

A Room-Temperature, Solution Phase Method for the Synthesis of Mesoporous Metal Chalcogenide Nanocrystal-Based Thin Films with Precisely Controlled Grain Sizes

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(5) Supporting Information

ABSTRACT: Block copolymer templating of ligand-stripped nanocrystals followed by thermal degradation of the polymer template is a robust method that has been applied in making a variety of mesoporous nanocrystal-based films. However, the use of thermal processing to remove the polymer template can have detrimental effects on other material properties such as grain size and crystal structure that affect size-dependent properties such as the band gap. Here we present a new method for forming mesoporous films of cadmium and lead chalcogenide nanocrystals that avoids thermal processing. In our method, nanocrystals are first assembled with a diblock copolymer template. The resulting films are then soaked in a solution of a small molecule cross-linking agent to lock the



nanocrystals into the structure. Finally, the polymer template is gently dissolved out of the film, leaving behind a porous film of nanocrystals. These films show disordered but homogeneous porosity, quantified by electron microscopy and ellipsometric porosimetry. Importantly, both X-ray diffraction and optical absorption spectroscopy indicate that the initial nanocrystal size is fully preserved in the final porous structure. This new synthetic method has exciting potential as a building block for composite structures where precise control of quantum confinement effects is needed.

INTRODUCTION

The overarching goal of nanoscience research has been to precisely control the unique size-dependent properties of nanomaterials. More specifically, preserving the inherent properties of the materials such as grain size, crystallinity and composition, while being able to precisely control nanoscale architecture, is necessary for many applications. Nanomaterials with precisely controlled properties and architecture could lead to improvements in applications ranging from catalysis,¹ photocatalysis,^{2–5} and electrochemical charge storage⁶ to photovoltaics.^{7–9}

Semiconductor nanocrystals, or quantum dots, make up a particularly interesting class of materials for a wide variety of applications.^{8,10–17} For example, tunable band gaps^{18,19} and the capacity for barrier-less carrier multiplication^{20–23} could revolutionize photovoltaics, among other fields. While the size-dependent optical properties provide a wealth of tunability, the small size also depresses the melting point in nanocrystals compared to those of their bulk counterparts, which limits temperatures at which nanocrystal-based devices can be processed while still maintaining their favorable size-dependent properties.²⁴

For many applications, precise control over both film morphology and the properties of the individual nanocrystals

is necessary. For example, there is a double necessity to maintain precisely controlled small size and narrow nanocrystal size distributions for applications in quantum dot photovoltaics.^{22,25} In other applications, it has been shown that decreasing the size of nanocrystals improves the thermoelectric properties of semiconducting nanocrystal-based films.^{26,27} Thus, the ability to precisely control both film morphology and nanocrystal size could lead to improved devices.

Synthetic methods for producing a variety of semiconductor nanocrystals with precise control over size, composition, crystal structure, and shape have been previously developed; here we include only a small subset of the many available synthetic methods.^{28–36} A majority of these syntheses leave long organic ligands on the nanocrystal surface to control kinetics during nanocrystal growth, prevent nanocrystal aggregation, and maintain colloid stability. These ligands have limited the use of these nanocrystals in electronic devices, mostly because of their insulating nature and the fact that they keep the nanocrystals fairly far apart. It has been shown, however, that small bidentate ligands can replace the long aliphatic ligands to

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shorten interparticle spacing and improve the electrical conductivity in nanocrystal films, allowing for their expanded use in device applications.^{15,37–45} Ligand exchange generally results in a volume contraction, however, so repeated multilayer deposition is required to produce homogeneous films using these methods.

Given that our goal is to control both size and mesoscale architecture in semiconductor nanocrystal assemblies, we need a method for controlling nanocrystal size, assembly, and connectivity in nanocrystal-derived solids. Recently, some beautiful sol–gel methods for assembling semiconductor nanocrystals into porous aerogels with retention of their quantum confined properties have been developed.^{46–50} While these materials have a large surface area and connected porosity, in general they are characterized by a broad pore size distribution that ranges from mesopores to macropores ($\sim 2-120 \text{ nm}$). Although these methods provide precise control over nanocrystal size, and thus optical properties, a method for the assembly of semiconductor nanocrystals with smaller, more homogeneous porosity, ideally in the thin film format, is desirable.

To accomplish this goal, we build upon recent progress in the field of assembling nanocrystals into porous thin films using block copolymers as a template.⁵¹⁻⁶¹ Most of the more recent papers in this field take advantage of synthetic advances that have led to the development of ligand-stripped or "bare" nanocrystals.⁶²⁻⁶⁵ In these methods, a reactive molecule interacts with anionic surface ligands, causing them to desorb from the surface; this leaves uncompensated cationic sites on the nanocrystal surfaces that are charge balanced by some anionic component of the reactive stripping agent. Despite the absence of ligands, the nanocrystals do not aggregate because of electrostatic repulsion between individual charged nanocrystals. To make these nanocrystals into mesoporous films, amphiphilic diblock copolymers are dissolved in polar solvents where they form micelles and are combined with ligand-stripped nanocrystals. Upon deposition onto a substrate and solvent evaporation, the ligand-stripped nanocrystals co-assemble with the polymer micelles. Typically, the films are then heated to remove the polymer template, leaving behind an open porous network of the inorganic material. Partial sintering of the nanocrystals during thermal processing provides mechanical robustness, which prevents the porous structure from collapsing. This method is very robust and allows for the synthesis of materials with large pore volume fractions from a broad range of materials.⁵¹⁻⁵

While the current method for producing mesoporous films from nanocrystals can provide exquisite control of film morphology, the effects of thermal processing can be detrimental to other material properties, such as grain size. Previously, we used thermal processing to remove the polymer template from mesoporous CdSe.⁵¹ X-ray diffraction (XRD) showed the presence of ~ 5 nm grains, which corresponds to the size of an individual nanocrystal, as well as larger 18 nm grains in these films after thermal processing. This grain growth caused the loss of a well-defined first excitation peak in the UV-visible absorption spectrum, which is indicative of a loss of well-defined nanocrystal size. A red shift of the absorption onset was also observed, again caused by the grain growth. Milliron and co-workers also used heat treatment to remove the polymer template from their mesoporous CdSe and observed similar trends.⁵³ Unfortunately, the current copolymers used to template semiconductor nanocrystals need to be heated to

~400 °C to be completely thermally degraded and produce open pores. 51,53 As a result, the deleterious effects on the nanocrystals' grain size and the template removal cannot be separated if thermal processing is used.

