Simultaneous Ligand and Cation Exchange in PbSe/CdSe nanocrystal films

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ABSTRACT

Trap states formed at the surface of colloidal semiconductor nanocrystals can have deleterious impact on performance in emerging optoelectronic applications. To mitigate surface traps in nanocrystal thin films we investigated simultaneous surface passivation and ligand exchange for PbSe nanocrystal films via treatment with a cadmium acetate solution. We show that a kinetically limited surface cation exchange produces a thin $\text{Cd}_x\text{Pb}_{1-x}\text{Se}$ shell that effectively passivates the nanocrystal surface as confirmed by increased photoluminescence intensity and photoluminescence lifetime. Ligand exchange to acetate ligands is confirmed via Fourier transform infrared spectroscopy and grazing incidence small angle X-ray scattering. We studied the impact of the cadmium acetate treatment on interparticle coupling and found that the reduced interparticle spacing and limited shell thickness leads to increased Förster resonant energy transfer in nanocrystal films. Simultaneous cation/ligand exchange enables the production of

heterostructured nanocrystal films with properties like Quasi-Type II nanocrystals synthesized in solution.

INTRODUCTION

Recent years have borne witness to tremendous progress in the fabrication of colloidal semiconductor nanocrystals (NCs) with precise control over size, shape, and composition. Availability of these materials has led to a surge of promising proof-of-concept devices that exploit their tunable optical and electronic properties [1-4]. An emerging consensus from the work on these devices is that sustained progress towards their technological potential requires deeper understanding and rigorous control over the surface states. Specifically in optoelectronics, surface states have been implicated as the cause for limited lifetime and mobility of carriers leading to reduced performance of devices[5, 6].

A common method to mitigate surface states is through the synthesis of core-shell NCs. Depending upon the specific alignment between the energy levels of the core and shell, one or both carrier types can be confined to the core and thereby isolated from surface trap states.[7, 8] These structures are particularly desirable for applications where a high fluorescence quantum yield (QY) is required such as LEDs[1, 9] and in biolabeling[10, 11]. This technique has been successful for a variety of materials systems, such as CdSe/ZnS[12] and PbX/CdX (X=S, Se, Te) [13, 14] and has been extended to multi-shelled and alloyed shelled NCs[15, 16]. Beyond increased QY, PbSe/CdSe NCs have been shown to have impressive multiple exciton generation (MEG) capabilities due to stabilization of high energy holes in the CdSe shell[17]. These NCs are currently the best performing MEG materials, surpassing PbSe nanorods[18]. PbS/CdS core-shell particles have also shown improved open circuit voltage (V_{oc}) in solar cells compared to

core-only devices[19, 20] as well as reduced turn on voltage and increased efficiency in IR LEDs.[21, 22]

In parallel to the development of core-shell structures, other passivation strategies have been studied to improve the surface passivation of NCs and NC thin films. In particular, passivation methods involving inorganic or atomic species as ligands have enabled significant advances to passivate the surface while at the same time reducing interparticle spacing to enhance charge transport through the NC film.[23, 24]. The most successful atomic ligands in PV applications have been halides (Cl, I, Br) incorporated either during synthesis or as part of a ligand exchange procedure[23, 25]. The results of these treatments have been an increase in the efficiency of NC solar cells via increased V_{oc} , again attributed to passivation of trap states. Other atomic passivation schemes have been investigated with the same goals. Sequential treatments with ionic solutions of chalcogenide and lead that remove capping ligands and passivate surfaces have been shown to produce inorganically connected lead chalcogenide NC thin films with mobilities above $4 \text{ cm}^2/\text{Vs}$ [26]. Passivation of NC surfaces via atomic layer deposition also enables high mobilities in NC assemblies as well as MEG approaching solution phase yields[27, 28]. In these completely inorganic nanocrystal arrays, carrier trapping and scattering is reduced.

Given the sensitive nature of the NC surface, minimizing the processing steps between synthesis and device operation is desirable to avoid degrading the NC surface. In this work we present a single step process that simultaneously passivates NC surfaces via limited cation exchange as well as decreases interparticle spacing via ligand exchange. Treatment of PbSe NCs with cadmium acetate (CdAc) results in increased steady state PL intensity indicating passivation

of trap states on the surface of NCs as well as increased energy transfer in NC films due to the reduction of interparticle spacing.

