Size-dependent ligand exchange of colloidal CdSe nanocrystals with $S^{2-}$ ions†

Limin Liu,ab Xianfeng Zhang,a Li Ji,b Hanwen Li,a Huijuan Yu,a Fangjie Xu,b Jianhua Hu,a Dong Yang*a and Angang Dong*b

In the surface treatment of colloidal nanocrystals (NCs), $S^{2-}$ ions have been widely employed as metal-free atomic ligands to efficiently replace the original long hydrocarbon ligands. Prior studies exclusively show that $S^{2-}$ ions considerably quench the photoluminescence (PL) of semiconductor NCs (e.g., CdSe and PbS) during ligand exchange. Here we report that the influence of $S^{2-}$ treatment on the luminescent properties of CdSe NCs is highly dependent on the NC size. We observe an unexpected PL brightening phenomenon when small CdSe NCs (<4 nm) are subject to $S^{2-}$ treatment followed by incubation in the presence of air and light irradiation, whereas PL enhancement is not observed in large CdSe NCs (>4 nm) treated under the same conditions. Systematic characterization establishes the evolution of CdSe/CdS core–shell structures in small CdSe NCs arising from anion exchange between $Se^{2-}$ and $S^{2-}$, which in conjunction with the subsequent incubation process accounts for the PL enhancement. Notably, 2.1 nm CdSe NCs treated with (NH$_4$)$_2$S exhibit a PL quantum yield (QY) as high as ~40% after 2 days of incubation, which is comparable to that of conventional hydrophobic CdSe/CdS core–shell NCs synthesized at high temperatures. Our studies demonstrate that $S^{2-}$ ions can substantially substitute $Se^{2-}$ in small CdSe NCs in addition to replacing the surface-coating ligands, enabling highly luminescent, hydrophilic CdSe/CdS core–shell NCs at room temperature.

Introduction

Colloidal nanocrystals (NCs) have been the subject of intensive investigation due to their unique size-dependent properties and wide device applications.1–4 Controlled synthesis of high-quality NCs generally requires the use of long hydrocarbon molecules such as tri-n-octylphosphine oxide (TOPO) and oleic acid (OA) as ligands.5–7 In addition to serving as stabilizers to prevent NC aggregation, the surface-capping ligands also provide chemical passivation, which has a significant influence on the physiochemical properties of NCs.8–11 Surface chemistry is particularly important for luminescent semiconductor NCs, as a good passivation layer can reduce the density of surface trap states and improve the stability of NCs against photo-degradation, enabling high and stable fluorescence quantum efficiencies.12–14 However, the existence of the long insulating ligands dramatically inhibits electronic communications between NCs in solution-cast films, significantly limiting their device applications.15–18,19 To overcome this problem, considerable attention has been paid to the surface modification of colloidal NCs in the past few years,1 with a main purpose to promote charge transport through NC films. Ligand exchange is a commonly used strategy, in which the original long ligands are replaced by shorter ones through a solution- or solid-phase process while preserving the morphology and properties of individual NCs.1,20–27 A variety of small organic and inorganic species, including hydrazine,18 NOBF$_4$,21 thiocyanates,22 molecular metal chalcogenide complexes,23 halides,24 and chalcogenides,25–27 have been utilized to treat NCs, and the enhanced NC coupling resulted from ligand exchange has enabled the development of a number of electronic and optoelectronic devices.20,19

