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Highly Reactive Se Precursor for the Phosphine-Free Synthesis of Metal Selenide Nanocrystals

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Herein we present a general phosphine-free synthesis of metal selenide nanocrystals. In this method, reduction of elemental Se with sodium borohydride in the presence of hydrophobic alkylamines generated hydrophobic alkylammonium selenide species in situ. The phosphine-free Se precursor was found to be highly reactive and suitable for the synthesis of various metal selenide nanocrystals. Its high reactivity was also exploited to derive core−shell CdSe@CdS quantum dots (QDs) in one-pot synthesis, without the need for prior purification of CdSe cores. This provided a greener and less expensive route to the large-scale synthesis of metal selenide QDs. Our approach also presented a facile route for tuning the surface properties of metal selenides. It was found that the presence of excess elemental sulfur could quench the luminescence of QDs by the trapping of surface electrons. However, the luminescence could be photoactivated via ultraviolet (UV) irradiation. This deactivation−photoactivation process was reversible, and could be applied toward generating a designed photoluminescent pattern on a solid substrate.

Introduction

Metal selenide QDs have generated intense interest in applications such as opto-electronics (e.g., light-emitting diodes (LEDs)[1,2] and photovoltaics[3,4]) and bioimaging. To achieve the widespread use of QD-based devices and systems, it would be important to develop safe, economical, and environmentally friendly large-scale syntheses of high-quality QDs. Current colloidal syntheses of QDs may be categorized by (i) those conducted at low temperatures in water and (ii) those performed at high temperatures in organic solvents. The aqueous synthesis typically involves the reaction of an aqueous cadmium salt with sodium selenide.[5,6] The solvent and precursors are benign and inexpensive. However, the photoluminescence (PL) quantum yield (QY) of the product is often low owing to a large number of defect states, and the photostability is also poor due to the difficulty in forming a passivating layer against oxidation. The high-temperature synthesis usually involves the reaction of an organic cadmium compound with a phosphine complex of selenium.[7−10] The product often exhibits high PL QY and photostability. However, toxic and expensive organometallic compounds (e.g., dimethylcadmium) and phosphines (e.g., trioctylphosphine (TOP) and tributylphosphine (TBP)) are used as precursors.

Organometallic cadmium precursors have been replaced with the more benign organic cadmium salts, e.g., cadmium stearate.[9,10] The Se precursor, on the other hand, is still almost invariably a Se−phosphine complex. This has prompted some groups to develop alternative Se precursors that involve the dissolution of elemental selenium by prolonged heating in organic solvents[11,12] or by using hydrogen selenide gas.[13] Herein, we presented an alternative route for synthesizing the organic selenide salt directly in phosphine-free organic solvents. In this method, reduction of elemental Se with sodium borohydride ($NaBH_4$) in the presence of hydrophobic alkylamines (e.g., oleylamine (OLA)) generated hydrophobic alkylammonium selenide species in situ. The phosphine-free Se precursor was found to be highly reactive, and suitable for the synthesis of various metal selenide nanocrystals. Its high reactivity was also exploited to derive core−shell CdSe@CdS QDs in one-pot synthesis, without the need for prior purification of CdSe cores. This provided a greener and less expensive route to the large-scale synthesis of metal selenide QDs.

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Experimental Section

Chemicals. Cadmium oxide (CdO, ≥ 99%), lead acetate trihydrate ($Pb(OAc)_2 \cdot 3H_2O$, ≥99.5%), zinc stearate trihydrate ($(Zn(stearate)_2 \cdot 3H_2O$, technical grade), silver nitrate ($AgNO_3$, ≥99%), copper(I) acetate (CuOAc, 97%), indium acetate ($In(OAc)_3$, 99.99%), octadecylphosphonic acid (ODPA, 97%), OLA (technical grade, 70%), oleic acid (OA, ≥93%), Se powder (≥99%), S (≥99.5%), $NaBH_4$ (98%), tetrabutylammonium borohydride (TBAB, 98%), acetone (98%), toluene (99%), and chloroform (98%) were purchased from Sigma-Aldrich and used as received.

