Thermally Degradable Ligands for Nanocrystals

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ABSTRACT We exchanged the oleate ligands on as-prepared PbSe/CdSe core/shell nanocrystals with octyldithiocarbamate to enable the removal of insulating ligands by gentle heating. The octyldithiocarbamate ligand could readily be stripped from the surface by heating briefly to temperatures from 140 to 205 °C, which is substantially lower than the temperature (330 °C) required to remove oleate from the nanocrystal surface. X-ray diffraction and transmission electron microscopy reveal that the nanocrystals sinter around 250 °C, resulting in a loss of quantum confinement. Heating for 1 min to 205 °C removed 92% of the organics from the surface. We could therefore prepare densely packed films of quantum-confined nanocrystals *via* dithiocarbamate treatment. Conductivity increased by up to 4 orders of magnitude after annealing. In addition to PbSe/CdSe core/shell nanocrystals, we also examined the applicability of our ligand removal procedure to CdSe nanocrystals.

Due to the unique electronic, magnetic, and optical properties of semiconductor nanocrystals, researchers have been working to exploit them in devices such as light-emitting diodes, solar cells, and photodetectors.[1−3] Typically, these devices require two characteristics that are hard to achieve simultaneously. Namely, the nanocrystals should be distinct particles that exhibit quantum confinement of the charge carriers, and they should be strongly coupled to neighboring particles when they are assembled into a film. Quantum confinement allows the electronic properties to be tuned with size, while electronic coupling facilitates charge transport in the device. Unfortunately, achieving both of these goals can be difficult because of bulky surface ligands. These ligands are necessary to control nanocrystal size and shape during growth and stabilize the nanocrystal dispersion during subsequent processing, but they also keep the nanocrystals separated from adjacent particles.

A variety of chemical and thermal treatments have been investigated to bring nanocrystals closer together and increase their conductivity. One approach is to deposit nanocrystals with long-chain ligands on a device and then replace the ligands with short-chain nucleophiles such as hydrazine,[4] ethanedithiol,[5] methylamine,[6] or sodium hydroxide.[7] These postdeposition treatments can increase conductivity by many orders of magnitude. However, they suffer several disadvantages: the electronic properties of nanocrystals are extremely sensitive to small variations in processing conditions; the chemicals are typically caustic, which can damage other device components (for example, conducting polymers); the chemicals are often toxic; and the removal of long-chain ligands after deposition causes cracking in nanocrystal films, necessitating multiple depositions.[5]

A second approach is to anneal the nanocrystal film at elevated temperatures. The simplest method is to prepare a film directly from as-synthesized nanocrystals and then heat under vacuum. Unfortunately, it is not possible to remove standard ligands without sintering the nanocrystals.[8] A more complex scheme is to exchange the ligands in solution with weakly binding, small molecules such as pyridine[9] or butylamine,[10] deposit the nanocrystals as a film, then heat under vacuum to desorb some of the ligands. Unfortunately, dispersions made with small molecules on the surface have poor stability[11] and require lengthy anneals to remove a significant fraction of the ligands.[12] Alternatively, films of as-synthesized particles can be annealed under reactive conditions such as forming gas or an air plasma to remove the surface ligands.[13,14]
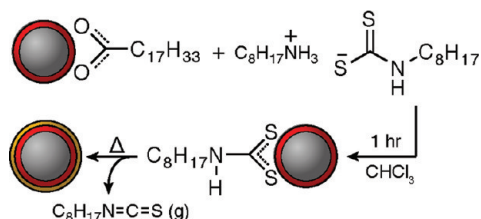
Scheme 1. Proposed exchange mechanism. The oleate ligands on as-synthesized PbSe/CdSe core/shell nanocrystals are exchanged with octyldithiocarbamate in solution, deposited as films, then heated to strip the ligands. A likely degradation pathway is shown. Gray represents the PbSe core, red the CdSe shell, and yellow the likely sulfur overcoating.

A third approach is to exchange semiconductor nanocrystals with ligands that contain additional chemical functionality. For example, a ligand terminated by the *tert*-butyoxylcarbonyl (BOC)-protecting group has been studied.[15] These molecules can be shortened either thermally or using an ultraviolet acid generator, an effect that has been utilized to improve the performance of hybrid polymer−nanocrystal photovoltaics.[16] Another idea is to cap nanocrystals with molecular chalcogenides that convert to semiconductors on heating to create highly conducting composite materials.[17] The additional functionality of these ligands allows the production of previously inaccessible composite materials.