MATERIALS AND METHODS

Materials

Lead oxide (99.99%), selenium (99.999%, powder), trioctylphosphine (90%, technical grade), oleic acid (OA 70%, technical grade), 1-octadecene (ODE 90%), diphenylphosphine (98%), and anhydrous ethanol (200 proof) were all purchased from Sigma-Aldrich. Cadmium acetate dihydrate(99.999%) was purchased from Alfa Aesar. All chemicals were used without further purification.

NC synthesis and film formation

PbSe NCs were prepared by using a modified procedure adopted from the method of Yu *et al*[29]. In a typical synthesis, a 50 mL three-neck flask was loaded with 892 mg of PbO, 3.2 g of oleic acid, and 15.5 g of 1-octadecene and heated to 120 °C under vacuum with stirring for 1.5 h until the solution was transparent and colorless. The lead oleate precursor was transferred into a septa-capped vial and purged with nitrogen for 1 h at 150 °C before transferring into a glovebox for the remainder of the synthesis. Lead oleate (3 mL) was introduced into a 20 mL vial and heated to 100 °C for 15 min on a hot plate. In a separate vial, 750 µL of 1.25 M selenium in tri-*n*-octylphosphine was mixed thoroughly with 15 µL of diphenylphosphine and loaded into a syringe. When the lead oleate solution reached injection temperature, the selenium precursor was swiftly injected into the vial. Injection temperatures and reaction times were varied to tune the NCs to the desired size. To quench the reaction, the vial was immediately submerged into a cold ethanol bath and injected with 3.5 mL of anhydrous ethanol to arrest the

NC annealing. The NCs were isolated from the crude solution by centrifugation and precipitated twice more with toluene/acetonitrile as the solvent/antisolvent pair.

NC films were prepared by spincoating a 20 mg/ml solution of NCs at 2000 rpm for 30s onto glass slides for optical absorption and PL measurements. Cation/Ligand exchange was performed by submerging a NC film into a 20 mM solution of Cadmium acetate in ethanol for 30s followed by a 30s rinse in ethanol. Mixed NC films were prepared by mixing two stock NC solutions together in an appropriate ratio. The molar concentration of NC solutions was determined following the procedure detailed by Moreels *et al*[30]. All processing was performed in a nitrogen glovebox to avoid oxidation.

Characterization

Optical absorption measurements were collected with a Cary 5000 UV-Vis-NIR spectrometer. TEM images were acquired using a FEI Tecnai T12 at 120 kV. GISAXS was performed at the D1 beamline of the Cornell High Energy Synchrotron Source (CHESS) using monochromatic radiation of wavelength 1.161 Å and a bandwidth $\Delta\lambda/\lambda = 1.5\%$. The X-ray beam was produced by a hardbent dipole magnet of the Cornell storage ring and monochromatized with Mo:B₄C synthetic multilayers with a period of 30 Å. GISAXS images were collected by a MedOptics fiber coupled CCD camera with a pixel size of 46.9 μm by 46.9 μm and a total of 1024 by 1024 pixels with 14-bit dynamical range per pixel. The sample to detector distance was 900 mm, as calibrated by a silver behenate powder standard. Images were dark current corrected, distortion corrected, and flat field corrected by the acquisition software. The incident angle of the X-ray beam was 0.25°. Scattering images were calibrated using the Fit2D software[31]

The photoluminescence was measured using a home-built spectrophotometer. In the continuous measurement, a 638 nm diode laser with typical intensity of 30 mW/cm² was used for

excitation. In the PL lifetime measurement, a pulse train of 1 kHz repetition rate, 800 nm wavelength, and <1 ps pulse duration was used as the excitation source. The emitted light was collected, passed through a monochromator for wavelength filtering, and then temporally resolved using a fast InGaAs photomultiplier detector, with the temporal resolution of 1 ns.

RESULTS AND DISCUSSION

We focused our study on colloidal PbSe NCs with a diameter of 4.0 nm $\pm$.35 nm. Figure 1 shows the absorption spectra of the PbSe NC films before and after CdAc treatment. The excitonic peak blue shifts and broadens after a 30s soak in an ethanolic solution of CdAc. We interpret the blue shift as increased quantum confinement compared to untreated films. Previous studies have shown that cadmium can replace lead in PbX (X=S,Se,Te) NCs, consuming the originally synthesized NC and producing a CdX shell[13, 14, 32]. TEM of particles before and after CdAc treatment show no change in size after treatment, indicating that the treatment did not etch the surface of the particle. We conclude that cation exchange has produced a PbSe/CdSe heterostructure, as has been observed via HRTEM in earlier studies[33].