Despite its detrimental effects, thermal processing has previously been necessary because it both fuses nanocrystals, giving the film mechanical rigidity, and removes the polymer template.^{51,52} As previously discussed, small bidentate ligands have been used to decrease interparticle spacing, showing that they can strongly bind the particles together.^{15,39} This makes small molecule cross-linking agents a promising alternative to thermal treatments to form a robust nanocrystal network. If nanocrystals can be well cross-linked using bidentate ligands, then the polymer template can be removed by simply washing it out of the pores.⁵ In our case, the distance between two nanoparticles is already small because of the ligand stripping treatments. Thus, upon treatment with small bidentate ligands, there should be negligible volume contraction. The flexibility of nanoporous networks is also likely to help accommodate any volume change that does occur upon cross-linking.60

The cadmium chalcogenide nanocrystals investigated by the porous materials community so far provide a good model system for developing new methods for assembling nanocrystals into porous structures because of their impressive chemical stability toward different ligand treatments and their wellstudied, size-dependent optical properties. The lead chalcogenides (PbS and PbSe) are also of great interest for applications such as solar energy harvesting because of their much smaller bulk band gaps and large Bohr exciton radii, which subsequently allow for a size tunable bandgap throughout the near-infrared (NIR) region.⁶⁷ Despite these attractive advantages, these Pb-based nanocrystals do not have the same chemical stability that the cadmium chalcogenides exhibit. Indeed, in many of the reported methods developed to produce cationic, "naked" nanocrystals, the lead chalcogenides were not explored or it was reported that the methods failed to produce stable colloidal dispersions for the lead chalcogenides. 62,63,65 One recent exception stands out; researchers used Lewis acidbase adducts of BF_3 to produce stable, ligand-stripped, dispersions of ~6 nm PbSe nanocrystals.⁶⁴ This advance provides a path forward for preparing open, mesoporous films of NIR PbX-based nanocrystals. Gentle cross-linking and template removal likely will be necessary for the fabrication of these sensitive materials.

In this work, we thus show that ethanedithiol and 3mercaptopropionic acid, two standard bidentate nanocrystal cross-linkers,^{15,39} can be used to cross-link both CdS and CdSe nanocrystals using both ether- and acrylamide-based block copolymer templates. After cross-linking, we show that the polymer template can be removed by soaking the films in appropriate solvents. Because no thermal processing is used, the size-dependent optical properties of the original nanocrystals are well maintained. Further, we show that this method can be expanded to sensitive NIR active PbS/CdS core/shell nanocrystals. We thus present a method for organizing nanocrystals into porous networks while fully preserving quantum confinement effects.

EXPERIMENTAL SECTION

Materials. The following chemicals were used as received: tetraethylthiuram disulfide (97%, Alfa Aesar), 2,2'-dithiobis-(benzothiazole) (99%, Aldrich), tetradecanoic acid (98%, Alfa Aesar), cadmium acetate dihydrate (98%, Alfa Aesar), cadmium



Scheme 1. Assembly of Nanocrystals into Porous Thin Films by Cross-Linking Polymer-Templated Nanocrystals

oxide (99%, Strem), sulfur powder (99.5%, Alfa Aesar), selenium powder (99.5%, Strem), oleic acid (90%, Fischer), 1-ocadecene (90%, Acros), trioctylphosphine (90%, Aldrich), 1,2-ethanedithiol (95%, Acros), and 3-mercaptopropionic acid (>99%, Acros). Poly(ethylene oxide)-*block*-poly(butylene oxide) with a PEO(6500)-*b*-PBO(5000) mass ratio and a PDI of 1.09 was purchased from Advanced Polymer Materials Inc. Polystyrene-*block*-poly(dimethyacrylamide) with a PS(51000)-*b*-PDMA(8500) mass ratio and a PDI of 1.3 was purchased from Polymer Source Inc.

Nanocrystal Synthesis. CdS nanocrystals were synthesized using slight modifications to literature procedures.³¹ Briefly, cadmium acetate dihydrate (1 mmol, 269 mg), sulfur (0.5 mmol, 16 mg), tetradecanoic acid (2 mmol, 451 mg), and tetraethylthiuram disulfide (TETD) (0.06 mmol, 17 mg) were added to a three-neck flask. Next, 2,2'-dithiobis(benzothiazole) (DTBT) was added, and the amount of DTBT was used to control the size of the nanocrystals. A 1:3 TETD:DTBT molar ratio was used for larger (~5 nm) CdS nanocrystals, and a 2:1 ratio was used for smaller (~3 nm) CdS nanocrystals. This reaction mixture was dissolved in 50 mL of octadecene and stirred at 120 °C under flowing argon for 2 h. The temperature was increased to 240 °C with a ramp rate of ~10 °C/min and held for an additional 2.5 h under flowing argon. After cooling to room temperature, the nanocrystals were collected by centrifugation at 4000 rpm for 10 min. It was found that the nanocrystals were not dispersible with the native tetradecanoic acid ligands; however, adding excess oleic acid to the pelleted solid followed by sonication brought the nanocrystals into solution, and the nanocrystals were then purified by three cycles of dissolution in hexanes, followed by precipitation using ethanol. CdSe nanocrystals were synthesized according to reported procedures, and the only modifications were that the reaction was performed under argon protection and the reaction was scaled up 5-fold.⁶⁸ PbS/CdS core/shell nanocrystals were synthesized according to reported procedures.⁶

Ligand Stripping. For CdS and CdSe nanocrystals, organic ligands were stripped from the nanocrystal surfaces using Me₃OBF₄ or Et₃OBF₄ (Meerwein's salts) according to recently reported procedures.⁶³ Typically, half the products from a CdS synthesis dispersed in ~15 mg/mL hexanes were mixed with a 40 mg/mL solution of Meerwein's salt dissolved in acetonitrile. The Meerwein's salt solution was added until the nanocrystals precipitated from the solution (~0.5 mL). Chloroform was added, and the nanocrystals were pelleted by centrifugation. The supernatant was discarded, and the nanocrystals were dissolved in 2 mL of DMF for subsequent use. We found that the nanocrystals were more easily degraded by an excessive stripping agent when using Me₃OBF₄; however, both reagents were used to prepare ligand-stripped nanocrystals for this work. Native ligands were stripped from the PbS/CdS core/shell nanocrystals under equilibrium conditions by Lewis acid-base adducts of born trifluoride using the methods recently developed by Helms and co-workers.⁶⁴ After

removal of the organic ligands, the nanocrystals were dissolved in DMF with a concentration of \sim 20 mg/mL.