Among various small species recently developed for ligand exchange, $S^{2-}$ ions are emerging as a class of inorganic atomic ligands that are particularly suitable for surface treatment of semiconductor NCs.25–27 In this regard, $S^{2-}$ ions replace the original organic ligands, resulting into hydrophilic, $S^{2-}$-passivated NCs that are dispersible in polar solvents having high dielectric constants such as formamide (FA).27 Notably, this facile ligand-exchange process can be accomplished within seconds with high exchange efficiencies, presumably due to the strong binding affinity between $S^{2-}$ and the partially coordinated metal cations at NC surface.28 Since the first demonstration by Talapin and coworkers,25 $S^{2-}$ ligands have been widely...
applied to the surface modification of semiconductor NCs.\textsuperscript{26–30} Moreover, CdSe and PbSe NCs treated with S\textsuperscript{2−} have been used to construct electronic and optoelectronic devices with enhanced performance.\textsuperscript{28–30} Despite these benefits, S\textsuperscript{2−}-ligand exchange has been demonstrated to be detrimental for the luminescent properties of semiconductor NCs.\textsuperscript{25–27} For instance, Talapin and coworkers reported that the PL quantum yield (QY) of 5.5 nm, OA-capped CdSe NCs dropped from 13 to 2% upon S\textsuperscript{2−} treatment,\textsuperscript{25} and 4.2 nm, S\textsuperscript{2−}-treated CdSe NCs exhibited an even lower QY at 0.7%.\textsuperscript{27} Similarly, Robinson and coworkers showed that the PL intensity of PbS NC films treated with (NH\textsubscript{4})\textsubscript{2}S gradually decreased with treatment time.\textsuperscript{26} In addition, the PL lifetime was observed to decrease after S\textsuperscript{2−} treatment by both groups,\textsuperscript{25,26} indicating that the reduced QY in CdSe and PbS NCs could be caused by non-radiative recombination channels arising from surface defects introduced by S\textsuperscript{2−} ligands. Although the exact quenching mechanism is yet to be explored, prior studies unambiguously demonstrate that S\textsuperscript{2−} treatment considerably quenches the PL of semiconductor NCs, which is undesirable for applications that require high quantum efficiencies such as light-emitting devices\textsuperscript{31} and biological labeling.\textsuperscript{32}

In this work, we report systematic studies of S\textsuperscript{2−}-ligand exchange of CdSe NCs with various sizes and reveal a striking size-dependent influence of S\textsuperscript{2−} treatment on the luminescent properties of CdSe NCs. In contrast to the quenching results reported previously,\textsuperscript{25–27} we have found that S\textsuperscript{2−} treatment can significantly enhance the PL of CdSe NCs having sizes less than 4 nm upon incubation in the presence of air and light irradiation, whereas PL enhancement is not observed in large CdSe NCs (>4 nm) treated under the same conditions. This unexpected brightening phenomenon is attributed to the evolution of CdSe/CdS core–shell structures in small CdSe NCs, in which the thin CdS shell is formed by anion exchange between Se\textsuperscript{2−} and S\textsuperscript{2−} occurring during ligand exchange, as consistently confirmed by absorption and PL spectroscopies, X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy (EDS). In addition, both air and light irradiation prove to be critical parameters that dictate the PL enhancement in S\textsuperscript{2−}-treated CdSe NCs, presumably due to the photochemical annealing of structural defects initially presenting at CdSe/CdS interfaces.\textsuperscript{33,34} Notably, 2.1 nm CdSe NCs treated with (NH\textsubscript{4})\textsubscript{2}S exhibit a PL QY as high as ~40%, which is comparable to that of high-quality hydrophobic CdSe/CdS core–shell NCs obtained by high-temperature colloidal synthesis.\textsuperscript{34,35} Our studies establish that S\textsuperscript{2−} treatment can be employed as a new route to synthesize highly luminescent CdSe/CdS core–shell NCs at room temperature.

**Experimental section**

**Materials**

Selenium powder (Se, 99.5%), oleic acid (OA, 90%), oleylamine (OAm, 70%), 1-octadecene (ODE, 90%), tri-n-octylphosphine (TOP, 90%), and tri-n-octylphosphine oxide (TOPO, 90%) were purchased from Sigma-Aldrich. Cadmium oxide (CdO, 99.99%) and ammonium sulfide [(NH\textsubscript{4})\textsubscript{2}S] solution (40–48 wt% in water) were purchased from Aladdin. Formamide (FA) and potassium sulfide (K\textsubscript{2}S) were purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were used without further purification.

**Synthesis of CdSe NCs with different sizes**

All preparative procedures were conducted using standard Schlenk-line techniques under N\textsubscript{2}.