CdSe Synthesis. In total, 26 mg of CdO (0.2 mmol), 130 mg of ODPA (0.4 mmol), and 5 mL of OLA were heated to 300 °C under Ar flow until the reactants were completely dissolved; the solution was then cooled to 240 °C. The Se solution was prepared by dissolving 4 mg of Se powder (0.05 mmol) and 2 mg of $NaBH_4$ (0.05 mmol) in 2 mL of OLA. It was injected into the reaction mixture with rapid stirring. The nanocrystals were obtained with ripening at 300 °C for a set period of time following the Se solution injection. Absorption and PL spectra were recorded for aliquots of these nanocrystals. The nanocrystals were precipitated, washed twice using acetone, and redispersed in toluene or chloroform.

Ag_2Se Synthesis. In total, 34 mg of $AgNO_3$ (0.2 mmol) and 5 mL of OLA were heated to 100 °C under Ar flow until the reactants were completely dissolved. The Se solution was prepared by the dissolution of 16 mg of Se (0.2 mmol) and 8 mg of $NaBH_4$ (0.2 mmol) in 2 mL of OLA. It was injected into the reaction media with rapid stirring. The mixture was heated at 100 °C for another 5 min and then cooled to room temperature. The Ag_2Se nanocrystals were precipitated, washed twice using acetone, and redispersed in toluene or chloroform.

PbSe Synthesis. In total, 76 mg of $Pb(OAc)_2 \cdot 3H_2O$ (0.2 mmol), 0.2 mL of OA, and 5 mL of OLA were heated to 240 °C under Ar flow until the reactants were completely dissolved. The Se solution was prepared by the dissolution of 8 mg of Se (0.1 mmol) and 4 mg of $NaBH_4$ (0.1 mmol) in 2 mL of OLA. It was injected into the reaction media with rapid stirring. The mixture was heated at 240 °C for one more minute and then cooled to room temperature. The PbSe nanocrystals were precipitated, washed twice using acetone, and redispersed in toluene or chloroform.

ZnSe Synthesis. In total, 126 mg of $Zn(stearate)_2 \cdot 3H_2O$ (0.2 mmol) and 5 mL of OLA were heated to 240 °C under Ar flow until the reactants were completely dissolved. The Se solution was prepared by the dissolution of 8 mg of Se (0.1 mmol) and 4 mg of $NaBH_4$ (0.1 mmol) in 2 mL of OLA. It was injected into the reaction media with rapid stirring. The mixture was heated at 240 °C for another 5 min and then cooled to room temperature. The ZnSe nanocrystals were precipitated, washed twice using acetone, and redispersed in toluene or chloroform.

$CuInSe_2$ Synthesis. In total 12 mg of CuOAc (0.1 mmol), 29 mg of $In(OAc)_3$ (0.1 mmol), and 5 mL of OLA were heated to 240 °C under Ar flow until the reactants were completely dissolved. The Se solution was prepared by the dissolution of 8 mg of Se (0.1 mmol) and 4 mg of $NaBH_4$ (0.1 mmol) in 2 mL of OLA. It was injected into the reaction media with rapid stirring. The mixture was heated at 240 °C for another 5 min and then cooled to room temperature. The $CuInSe_2$ nanocrystals were precipitated, washed twice using acetone, and redispersed in toluene or chloroform.

CdSe@CdS Synthesis. In total, 26 mg of CdO (0.2 mmol), 130 mg of ODPA (0.4 mmol), and 5 mL of OLA were heated to 300 °C under Ar flow until the reactants were completely dissolved, and then the solution was cooled to 240 °C. The Se solution was prepared by dissolving 4 mg of Se powder (0.05 mmol) and 2 mg of $NaBH_4$ (0.05 mmol) in 2 mL of OLA. It was injected into the reaction mixture with rapid stirring. Next, the temperature for the reaction system was reduced to 220 °C right away, where the mixture was kept for 1 min. The S solution was prepared by dissolving 1.5 mg of elemental sulfur (0.05 mmol) in 2 mL of OLA. It was injected into the reaction mixture dropwise with rapid stirring. The mixture was heated at 220 °C for another 5 min and then cooled to room temperature. The resulting CdSe@CdS nanocrystals were precipitated, washed twice using acetone, and redispersed in 10 mL of chloroform (to obtain a nominal CdSe concentration of 5 mM).