Nanocrystals with dodecanethiol ligands for optical absorption studies were prepared by exposing ligand-stripped nanocrystals in DMF to a solution of dodecanethiol dissolved in hexanes. The resulting biphasic mixture was vigorously stirred until the nanocrystals were transferred to the hexanes, as indicated by a color change in the hexane layer from clear to yellow. The hexane layer was isolated, and the nanocrystals were purified by precipitation with ethanol followed by resuspension in hexanes to remove excess dodecanethiol.

Film Synthesis. In a typical synthesis of a mesoporous film, 5 mg of PEO-b-PBO was dissolved in ~0.2 mL of ethanol with gentle heating and sonication. Next, 0.8 mL of ~5 nm diameter ligandstripped nanocrystals in DMF (described above) was added to the polymer solution. After being stirred for ~1 h, followed by brief sonication, this solution was used to deposit films via spin coating at 1000 rpm for 90 s onto oxygen plasma-cleaned (100) silicon substrates for diffraction, ellipsometric porosimetry, X-ray photoelectron spectroscopy (XPS), or electron microscopy, or onto clean glass slides for optical absorption measurements. After spin coating, the films were quickly placed in a septum-capped vial and purged with argon. A 10% (v/v) solution of either ethanedithiol (EDT) or 3-mercaptopropionic acid (MPA) in methanol was then added to the vial. Approximately 2 mL of the bidentate ligand solutions was used for a 1 cm² film. Caution: Ethanedithiol is highly toxic. The films were allowed to soak in this solution for 24 h without stirring or agitation. After being soaked in the cross-linking solution, the films were washed twice with ethanol by gently flowing ethanol over the film and soaked in ethanol for an additional 48 h to remove the polymer template. The films were then dried and stored in septa-capped vials flushed with argon. These films were used without further processing for all subsequent characterization.

The procedures for synthesizing films templated using PS-*b*-PDMA were similar to the descriptions included above, with the exception that the polymer was dissolved in DMF initially rather than ethanol. In addition, 0.2 mL of *N*-methyl-2-pyrrolidone (NMP) was added to the polymer/nanocrystal solution to facilitate better wetting of the solution on the substrates. Cross-linking with MPA and EDT was performed as described above; however, the template was removed by soaking the films in DMF because of the low solubility of PS-*b*-PDMA in ethanol.

Films for UV-visible absorption spectroscopy and wide angle X-ray scattering (WAXS) and those made with PbS/CdS core/shell nanocrystals were prepared under air free conditions by spin coating the samples in a nitrogen atmosphere glovebox and sealing them in septa vials. The vials were removed from the glovebox where the cross-linking solutions were added and removed using septa syringe techniques under a dry argon flow. In most cases, some optimization of nanocrystal:polymer template ratios was needed to produce films



Figure 1. Top view SEM images of spin-coated porous films of nanocrystals using different polymers and cross-linkers. (a and b) PEO-b-PBO-templated \sim 5 nm CdS nanocrystals cross-linked with EDT and MPA, respectively. (c) CdS nanocrystals (\sim 5 nm) templated with PS-b-PDMA and cross-linked with MPA. (d) CdSe nanocrystals (\sim 4 nm) templated with PEO-b-PBO and cross-linked with EDT.

with homogeneous porosity because other factors, such as the size of nanocrystals, can affect the ideal ratio.

Characterization. Scanning electron microscopy (SEM) images were obtained using a JEOL model 6700F electron microscope with an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) micrographs of the PbS/CdS core/shell particles were collected using an FEI Tecnai T20 G2 S-TWIN TEM instrument operating at 200 kV. To improve contrast, samples were supported on three- to five-layer graphene-spanning holes in Quantifoil R1.2/1.3 holey carbon grids. These grids were prepared using the direct transfer method.⁷⁰ TEM micrographs of the ligand-stripped particles were collected using an FEI T12 TEM instrument operating at 120 kV. Two-dimensional (2D) WAXS data were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) using beamline 11-3. Measurements were taken in reflection mode with the incoming beam near grazing incidence and an X-ray energy of 1.27 keV. Transmission absorbance spectra were recorded on an Agilent HP 8452A UV-vis spectrophotometer. Ellipsometric porosimetry was performed on a PS-1000 instrument from Semilab using toluene as the adsorbate. A UVvisible CCD detector adapted to a grating spectrograph analyzed the signal reflected by the sample. The light source was a 75 W Hamamatsu xenon lamp, and measurements were taken in the spectral range from 1.24 to 4.5 eV with an angle of incidence of 60°. Data analysis was performed using the associated WinElli II software with the assumption of cylindrical pores. XPS analysis was performed using a Kratos Axis Ultra DLD instrument with a monochromatic Al K α radiation source. The charge neutralizer filament was used to control charging of the sample; a 20 eV pass energy was used with a 0.1 eV step size for high-resolution scans, and scans were calibrated using the C 1s peak shifted to 284.8 eV.