2.1 nm NCs capped with OA and TOP. In a typical synthesis, 256 mg of CdO and 3.5 mL of OA mixed in 40 mL of ODE were heated to 220 °C until the solution became clear. Then the solution was cooled to 120 °C and degassed to remove residual water. Under N\textsubscript{2}, a solution of Se precursor containing 316 mg of Se and 2 mL of TOP was injected. The reaction was allowed to proceed at this temperature for 10 min. After cooling down to room temperature, ethanol and isopropanol were added to precipitate CdSe NCs, and the precipitated NCs were redissolved in hexane to form a stable colloidal solution.

3.1 nm CdSe NCs capped with OA and OAm. 3.1 nm CdSe NCs were prepared according to the procedure reported elsewhere.\textsuperscript{36}

4.3 nm CdSe NCs capped with OA, OAm, and TOP. 4.3 nm CdSe NCs were prepared according to a literature method.\textsuperscript{26}

7.7 nm CdSe NCs capped with OA, OAm, and TOP. A stock solution of TOPSe solution was prepared by dissolving 158 mg of Se in 1.4 mL of TOP. In a typical synthesis, 128 mg of CdO and 1.75 mL of OA were heated in 20 mL of ODE at 220 °C until the solution became clear. The solution was cooled to 110 °C and 3.5 mL of OAm was added. After degassing for 1 h, the flask was heated to 320 °C, at which point 0.44 g of TOPSe was injected and the reaction was allowed to proceed at this temperature for 8 min. In the next 30 min, the remaining TOPSe precursor was added dropwise into the reaction solution. After cooling down to room temperature, ethanol and isopropanol were added to precipitate CdSe NCs, and the precipitated NCs were redissolved in hexane to form a stable colloidal solution.

**Ligand exchange of CdSe NCs with S\textsuperscript{2−} ions**

The ligand exchange of CdSe NCs with S\textsuperscript{2−} ions was carried out by a procedure described by Talapin and coworkers.\textsuperscript{25}

Ligand exchange with (NH\textsubscript{4})\textsubscript{2}S. A stock solution of (NH\textsubscript{4})\textsubscript{2}S in FA was prepared by adding 10 μL of (NH\textsubscript{4})\textsubscript{2}S aqueous solution into 1 mL of FA. In a typical experiment, 5 mL of CdSe NC solution (~0.01 M) in hexane was mixed with 1 mL of (NH\textsubscript{4})\textsubscript{2}S solution in FA. The resulting mixture was stirred for 10 min, during which the occurrence of ligand exchange was evidenced by the complete transfer of CdSe NCs into the FA phase. Upon phase transfer, CdSe NCs were isolated by repeated washing and centrifugation with acetone, and the precipitated NCs was redispersed in FA to form a stable colloidal solution for further characterization.

Ligand exchange with K\textsubscript{2}S. The ligand-exchange process using K\textsubscript{2}S differs slightly from the case of (NH\textsubscript{4})\textsubscript{2}S treatment. In a typical procedure, 5 mL of CdSe NC solution (~0.01 M) in hexane was mixed with 1.5 mL of K\textsubscript{2}S solution (5 mg mL\textsuperscript{−1}) in FA in a N\textsubscript{2}-purged glovebox. After 10 min of stirring, the ligand-
exchanged CdSe NCs were isolated by repeated washing and centrifugation, with FA and acetone as solvent and nonsolvent, respectively. The precipitated NCs were redispersed in FA for further characterization.

**PL enhancement in S\(^2^-\)-treated CdSe NCs**

The photoannealing of S\(^2^-\)-treated CdSe NCs was conducted in air, unless otherwise specified. The S\(^2^-\)-treated CdSe NCs dispersed in FA were incubated in the presence of steady light irradiation provided by room lights or a 7 W incandescent lamp. The PL spectra were acquired at different time intervals to monitor the photoenhancement process.