Luminescence Quenching. A volume of 0.2 mL of the CdSe@CdS colloidal solution was diluted with 0.8 mL of chloroform to obtain a nominal CdSe concentration of 1 mM. The S solution was prepared by dissolving 1.5 mg of elemental sulfur (0.05 mmol) in 2 mL of OLA. A drop of the S solution was then added to the CdSe@CdS solution to quench the QD luminescence. The resulting sample was designated as CdSe@CdS with excess sulfur.

Two-Photon Laser Writing and Imaging. A chloroform solution of CdSe@CdS with excess sulfur was spin-coated onto a glass coverslip. Two-photon laser writing of a specific pattern on the coated coverslip and luminescence imaging were performed using a Zeiss LSM 510-Meta laser scanning microscope with a Ti:Sapphire laser (Mai Tai BB, Spectra-Physics) as the excitation source at 900 nm.

Transmission Electron Microscopy (TEM) Characterization. TEM was performed on a FEI Tecnai G^2 F20 electron microscope operated at 200 kV with the software package for automated electron tomography. For TEM studies, a drop of the nanoparticle solution was dispensed onto a 3 mm carbon-coated copper grid. Excess solution was removed by an absorbent paper, and the sample was dried under vacuum at room temperature.

X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) Characterizations. XRD patterns were obtained using a Siemens D5005 diffractometer. XPS analysis was conducted on a VG ESCALAB MKII spectrometer. The QDs were precipitated from the toluene solution using acetone, recovered by centrifugation, and washed with acetone several times to remove nonspecifically bonded OLA. They were dried at room temperature in vacuum before the XRD and XPS characterizations.

Results and Discussion

The scheme for synthesizing phosphine-free QDs is illustrated in Figure 1. Our protocol employed $NaBH_4$ to facilitate the dissolution of Se powder in OLA at room temperature. The dissolution of Se in OLA using $NaBH_4$ was derived from a phase transfer protocol. We found that Se powder reduced by $NaBH_4$ in the aqueous phase could be transferred to organic solvent easily using amine as the transfer agent. Subsequently, this transfer protocol was devised to synthesize the organic selenide salt directly in organic solvents. In the presence of $NaBH_4$, Se powder was first reduced into Se^{2-}, which could be dissolved in OLA to generate a colorless solution. The Se precursor solution in OLA was labeled as OLA-Se. Without $NaBH_4$, Se could only be dissolved in OLA after extended heating under continuous Ar flow, analogous to the dissolution of Se powder in octadecene[11] and olive oil.[12]

Figure 2a shows the photographs of the CdSe colloidal solution in toluene under UV excitation. The CdSe nanocrystals derived 1, 8, 16, 32, 64, 128, 256, and 512 min after

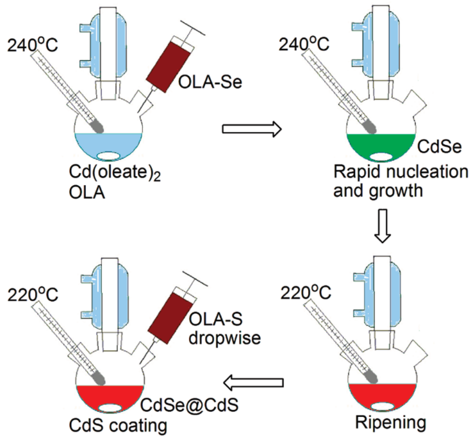

Figure 1. Schematic for the synthesis of phosphine-free CdSe@CdS QDs.