RESULTS AND DISCUSSION

In this work, our goal was to mitigate the negative effects of thermal processing on nanocrystal properties by removing the need for heat treatments during the synthesis of mesoporous films made from nanocrystals. Scheme 1 gives an overview of our method for porous film formation. First, ligand-stripped nanocrystal solutions were combined with amphiphilic diblock copolymer solutions. Films were deposited by spin coating onto suitable substrates where the nanocrystals co-assembled with polymer micelles to form organic/inorganic composites. The resulting films were then soaked in solutions of bidentate crosslinking ligands to bind the nanocrystals together. The crosslinking solutions used were much more concentrated than those used for layer-by-layer deposition of dense nanocrystal solids.^{39,40} To preserve the porous structure of the films, the rate of nanocrystal cross-linking must be faster than the rate of polymer template diffusion out of the film, so more concentrated solutions of the cross-linking molecules were used to accelerate the cross-linking kinetics. In addition, the solvent used for the cross-linking was specifically chosen to dissolve the cross-linking agent, while having minimal nanocrystal and polymer solubility. The films were soaked in the solution of cross-linking molecules for 24 h to ensure complete cross-linking of the nanocrystals. After cross-linking, the polymer template was removed by soaking the resulting films for 48 h in a good solvent for the polymer template. In both cases, the time the films were soaked was chosen to ensure



Figure 2. Toluene adsorption isotherms for (a) CdS and (c) CdSe templated with PEO-*b*-PBO and cross-linked with EDT. Corresponding pore radius distributions for (b) CdS and (d) CdSe calculated from a Kelvin model fit for mesopores. CdS data correspond to the SEM image in Figure 1a and CdSe data to the SEM image in Figure 1d.

completeness of reaction; the reactions could proceed much faster, but shorter times were not investigated.

The most direct evidence of the porous structure of our films comes from top view SEM images. Figure 1 presents top view SEM images of mesoporous films of cross-linked nanocrystals made using different cross-linkers, different polymer templates, and different nanocrystal building blocks. Despite the lack of thermal processing, it is difficult to see individual nanocrystals in the pore walls because the organic cross-linkers coat the nanocrystals. However, in all cases, we observe disordered but homogeneous porosity. The disorder is likely a combination of disorder in the initial polymer/nanocrystal composite and disorder introduced during cross-linking and polymer removal. Unfortunately, we were unable to observe any long-range order by small angle X-ray scattering. Other polymers specifically designed to produce more ordered pore structures with nonoxide nanocrystals could be used to achieve more ordered mesopores.

To understand the effect of different cross-linking ligands, we prepared identical PEO-*b*-PBO-templated films and treated them with either 3-mercaptopropionic acid (MPA) or 1,2-ethanedithiol (EDT) in methanol and washed out the polymer template using ethanol. Figure 1a shows a top view SEM image of an MPA cross-linked film made from ~5 nm CdS nanocrystals, and Figure 1b shows a top view image of an EDT cross-linked film made using the same nanocrystals.

Qualitatively, there are minimal differences in the film morphology between the two different cross-linkers used. Observation of the bound thiolate by XPS (Figure S1A) shows that the cross-linking ligands remain bound after the procedure to wash out the polymer template. Because the morphology appears to be independent of cross-linker and the linking molecules remain bound, our method could be general to many bidentate small molecule cross-linkers, including hydrazine, ethylenediamine, and diacids. Importantly, these different small molecules can be used to tune electronic properties of nanocrystal solids.^{37–39,45}

While SEM provides evidence of the mesoscale structure, it does not provide any information about the internal threedimensional structure of the nanocrystal assemblies, and importantly, it does not prove removal of the polymer template. To address this, we analyzed the mesoporosity using ellipsometric porosimetry with toluene as the adsorbate.⁷¹ Figure 2a shows an adsorption isotherm for PEO-*b*-PBOtemplated CdS. This sample shows ~20% solvent accessible pore volume, which is in reasonable agreement with SEM images (Figure 1a). The pore radius distribution (Figure 2b) was determined from a Kelvin model fit of the adsorption data. The average pore radius measured was ~9 nm, which is in good agreement with SEM images for this sample (Figure 1a). Similar results were seen for mesoporous CdSe (Figure 2c,d); however, in this case, a larger solvent accessible pore volume $(\sim 30\%)$ was observed, along with a slightly larger average pore radius (~ 12 nm). These results are again in good agreement with SEM images, where the CdSe films (Figure 1d) show an average pore size slightly larger than that of the CdS films (Figure 1a).

The differences in porosity between these two samples are attributed to different polymer template:nanocrystal ratios used in the synthesis of these specific samples (0.5 mg of polymer/ mg of as-synthesized nanocrystals for the CdS samples vs 0.7 mg of polymer for the CdSe sample). The variation in pore size is in good agreement with previous examples of polymertemplated nanocrystal films where the polymer:nanocrystal ratio was systematically explored.⁵⁴ The SEM images and the porosimetry together provide strong evidence of the existence of homogeneous, nanoscale porosity of our films. These data thus indicate that the polymer template was indeed successfully removed using our solution phase methods. While our films show good porosity, it is lower than the highest values of 50% solvent accessible porosity we have achieved using thermal decomposition of the same polymer template.⁵¹ In the case of thermal decomposition, the total porosity is a combination of mesopores resulting from the polymer template and micropores stemming from spaces between individual nanocrystals. In this case, the spaces between individual nanocrystals are occupied with cross-linking molecules and therefore cannot be accessed by adsorbate molecules, which could partly account for the smaller solvent accessible pore volume. Other differences could arise from variations in the nanocrystal:template ratio.

Further evidence of the removal of the polymer template comes from evaluation of C 1s signals from XPS. Because PEOb-PBO contains many ether linkages, the intensity of the C-O signal with a binding energy of 286.3 eV can be used to probe the amount of remaining polymer template. A C 1s XPS spectrum for an EDT cross-linked film of PbS/CdS nanocrystals (Figure S1A) shows signal primarily from C-C species that could arise from both contamination of the sample with adventitious carbon from the atmosphere and carbon in the dithiol. A small shoulder attributed to C-O species that we attribute to small amounts of residual polymer is also observed. By comparing this signal to the C–O signal from a sample of pure PEO-b-PBO (Figure S1C), it is easy to see that the ratio of C-O carbon to C-C carbon is much higher in the pure polymer sample than in our films. This qualitatively shows that most of the polymer template is removed. We then quantified the amount of remaining polymer by determining the atom percent of C-O carbon and comparing it to the atom percent of sulfur from the XPS data. On the basis of the unique distribution of aliphatic and C-O carbons in PEO-b-PBO, we calculated the mass of polymer from the C-O signal and compared it to the mass of metal sulfide nanocrystals calculated from the atom percent of sulfur. Through this analysis, we determine there is ~0.1 wt % polymer remaining in our samples, compared to ~ 30 wt % in the as-formed films, indicating that the polymer template is thoroughly removed.