**Instrumentation**

TEM images were obtained on a Tecnai G2 F20 S-Twin microscope operated at 200 kV. FTIR spectra were recorded on a PerkinElmer Spectrum Two spectrometer. Scanning electron microscopy (SEM) images and EDS spectra were recorded using a Zeiss Ultra-55 microscope operated at 5 and 10 kV, respectively. XRD was carried out on a Bruker D4 X-ray diffractometer (Cu K\(\alpha\) irradiation, \(\lambda = 1.541 \text{ Å}\)). UV-visible absorption spectra were collected using a Shimadzu UV-3600 spectrophotometer. Steady state PL measurements were conducted on a PTI QM40 spectrometer using a xenon lamp as the source. The absolute PL QY was obtained using integrating sphere measurements, with all NC specimens measured at absorption density below 0.05 at the excitation wavelength. The PL lifetime measurements were carried out on FLS920 spectrometer.

**Results and discussion**

**Size dependence in S\(^2^-\)-ligand exchange of CdSe NCs**

The monodisperse and size-tunable CdSe NCs used in this work are synthesized by the established literature methods.\(^{26,36}\) To systematically examine the size dependence in S\(^2^-\)-ligand exchange, four different-sized CdSe NC specimens having an average diameter of 2.1 ± 0.4, 3.1 ± 0.4, 4.3 ± 0.5, and 7.7 ± 0.5 nm, respectively, are investigated in this work. The first three NC samples possess a zinc-blende (ZB) crystal structure, whereas 7.7 nm CdSe NCs predominately adopt a wurtzite (WZ) crystal structure (Fig. S1, ESI†). (NH\(_4\))\(_2\)S or K\(_2\)S is used for ligand exchange for all NC samples, which is carried out at room temperature with a duration of 10 min, following the procedure reported previously.\(^{25}\) Upon the complete removal of excess S\(^2^-\) by thorough washing, the ligand-exchanged CdSe NCs are dispersed in FA for further characterization. To enhance PL, the S\(^2^-\)-treated CdSe NCs stored in FA are exposed to air and room lights for 2 days before PL measurements.

(NH\(_4\))\(_2\)S is chosen to demonstrate S\(^2^-\) treatment, although a similar size-dependent behavior is also observed when K\(_2\)S is used for ligand exchange. For all samples, FTIR spectra confirm that the original organic ligands are nearly completely removed after 10 min of S\(^2^-\) treatment (Fig. S2†), suggesting that the ligand-exchange efficiencies are independent of the sizes, crystal structures, and organic capping ligands of CdSe NCs.

![Fig. 1](image1)

Transmission electron microscopy (TEM, Fig. 1) and the corresponding statistical analyses (Fig. S3†) indicate that the size of the S\(^2^-\)-treated CdSe NCs is almost identical to that of the
original NCs. Fig. 2 shows the representative absorption and PL spectra of CdSe NCs before and after S\textsuperscript{2−} treatment. As mentioned above, the PL spectra and QY of the S\textsuperscript{2−}-treated CdSe NCs are measured after 2 days of incubation in the presence of air and room lights. For 7.7 and 4.3 nm CdSe NCs, the excitonic features in their absorption spectra do not change noticeably after (NH\textsubscript{4})\textsubscript{2}S treatment (Fig. 2a and b). In addition, both samples retain their band-edge PL without obvious shift in peak position. However, both the PL QY and lifetime decrease upon ligand exchange (Table 1 and Fig. S4†), suggesting that S\textsuperscript{2−} treatment degrades the surface passivation of 7.7 and 4.3 nm CdSe NCs. The decreased PL QY and lifetime are consistent with previously reported results based on 5.5 and 4.2 nm CdSe NCs\textsuperscript{25,27} indicating that S\textsuperscript{2−} treatment indeed has an adverse effect on the luminescent properties of CdSe NCs having sizes larger than 4 nm.