the injection of OLA-Se precursor at 250 °C were precipitated by the addition of acetone and redispersed in toluene. The resulting absorption and normalized PL spectra for the aliquots taken at various times after the injection of OLA-Se precursors are illustrated in Figure 2b,c. The sharp features in the absorption spectra indicated a narrow size distribution for the CdSe samples,[14,15] which was further confirmed by the narrow full width at half-maximum (fwhm = 25−28 nm) of the emission band. A TEM image of the CdSe nanocrystals derived 512 min after the injection of OLA-Se precursor is shown in Figure 2d. The average TEM particle size and relative standard deviation of the nanocrystals were 5.1 nm and 4.8%, respectively. The narrow size distribution of nanocrystals resulted in the formation of two-dimensional (2D) close-packed hexagonal arrays on the TEM grid. Figure 2e illustrates the high-resolution TEM (HRTEM) image of the same CdSe sample, indicating that the as-prepared CdSe nanocrystals were highly crystalline. This was consistent with the powder X-ray diffraction (XRD) pattern of the sample (Supporting Information, Figure S1), which confirmed the cubic crystal structure of CdSe. These findings demonstrated that high-quality CdSe nanocrystals were successfully obtained using the phosphine-free Se precursor. Compared to other phosphine-free methods,[11−13] whereby the Se was dissolved in organic solvents by prolonged heating, this room-temperature preparation of Se solution provided for a facile synthesis that also conserved energy and time.

The phosphine-free Se precursor was found to be highly reactive and suitable for the synthesis of a wide range of metal selenide nanocrystals, including Ag_2Se, PbSe, ZnSe, and $CuInSe_2$. The experimental conditions were only slightly different from that for CdSe synthesis. Figure 3 shows the TEM and HRTEM images of the crystalline metal selenide samples. The successful syntheses of Ag_2Se, cubic PbSe and ZnSe, and tetragonal $CuInSe_2$ nanocrystals were also demonstrated by XRD (Supporting Information, Figure S2). Unlike the spherical morphology of other metal selenides, bimetallic selenide $CuInSe_2$ nanocrystals were mostly triangular or cubic (Figure 3g,h). This could have resulted from the existence of preferential particle growth directions, probably caused by the anisotropic adsorption of OLA on the surface of the growing $CuInSe_2$ nanocrystals.

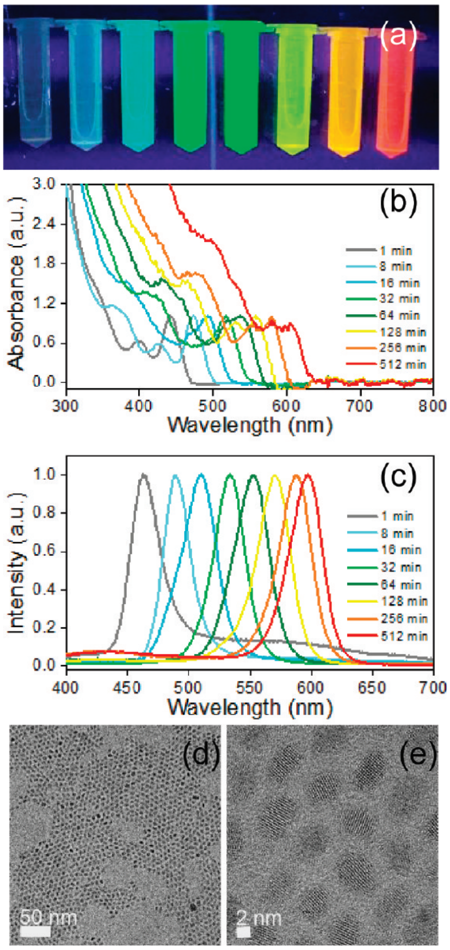

Figure 2. (a) Photographs showing the as-prepared CdSe nanocrystals obtained 1, 8, 16, 32, 64, 128, 256, and 512 min after the Se precursor injection (left to right). (b) Absorption and (c) normalized PL spectra of the aliquots obtained from the time specified after the Se precursor injection. (d) TEM and (e) HRTEM images of the CdSe nanocrystals derived 512 min after the Se precursor injection.