Figure 1: a) Optical absorption of PbSe nanocrystal films with Pb-oleate surface termination (black) and Cd-acetate surface termination (green) the blueshift in peak formation indicates increased exciton confinement due to cation exchange. b,c) TEM images of Pb-oleate and Cd-Acetate terminated NCs respectively

To explain the blue shift of the excitonic peak we use, as a first approximation, a continuum model to represent the core-shell structure and assume uniform coverage of a CdSe layer. Previous studies of PbX/CdX core shell systems have matched PbSe core sizes observed in TEM to the empirical curve of energy *versus* size developed by Moreels *et al*[30, 34-36]. From the change in excitonic absorption peak, this model predicts a 0.15 nm reduction in the radius of the PbSe core; this would correspond to a uniform CdSe shell of half the Pb-Se bond length. Clearly, the simple continuum model leads to a non-physical result. Instead of forming a well-

defined core-shell structure, we conclude that the cation exchange must be limited to a submonolayer during the treatment.

Moreover, a more accurate description of the PbX/CdS heterostructure must also take NC shape and faceting into account. PbSe NCs are commonly considered as stoichiometric cores, with a metal rich surface layer including Pb terminated {111} facets.[37, 38] A model of a PbSe NC with {100} and {111} facets truncated at 2 nm from the center of the NC, shown in Figure 2a, has 40% of the cations on the surface. Energy dispersive X-ray spectroscopy (Figure S1) indicates that Cd makes up 23% of the cations in the CdAc treated film, in agreement with the shift in excitonic peak that indicates about half a monolayer of surface cation exchange. High-resolution TEM studies of PbX/CdX core/shell structures have shown preferential cation exchange on the {111} crystal facets[33]. Given this model of a PbSe NC, and evidence for preferential cation exchange on {111} facets in previous studies, we suggest that the submonolayer exchange may occur predominantly on the {111} facets of a NC. Figure 2a shows a model of a PbSe NC before and after cation exchange limited to the Pb terminated {111} facets.

To improve our understanding of the optical properties of CdAc-treated PbSe NC films, we examined the photoluminescence (PL) of NC films. The Quasi-Type II energy level alignment in PbSe/CdSe is predicted to result in delocalization of electrons throughout the heterostructure whereas holes remain confined to the PbSe core[34]. In light of this energy level alignment in the heterostructure, we can interpret increase in PL in PbSe/CdSe heterostructures compared to the initial PbSe system as a reduction of hole trapping at surface states due to increased confinement[8, 17, 34, 39]. Figure 2b,c shows that CdAc treated 4 nm PbSe NC films exhibit increased PL and increased PL lifetime compared to untreated NC films, as shown in

Figure 2b and 2c. The magnitude of the increase in PL ($\sim 3X$ increase) agrees well with the solution based measurements performed on PbSe/CdSe core-shell particles with submonolayer thickness obtained following 19 hours of cation exchange[14]. This comparison confirms our interpretation of the blueshift in absorption, that CdAc treatment leads to formation of a PbSe/CdSe heterostructured film.

Figure 2: a) Atomistic models of a PbSe NC before and after submonolayer cation exchange. Lead cations are black, cadmium cations are green. b) Photoluminescence spectra of 4 nm OA passivated and CdAc passivated

NC films. The blueshift and increase in PL intensity indicate surface passivation via cation exchange. c) Time resolved PL of these films measured at the peak emission wavelength showing increased lifetime following cation/ligand exchange.

The significant change of the PbSe NC optical properties in response to the CdAc treatment leads to the question: *What is the fate of the oleate ligand that was initially bound to the PbSe NC surface?* In wet chemical PbSe/CdSe core-shell synthesis, Cd is supplied by Cd-oleate and so oleate and oleic acid ligands are plentiful in solution and continue to passivate the surface and provide colloidal stability to the NCs after cation exchange. In contrast, our work employs CdAc, so we hypothesized that the acetate might displace the longer chain oleate from the NC surface. FTIR absorption spectra in Figure 3a show a 70% reduction in the integrated intensity of C-H stretches near 2900 cm^{-1} which come predominantly from the aliphatic tail of oleate ligands, while the carboxylate stretching peaks near 1550 and 1400 cm^{-1} common to both oleate and acetate are retained. The decrease, but not complete absence, of the C-H stretching peaks indicates an incomplete ligand exchange with oleate ligands still in the film after CdAc treatment. If cation exchange occurs via a Z-type ligand exchange of neutral metal carboxylate complexes, the carboxylate ligands will be exchanged simultaneously with the cations. In addition, the solvent, ethanol, has been shown to remove Z-type ligands from NC surfaces and may enhance the rate of cation/ligand exchange[40].

