Evolution of PL QY of CdSe/SCdS core/shell QDs during the surface treatment. (c) Evolution of transient PL of CdSe/SCdS core/shell QDs at different stages.

the degassing procedure—either Ar bubbling or UV irradiation. Consequently, addition of cadmium carboxylates into the solutions with the QDs finally boosted the PL QY of the QDs to near unity (Figure 4b). Transient PL measurements confirmed removal of the traps by this three-step surface treatment (Figure 4c). The lifetime of the monoexponential PL decay dynamics for the resulting QDs was found to be identical to that of the QDs from the surface-treatment coupled single-precursor approach, i.e., 24 ns for the CdSe/SCdS core/shell QDs with 3 nm CdSe as the core nanocrystals dispersed in hexane.

Shell-Thickness Dependence of Isolation Effects of CdS Shell to the Surface Traps. The PL QY of three series of CdSe/CdS core/shell QDs with 0–10 monolayers of CdS shell was compared to understand the shell-thickness effects on different types of surface traps (Figure 5a). Parts a (red circles)

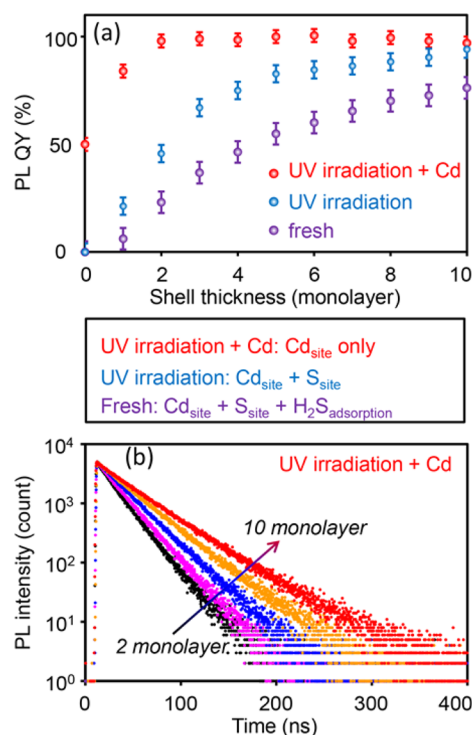


Figure 5. (a) Shell-thickness dependent PL QY of the CdSe/CdS core/shell QDs at different stages. (b) Shell-thickness dependent transient PL of the final products from the phosphine-free scheme in Figure 3.

and b of Figure 5 respectively show that the fully treated QDs with 2–10 monolayers of CdS shells from the phosphine-free scheme in Figure 3 all possessed ~100% PL QY and monoexponential PL decay dynamics. With high photon counts (5000), all PL decay curves could be fitted with monoexponential decay kinetics with the goodness-of-fit (χ^2_R) being 1.000–1.150. These results suggested that there should be no interior electronic traps within an inorganic nanocrystal, including the core–shell interface.

Among the series of QDs treated with UV irradiation only (the blue circles in Figure 5a), the PL QY for the QDs without a CdS shell was near zero and it reached ~95% for CdSe/10CdS core/shell QDs. According to the results above, this series of QDs should only possess the surface hole traps caused by the unpassivated surface anionic sites, given the cationic sites being ineffective for the QDs with ≥ 2 monolayers of the CdS

shells. Results in Figure 5a (blue circles) implied that this type of surface hole traps was quite efficient and only thick shells could isolate them from the photogenerated excitons. In comparison, hole traps associated with the surface thiol ligands became insignificant when the thickness of the CdS shells was more than ~ 6 monolayers.⁴⁵

The series labeled as “fresh” in Figure 5a possessed the lowest PL QY. Especially, while the PL QY of the degassed CdSe/10CdS core/shell QDs (labeled as “UV irradiation” in Figure 5a) was near-unity, the PL QY of the corresponding QDs in the “fresh” series could only reach $\sim 75\%$. Moreover, additional H₂S could completely quench the PL of CdSe/5CdS core/shell QDs (see Figure 4b and Figure S3 (Supporting Information)). All of these results suggested that up to 10 monolayers of the CdS shells would be inefficient barriers between the photogenerated holes and the surface adsorbed H₂S.