This phosphine-free Se precursor further facilitated the synthesis of metal selenide QDs with a core−shell structure. For example, to derive core−shell CdSe@CdS, the reaction mixture containing Cd and Se precursors at a molar ratio of 4:1 was heated at 220 °C for 10 min for the ripening of CdSe nanocrystals, followed by the dropwise addition of S solution in OLA (labeled as OLA-S) with rapid stirring. This one-pot synthesis of core−shell CdSe@CdS nanocrystals relied on the fact that the OLA-Se precursor used was highly reactive and rapidly consumed. Hence, the CdS coating could be achieved without prior purification of the CdSe cores, unlike the conventional approaches with TOP-Se as the Se precursor.[16,17]

Figure 4a shows the photographs of the core−shell CdSe@CdS colloidal solutions in toluene under UV excitation. 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 equiv of CdS

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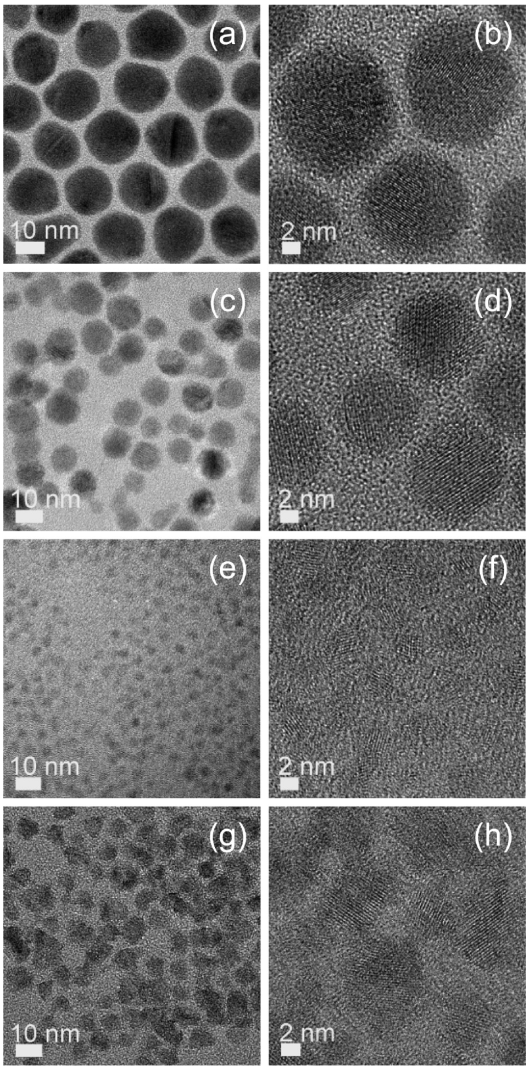

Figure 3. (a, c, e, g) TEM and (b, d, f, h) HRTEM images of (a, b) Ag_2Se, (c, d) PbSe, (e, f) ZnSe, and (g, h) $CuInSe_2$ nanocrystals synthesized with OLA-Se precursor.