We next examined the structure of the films using wide angle X-ray scattering (WAXS) and optical absorption spectroscopy. WAXS was used to determine the crystal structure and average crystallite size of freshly ligand-stripped nanocrystals and of the nanocrystals in the porous films. Figure 3A shows WAXS patterns for CdS nanocrystals in different environments. Part a shows WAXS patterns for ligand-stripped CdS nanocrystals that can be indexed to zinc blende CdS. Wurtzite CdS could



Figure 3. (A) Wide angle XRD patterns obtained by integrating twodimensional (2D) WAXS patterns of CdS nanocrystals after different ligand treatments: (a) ligand-stripped CdS nanocrystals, (b) templated CdS nanocrystal film cross-linked with EDT, and (c) templated CdS nanocrystal film cross-linked with MPA. The stick pattern corresponds to zinc blende CdS (JCPDS Card 00-010-0454). (B) Wide angle XRD patterns obtained by integrating 2D WAXS patterns of CdSe nanocrystals after different ligand treatments: (a) ligand-stripped CdS nanocrystals and (b) templated CdS nanocrystal film cross-linked with EDT. The stick pattern corresponds to zinc blende CdSe (JCPDS Card 00-019-0191). Good nanocrystal size retention is observed for all samples across all processing conditions.

give a very similar pattern; however, the peak at 1.86 Å⁻¹ would be a convolution of three peaks and would thus be broader than the peak seen at 3.1 Å⁻¹. Also, wurtzite CdS shows a peak at 2.6



Figure 4. (a) Solution phase optical absorption for CdS nanocrystals with different capping ligands. (b and c) Absorption for large (\sim 5 nm) and small (\sim 3 nm) CdS, respectively, templated into porous films and cross-linked with different molecules. (d) Absorption for CdSe-based porous films cross-linked with different molecules. As-synthesized traces correspond to solution phase absorption of nanocrystals homogeneously dissolved in hexanes.

 $Å^{-1}$, which is not seen in our patterns. The diffraction patterns show broad peaks consistent with their small crystallite size. We found that by fitting the peaks and applying the Scherrer equation modified for q space and assuming spherical crystallites,⁷² we determined a crystallite size of \sim 4.1 nm. Porous films cross-linked with EDT were prepared from the same nanocrystal batch. WAXS patterns for the film (panel A, part b) shows an identical pattern with minimal changes to the peak broadening or peak positions, which indicates essentially no changes to the crystal structure and crystallite size due to oxidation, etching, or sintering. EDT-derived porous films showed a Scherrer crystallite size of 4.1 nm, in excellent agreement with that of the isolated nanocrystals. In the case of CdS nanocrystals cross-linked with MPA, we calculate a Scherrer size of 4.2 nm, which further indicates the retention of size throughout processing with different ligands. Any variations in size are well within the uncertainty of the measurement. CdSe nanocrystals (Figure 3B) showed similar trends. In this case, we calculated a Scherrer size of 3.3 nm for the ligand-stripped CdSe and a size of 3.2 nm for CdSe crosslinked with EDT. On the basis of WAXS, we thus conclude that there is no measurable change in the crystal structure or size of the nanocrystals during formation of the mesoporous network. By avoiding heat treatments in this method for making mesoporous films, we fully preserve the crystallite size in the resulting film.

UV-visible absorption spectroscopy was employed to investigate the effects of film processing on the nanocrystal optical properties. Absorption is also highly sensitive to changes in nanocrystal size, so it is a good double check of the conclusion from WAXS. On the basis of the preservation of nanocrystal size, we expect to see minimal differences between the optical absorption of the as-synthesized nanocrystals and the optical absorption of those in the porous films due to nanocrystal size effects. However, the optical absorption, and in particular the position of the first exciton peak, of nanocrystals is also affected by other factors such as the surface ligands and the spacing between the individual nanocrystals, which can change the dielectric environment surrounding the nanocrystals and causes coupling between quantum dots. In this system, the ligand environment changes from the oleic acid ligands used in the synthesis to a charge stabilization and finally to a thiol ligand bound to the surface.

To understand the ligand effects, we first prepared multiple solutions of CdS nanocrystals from the same batch with different surface ligands. We specifically examined nanocrystals with oleic acid ligands, as charge-stabilized nanocrystals in DMF, and with dodecanethiol ligands to mimic the surface effect of EDT or MPA. We then performed solution phase absorption measurements to remove electronic coupling effects. UV-vis absorption (Figure 4a) shows a blue shift of 2 nm in wavelength from the nanocrystals with the native ligands to ligand-stripped nanocrystals. This could result from either a negative solvatochromatic shift due to the higher dielectric constant of DMF compared to that of hexanes or an altered spherical potential confining the exciton wave function due to ligand effects. Upon conversion from charge-stabilized nanocrystals to thiol-capped nanocrystals, there is a 1 nm red shift. The addition of a sulfur from the thiol to the surface of the nanocrystals will slightly increase the size of the nanocrystal, which could explain the red shift. One peculiarity of the absorption spectra is the decreased intensity of the second absorption peak for ligand-stripped and thiol-capped nanocrystals. This effect was also seen in other nanocrystal surface treatments using inorganic ligands as the capping agents^{65,73} but has not been fully explained. We suspect that this mode has significant p character; thus, its oscillator strength will be more influenced by surface modifications.^{74,75} Overall, while some changes in absorption spectra do occur with different ligand environments, the effect is weak.