CONCLUSION

Previous studies on plain CdSe core QDs revealed that the electron traps are associated with surface Cd sites but the nature of the surface hole traps was not clear. Here, CdS shells with variable yet controlled thickness were applied as the probe for identification of various electronic traps on single-crystalline CdSe/CdS core/shell QDs. The results not only confirmed the nature of electron traps being Cd sites but also suggested two types of surface hole traps commonly encountered in synthesis of II–VI core/shell QDs, namely, the surface adsorbed H₂S and unpassivated surface anionic sites. Furthermore, the relative trapping efficiency of all types of surface electronic traps was identified with the well-known surface thiol (thiolate) ligands as the reference, namely, the adsorbed H₂S > unpassivated surface anionic sites > thiolates \gg electron traps. Their exact energetic levels, however, need to be confirmed with further studies. With the help of shell isolation of the electron traps, practical and simple surface treatment procedures were developed to remove those detrimental yet extrinsic traps, i.e., the two types of hole traps. The results presented here shed new light on both synthesis and processing of colloidal QDs. For synthesis, toxic, pyrophoric, yet commonly used organophosphine ligands were confirmed to be unnecessary for both single-precursor and SILAR approaches to obtain durable CdSe/CdS core/shell QDs with near-unity PL QY and monoexponential PL decay dynamics.

EXPERIMENTAL SECTION

Chemicals. Stearic acid (HSt, 90+%), cadmium oxide (CdO, 99.998%), selenium powder (Se, 200 mesh, 99.999%), 1-octadecene (ODE, 90%), tetramethylammonium hydroxide (TMAH, 98%), octylamine (98%), dodecane (99%), oleic acid (HOI, 90%), and dodecanethiol (98%) were purchased from Alfa-Aesar. Tributylphosphine (TBP) and oleylamine (C₁₈ content 80–90%) were purchased from Acros. Cadmium acetate dihydrate (CdAc₂·2H₂O, 98.5%) was purchased from Shanghai Tingxin Reagents. Sodium diethyldithiocarbamate trihydrate (NaDDTC·3H₂O, 99%) was purchased from Aladdin Reagents. Cadmium formate (Cd(Fo)₂, 99.9%) was purchased from Aldrich. Acetone, toluene, methanol, and hexane were purchased from Sinopharm Chemical Reagents. All chemicals were used directly without any further purification unless otherwise stated.

Precursor Preparation. Cadmium diethyldithiocarbamate (Cd(DDTC)₂) and cadmium stearate (CdSt₂) were prepared following the literature.³⁴ Synthesis of cadmium oleate (Cd(OI)₂) was as follows. CdO (10 mmol) and 40 mmol of HOI were mixed in a 25 mL flask. After stirring and argon bubbling for 10 min, the mixture in the flask

was heated to 240 °C to obtain a clear solution. The mixture was allowed to cool down to 50 °C, and then added into 100 mL of acetone slowly. White precipitate of Cd(OI)₂ immediately formed and was collected through filtration. The solid on filter paper was washed three times with acetone and then dried under a vacuum overnight at room temperature before using.

The single-source precursor solution was prepared by dissolving 1.5 mmol of Cd(DDTC)₂ in a mixture of 5 mL of dodecane and 5 mL of oleylamine. The Cd(OI)₂ solution was prepared by dissolving 1.5 mmol of Cd(OI)₂ in a mixture of 1 mL of oleylamine and 9 mL of ODE. The Se-suspension in ODE (Se-SUS) was prepared by dispersing 0.30 mmol of Se powder in 3 mL of ODE by sonication. ODE-S solution was prepared by dissolving 1.5 mmol of elemental sulfur in 10 mL of ODE. Cadmium formate (Cd(Fo)₂) solution was prepared by dissolving 0.3 mmol of Cd(Fo)₂ in 2 mL of octylamine by sonication. H₂S was produced by the reaction of elemental S with octylamine at 100 °C, which was either directly carried into the reaction flask by Ar flow or collected by oleylamine to saturation (0.1 mmol/mL) for future use.