It is interesting to note that the influence of S\textsuperscript{2−} treatment on the optical properties of CdSe NCs is different when the NC size gets smaller. As shown in Fig. 2c, the excitonic feature is red shifted by 8 nm in the absorption spectra of 3.1 nm CdSe NCs, with the PL peak shifted from 581 to 589 nm. More pronounced spectra shifting is observed when we further decrease the size of CdSe NCs. In the case of 2.1 nm CdSe NCs (Fig. 2d), a large red shift of ~40 nm is observed in absorption and PL spectra, respectively. More importantly, the PL quantum efficiencies of both NC samples are dramatically improved, which is in sharp contrast to the quenching phenomenon described above. The PL QY of 3.1 nm CdSe NCs is increased from 1.9 to 9.4%, while 2.1 nm CdSe NCs exhibit a QY as high as ~40% upon S\textsuperscript{2−} treatment, representing a 25-fold increase over the initial QY (~1.6%, Table 1). The improved PL quantum efficiencies are also evident by comparing the luminescent photographs of NC solutions before and after ligand exchange (Fig. 2c and d, insets). In addition to the improved QY, (NH\textsubscript{4})\textsubscript{2}S treatment also leads to an increase in PL lifetime for 3.1 and 2.1 nm CdSe NC samples (Table 1 and Fig. S4†). Given the PL quenching results obtained from 7.7 and 4.3 nm CdSe NCs, it is thus concluded that the influence of (NH\textsubscript{4})\textsubscript{2}S treatment on the luminescent properties of CdSe NCs is highly dependent on the NC size. Using K\textsubscript{2}S for ligand exchange also improves the PL QY for small CdSe NCs (<4 nm) while quenching the PL for larger ones (>4 nm), although the PL enhancement is not as significant as the case of (NH\textsubscript{4})\textsubscript{2}S treatment (Table S1 and Fig. S3†).

To understand the origin of this size-dependent behavior, XRD is performed to analyze the structural changes of CdSe NCs induced by S\textsuperscript{2−} treatment. Fig. 3 shows the XRD patterns of S\textsuperscript{2−}-treated CdSe NCs with varying sizes as well as the standard JCPDS stick patterns of CdSe and CdS bulk phases. The XRD patterns of individual CdSe NC samples before and after S\textsuperscript{2−} treatment are also shown in Fig. S1.† Despite different crystal structures, the diffraction peaks of 7.7 and 4.3 nm CdSe NCs do not shift upon ligand exchange, matching the corresponding CdS bulk phases (Fig. 3, green and pink curves). In contrast, the diffraction peaks of 3.1 nm, S\textsuperscript{2−}-treated CdSe NCs systematically shift toward larger angles and lie in between those inherent to CdSe and CdS bulk phases (Fig. 3, blue curve). An even further shift is observed in the case of 2.1 nm, S\textsuperscript{2−}-treated CdSe NCs, which display an XRD pattern nearly matching the CdS bulk phase (Fig. 3, red curve). As has been proposed previously, such a pronounced shift in XRD patterns could be ascribed to the formation of CdSe\textsubscript{x}S\textsubscript{1−x} alloys\textsuperscript{37} or CdSe/CdS core–shell structures.\textsuperscript{38} However, the large red shifts observed in absorption and PL spectra in Fig. 2c and d rule out the alloy formation, because ternary alloyed CdSe\textsubscript{x}S\textsubscript{1−x} NCs are expected to exhibit absorption and PL spectra that are blue shifted with respect to those of CdSe NCs due to the widened band gap energy.\textsuperscript{39,40} Therefore, XRD combined with absorption and PL spectroscopies strongly suggests the formation of CdSe/CdS core–shell structures in small S\textsuperscript{2−}-treated CdSe NCs.\textsuperscript{41,42} It is noteworthy that our findings are in agreement with the results recently reported by Dukovic and coworkers,\textsuperscript{43} who

<table>
<thead>
<tr>
<th>NC size (nm)</th>
<th>PL QY (%) Before treatment</th>
<th>PL QY (%) After treatment</th>
<th>PL lifetime (ns) Before treatment</th>
<th>PL lifetime (ns) After treatment</th>
</tr>
</thead>
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<td>7.7</td>
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<td>0.3</td>
<td>16</td>
<td>9</td>
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<td>9.4</td>
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<td>2.1</td>
<td>1.6</td>
<td>39.8</td>
<td>43</td>
<td>58</td>
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</table>

Fig. 3 XRD patterns of (NH\textsubscript{4})\textsubscript{2}S-treated CdSe NCs with different sizes. The XRD stick patterns of bulk CdSe (top) and CdS (bottom) phases are provided for comparison.
demonstrated by experiments and calculations that CdTe NCs treated with chalcogenide ions (S\(^2^-\), Se\(^2^-\), and Te\(^2^-\)) could be regarded as core–shell NCs with thin ligand shells.