To determine how the change in ligand coverage and composition impacts interparticle spacing, we turned to grazing-incidence small-angle X-ray scattering (GISAXS) of NC thin films. GISAXS shows that the CdAc treatment significantly reduces the nearest neighbor separation of 7.1 nm in the OA passivated film to 5.5 nm in the CdAc passivated films. The surface to surface spacing after cation/ligand exchange is larger than expected for acetate passivated particles[41], which we attribute to the incomplete ligand exchange that occurs.

Notably, the scattering data also show that long-range ordering is substantially preserved although an unambiguous identification of the superlattice symmetry after cation/ligand exchange is not possible. The reduced interparticle separation measured by GISAXS is consistent with the intimate spacing between NCs evident from TEM (Figure 1).

Figure 3: Ligands are also exchanged during CdAc treatment. a) FTIR absorption of NC assemblies shows loss of C-H stretching peaks, but retention of carboxylate binding group at the NC surface. b) As a result of the ligand exchange, NC spacing is reduced in NC films as evidenced by a shift in GISAXS to higher q values. Major ticks indicate 1 nm^{-1}

Collectively, the reduced interparticle spacing (from GISAXS) and reduced surface trapping (from PL) suggests that charge transport may be improved. To investigate interparticle electronic coupling, we take advantage of the increased PL intensity of cation/ligand exchanged

films to study exciton transport via steady state and time resolved photoluminescence (TRPL). We prepared films containing large bandgap particles (1.2 eV, 2.6 nm) and small bandgap (.95 eV, 4 nm) particles in a 100:1 ratio. The larger particles act as luminescent traps which accept excitons from the donor NCs[42]. The 0.25 eV (~ 10 kT) difference in energy gap between the acceptors and the surrounding matrix of smaller NC will suppress exciton transport away from the acceptor particles. Figure 4a shows the alignment between the conduction and valence bands of donor and acceptor particles based on the work of Jasieniak *et al*[43].

Figure 4: Mixed films of donor (2.6 nm) and acceptor (4 nm) particles a) Energy level alignment and particle spacing between donor and acceptors before (left) and after (right) CdAc treatment. Particle size and energy alignment match the sizes determined from TEM. b) Photoluminescence from mixed NC films showing increased acceptor emission after cation/ligand exchange. Spectra are normalized by the total PL emission.

Since the majority of excitons are generated in the donor matrix, we can monitor emission from acceptor particles as a convenient measure of the ability of carriers to diffuse in the mixed NC films. We use the model developed by Zhitmirsky *et al* in equation 1 to analyze the steady state emission from mixed NC films[42].

$$\tau_{Film}^{-1} = \tau_D^{-1} + vN_A\sigma_A + vN_T\sigma_T \quad (1)$$

Where τ represents the average lifetime of the film as a whole and the donor matrix respectively, v is the velocity of carriers, N is the density of acceptors or traps, and σ is the capture cross section. The first term represents radiative relaxation in the matrix, the second transport to and radiative relaxation in acceptor particles, and the third term nonradiative relaxation via traps. By normalizing to the total PL emission, we can look specifically at the radiative pathways. Figure 4b shows that 55% of the emission comes from acceptor particles in NC films prior to CdAc treatment. Cation/ligand exchange significantly increases the amount of recombination occurring in the acceptor particles, up to 82% of the total emission. Assuming that the capture cross section of acceptors does not change, the increase in emission from the acceptor particles must result from some combination of an increase in the radiative lifetime of NCs and increased carrier velocity after CdAc treatment.

We probed transient PL to better understand the underlying energy and charge transport mechanism responsible for the change in PL. Specifically, the transient nature of the emission from the acceptor can provide insight into the nature of electronic coupling to the surrounding donor NCs. Time resolved photoluminescence (TRPL) measurements of the acceptor emission reveal a rise in PL intensity during the first 300 ns (Figure 5); this is a signature of Förster resonant energy transfer (FRET) in NC assemblies[44-46]. To quantify the growth and decay of PL intensity, we fit the beginning of the TRPL traces with a biexponential containing one rising

and one decaying term. The characteristic rise time decreases from 62 ns to 15 ns following CdAc treatment; this indicates that the rate of exciton transfer is increased.