Synthesis of QDs. Synthesis of CdSe QDs. In a typical synthesis, CdSt₂ (0.2 mmol) and 3.5 mL of ODE were loaded into a 25 mL three-neck flask. After stirring and argon bubbling for 10 min, the mixture was heated to 250 °C to form a clear solution. Freshly prepared Se-SUS (containing 0.05 mmol of elemental selenium, 0.5 mL) was injected quickly into the reaction flask at 250 °C. The reaction temperature was remained at 250 °C for further growth. After growth for ~ 8 min, Se-SUS was added dropwise until the absorption peak of the CdSe QDs reached 550 nm. Usually, 0.1–0.2 mL of Se-SUS (0.01–0.02 mmol of elemental selenium) was needed for the second step. The reaction mixture was allowed to cool down to 50 °C. An *in situ* purification procedure was employed to purify the nanocrystals. Into the reaction flask, 0.2 mL of octylamine, 4 mL of hexane, and 8 mL of methanol were added to the CdSe reaction solution at 50 °C and stirred for 2.5 min. The mixture would separate into two layers after stirring was turned off; the colorless methanol layer at the bottom of the flask was removed by syringe. This extraction procedure was repeated four times, while octylamine was only added for the first and third time. Hexane and trace amounts of methanol left in the flask were removed by argon bubbling at about 60 °C.

Synthesis of CdSe/CdS Core/Shell QDs through Single-Precursor Approach. In a typical synthesis, dodecane (1.2 mL) and 3.8 mL of oleylamine were added into the purified CdSe core solution (3×10^{-7} mol of CdSe QDs) under argon flow, and then, the mixture was heated to 80 °C. The amount of precursor solution for each injection was estimated by extinction coefficients and calibrated by the TEM measurements.³⁴ For example, for a reaction with 3×10^{-7} mol of 3.0 nm CdSe core, the amount for six consecutive injections of the precursor solution was calibrated as 0.08, 0.11, 0.15, 0.20, 0.26, and 0.32 mL, respectively. From the seventh monolayer of the CdS shell, the precursor solution was changed to a mixture of Cd(DDTC)₂ and Cd(OI)₂ with a mole ratio of 4:1. This mixed precursor solution in an amount of 0.39, 0.46, 0.54, and 0.63 mL was used for the growth of seventh, eighth, ninth, and tenth monolayers of the CdS shells, respectively. For each monolayer, addition of the precursor solutions was at 80 °C and growth was at 160 °C for 20 min.

Synthesis of CdSe/CdS Core/Shell QDs with the TC-SILAR Method. The thermal-cycling coupled SILAR (TC-SILAR) method was modified from the existing ones in the literature.⁵⁵ In a typical synthesis, oleylamine (2 mL) and ODE were added into the solution of the purified CdSe core QDs (3×10^{-7} mol of CdSe QDs) and the total volume was 6 mL. The calculated amounts of CdOI₂ and ODE-S solutions were added at 120 °C sequentially. After addition of every run of precursor, growth of CdS shell was initiated by increasing the temperature to 240 °C for 20 min. After a targeted shell thickness was achieved, the reaction was stopped and the solution was allowed to be cooled in air to room temperature.

Surface Treatment of CdSe/CdS Core/Shell QDs Coupled with the Single-Precursor Approach. After the CdSe/CdS core/shell QDs with targeted shell thickness were synthesized with the

single-precursor approach described above, Ar bubbling at 150 °C was carried out for 15 min to remove a sufficient amount of hydrogen sulfide in the flask. Consequently, the temperature of the reaction mixture was reduced to room temperature in air. The Cd(Fo)₂ solution was added with the amount of Cd(Fo)₂ sufficient for the next monolayer of the CdS shell. Time for the Cd(Fo)₂ treatment depended on the reaction temperature. For example, 10 min was enough when the temperature was ~50 °C.

Surface Treatment of CdSe/CdS Core/Shell QDs Coupled with the SILAR Approach. After the designated thickness of the CdS shells was achieved using the TC-SILAR method described above, ODE-S solution with the amount of S sufficient for two monolayers of shell growth was added at the reaction temperature. The PL of the CdSe/CdS core/shell QDs would be quenched immediately and then slowly recovered as time went by. During the recovering of the PL, the reaction mixture was allowed to cool down to 150 °C and was maintained at 150 °C for 20 min for degassing by Ar bubbling. For the degassed solution of the QDs, the following Cd(Fo)₂ treatment was carried out in the same manner as described above.

Precipitation of CdSe/CdS Core/Shell QDs. For precipitation with acetonitrile, the crude reaction solution was mixed with chloroform with a volume ratio of 1:1. Acetonitrile was added at an appropriated amount to completely precipitate the QDs. The mixture was centrifuged at 4000 r/m, and the solution phase was discarded. The precipitation was repeated again by dispersing the QDs in hexane to ensure all side products were excluded. For precipitation with methanol, the crude reaction solution was mixed with methanol with a volume ratio of 1:2. This mixture was centrifuged at 4000 r/m for 5 min, and the solution phase was discarded. For the second precipitation, QDs were first dispersed in hexane; then, a mixture of methanol and acetone (1:1 volume ratio) was added to precipitate the QDs. The addition of acetone was to ensure a homogeneous phase for the supernatant.

