Assembling nanocrystal superstructures

Marino, E.

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Repairing Nanoparticle Surface Defects

There’s light enough for what I’ve got to do.

— Charles Dickens

Optoelectronic devices based on semiconductor nanoparticles require the use of conductive ligands; however, replacing the native, insulating ligands with conductive metal chalcogenide complexes introduces structural defects within the crystalline nanostructure that act as traps for charge carriers. We utilized atomically thin semiconductor nanoplatelets as a convenient platform for studying, both microscopically and spectroscopically, the development of defects during ligand exchange with the conductive ligands Na$_4$SnS$_4$ and (NH$_4$)$_4$Sn$_2$S$_6$. We show that these defects can be repaired via mild chemical or thermal routes, through the addition of L-type ligands or wet annealing, respectively. This results in a higher-quality, conductive, colloidally stable nanomaterial that may be used for active films in optoelectronic devices.
Chapter 5. Repairing Nanoparticle Surface Defects

5.1 Introduction

Colloidal semiconductor nanocrystals (NCs) represent a versatile class of materials with unique optoelectronic properties that are fundamentally defined by their nanometric confinement. The use of NCs in optoelectronic devices ranges from optical displays, [117,118] and transistors, [26,119] to solar cells. [120,121] Specifically, photovoltaic devices fabricated from NCs are amenable to inexpensive room-temperature solution processing, with the promise of yielding large-scale thin films. [122] Power conversion by a solar cell requires, in sequence, light absorption, charge carrier separation, charge transport to, and extraction at the contacts. Whereas light absorption can be optimized by the choice of material, for example, by tuning the NC composition, size, and shape, charge carrier separation and transport within the macroscopic film are limited by the NC surface properties, requiring the presence of conductive pathways, or bonds, between individual nanocrystals.

Metal chalcogenide complexes have been used as conductive surface ligands to improve charge transport in devices; [123,124] however, replacing the native insulating ligands requires an often detrimental ligand exchange (LE) process, which greatly reduces the photoluminescence quantum yield, $PLQY$, by orders of magnitude and decreases the long-term colloidal stability from years to days. [123,124] Insight into the LE process through investigation of a model system would thus be greatly beneficial.

Atomically thin semiconductor nanoplatelets (NPs) [125–128] exhibit superior uniformity in their confining dimension, which is reflected by the coincidence of their ensemble and single-particle PL spectra. [128] This key feature results in exceedingly sharp excitonic absorption peaks and band-edge emission with no Stokes shift, which was recently exploited for stimulated emission studies. [64,129] Herein, we utilized NPs as a model system for studying the development of structural defects during LE. Defects in NPs become particularly apparent both topologically and in their PL spectra whereas equivalent changes in quantum dots may be concealed in their intrinsic polydispersity, and thus NPs offer a unique opportunity for investigating LE-induced damage. Surprisingly, we find that defects caused by LE are healed through mild treatments, leading to the recovery of the native structural integrity and most of the initial $PLQY$ of the NPs.

5.2 Experimental details

We synthesized CdSe NPs with monodisperse lateral dimensions of $94 \pm 9nm \times 15.5 \pm 1.5nm$: The sharp absorption transition at 514 nm is indicative of a thickness of 4.5 atomic monolayers, corresponding to 1.2 nm, Figure 5.1a. [65,66] The top and bottom facets of NPs, (001) facets of zinc blende CdSe, [129] are Cd-terminated and
5.2. Experimental details

Figure 5.1: CdSe NPs before and after ligand exchange (LE) with Na₄SnS₄. (a1-a5) Bright-field STEM and (a6) high-resolution HAADF images of pristine NPs with OA as the ligand. (b) Absorbance (solid lines) and PL (dotted lines) spectra of pristine and LE NPs. The PL intensity of the ligand exchanged NPs has been multiplied by 500. (c) DC conductivity measurements on thin films of pristine and LE NPs. (d1-d5) Bright-field STEM and d6) high-resolution HAADF images of damaged NPs with (NH₄)₄Sn₂S₆ as the ligand. Black scale bars: 20 nm; white scale bars: 5 nm.
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Figure 5.2: Dynamic light scattering on CdSe nanoplatelets. Scattered light intensity correlation curves from NPs before (left) and after (right) ligand exchange. Grey lines indicate the fit with a single exponential decay of type $e^{\frac{-t}{\tau}}$ where $R_H = \left(\frac{k_B T}{6 \pi \eta q^2}\right)\tau$ is the hydrodynamic radius of nanoplatelets, $\eta$ the solvent's viscosity, and $q$ the scattering wavevector.