For porous nanocrystal films treated with bidentate ligands, the small shifts due to changes in the ligand environment will be superimposed with the effects from decreasing the interparticle spacing. Figure 3B shows UV–vis absorption for large (~5 nm) nanocrystals with oleic acid ligands in hexanes, and for porous films templated with PEO-*b*-PBO and treated with MPA and EDT. The absorption spectra for the films were corrected for a small scattering background due to film imperfections to facilitate comparison. There is an ~5 nm red shift from the as-synthesized nanocrystals going to the cross-linked porous films. Similar trends are seen for smaller CdS (~4 nm) for EDT-cross-linked films (Figure 4c). However, the same trend is not seen for MPA-cross-linked films for the smaller nanocrystals.

To understand the cause of the red shift in EDT-treated films, we consider related systems. PbSe nanocrystals crosslinked with EDT show a similar red shift, and it has been suggested that this red shift arises from a combination of changes to (i) the dielectric constant at the surface of the nanocrystals, (ii) radiative electronic coupling, and (iii) increased wave function overlap.³⁹ More recent work has shown that the red shift is predominantly a result of changes to the dielectric environment surrounding each quantum dot $(\sim 88\%)$, with a smaller contribution from electronic or transition dipole coupling.⁷⁶ The effects of the increased dielectric constant may be stronger for PbSe than for CdSe or CdS because of the larger Bohr exciton radius of PbSe, meaning the exciton will be located closer to the nanocrystal surface for PbSe and subsequently be more sensitive to surface effects.⁷⁷ Nonetheless, red shifts of the absorption peak in close-packed films of CdSe nanocrystals capped with tributyl phosphine/ tributyl phosphine oxide (TBP/TBPO) ligands have been observed and attributed to changes to the dielectric environment around the nanocrystals.⁷⁸ However, in this case, shifts were smaller than the ones we observe here because the TBP/ TBPO ligands are much larger than EDT.⁷⁸ We thus conclude that the red shifts observed in our samples are a result of decreased interparticle spacing, which predominantly changes the dielectric environment of the nanocrystals, thus causing their absorption to red shift.

We also looked at the absorption of porous CdSe films crosslinked with both EDT and MPA (Figure 4d). Here, there is no red shift in the cross-linked films. However, CdSe is more sensitive to oxidation than CdS, especially when both are ligand-stripped. Any oxidation of the nanocrystals will blue shift the absorption, so the effects due to oxidation and coupling have opposite effects on the position of the first excitation peak and could cancel out.⁷⁷ In support of this idea, CdSe-based films made in air showed clearly observable blue shifts (data not shown), confirming that the presence of air can blue shift the position of the first excitation peak. We note that while some measurable changes in our optical absorption spectra of both CdS and CdSe can be observed, all changes are small compared to the changes previously observed using thermal treatments, where red shifts of up to 100 nm were observed.⁵¹ Others have used less aggressive thermal treatments and saw smaller red shifts (~15 nm), but even those changes are much more significant than the ones shown here.⁵³ While those less aggressive thermal treatments mitigated some of the effects of grain growth, it is unclear whether the polymer template was fully removed and a truly open porosity was achieved at those more modest temperatures, as porosimetry was not used to confirm an open pore volume and the temperature was somewhat lower than the polymer decomposition temperature.⁵³ This discussion serves to emphasize that the methods presented here allow for precise control over the optical properties of porous films, combined with fully accessible porosity.

In addition to information about the size of the nanocrystals, optical absorption can also provide information about the size distribution of the nanocrystals in a sample. The right halfwidth at half-maximum (RHWHM) of the first exciton peak has been used to quantify the size distribution of quantum dot samples in solution.^{19,79} Because the position of this peak is dependent on size, absorption from nanocrystals larger and smaller than the average will broaden the absorption peak in a polydisperse sample. The RHWHM values of the first excitation peak for the as-synthesized nanocrystals in solution and for the porous films were measured, and in the case of the ~5 nm diameter CdS nanocrystals, we found the RHWHM values to be 12.8, 12.6, and 12.8 nm for as-synthesized nanocrystals, EDT-cross-linked porous films, and MPA-crosslinked porous films, respectively. Similar trends were observed for the smaller ~4 nm CdS. One might expect some broadening due to wave function overlap, but as discussed above, the dominant optical changes resulting from nanocrystal assembly are dielectric changes; therefore, the effect of wave function overlap is expected to be small. We note that similar trends (i.e., a red shift in peak position but no peak broadening) have also been observed for dense EDT-cross-linked PbSe films.³⁹ The minimal changes to the RHWHM of the first exciton peak show that there are minimal changes to the size distribution of the nanocrystals in our samples, which is important for many optoelectronic applications.²

Next we wanted to expand out method to more sensitive NIR particles to take advantage of the gentle process we have developed. While the "gentle" BF₃ ligand stripping procedure developed by Helms and co-workers is a synthetic break-through and could guide the development of new strategies for producing naked nanocrystals, it was only verified for large PbSe nanocrystals.⁶⁴ Large PbSe nanocrystals have a band gap that is too small for use in solar energy harvesting because of the limited open circuit voltage. When we used small (~3 nm) PbS nanocrystals, which have ideal band gaps for use in single-junction solar cells, we were unable to obtain stable colloidal



Figure 5. (A) Visible–NIR absorption of PbS and PbS/CdS core/shell nanocrystals in different ligand environments. The difference in the position of the first excition peak between the PbS and PbS/CdS nanocrystals is used to estimate the shell thickness. All spectra except those of the PbS/CdS EDT film were recorded in dilute solution. Because of the lack of distinct excitonic features for the PbS/CdS BF₄ and PbS/CdS EDT samples, spectra were normalized at 800 nm. The inset is a photograph of the clear solution of ligand-stripped PbS/CdS core/shell nanocrystals in DMF. (B) Low-magnification TEM image of PbS/CdS core/shell particles with oleate ligands. Inset are HRTEM images and corresponding FFTs of particles along the $\langle 100 \rangle$ and $\langle 111 \rangle$ zone axes. (C) Low-magnification TEM image after treatment with BF₃⁻ in DMF. (D) Wide angle XRD patterns obtained by integrating 2D WAXS patterns of PbS/CdS core/shell nanocrystals with different ligand environments: (a) as-synthesized PbS/CdS core/shell nanocrystals, (b) nanocrystals from the same batch after treatment with BF₃ in DMF, and (c) a porous film of PbS/CdS nanocrystals after treatment with EDT. (E) Top view SEM image of PbS/CdS core/shell nanocrystals assembled into an open porous structure using PEO-*b*-PBO as the pore template. (F) Toluene adsorption isotherms for a porous PbS/CdS nanocrystal film cross-linked with EDT and (inset) the corresponding pore radius distribution. This data was collected on films made in the same batch as the sample shown in panel E.