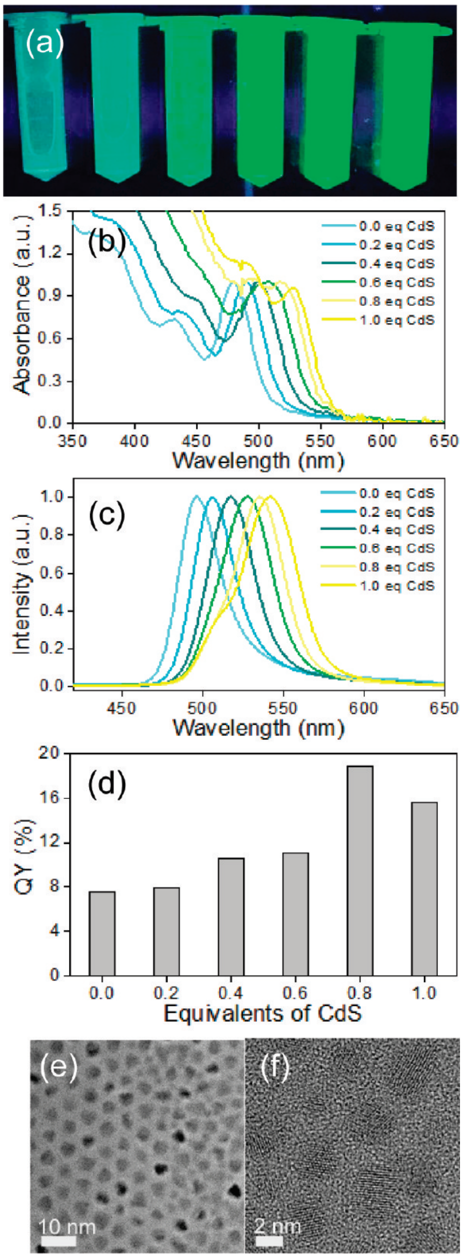

Figure 4. (a) Photographs showing the as-prepared core–shell CdSe@CdS nanocrystals prepared with the addition of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 equiv of CdS (left to right). (b) Absorption and (c) normalized PL spectra of the aliquots derived from the different equivalents of CdS specified. (d) QYs of the CdSe@CdS nanocrystals prepared with the different equivalents of CdS specified. (e, f) TEM and HRTEM images of the CdSe@CdS nanocrystals prepared with the addition of 1.0 equiv of CdS.

were introduced. With control of the thickness of the CdS shell, the color of the CdSe QDs could be tuned. The absorption spectrum showed a slight broadening caused by the size increase during the growth of the CdS shell (Figure 4b). The corresponding PL spectra (Figure 4c) revealed band-edge luminescence for QDs of all CdS shell thicknesses; no deep trap luminescence was detected. The CdS coating markedly improved the fluorescence of the CdSe QDs. Figure 4d shows that the QY was optimized when the CdSe cores were coated by 0.8 equiv of CdS. TEM and HRTEM images of CdSe@CdS nanocrystals derived with the use of 1.0 equiv of CdS are shown in Figure 4e,f. After CdS coating, the nanoparticles became less regular in morphology and had an increase in particle size from ~3.2 nm (Supporting Information, Figure S3) to ~4.8 nm. Since the lattice mismatch between CdSe and CdS is only ~3.9%,[16] the core–shell structure was difficult to determine accurately using TEM. However, the formation of core–shell CdSe@CdS nanoparticles could be confirmed by the elemental profile via energy-dispersive X-ray (EDX) analysis. As shown in the Supporting Information, Figure S4, Cd and S signals were noted across the entire particle, whereas Se signal was obtained only across the ~3 nm core.

Analogous to the Se-rich CdSe nanocrystals,[18] the addition of excess sulfur to the colloidal CdSe@CdS solution in toluene would quench the QD luminescence (Figure 5a). The PL could be recovered by exposing the QDs with excess sulfur to UV light (365 nm, 2 mW/mm^2). The deactivation–photoactivation process was reversible by the alternate addition of sulfur and UV irradiation (Figure 5b). Cohen

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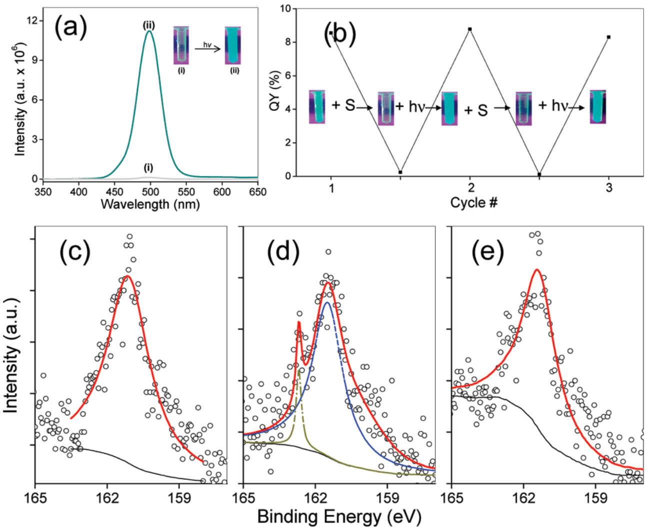

Figure 5. (a) PL spectra and (inset) photographs of CdSe@CdS QDs with excess sulfur (i) before and (ii) after 30 s of UV irradiation (365 nm). (b) Reversibility of the deactivation−photoactivation process induced by sulfur addition and UV irradiation, respectively, as illustrated by the photographs and QYs of CdSe@CdS QDs with excess sulfur. XPS S 2p spectra of (c) CdSe@CdS QDs without excess sulfur and CdSe@CdS QDs with excess sulfur (d) before and (e) after UV irradiation.

and co-workers[19] have demonstrated the photoactivation of core−shell CdTe@CdS nanocrystals functionalized with *ortho*-nitrobenzyl (ONB) groups. These QDs were nonluminescent under typical microscopic illumination but could be activated with strong pulses of UV light. However, their system involved the use of complex organic molecules, and no reversible deactivation−photoactivation process was reported.