passivated by oleate ligands (OA). OA ligands belong to the category of X-type ligands, or one-electron donors, since they can participate in a two-electron bond with an atom on the surface of a NC by donating one electron from a ligating atom. [40, 130] In the case of OA, the ligating atom is the deprotonated oxygen of the carboxylate which donates its unpaired electron. These OA ligands provide NPs with colloidal stability in non-polar solvents by steric stabilization but induce stacking of the NPs upon drying, Figure 5.1a. Replacing the insulating OA ligands with conductive metal chalcogenide complexes is a necessary step to achieve sufficient electronic transport in thin films. [123, 131, 132] To this end, we used a two-phase system in which a solution of thiostannate ligands ($Na_4SnS_4$ or $(NH_4)_4Sn_2S_6$) in a polar solvent, such as an aqueous solution of $NH_4OH$, was placed in contact with a dispersion of NPs in hexane. Stirring the mixture allowed for LE to proceed until the NPs had fully migrated to the polar phase. After ligand exchange, the NPs were still well dispersed as shown by dynamic light scattering (DLS) measurements, which revealed only minor changes in the hydrodynamic radius between pristine and LE NPs, as shown in Figure 5.2.

5.3 Results and Discussion

5.3.1 Effects of ligand exchange

Remarkably, DC conductivity studies showed that the conductance of a non-annealed thin film of LE NPs is up to three orders of magnitude higher than that of pristine NPs, resulting in an electron mobility value of approximately $0.5 \times 10^{-3} cm^2 V^{-1} s^{-1}$.
Figure 5.3: Ligand exchange and structural consequences on NPs. (a) Schematics illustrating the L-promoted Z-type ligand displacement process described in the text. (b) HAADF STEM image indicating the line scanned for calibrated thickness measurement shown in (c). The line purposely crosses a macroscopic puncture in the NP. (c) Measured intensity as a function of distance. To provide an estimate of the total thickness variation of the NPs after ligand exchange, we analyzed STEM images and compared them with the results of image simulations. The STEM images were then converted to an absolute intensity scale using a detector normalization, such that intensities in the image are a fraction of the total incident beam intensity. [133-135] (Figures 5.1c). Concomitant with the strong increase in conductance, however, a dramatic degradation of structural integrity was observed for the ligand exchanged NPs, seen as punctures in the atomic crystal lattice (Figures 5.1d); at the same time, the PLQY greatly decreased (Figure 5.1b). The direct observation of the development and propagation of surface defects is enabled by the exceptionally thin NPs as the removal of just a few atoms from the (001) facets strains the lattice, inducing perforations. [66] The aqueous solution of NH$_4$OH, itself an L-type (two-electron donor) promoter ligand, allows the LE with thiostannate ligands to proceed rapidly, likely following a process known as L-promoted Z-type ligand displacement (Figure 5.3a). [40] Specifically, the addition of L-type ligands can simultaneously promote the removal of Cd(OA)$_2$ complexes as L – Cd(OA)$_2$ soluble species, and passivate the under-coordinated Cd$^{2+}$ sites as CdL. This process intrinsically supports NP degradation. Calibrated thickness measurements performed with HAADF STEM showed that at least 50% of the material was removed from damaged areas (Figure 5.3b,c). These results highlight the mobility of surface atoms in such II–VI NCs. We found this structural and PLQY degradation to be quite general. The displacement potency of a ligand depends on multiple attributes, such as electronic effects, chelation, and steric properties. [40] We investigated the influence of steric effects on displacement potency by replacing NH$_4$OH with promoter ligands pyridine, 3-methylpyridine (3MP),
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Figure 5.4: Influence of the composition of the polar phase on the visual integrity of ligand exchanged NPs. Bright field STEM images of NPs after LE using the indicated solvent as polar phase during LE. Scale bars indicate 50 nm.

or 2,6-dimethylpyridine (DMP), all L-type ligands, and found that all LE treatments resulted in perforation of the NPs; furthermore, treatment with DMP also resulted in material rearrangement from the NP core onto the surface (Figure 5.4). This structural damage always correlated with a dramatic decrease in PLQY, to $\sim 0.02\%$, with respect to the original pristine NPs with oleate ligands, 10%. We also studied LE-induced damage in the absence of promoter ligands that may trigger L-promoted Z-type ligand displacement, by altering the composition of the polar phase from pure water ($\epsilon \approx 80$) to N-methylformamide (NMF, $\epsilon \approx 182$). Interestingly, while the use of water still resulted in heavily damaged NPs, NMF did not induce visible perforations (Figure 5.4). This finding supports a recent study that described the removal of OA ligands only rather than Cd(OA)$_2$ complexes upon LE with thiostannate complexes when using NMF, therefore leaving the Cd-rich surface intact. [132] Nevertheless, the PLQY dramatically decreased to approximately 0.01%. Thus while a judicious choice of the polar component during LE can reduce structural damage, the effects on the spectroscopic properties remain deleterious.