dispersions. We suspect that the smaller sized nanocrystals have much higher surface energies and cannot accommodate a ligand free, naked surface. To address this problem, we hypothesized that a thin cadmium sulfide shell on the surface of the PbS nanocrystals would stabilize the surface and allow us to obtain stable dispersions of PbS nanocrystals. We thus synthesized PbS/CdS core/shell nanocrystals using a partial cation exchange approach that has been fully characterized elsewhere.⁶⁹ In these nanocrystals, the shell is grown by replacement of Pb2+ with Cd2+ on the surface. Thus, the effective size of the PbS core decreases as the shell grows. Because the position of the first excition peak is determined by the size of the PbS core, the shell thickness can be calculated on the basis of the blue shift of the first exciton peak using the empirical fit for the size dependence of the exciton peak.¹⁸ On the basis of the blue shift observed for our PbS nanocrystals after shell growth (Figure 5A, black and red traces), we estimate a shell thickness of 0.3 nm. We targeted 0.3 nm thick CdS shells to ensure complete coverage of CdS on the surface, but at the

same time keeping the shell thin enough for charge transport between nanocrystals to be possible.

TEM of the PbS/CdS core/shell particles (Figure 5B) shows a narrow size distribution after the shell growth reactions. Because of the thin nature of the shell and the nearly indistinguishable lattice parameters of PbS and CdS, determining the shell thickness of the particles by HRTEM is difficult. However, the different crystal structures (rock salt vs zinc blende) of the core and shell materials allow for the visualization of the two domains based on the symmetry of HRTEM lattice fringes and the coherent alignment of the two materials. 80 On the basis of this, along the $\langle 100\rangle$ zone axis, both PbS and CdS are expected to have square lattices that are offset by 45° with a lattice spacing of 2.96 Å for the (200) planes of the PbS and 2.05 Å for the (220) planes of the CdS shell. In our HRTEM image along the $\langle 100 \rangle$ zone axis (Figure 5B, left inset), we observe well-defined fringes of the PbS core that do not extend to the edge of the particle. We assign the diffuse shell, which can be easily distinguished from the lowbackground graphene support, to the CdS layer on the surface.

We suspect the lattice fringes from the shell cannot be resolved because of its thin nature and the small lattice fringe spacing, which is approaching the resolution limit of the TEM used. Along the $\langle 111 \rangle$ zone axis, PbS and CdS have the same projection; thus, we should expect lattice fringes to extend to the surface of the nanocrystal, which is what we observe by HRTEM (Figure 5B, right inset). Additional TEM images and visualization of the core and shell crystal structures viewed down different zone axes are shown in Figure S2. We note that not all of the particles observed by HRTEM were defect free (Figure S3) like the ones shown in Figure 5A. It is unclear if this is expected for these types of particles because papers reporting their synthesis show HRTEM from only a few particles.⁶⁹ While TEM can provide detailed information about individual particles, it is difficult to extract information from the "average" nanocrystal. Optical methods are thus more reliable for determining average shell thickness.⁶⁹

We then stripped the oleic acid ligands off the nanocrystal surface using the BF₃/DMF Lewis acid–base adducts discussed above.⁶⁴ Using this method, we were able to obtain dispersions of ligand-stripped PbS/CdS core/shell nanocrystals in DMF (inset of Figure 5A) that did not scatter light and were stable for several days in a nitrogen-filled glovebox. Optical absorption from the ligand-stripped PbS/CdS nanocrystals (Figure 5A, blue trace) shows that the well-defined excitonic features are lost upon ligand stripping, indicating more polydisperse samples. In agreement with this fact, TEM also shows a broader size distribution for ligand-stripped nanocrystals (Figure 5C).

Comparing the WAXS patterns for the as-synthesized PbS/ CdS core/shell nanocrystals and the ligand-stripped nanocrystals (Figure 5D, traces a and b, respectively) shows a decrease in the intensity of the peak at ~ 2.2 q after ligand stripping. The close proximity of the PbS and CdS causes constructive interference between the core and shell materials, which makes the diffraction patterns appear as a weighted average of the two reference patterns, in agreement with the results of XRD simulation presented elsewhere.⁶⁹ On this basis, we can use the intensity of the (002) reflection (peak at ~ 2.2 q) as a way to determine the relative amounts of the two materials because the CdS phase has a much lower intensity for that reflection; the loss of intensity suggests a loss of Pb²⁺ from the system. We suspect the sharp peaks from 2.5 q to 3.5 q are from residual Lewis acid-base adducts of BF₃, which are a byproduct of the reaction. We were not able to match them with any known reference patterns, however. The changes to the optical properties and the possible loss of lead could come from etching of the nanocrystals by trace amounts of HBF4, a byproduct of ligand stripping if trace amounts of water are available.⁶⁴ We note that there are no data available in the literature on the optical properties of ligand-stripped PbSe or PbS, so it is not possible to tell if these dramatic changes in optical absorption are expected upon ligand stripping.

While ligand stripping causes changes to the structural and optical properties of the nanocrystals, the goal of this paper is to develop new methods of processing nanocrystals into porous structures without altering their properties. In comparing the vis—NIR absorption of the ligand-stripped nanocrystals with that of a porous film of nanocrystals (Figure 5A) treated with EDT, we find that minimal changes are seen, indicating the optical properties of the nanocrystals are maintained. There is a slight red shift of the absorption onset that is expected on the basis of the increased dielectric constant surrounding the

nanocrystals when they are incorporated into a film.⁷⁶ Furthermore, we do not observe any changes to the wide angle diffraction during the processing used to make porous films of nanocrystals (Figure 5D, traces b and c). This evidence further shows that our process for making porous films of nanocrystals can be expanded to other, less well-behaved, systems while still maintaining the properties of the ligand-stripped nanocrystal building blocks. Further work still needs to be done, however, to develop general methods for synthesizing ligand free "naked" nanocrystals for these highly reactive systems without altering their delicate optical and electronic properties.