EDS is employed to quantify the composition of CdSe NCs before and after ligand exchange (Fig. S6\(^\dagger\)). All the S\(^2^-\)-treated CdSe NC samples are subject to repeated washing and centrifugation to remove residual S\(^2^-\) ions, and to ensure more accurate measurements, EDS spectra are collected from multiple regions and the average Cd, Se, and S atomic percentages are used to determine the composition of each sample. As shown in Table 2, the atomic ratio of Cd/Se in original CdSe NCs is close to 1 : 1, while S\(^2^-\) treatment leads to a decrease in Se atomic percentage accompanied by an increase in S atomic percentage for all CdSe NC specimens. The considerably increased Cd/Se ratios upon ligand exchange suggest that Se\(^2^-\) ions in NC lattices have been partially substituted by S\(^2^-\), presumably through an anion-exchange reaction.\(^{44}\) Note that in all cases, the atomic ratio of Cd/(Se + S\(_{\text{total}}\)) after S\(^2^-\) treatment is still close to 1 : 1, implying that the content of the surface-bound S\(^2^-\) ligands (S\(_{\text{l}}\)) contributes insignificantly to the total S content (S\(_{\text{total}}\)). The S atomic percentage in NC lattices (S\(_{\text{NC}}\)) arising from anion exchange can be roughly calculated (Table 2), considering that the atomic ratio of Cd/(Se + S\(_{\text{NC}}\)) in S\(^2^-\)-treated CdSe NCs is equal to the initial Cd/Se ratio before S\(^2^-\) treatment. The S\(_{\text{NC}}\) values determined are then plotted as a function of NC diameters in Fig. 4, which clearly shows that the degree of anion exchange is highly sensitive to the size of NCs. For example, \(\sim 43.57\%\) of Se\(^2^-\) ions in 2.1 nm CdSe NCs undergo anion exchange during S\(^2^-\) treatment, whereas only \(\sim 8.51\%\) of Se\(^2^-\) ions in 7.7 nm CdSe NCs are replaced by S\(^2^-\) under the same conditions (Table 2). The higher degree of anion exchange in smaller CdSe NCs could be attributed to their higher surface to volume ratios, as anion exchange is expected to proceed from NC surface through inward diffusion, similar to the case of cation-exchange reactions.\(^{45,46}\) The degree of anion exchange resulted from K\(_2\)S treatment is also dependent on the size of CdSe NCs (Fig. S7\(^\dagger\)).

The thickness of CdS shells can be estimated by comparing the volume of the CdSe core and the CdS shell,\(^{47}\) assuming that CdS shells formed on the surface of CdSe NCs are smooth and continuous (Fig. S8\(^\dagger\)). As listed in Table 2, the thickness of CdS shells in 7.7, 4.3, 3.1, and 2.1 nm CdSe NCs is determined to be 0.11, 0.10, 0.23, and 0.18 nm, respectively. Given that a monolayer of CdS is about 0.21 nm in thickness,\(^{47}\) we speculate that S\(^2^-\) treatment leads to the formation of a monolayer CdS shell in small CdSe NCs (2.1 and 3.1 nm), whereas in the case of large CdSe NCs (4.3 and 7.7 nm), the resulting CdS shell is not thick enough to support a complete monolayer. The incomplete CdS coating also explains the PL quenching phenomenon observed in large CdSe NCs. We should point out that even in the case of small CdSe NCs with a large S content, the slight contrast difference between CdSe and CdS makes it hard to distinguish the core and the shell by TEM.