The point dipole FRET equation shown in equation 2 is commonly used to analyze FRET in NC assemblies and has shown success in interpreting the observed energy transfer.

$$k_{FRET} = \frac{1}{\tau_D} \left(\frac{R_o}{R} \right)^6 \quad (2)$$

Where k_{FRET} is the energy transfer rate, τ_D is the donor lifetime, R_o is the Förster radius and R is the distance between the point dipoles. We note that the actual dependence of FRET on interparticle spacing in assemblies may deviate from the R^6 dependence of the standard expression. The Förster radius is influenced by the spectral overlap between donor emission and acceptor absorption. Although both emission and absorption spectra shift due to cation exchange, the shift is nearly the same, leading to only a 5% increase in spectral overlap after cation/ligand exchange (see SI for details of the calculation). Based on the reduced interparticle spacing revealed by our GISAXS measurements (Figure 3b,c), the standard FRET model predicts a 4.8 fold increase in energy transfer rate following CdAc treatment; this prediction is consistent with the 4.1 fold increase in energy transfer rate found in TRPL measurements.

Figure 5: Time resolved photoluminescence of acceptors a) Acceptor particles exhibit a rising transient indicative of Förster resonant energy transfer. Inset: time constants for the rising and decaying component of a biexponential fit to the data. b) Full TRPL traces show single exponential decay before treatment, with an additional long lifetime (~ 3 μ s) after treatment

As the acceptor particles are surrounded by a matrix of higher band gap particles, exciton transport away from the acceptors should be significantly reduced. This enables direct observation of the effect of CdAc treatment on the lifetime of excitons in PbSe films independent

of the increased energy transfer rates that may confound measurements of films composed of a single size of NCs, where FRET can occur even with a narrow size distribution[44]. The transient emission of the untreated films are well fit by a single exponential decay with a time constant of 720 ns. After CdAc treatment, the initial decay remains the same but an additional long lifetime component appears with a lifetime of 2850 ns. The short lifetime component is typical of oleate passivated PbSe NCs measured in solution while the long lifetime component agrees with values measured for PbSe/CdSe core shell particles in solution[34, 47]. The TRPL data therefore supports our assumption that transport away from acceptor NCs is significantly reduced and that these TRPL measurements represent the carrier dynamics in an isolated bright particle in the NC films.

The TRPL data merit further discussion on context of the steady state PL data shown in Figure 2. We note that the increased lifetime of CdAc acceptors is not sufficient to explain the ~3.5 fold increase in PL. The ~3 μ s decay component only accounts for 7% of the PL decay. To describe this discrepancy, we emphasize that TRPL measurements only measure bright particles. Any dark particles (with trap states) will have an effect on the ensemble film measurements by increasing the non-radiative decay rate, but not on the TRPL measurements of isolated particles. For a single component film, equation 1 can be modified by removing the acceptor recombination term

$$\tau_{Film}^{-1} = \tau_{NC}^{-1} + \nu N_T \sigma_T \quad (3)$$

Here τ_{Film} is obtained from Figure 2c, and τ_{NC} represents both radiative and nonradiative relaxation pathways in the bright NCs as measured in Figure 5b. The relationship in equation 3 therefore provides a convenient measure of the trap density due to dark particles under two assumptions. First, we interpret the 4.1 fold improvement in energy transfer rate as an indication

of relative increase in exciton velocity due to CdAc treatment and secondly assume that the capture cross section is constant. Based on these assumptions, we find that CdAc treatment reduces the trap density by over an order of magnitude ($n_{OA}/n_{CdAc}=12$). We can therefore conclude that the CdAc treatment significantly improves the surface passivation of PbSe NCs. The combination of improved surface passivation and improved energy transfer rates make simultaneous cation and ligand exchange an attractive processing tool for optoelectronic applications. In particular, we believe LED applications may benefit from the increase in PL intensity combined with improved energy transfer rates.

CONCLUSIONS

We have shown that by exposing a PbSe NC thin film to an ethanolic solution of cadmium acetate both cation and ligand exchange occur on the surface of the NCs simultaneously. This results in NC films that show increased PL as well as improved PL lifetime. The exchange from oleate to acetate ligands leads to reduced interparticle spacing and a corresponding 4.1 fold increase in Förster resonant energy transfer rate in NC films. Comparison of TRPL lifetime measurements of particles isolated in a higher bandgap matrix to single component films of the same particles indicates that the trap density is reduced by an order of magnitude following cation/ligand exchange. Based on observations of increased PLQY, increased PL lifetime, and increased energy transfer, we conclude that with a single processing step we have created a coupled artificial solid composed of heterostructured PbSe/CdSe NCs.

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