Herein, we describe the use of an alternative ligand that can stabilize nanocrystals but has additional functionality so it can be easily stripped from the surface. Previous research on CdSe/ZnS core/shell nanocrystals as well as molecular complexes suggested that the dithiocarbamate group would provide excellent stability for a variety of nanocrystal dispersions.[18−20] In addition, metal dithiocarbamates decompose with mild
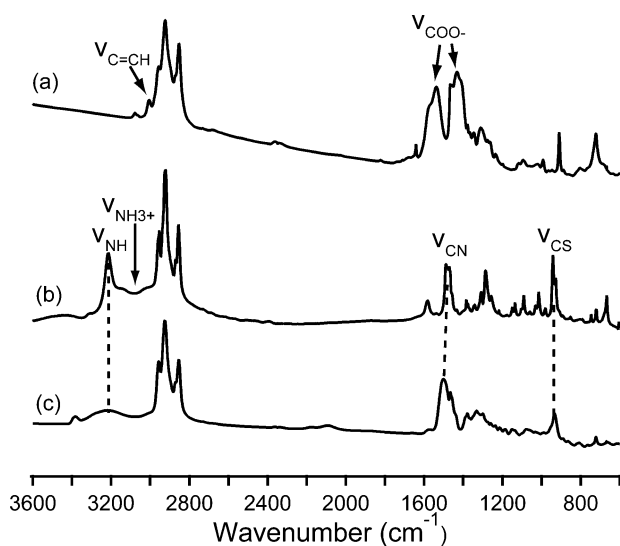

Figure 1. Infrared absorbance spectra of (a) as-synthesized PbSe/CdSe core/shell nanocrystals, (b) the octylammonium octyldithiocarbamate ligand used for the exchange, and (c) the same PbSe/CdSe nanocrystals as in (a) after ligand exchange. Peaks were assigned from the literature.[24,25]

heating to the corresponding metal sulfides and gaseous byproducts,[20,21] providing a simple route to strip ligands from the nanocrystal surface. While secondary dithiocarbamates have been better studied, primary dithiocarbamates are known to degrade at lower temperatures.[20,22] Dithiocarbamates are also relatively nontoxic, in contrast to many current chemical treatments. We therefore devised a new procedure (Scheme 1) in which nanocrystals are treated with a primary dithiocarbamate, deposited as a film, and gently heated to decompose the ligands and bring the particles into closer contact. For our model system, we focused on octyldithiocarbamate and PbSe/CdSe core/shell particles. PbSe/CdSe nanocrystals were chosen because they have recently been reported to be more thermally stable than PbSe particles[23] and their electrical properties had not previously been studied. The applicability of our approach to other common nanocrystals is also discussed.

RESULTS AND DISCUSSION

Ligand Exchange. Octylammonium octyldithiocarbamate was easily prepared in large quantities *via* standard procedures.[20] We synthesized PbSe/CdSe core/shell nanocrystals by surface cation exchange on PbSe nanocrystals following modified literature methods.[23] We exchanged the ligands on the surface of the as-synthesized particles with octylammonium octyldithiocarbamate by stirring the nanocrystal dispersion in an excess of dithiocarbamate in chloroform. The nanocrystals were stable indefinitely (at least 6 months) in the dark and for weeks when stored in the light, as measured by their ability to pass through a filter with 0.2 μm pores and because no agglomerates were observed in transmission electron microscopy (TEM). For a dispersion stored in the light for 2 weeks, we also saw a negligible increase in the infrared (IR) vibrations due to isothiocyanate, which is the probable degradation product of primary dithiocarbamates. These dispersions were easy to handle and could be flocculated and redispersed.

The exchanges were followed using Fourier transform infrared (FTIR) spectroscopy, as shown for representative PbSe/CdSe nanocrystals in Figure 1. As synthesized, the PbSe/CdSe nanocrystals exhibited stretching modes consistent with a surface capped by oleic acid. After exchange with octylammonium octyldithiocarbamate, the carboxylate stretches at 1538 and 1430 cm^{-1} and vinylic C−H stretches at 3005 cm^{-1} vanished and were replaced with stretches assigned to the dithiocarbamate ligand at 1502 and 933 cm^{-1}.[24,25] The vibration due to the octylammonium counterion around 3100 cm^{-1} also disappeared, although minor amine stretches might be hidden by the strong primary dithiocarbamate NH peak at 3200 cm^{-1}. The replacement of oleate with octyldithiocarbamate is unsurprising, as dithiocarbamates bind strongly to most metals.[20]
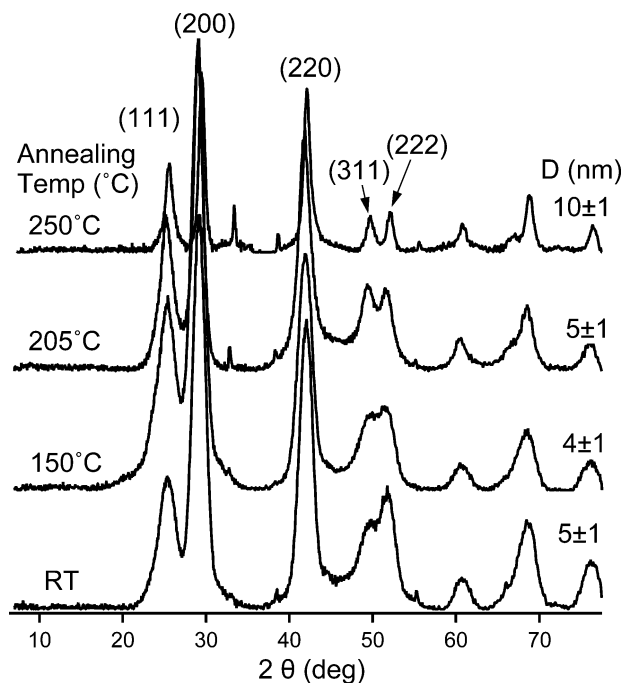
Figure 2. X-ray diffraction patterns for films of dithiocarbamate-treated PbSe/CdSe core/shell nanocrystals annealed for 1 min at the temperatures shown. A pattern obtained for a sample kept at room temperature (RT) is shown for comparison. The temperatures were chosen to match ligand-loss steps obtained by thermal analysis. Nanocrystal diameters shown on the right are derived from fitting the width of the (220) peak using the JADE 8.0 software package. Despite the short annealing time, the nanocrystals start to sinter by 250 °C.