5.3.2 Healing strategies for nanoplatelets

We therefore studied the healing of NPs after LE in the presence of NH$_4$OH. Unexpectedly, upon addition of DMP to an already damaged dispersion of NPs with Na$_2$SnS$_4$ as the ligand, we observed the recovery of the structural integrity and the healing of holes, with no measurable changes in the NP lateral dimensions (Figures 5.5a). Additionally, the PLQY underwent a tenfold increase, indicative of the recovery of crystalline integrity of the NPs together with an improved surface passivation, and the absorption spectrum was slightly blue-shifted as a result of the effective de-
5.3. Results and Discussion

Figure 5.5: Healing defects in the NP crystal lattice with DMP. (a1-a6) Bright-field STEM images of repaired NPs after DMP treatment with Na₄SnS₄ as the ligand. Scale bars: 20 nm (a1-a5) and 200 nm (a6). (b) Absorbance (solid lines, normalized) and PL (dotted lines) spectra of NPs after LE and after DMP treatment. (c) Wet annealing (WA) of NPs at 100°C. Absorbance (solid lines) and PL (dotted lines) normalized spectra for pristine NPs, after LE with Na₄SnS₄, and during WA. (d) Bright-field STEM images of NPs after 5 min (d1), 20 min (d2), and 60 min (d3) of WA. Scale bars: 50 nm.
crease in the local NP thickness through the removal of rough areas (Figure 5.5b). As

**Figure 5.6: Wet annealing treatment induces NP necking.** (a) STEM image of NPs after WA (20 min). The inset shows the area described by the square magnified tenfold. Necking sites are clearly visible. Scale bar indicates 200 nm. (b) Normalized distribution function of hydrodynamic radii of NPs after WA treatment (20 min). The distribution is the result of the multi-exponential fitting of the scattered light correlation curve obtained with DLS.

an alternative to chemical treatments, we also explored temperature treatments without DMP as the healing process should depend on the thermal energy supplied. We investigated this by performing a wet annealing treatment, WA, starting from a dispersion of damaged NPs in water and increasing the temperature of the solution to 100°C. Immediately thereafter, the dispersion slightly changed in color; we continued to follow the structural and spectroscopic changes by taking aliquots every few minutes (Figure 5.5c). After 5 min of WA, the absorption and PL peaks underwent a red shift of about 10 nm, suggesting structural modification of the NPs; remarkably, the PLQY recovered by a factor of 230 compared to the values measured after LE, reaching 4.5%. As the WA proceeded, the absorption and PL peaks were red-shifted by an additional ca. 5 nm after 10 min; the excitonic peaks of the absorption lost definition, the scattering was enhanced, and the PL spectrum broadened. Direct visualization of the NPs after WA by STEM revealed surface reconstruction, yielding whole NPs (Figure 5.5d). Similarly to the DMP treatment, WA leads to NP recovery, confirming the enhancement of the surface mobility under mild conditions. The process eventually triggered growth on side facets, bridging NPs together, as demonstrated by STEM images, where the necking sites can be easily identified, and DLS, resulting in a distribution of hydrodynamic radii with a wide tail at high radii indicating aggregation (Figure 5.6). Allowing the WA to continue further resulted in the lateral thinning of the NPs along the [1 -1 0] direction and in material overgrowth (Figure 5.5d3). Side facets are more favorable to growth and more resistant towards
dissolution than top facets owing to both the formation of one extra Cd-Se bond \[66\] and a smaller nucleation energy barrier, as shown in recent work. \[136\] If used in a controlled way, this process can yield surface healing or soldering of NPs.

### 5.3.3 Spectroscopic monitoring of nanoplatelet damage and healing

Pristine NPs passivated with OA showed a second broad PL band at longer wavelengths accompanying the sharp emission profile at the band edge, Figure 5.7a, resulting from the presence of deep traps. \[137\] Even in pristine NPs, the \(PLQY\) of this band is comparable to that of the main emission (ca. 5%). Further disrupting the structural integrity of NPs should result in an increase in the number of defects, and indeed, after LE in the presence of the L-type ligand \(\text{NH}_4\text{OH}\), the defect band strongly increased relative to the band-edge peak (Figure 5.7a,b). Remarkably, the nanoscale surface recovery upon DMP addition resulted in a large decrease in the defect band relatively to the main emission peak (Figure 5.7b). WA treatment had an even more drastic effect on the recovery of LE-damaged NPs (Figure 5.7c): After only 5\(\text{min}\) of treatment, the defect band had strongly decreased with respect to the main peak, concomitant with a recovery of the PL of the primary emission. Interestingly, as the annealing proceeded, the intensity of the defect PL band slowly increased. This evolution of the PL spectra directly relates to the structural recovery observed by STEM (Figure 5.5d2,d3). While short annealing was beneficial to surface recovery, longer treatment resulted in the overgrowth of material on the NP surface, generating a soldered network.