Effects of Amines on PL quenching of the QDs by H₂S. Two batches of CdSe/5CdS core/shell QDs from the same reaction were used for this study. One batch of the QDs was purified using the acetonitrile precipitation described above and then dissolved in pure hexane. The other batch was directly from the crude solution and diluted with hexane to the same concentration of the QDs. After bubbling H₂S gas for 15 s, PL spectra of these two solutions were collected to monitor the evolution of their PL intensity.

Correlation of Concentration of H₂S in the Gas Phase and PL Intensity of the QDs in the Solution. For the data in Figure S5, CdSe/5CdS core/shell QDs were synthesized following the typical procedure with some modification for the fifth monolayer of epitaxy. Specifically, after the precursor solution was added at 80 °C, the solution was heated up following the usual procedure. Heating was stopped at about 120 °C after the PL peak position shifted to about 611 nm, indicating full epitaxy as expected. Subsequently, Ar was bubbled into the reaction solution. At a given time interval, the exhausted gas was introduced into a glass vial with a piece of wet lead acetate testing paper for 1.5 min, and a PL spectrum of the QDs in the solution was recorded during this time interval.

Optical Measurements. UV–vis spectra were taken on an Analytik Jena S600 UV–vis spectrophotometer. PL spectra were recorded using an Edinburgh Instrument FLS920. The absolute PL QY was measured using an Ocean Optics FOIS-1 integrating sphere coupled with a QE65000 spectrometer. Transient PL was measured on a time-correlated single-photon counting (TCSPC) spectrofluorometer (FLS920, Edinburgh Instrument, U.K.) at room temperature. The nanocrystal samples were diluted in hexane solution and excited by a 405 nm picosecond laser diode with a 2 MHz repetition rate.

Fourier Transform Infrared (FTIR) Measurements. After purification, the QDs were dispersed in a small amount of hexane. Several drops of this concentrated solution were placed onto a CaF₂ platelet and allowed the solvent to evaporate. Air was used as the reference for the FTIR measurements using a Nicolet 380 spectrometer.

Nuclear Magnetic Resonance (NMR) Measurements. NMR spectra were obtained on a Bruker AVANCE III 500. The QDs were

precipitated twice by acetonitrile as mentioned above from about 5 mL of crude reaction solution. The precipitation was dried overnight at room temperature, and then dissolved by chloroform-d for measurements.

Transmission Electron Microscopy (TEM). Low-resolution TEM images were taken on a Hitachi 7700 transmission electron microscope with an acceleration voltage of 80 kV using copper grids (400-mesh) coated with pure carbon support film.

X-ray Powder Diffraction (XRD). XRD patterns were obtained using a Rigaku Ultimate-IV X-ray diffractometer operating at 40 kV/40 mA using the Cu K α line ($\lambda = 1.5418 \text{ \AA}$). Powder samples for XRD measurements were prepared by the acetonitrile precipitation procedure. The final precipitate was separated by decantation of the solution waste and transferred onto a glass slide for XRD measurements.

Single Dot PL Measurements. PL intensity trajectories were obtained following a reported procedure.^{34,37} Briefly, samples were obtained by diluting an aliquot in a PMMA/toluene (2 wt % PMMA) solution. The mixed solution was spin-coated onto a clean glass coverslip. All single-dot optical measurements were performed using a home-built epi-illumination fluorescence microscope system equipped with a Zeiss 63 \times oil immersion objective (numerical aperture = 1.46) and suitable spectral filters. Samples were excited by a 405 nm ps pulse laser with 1 MHz repetition. The excitation power was calculated to ensure the QDs at a single-exciton level. The PL intensity trajectories of single dots were recorded by an Andor DU-897 EMCCD. The exposure time per frame was 30 ms. The PL intensity of each QD on each frame was determined by the mean of the gray values in an $\sim 1.4 \times 1.4 \mu\text{m}^2$ square containing the largest luminescence spot of the dot in all frames. Background intensity was determined by the mean of the gray values in a square of the same size close to the QD but without any luminescence signal from visible QDs.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b02909.

Additional experimental data and figures (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*xpeng@zju.edu.cn

Notes

The authors declare no competing financial interest.

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