It is also noteworthy that the reduced core size arising from the formation of CdS shells in small CdSe NCs can lead to a blue shift in absorption and PL spectra, the magnitude of which may not be overcompensated by that of the red shift caused by the CdS shell formation. In other words, the large red shift should be caused by some other reasons in addition to the formation of CdSe/CdS core–shell structures. We note that CdSe NCs, especially 3.1 and 2.1 nm CdSe NCs, tend to aggregate or even fuse after S\(^2^-\) treatment (Fig. 1c and d). Such NC aggregation and fusion could lead to a significant red shift, due to the enhanced interparticle interactions. We speculate that the magnitude of the red shift induced by the core–shell formation as well as NC aggregation and fusion eventually overcompensates that of the blue shift caused by the decreased core size, leading to the observed red shift in absorption and PL spectra.

### PL enhancement in S\(^2^-\)-treated CdSe NCs

While it is becoming increasingly evident that the formation of CdSe/CdS core–shell structures in small CdSe NCs is

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**Table 2** Compositional analysis of CdSe NCs before and after (NH\(_4\))\(_2\)S treatment

<table>
<thead>
<tr>
<th>NC size (nm)</th>
<th>Before treatment</th>
<th>After treatment</th>
<th>d(_{\text{CdS}}) (nm)</th>
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<tbody>
<tr>
<td></td>
<td>Cd (%)</td>
<td>Se (%)</td>
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<td>2.1</td>
<td>51.13</td>
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</table>

\(a\) The total content of S. \(b\) The atomic percentage of S in CdSe NCs arising from anion exchange. \(c\) The atomic percentage of S in surface-coating ligands. \(d\) The percentage of Se\(^2^-\) replaced by S\(^2^-\) by anion exchange: S\(_{\text{re}}\) = S\(_{\text{NC}}\)/(S\(_{\text{NC}}\) + Se). \(e\) The thickness of CdS shells.
responsible for the observed PL brightening, we stress that $S^{2-}$-treatment does not lead to an immediate improvement in PL quantum efficiencies. Instead, the PL QY of the $S^{2-}$-treated CdSe NCs is found to be gradually increased upon exposure to air and light irradiation, reaching the maximum after 2 days of incubation (Fig. 5a). Notably, this PL brightening is irreversible, as the QY remains high after putting the incubated CdSe NCs in dark in a N$_2$-purged glovebox for several days. It is also noteworthy that despite the significantly increased PL intensity, no drastic structural and compositional changes in $S^{2-}$-treated CdSe NCs are detectable during the course of incubation as indicated by XRD and EDS. The gradually declined PL QY upon prolonged exposure in Fig. 5a is probably attributed to photooxidation, as photooxidation typically leads to a decrease in NC size, in agreement with the gradual blue shifts in PL peak position.

To further investigate the brightening mechanism, a series of control experiments are carried out, in which the $S^{2-}$-treated CdSe NCs are exposed to different environments for 12 h before PL measurements. As shown in Fig. 5b, NC samples incubated in dark do not show apparent PL brightening regardless of the presence of air (Fig. 5b, pink and green curves), suggesting that light irradiation is an important parameter for PL enhancement. On the other hand, when the sample incubated in a N$_2$-purged glovebox is exposed to light irradiation, only a slight improvement in PL intensity is observed (Fig. 5b, blue curve), implying that air also plays a key role in PL brightening. Given that significant PL enhancement is achievable only when the $S^{2-}$-treated CdSe NCs are exposed to both air and light irradiation (Fig. 5b, red curve), we surmise that the complex interplay between these two parameters dictates the PL enhancement.