Annealing and Ligand Stripping. The goal of our dithiocarbamate treatment is to strip the insulating ligands through heating without losing quantum confinement. For this approach to be successful, the ligands must be removed before the nanocrystals sinter. Semiconductor nanocrystals have been shown to sinter at temperatures far below their bulk melting temperatures. For example, PbSe nanocrystals begin sintering around 200 °C when annealed in nitrogen.[6] We collected X-ray diffraction (XRD) patterns on dithiocarbamate-treated PbSe/CdSe nanocrystals (Figure 2) that reveal that the nanocrystals start growing between 205 and 250 °C when annealed for 1 min in nitrogen. Samples annealed at 150 °C for longer times (1 h) also grew slightly. Our data reveal that only quick, gentle thermal treatments avoid sintering of our particles. In general, the vulnerability of nanocrystals to such sintering motivates the search for new ligands that degrade at lower temperatures.

Using thermogravimetric analysis (TGA), we compared the temperatures at which the original oleate and our octyldithiocarbamate ligands could be removed from PbSe/CdSe nanocrystals. Figure 3 shows the TGA data and its first derivative for our samples as they are slowly heated. In the first derivative, we observe dips corresponding to a decrease in mass at specific temperatures, which we assign to ligand loss for the following reasons: (1) samples heated to the temperatures at which mass loss occurred in TGA also showed decreased intensity in ligand stretching modes in IR spectroscopy (Figure 4); (2) the inorganic core should not evaporate until much higher temperatures (the melting points of bulk PbSe and CdSe are 1264 and 1082 °C, respectively[26]); and (3) nanocrystal sintering should not result in a change in mass.

The TGA data confirmed that ligand loss occurs around 330 °C for the oleate-capped PbSe/CdSe nanocrystals. However, oleate-capped PbSe/CdSe nanocrystals heated to this temperature for 1 min sintered. In contrast, the thermal analyses of the octyldithiocarbamate-capped nanocrystals reveal ligand loss occurring in two lower temperature steps. The initial degradation step exhibited a 6% mass loss at 145 °C, which is 185 °C lower than the oleate-capped particles. The second step showed an additional 7% mass loss at 205 °C. An investigation of the degradation pathways of molecular complexes of primary alkyldithiocarbamates and Cd showed similar changes in TGA.[22] The total mass loss due to ligand decomposition was 12.5% for the octyldithiocarbamate-treated particles *versus* 25% for those that were oleate-capped. The lower percentage of mass loss for the dithiocarbamate ligand is expected because its carbon chain is significantly shorter than the oleate (8 *versus* 18 carbons). However, assuming that the same number of ligands per particle are in each sample and that all of the oleate mass was removed, we would predict a mass loss of 17.5% for the dithiocarbamate sample based purely on molecular weight differences. This suggests that either some of dithiocarbamate ligands have not decomposed (unlikely based on the IR results discussed below) or some mass remains after decomposition. For example, the degradation of octyldithiocarbamate can leave sulfur on the particle surface. If this occurs, it may actually be advantageous as CdS shells as thin as 0.8 monolayers are known to enhance the quantum yield and photostability of CdSe nanocrystals.[12] Although our shells would be even thinner (0.5 monolayers), such a sulfur coating could still provide some of these benefits.