The effect of the recovery processes on the \(PLQY\) are summarized in Figure 5.7d. Varying the composition of the polar phase during LE affects the \(PLQY\) by up to one order of magnitude. Specifically, while for pure water the band-edge \(PLQY\) is lower than the defect band contribution, for NMF, it is higher by a factor of 15; these results are supported by, respectively, the presence and lack of perforations in the crystalline structure of the NPs, topological indicators of surface quality (Figure 5.4). Still, DMP- and WA-healed NPs outperform visually undamaged NMF LE NPs by at least one order of magnitude in terms of the \(PLQY\) (Figure 5.7d). Additionally, such NMF LE NPs can also be repaired by using the reported DMP and WA recovery routes; also in this case, the \(PLQY\) increased significantly, consistent with the \(\text{NH}_4\text{OH}\) LE NPs after recovery (data not shown). The effect of structural recovery on the optoelectronic properties was further investigated by time-resolved microwave conductivity (TRMC) measurements, which probe the conductivity within individual NPs. The mean path length of charge carriers measured by this technique is about 30 nm; \[55\] therefore, TRMC measurements uncover the dynamics of photogenerated carriers on the length scale of a single NP. The values for charge carrier mobility in treated NPs correlate well with the \(PLQY\) (Figures 5.8), confirming that LE introduces traps that can be healed by a mild treatment of the NPs. Importantly, this shows that independent of
Figure 5.7: Analysis of the photoluminescence (PL) of nanoplatelets. (a) Normalized PL spectra of pristine nanoplatelets with Lorentzian and Gaussian fits (gray lines) for the band-edge and trap state emissions, respectively. Note the log/lin scaling. (b) Normalized PL spectra of nanoplatelets after LE and after DMP treatment with Gaussian fits. (c) Normalized PL spectra of nanoplatelets during WA. (d) Nanoplatelet PLQYs for band-edge (circles) and defect band (squares) emissions for all treatments.
5.4. Conclusions

In conclusion, we have demonstrated that CdSe NPs can be used as a convenient model system for studying how LE affects the structural and optical properties of semiconductor nanostructures. While LE with conductive molecular ligands has thus far been mostly limited to quantum dots, [131,132] NPs provide a stringent test case owing to their superior PL linewidth, large surface area, and convenient flat imaging geometry. As LE on QDs results in a drop in PLQY similar to that observed for our NPs (Figure 5.9), we believe that these results apply to QDs as well. However, the recovery via chemical route seems to result in a PLQY enhancement relatively lower than measured with NPs (Figure 5.9b). Even more surprisingly, the recovery via thermal route does not result in the enhancement in PLQY but rather in a decrease. We can tentatively justify these discrepancies with the large difference in surface area among NPs and QDs: a NP has roughly 130 times more surface than the QDs studied here. Further studies might be necessary to prove the validity of LE recovery routes.
Figure 5.9: Spectroscopic properties of CdSe quantum dots exposed to the surface treatments investigated in this chapter. (a) Absorption spectra of quantum dots before LE, after NH$_4$OH-based LE, and after recovery with 3% and 33% $v/v$ DMP in H$_2$O. (b) Absorption spectra of quantum dots during WA treatment, as compared to pristine and post-LE conditions. (c) PLQY of band-edge emission from quantum dots for all the considered treatments.
for spherical QDs.

We have established that LE reactions cause a disruption of the atomic lattice of NCs, thereby introducing defects that quench the PLQY. The composition of the polar phase during the LE proves to be a key parameter in minimizing structural damage, with NMF giving the best results. By understanding the LE-induced structural disruption, we were able to drive the healing of NPs both structurally and spectroscopically by chemical (mild L-type ligands) and thermal (WA) routes. This resulted in a higher-quality and colloidally stable nanomaterial that may be self-assembled into novel structures such as superlattices [88][138] to be used as active films of optoelectronic devices. Future work to microscopically investigate these recovery routes on individual NPs may determine the exact nature of the trapped and recovered states similar to previous works. [139]