Herein the deactivation of QDs using excess sulfur further yielded insight into the surface chemistry of QDs. Studies with phosphine-free Se precursors have previously suggested that Se-rich QDs have lower QY due to the introduction of surface hole traps associated with the dangling bond orbitals of the Se^{2-} species.[18] This work showed that introduction of excess elemental sulfur could also reduce QY. X-ray photoelectron spectroscopy (XPS) S 2p spectrum showed that CdSe@CdS nanocrystals only exhibited one peak at 161.2 eV (Figure 5c), which could be indexed to S^{2-}. The spectrum of CdSe@CdS with excess sulfur could be deconvoluted into two peaks (Figure 5d). The more intense peak at 161.5 eV was attributed to S^{2-}, while the weaker peak at 162.7 eV could be assigned to S^0.[20] After UV irradiation, only one peak at 161.4 eV (corresponding to the S^{2-}) was observed in the S 2p spectrum of CdSe@CdS nanocrystals with excess sulfur (Figure 5e). The XPS analyses suggested that elemental sulfur was responsible for the quenching of QD luminescence and the low QY. UV irradiation resulted in the reduction of elemental sulfur, photoactivating the QDs.

Figure 6. Photograph of a photoluminescent pattern generated by two-photon laser writing on a solid substrate coated with CdSe@CdS QDs with excess sulfur. Scale bar represented 20 μm.

We have found that instead of using UV irradiation, the addition of a strong reducing agent, TBAB, to the CdSe@CdS colloidal solution with excess sulfur could also recovered the QD luminescence. These experimental results led to the unanticipated conclusion that the surface traps were associated with elemental sulfur and were thus electron traps; they led to PL quenching of QDs analogous to that by Lewis acid-like adsorbates.[21] Thus, this study presented an alternative interpretation of the QD deactivation−photoactivation process, in contrast to the discussions on oxidation of Se surface sites,[22] oxygen passivation,[23] photoinduced passivation by water,[24,25] and surface reconstruction.[26−28]

The deactivation−photoactivation of QDs could also be conducted on a solid substrate. Briefly, a drop of S solution in OLA was added to the QD solution in chloroform, quenching the QD luminescence. The resulting colloidal solution in chloroform was then spin-coated onto a glass coverslip and irradiated with a two-photon laser. The photoactivation of QDs via the reduction of elemental sulfur resulted in the designed pattern on the solid substrate (Figure 6).

Conclusions

In summary, we have demonstrated a phosphine-free protocol for synthesizing metal selenide nanocrystals. It employed $NaBH_4$ to facilitate Se powder dissolution in OLA at room temperature, bypassing the need for extended heating. The phosphine-free Se precursor has been successfully applied toward the synthesis of a variety of

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metal selenide nanocrystals. The high reactivity of the phosphine-free Se precursor was further used in the one-pot synthesis of core−shell CdSe@CdS QDs, without the need for prior purification of CdSe cores. This approach also presented a facile route for tuning the surface property of metal selenides. It was found that the presence of excess elemental sulfur could quench the luminescence of QDs by the trapping of surface electrons. However, the luminescence could be photoactivated via UV irradiation. This deactivation−photoactivation process was reversible and could be applied toward generating a photoluminescent pattern on a solid substrate.

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Supporting Information Available: XRD patterns of the QDs synthesized using the phosphine-free Se precursor, TEM and HRTEM images of nanocrystalline CdSe seeds for the growth of CdS shell, and EDX analysis of core−shell CdSe@CdS nanocrystal under the scanning transmission electron microscopy (STEM) mode (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.