IR spectra taken after briefly heating dithiocarbamate-treated nanocrystal films to the temperatures suggested by TGA confirms that the alkyl chain of primary dithiocarbamates can be removed from nanocrystal films with gentle heating, as shown in Figure 4. Integration of the alkyl stretches between 2800 and 3000 cm^{-1} shows a 92% decrease in the presence of the alkyl chain. Therefore, our TGA and FTIR results suggest that we can remove the insulating ligands from our films with quick, low-temperature heat treatments.
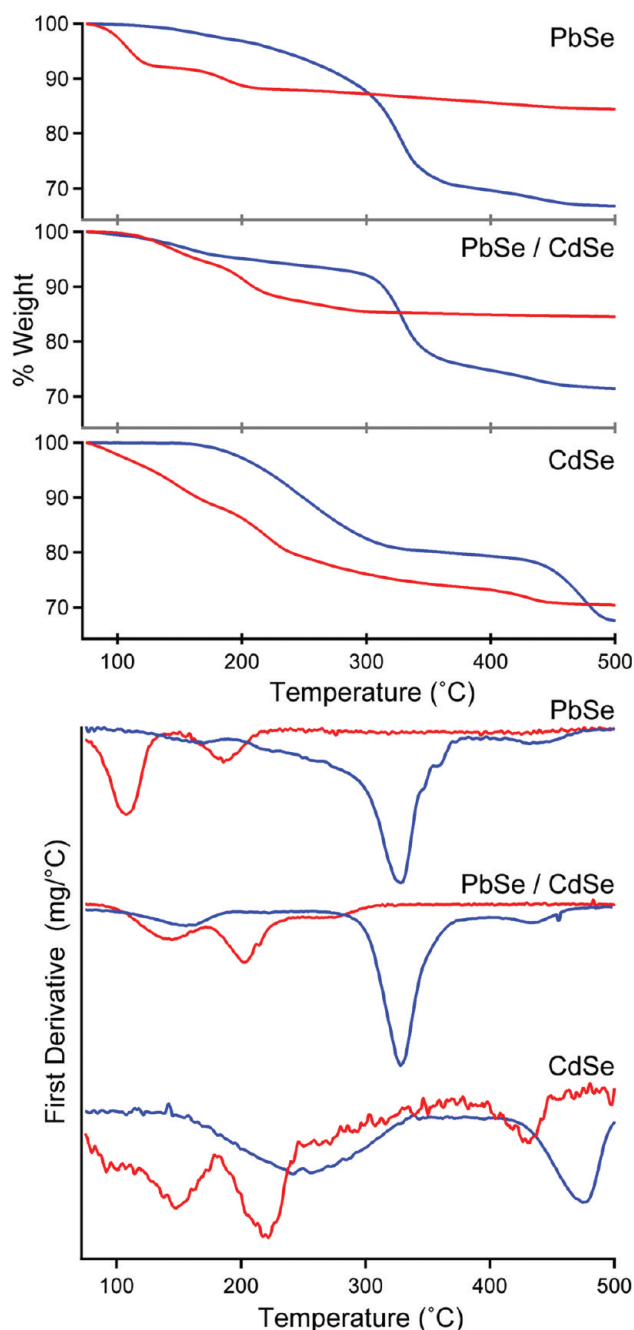
Figure 3. Thermogravimetric analyses (top) and their first derivatives (bottom) for three types of nanocrystals. Red curves represent the dithiocarbamate-capped nanocrystals, and blue curves represent the as-synthesized nanocrystals. For each data point, a second-order polynomial was fit to the surrounding ±0.5 °C and evaluated to obtain the first derivative.

Densification and Film Morphology. Next, we imaged submonolayer films of octyldithiocarbamate-treated PbSe/CdSe nanocrystals using transmission electron microscopy (TEM), as shown in Figure 5. In addition, we took low-magnification images across the TEM grid. The Fourier transform of these images provided the average interparticle spacing before and after mild heat treatment (Figure S1 in the Supporting Information). Before annealing, the particles are separated by a distance of

~1.5 nm. After heating to 150 °C for 1 min, the films become slightly more ordered. In addition, the interparticle spacing decreases to ~1 nm, although a couple of grid areas remained at the original spacing. When the ligands are stripped by heating at 205 °C, the particles touch, but lattice fringes show that they remain crystallographically distinct. All particle ordering is lost. By 250 °C, the lattice fringes show that the nanocrystals have sintered into much larger particles. This agrees with the crystallite sizes obtained from XRD (Figure 2). In addition, the first absorption feature in the near-IR optical spectrum disappears at 250 °C, further suggesting that the particles have lost quantum confinement (Figure S2 in the Supporting Information). Our results are consistent with previous TEM results on annealed PbSe, showing that nanocrystals first come into contact, then fuse into larger crystals through oriented attachment.[27]

A comparison of the sintering thresholds obtained from XRD and TEM (Figures 2 and 5) and the degradation temperatures of the various ligands shown by TGA (Figure 3) demonstrates the usefulness of our dithiocarbamate ligand exchange. We find that nanocrystals capped by standard surface molecules sinter when heated to the temperatures necessary to burn off the ligands. In contrast, ligands can be removed from octyldithiocarbamate-exchanged nanocrystals at temperatures up to 185 °C lower than the as-synthesized particles. This allows us to bring nanocrystals into contact before they sinter. We can therefore remove the insulating layer between nanocrystals while keeping individual particles in a quantum-confined regime.