Photoannealing is a commonly used strategy to improve the PL QY of core–shell nanostructures. For example, Buhro and coworkers reported that during surface treatment of CdTe nanowires with ethanethiol, photoannealing in the presence of O$_2$ promoted the formation of an epitaxial CdS shell on the nanowire surface by anion-exchange reactions between Te$_{2}\textsuperscript{2-}$ and S$_{2}\textsuperscript{2-}$. Likewise, Peng and co-workers observed PL brightening upon exposing CdSe/CdS core–shell NCs to light irradiation and oxygen. In our work, the evolution of CdS shells is found to be independent of air or light irradiation, as anion exchange between Se$_{2}\textsuperscript{2-}$ and S$_{2}\textsuperscript{2-}$ takes place even in the absence of air and light. However, PL brightening could be observed only when the $S^{2-}$-treated CdSe NCs are exposed to both air and light irradiation, as shown in Fig. 5b. Based on these observations, we speculate that light irradiation in the presence of air triggers structural reorganizations at CdSe/CdS interfaces through a photochemical process. This enables the elimination of structural defects originally presenting at CdSe/CdS interfaces, resulting in an ideal type-I heterostructure as schematically illustrated in Fig. 5c. We emphasize that such a minor structural change may not be detected by XRD. The presence of a considerable amount of structural defects at CdSe/CdS interfaces is reasonable if one considers that anion exchange takes place at room temperature, such that the resulting CdS shells may not be smooth and well-defined due to the presence of unexchanged Se$_{2}\textsuperscript{2-}$ and/or lattice mismatch between CdSe and CdS. In addition, light irradiation could also induce surface reconstructions, contributing to the PL enhancement by decreasing.

Fig. 5 (a) Plots of PL intensity and PL peak position of 2.1 nm, $S^{2-}$-treated CdSe NCs as a function of incubation time upon exposure to air and room lights. (b) PL spectra of 2.1 nm, $S^{2-}$-treated CdSe NCs which have been incubated under different conditions for 12 h. (c) Schematic illustration of $S^{2-}$-ligand exchange and photoenhancement, showing the evolution of CdSe/CdS core–shell structures in $S^{2-}$-treated CdSe NCs.

Fig. 6 (a) PL spectra of 2.1 nm, $S^{2-}$-treated CdSe NCs which have been incubated at different temperatures for 12 h. (b) Plots of PL intensity of 2.1 nm, $S^{2-}$-treated CdSe NCs as a function of time at different incubation temperatures.
the density of surface trap states.14-16 The improved interface and surface properties are also consistent with the increased PL lifetime as described above.

Finally, it is worth to mention that the PL enhancement in S2−-treated CdSe NCs can be accelerated by additional thermal annealing during the course of incubation. Fig. 6a shows the PL spectra collected from 2.1 nm, S2−-treated CdSe NCs which have been incubated at different temperatures for 12 h. Compared with the PL intensity of CdSe NCs incubated at room temperature (20 °C, Fig. 6a, black curve), incubation at 50 °C leads to a higher PL intensity without noticeable shift in PL peak position (Fig. 6a, red curve). In addition, the time required to achieve the maximum PL intensity is reduced to 1 day (Fig. 6b). Presumably, the accelerated PL enhancement is attributed to the facilitated interfacial and/or surface reconstructions induced by thermal annealing. Note that although the PL enhancement can be further accelerated by increasing the annealing temperature to 80 °C, the pronounced red shift (~13 nm) in PL spectra suggests the occurrence of NC aggregation or ripening (Fig. 6a, blue curve).

Conclusions

In summary, we have demonstrated that the influence of S2−-ligand exchange on the luminescent properties of CdSe NCs is highly dependent on the NC size. Our studies establish that during S2− treatment of small CdSe NCs (<4 nm), S2− ions can substantially substitute Se2− in NC lattices in addition to replacing the organic ligands at NC surface. This combined with the subsequent photoannealing process enables highly luminescent CdSe/CdS core–shell NCs that are dispersible in polar solvents. We note that the substantial replacement of Se2− by S2− could dramatically alter the electronic structures of CdSe NCs and therefore affect the resulting device performance, which may not be taken into consideration in previous studies.18-20 Although only CdSe NCs are explored in the current work, we anticipate that other types of semiconductor NCs may display similar size-dependent behaviors during ligand exchange with chalcogenide ions.

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Notes and references