Another important feature of our annealing treatment is its effect on the overall film morphology. Most chemical treatments produce rough, cracked films that must be backfilled with additional layers of nanocrystals to produce continuous films.[5,6] We studied the effect of annealing on octyldithiocarbamate-treated nanocrystal films spin-cast onto silicon using atomic force microscopy (AFM), as shown in Figure 6. The original PbSe/CdSe films appear to wet the substrate poorly (this is not generally true—for example, dithiocarbamate-treated CdSe wets the substrate well). After annealing, film roughness decreased by up to 31%. (This trend also held true in the case of films of octyldithiocarbamate-treated CdSe.) Importantly, the removal of dithiocarbamate did not induce cracking.

Conductivity and Transport of Annealed Films. By removing the insulating ligands from our nanocrystals we create densely packed films. These films show enhanced conductivity, as shown in Figure 7. After the original ligands were exchanged for octyldithiocarbamate on PbSe/CdSe nanocrystals, conductivity remained below our detection limit of 10^{-13} A. Once the films were heated under nitrogen to strip their ligands, current began to rise. After annealing for 1 min at 150 °C, the conductivity jumped to 7.3×10^{-8} S/cm. When films were heated
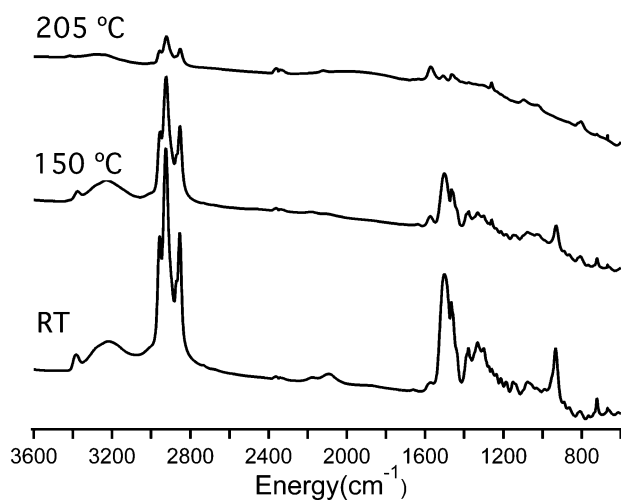
Figure 4. IR absorption spectra of a drop-cast film of dithiocarbamate-treated PbSe/CdSe core/shell nanocrystals heated for 1 min to the given temperatures. Data for the sample kept at room temperature (RT) are shown for comparison. Integration of the C−H stretching region from 2800 to 3000 cm^{-1} reveals that 50% of the organic components of the ligands are removed after the 150 °C anneal and 92% are removed after the 205 °C anneal.

to 205 °C for 1 min, which TEM revealed brought the particles into contact, it rose to 3.0×10^{-7} S/cm. A film that was heated until it sintered (1 min at 250 °C) showed the highest conductivity, 7.0×10^{-5} S/cm, but no longer exhibited quantum confinement. In contrast to films of the octyldithiocarbamate-treated nanocrystals, films of as-synthesized PbSe/CdSe nanocrystals did not conduct even when heated to 205 °C, just below the sintering point.

These results were obtained immediately after annealing. Better conductivities were obtained when films were either aged for 4 days in a nitrogen-filled glovebox or when vacuum was briefly (~5 min) applied. The increase in current was approximately equal for either treatment, and the effect was not cumulative (*i.e.*, applying vacuum after aging did not further increase conductivity), so we speculate that trace degradation products that negatively effect conductivity are being removed from the film. After vacuum treatment, final conductivities of 3.42×10^{-6} were obtained for the 205 °C sample. The annealed dithiocarbamate-treated films showed a weak gate effect with ambipolar transport characteristics (Figure S3 in the Supporting Information). To our knowledge, these are the first reported conductivity and transport measurements obtained on PbSe/CdSe core/shell nanocrystals. Overall, conductivities from our samples are about 2−3 orders of magnitude lower than from films of PbSe nanocrystals exposed to chemical treatments that do not involve hydrazine (which is believed to strongly dope the films).[4−6] Further experiments are required to determine the underlying reason for this decrease. For example, it could be intrinsic to PbSe/CdSe nanocrystals,

due to disorder introduced in the superlattice by rapid annealing or due to the role that other chemical treatments play in doping the films. This last issue will be discussed further below.

Dithiocarbamate Treatments of PbSe and CdSe Nanocrystals. In addition to treating PbSe/CdSe core/shell nanocrystals, we applied our dithiocarbamate treatment to PbSe and CdSe nanocrystals. PbSe and CdSe nanocrystals were prepared following modified literature procedures.[28−31] In the case of PbSe, FTIR indicated that octyldithiocarbamate replaced the original oleic acid on the nanocrystal surface, but the dispersions became unstable during precipitation. Therefore, further experiments with PbSe particles were limited. In contrast, CdSe nanocrystals were easily exchanged from phosphonic acids and anhydrides[32] to octyldithiocarbamate (Figure S4 in the Supporting Information), and the resulting dispersions were stable indefinitely (at least 8 months) in the dark or for weeks in the light.

We obtained thermal analyses on the PbSe and CdSe samples, as shown in Figure 3. As synthesized, the oleate on the PbSe nanocrystals degraded around 325 °C, which is similar to the oleate-capped PbSe/CdSe core/shell particles, while the ligands could be thermally removed from CdSe particles capped with phosphonic acid and anhydride around 250 °C. Also analogous to PbSe/CdSe, dithiocarbamate-capped PbSe and CdSe showed ligand removal in two steps with initial decomposition tem-
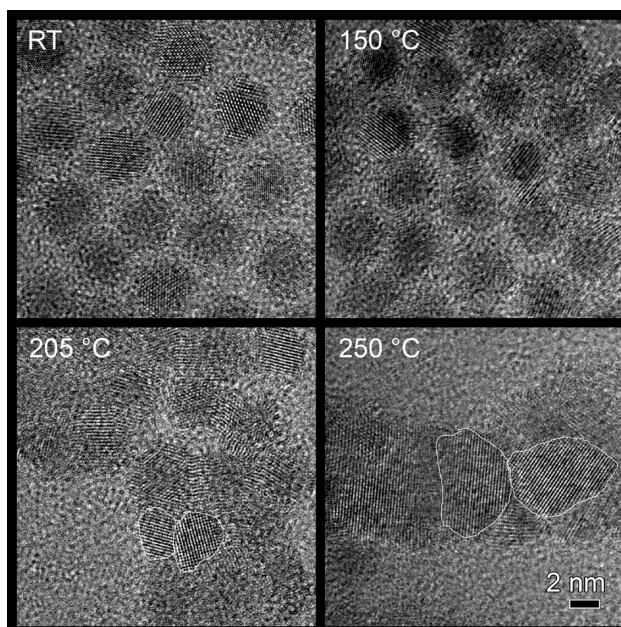

Figure 5. Bright-field transmission electron microscopy images of a submonolayer film of 5 nm PbSe/CdSe core/shell nanocrystals that were octyldithiocarbamate-treated. Sample grids were prepared by dip-coating from a 1 mg/mL dispersion in chloroform. Samples were heated for 1 min at the temperatures shown, except for the sample kept at room temperature (RT). The white lines are visual guides to outline the nanocrystals.
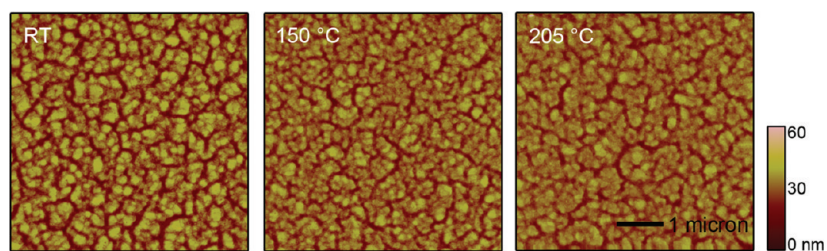
Figure 6. Tapping-mode atomic force micrographs of films of octyldithiocarbamate-treated 5 nm PbSe/CdSe core/shell nanocrystal films spin-coated from a 20 mg/mL chloroform dispersion onto silicon. The root-mean-square roughnesses are 6.84 nm for the film kept at room temperature (RT), 5.11 nm for the film treated at 150 °C, and 4.66 nm for the film treated at 205 °C.

peratures of 105 and 145 °C, respectively, much lower than required to remove the ligands from the as-synthesized particles. For the PbSe nanocrystals, two-thirds of the ligand loss occurred in the first step, while the mass losses are approximately equal between the two steps for CdSe, as in the case of PbSe/CdSe particles.

XRD patterns obtained on annealed CdSe films (Figure S5 in the Supporting Information) showed that the particles sintered between 150 and 220 °C. Because we can partially remove the ligands from CdSe at 145 °C, we can bring our particles into closer contact without sintering the nanocrystals. In contrast, CdSe nanocrystals capped with phosphonic acid and anhydride that were heated to 250 °C—the temperature necessary to strip the ligands—appeared to sinter and became gray. Spin-cast films of dithiocarbamate-treated CdSe nanocrystals appeared smooth by AFM before heat treatment (Figure S6 in the Supporting Information). After annealing, AFM showed that the films became even smoother. This effect was especially evident in the optical spectra of the film (Figure S7 in the Supporting Information). When a dithiocarbamate-treated CdSe film

Figure 7. Current−voltage (*I*−*V*) sweeps of 5 nm PbSe/CdSe core/shell nanocrystals, shown for a 20 μm long × 2 mm wide channel coated with a ∼45 nm thick spin-cast PbSe/CdSe nanocrystal film.

was annealed for 1 min at 150 °C, strong interference fringes appeared and the film attained a shiny finish to the eye, although it remained red and XRD indicated the particles did not sinter. In general, the effect of dithiocarbamate treatment and annealing on CdSe appears similar to what we observed for PbSe/CdSe core/shell nanocrystals.

We also performed numerous experiments to examine the effect of dithiocarbamate removal on the conductivity of films of CdSe nanocrystals. In contrast to the PbSe/CdSe core/shell nanocrystals, films of dithiocarbamate-capped CdSe nanocrystals always remained nonconductive (with conductivities $<10^{-10}$ S/cm) after thermal annealing. Only when the annealing temperature was sufficiently high that the particles sintered, did the films show conduction. At first, we hypothesized that this was because the dithiocarbamate did not fully decompose at the temperature of the anneal (1 min at 150 °C). However, further experiments showed that the same result was obtained for films of larger CdSe nanocrystals (3.7 nm in diameter) for which the sintering temperature shifted above 225 °C so that the films could be annealed at higher temperatures (2 min at 225 °C). This suggests that, although the dithiocarbamate ligands are being removed, conduction remains inhibited. The underlying cause is not yet understood. One outstanding issue is the role that small nucleophilic molecules such as hydrazine or ethanedithiol play in donating carriers to the films or filling traps.[4] Hydrazine is a strong reducing agent, and after hydrazine treatment, films of PbSe nanocrystals show strong n-type character, presumably due to remote doping of the nanocrystals by the hydrazine. The ambipolar transport in our films of PbSe/CdSe nanocrystals after annealing suggests that such effects are absent. If this is true, a combination of our dithiocarbamate treatment (for bringing the nanocrystals together) and another treatment (for inducing conductivity) may be required to optimize electrical transport. Further experiments are underway to test this idea.
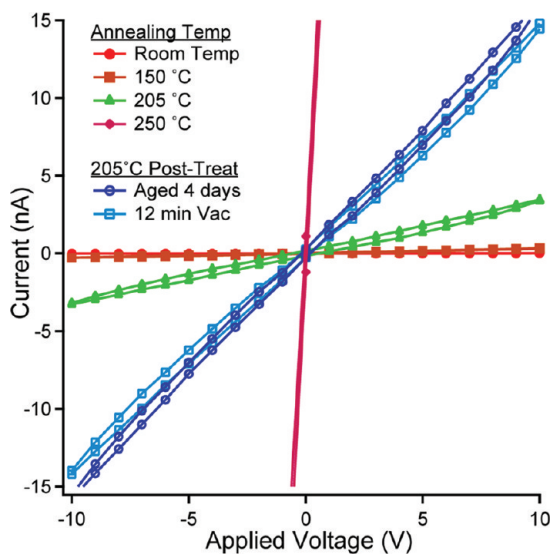
CONCLUSION

Thermal annealing is one way to strip insulating ligands and bring nanocrystals into closer contact. Un-

fortunately, many nanocrystals are susceptible to sintering when heated to the temperatures required to strip standard ligands, and such sintering destroys quantum confinement. We show that the ligands from octyldithiocarbamate-capped particles can be removed at low enough temperatures to avoid growth or sintering. We tested this approach on several common semiconductor nanocrystals. Of these, dithiocarbamate-treated PbSe/CdSe core/shell dispersions and CdSe dispersions showed robust colloidal stability. Octyldithiocarbamate could be easily removed from the nanocrystals by heat treatments at temperatures between 140 and 205 °C, temperatures at which PbSe/CdSe nanocrystals do not sinter or grow. We also demonstrated that the PbSe/CdSe particles moved closer together with removal of the octyldithiocarbamate, and films of such nanocrystals became smoother. In terms of electrical transport through these films, ligand-removal resulted in a 10 000-fold increase in conductivity, indicating an increased electronic coupling of the nanocrystals to their neighbors.

We expect our treatment to be applicable to a variety of semiconductor nanocrystals, as dithiocarbamates bind well to many metals.[20] Because the required heat treatment is relatively mild and avoids harsh chemicals, it could also be employed in new areas. For example, dithiocarbamate treatment could be used to bring nanocrystals into close contact in nanocrystal−organic semiconductor blends. In addition, the ambipolar transport suggests that dithiocarbamate treatment does not strongly dope the nanocrystals, allowing study of the fundamental properties of semiconductor nanocrystals. Thus, dithiocarbamate exchange and annealing adds complementary functionality to the treatments already available for obtaining electronically coupled films of nanocrystals.

EXPERIMENTAL SECTION

Materials. Lead(II) oxide (99.999%) and cadmium oxide (99.999%) were purchased from Strem and used as received. Selenium shot (99.99%), diphenylphosphine (98%), octylamine (99%), carbon disulfide (>99.9%), trioctylphosphine (90% technical grade), 1-octadecene (90% technical grade), and oleic acid (90% technical grade) were purchased from Sigma-Aldrich and used as received. Hexanes, chloroform, and methanol were obtained from VWR and dried over 4 Å molecular sieves. Toluene was obtained from VWR and dried on an MBraun solvent still. Acetone was obtained from Mallinckrodt and dried over 4 Å molecular sieves. Absolute ethanol was obtained from Pharmco−AAPER, dried over 4 Å molecular sieves, and distilled under nitrogen.

PbSe Nanocrystal Synthesis. PbSe nanocrystals were prepared following modified literature procedures.[30,31] PbO (2.50 g, 11.2 mmol), oleic acid (9.0 mL, 28.4 mmol), and 1-octadecene (36 mL) were degassed on a Schlenk line for 30 min, then the temperature was raised to 165 °C. When the solution went colorless, the temperature was lowered to 90 °C and the reaction was pumped on for 5 min to remove water. The temperature was raised to 185 °C under N_2, and a 1.00 M solution of selenium in trioctylphosphine (21.0 mL, 21.0 mmol) and diphenylphosphine (0.3 mL, 2.7 mmol) was swiftly injected. The solution went black in less than 1 s, and the nanocrystals were allowed to grow for 3 min at 140−150 °C. Then, 15 mL of ice-cold toluene was injected, and the solution was cooled to room temperature. The reaction mixture was transferred into a Schlenk flask and extracted twice with methanol *via* cannula, then brought into a nitrogen-filled glovebox, precipitated with acetone, centrifuged, and the supernatant was discarded. The resulting nanocrystals were redispersed in chloroform and stored in the glovebox. Yield = 2.0 g, diameter = 6.35 nm from optical spectra,[33] full width at half-maximum of lowest energy absorption feature = 36 meV.

PbSe/CdSe Core/Shell Preparation. PbSe/CdSe core/shell nanocrystals were prepared by partial cation exchange on the Schlenk line, following modified literature procedures.[23] CdO (3.0 g, 23.4 mmol), oleic acid (18.0 mL, 28.4 mmol), and 1-octadecene (44 mL) were degassed for 30 min, heated to 190 °C under N_2, then cautiously heated to 220 °C until the reaction went clear. **Warning: possibility of runaway reaction if overheated!** The temperature was lowered to 90 °C, and the flask was pumped on for 5 min to remove water. The temperature was raised to 100 °C, and 200 mg of PbSe nanocrystals in 2 mL of chloroform was injected. The reaction was stirred for 1 h, then cooled and purified as given above for PbSe nanocrystals. The particle diameter was 5 ± 1 nm by XRD.

Octylammonium Octyldithiocarbamate Synthesis. The preparation of alkylammonium alkyldithiocarbamates has long been known.[20] In our variation, octylamine (8.26 mL, 50.0 mmol) and hexanes were stirred over an ice bath. Carbon disulfide (1.65 mL, 25.0 mmol) was added dropwise. **Caution: carbon disulfide is volatile and noxious and should be used in a fume hood.** The reaction was stirred for 1 h, and the resulting crystalline product was filtered and washed three times with hexanes. The product was stored in air at −10 °C.

Ligand Exchange. In a nitrogen-filled glovebox, octylammonium octyldithiocarbamate (100 mg/mL) was added to PbSe/CdSe core/shell nanocrystals (50 mg/mL) in chloroform, and the mixture was stirred for 1 h. The reaction mixture was twice precipitated with methanol, centrifuged in sealed tubes outside the glovebox, and redispersed in chloroform. Samples were stored in the glovebox at room temperature.

Film Characterization. Thermal analyses were carried out on a Perkin-Elmer Diamond TGA. Films were prepared for FTIR spectroscopy by drop-casting on KBr windows in a nitrogen-filled glovebox. The IR cell was sealed, and spectra were obtained on a Nicolet Magna 560 spectrometer. Near-IR spectra were obtained in solution and on glass slides on a Varian Cary spectrophotometer. XRD patterns were obtained on a Bruker-AXS microdiffractometer using samples spin-cast (50 mg/mL, 1000 rpm, 30 s) on silicon or glass substrates. TEM images were obtained on a FEI Tecnai G2 F30 operating in bright-field mode at 200 keV. TEM samples were prepared by dipping carbon film/lacey carbon grids in a 1 mg/mL nanocrystal dispersion in chloroform and heating them for 1 min on a hot plate at the specified temperatures in a nitrogen-filled glovebox.

Electrical Characterization. For electrical characterization, films of PbSe/CdSe core/shell particles were spin-cast (30 s at 1700 rpm) from a 20 mg/mL dispersion in chloroform in a nitrogen-filled glovebox on Si/SiO₂ substrates with prepatterned source and drain electrodes (Cr/Au = 25/375 Å) and a prepatterned gate electrode (10 nm Al, 75 nm Au). Immediately after nanocrystal deposition, thermal treatment on the films was performed at the desired annealing temperatures (150, 205, or 250 °C) for 1 min. Afterward, two-terminal current−voltage ($I-V$) characteristics were measured in a Desert Cryogenics probe station under either nitrogen or vacuum. The source and drain biases were applied using Keithley 236 and 237 electrometers, respectively. Conductivities of the films were calculated from the slope of $I-V$ characteristics between −3 and 3 V and the given geometry of the channel. Channel width, length, and height were 2 mm, 20 μm, and 40 nm, respectively.

ARTICLE

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