The pore structure of the films made with PbS/CdS core/ shell nanocrystals shows structures similar to those made with cadmium chalcogenide nanocrystals. A top view SEM image (Figure 5E) of a porous PbS/CdS core/shell nanocrystal-based film templated with PEO-b-PBO shows a homogeneous pore size that is comparable to those made with CdS or CdSe nanocrystals. This indicates that the pore structure and material comprising the pore wall can be independently changed by using the appropriate choice of nanocrystal building blocks. Furthermore, porosimetry (Figure 5F) shows a 28% solvent accessible pore volume, confirming the pores are open and interconnected. The pore radius distribution determined by a Kelvin model fit (inset of Figure 5F) shows a peak at 20 nm and a relatively broad distribution that corresponds well with the pore sizes observed by SEM (Figure 5E). To the best of our knowledge, this is the first example of a film made from NIR active lead chalcogenide nanocrystals with interconnected, solvent accessible mesoporosity. These open pores could be filled with an acceptor material, which could lead to advances in quantum dot photovoltaics by allowing intimate mixing of donor and acceptor materials. This, in turn, would limit the distance excitons must diffuse before being separated at a heterojunction, while maintaining connected pathways to both electrodes.

CONCLUSION

In this work, we have developed a new technique for making porous films of nanocrystals without thermal treatments using block copolymer templating. We employ bidentate ligands to bind the nanocrystals together and simple washing to remove the polymer template. Our films show disordered but homogeneous porosity by SEM and good pore accessibility using ellipsometric porosimetry. In addition, WAXS and absorption spectroscopy show there is no change in the size of the nanocrystals constituting the film throughout the synthesis process. Our method thus provides a route to simultaneous control of the mesoscale architecture and the electronic properties of the nanocrystal building blocks that has not been achieved using thermal treatments. The generality of the method is demonstrated here using three different types of nanocrystals (CdS, CdSe, and PbS/CdS core/shell nanocrystals), two different block copolymers (PEO-b-PBO and PS-b-PDMA), and two different cross-linking agents (MPA and EDT).

To appreciate the potential impact of these methods, it is interesting to consider the fantastic array of kinetically trapped nanocrystals that have been synthesized, including core/shell particles,⁸¹ graded alloys,⁸² metastable crystal structures,^{83,84} and highly anisotropic shapes,^{85–87} many of which exhibit interesting and useful properties. Unfortunately, these kinetically trapped materials often convert to the thermodynamic

products upon mild heat treatment.^{87,88} Using the methods described here, open porous networks of these nanocrystals can potentially be made at room temperature, allowing metastable nanocrystals to be assembled into porous architectures. The only requirements are that a suitable surface treatment must be available to disperse the nanocrystals as ligand free charge-stabilized colloids in polar solvents, and finding an appropriate bidentate ligand for the given nanocrystal. While these constraints are significant, the method offers interesting possibilities for making novel photovoltaic, thermoelectric, electrochemical, and catalytic materials for which precise control over the mesoscale structure and nanocrystal properties are needed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.6b01681.

The SI contains XPS spectra and additional HRTEM images (PDF)

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REFERENCES

(1) Zaera, F. Nanostructured Materials for Applications in Heterogeneous Catalysis. *Chem. Soc. Rev.* 2013, 42, 2746–2762.

(2) Liu, C.; Dasgupta, N.; Yang, P. Semiconductor Nanowires for Artificial Photosynthesis. *Chem. Mater.* **2014**, *26*, 415–422.

(3) Zhang, Y.; Yuwono, A. H.; Wang, J.; Li, J. Enhanced Photocatalysis by Doping Cerium into Mesoporous Titania Thin Films. J. Phys. Chem. C 2009, 113, 21406–21412.

(4) Sreethawong, T.; Suzuki, Y.; Yoshikawa, S. Photocatalytic Evolution of Hydrogen over Mesoporous Supported NiO Photocatalyst Prepared by Single-Step Sol-gel Process with Surfactant Template. *Int. J. Hydrogen Energy* **2005**, *30*, 1053–1062.

(5) Vamvasakis, I.; Subrahmanyam, K. S.; Kanatzidis, M. G.; Armatas, G. S. Template-Directed Assembly of Metal-Chalcogenide Nanocrystals into Ordered Mesoporous Networks. *ACS Nano* **2015**, *9*, 4419–4426.

(6) Rauda, I. E.; Augustyn, V.; Dunn, B.; Tolbert, S. H. Enhancing Pseudocapacitive Charge Storage in Polymer Templated Mesoporous Materials. *Acc. Chem. Res.* **2013**, *46*, 1113–1124.

(7) Zhang, Y.; Xie, Z.; Wang, J. Supramolecular-Templated Thick Mesoporous Titania Films for Dye-Sensitized Solar Cells: Effect of Morphology on Performance. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2789–2795.

(8) Kamat, P. V. Quantum Dot Solar Cells. The Next Big Thing in Photovoltaics. J. Phys. Chem. Lett. 2013, 4, 908–918.

(9) Nozik, A. J. Nanoscience and Nanostructures for Photovoltaics and Solar Fuels. *Nano Lett.* **2010**, *10*, 2735–2741.

(10) Alivisatos, A. Perspectives on the Physical Chemistry of Semiconductor Nanocrystals. J. Phys. Chem. **1996**, 100, 13226–13239. (11) Kamat, P. V. Quantum Dot Solar Cells. Semiconductor Nanocrystals as Light Harvesters †. J. Phys. Chem. C **2008**, 112, 18737–18753.

(12) Nozik, a J.; Beard, M. C.; Luther, J. M.; Law, M.; Ellingson, R. J.; Johnson, J. C. Semiconductor Quantum Dots and Quantum Dot Arrays and Applications of Multiple Exciton Generation to Third-Generation Photovoltaic Solar Cells. *Chem. Rev.* **2010**, *110*, 6873– 6890.

(13) Maraghechi, P.; Labelle, A. J.; Kirmani, A. R.; Lan, X.; Adachi, M. M.; Thon, S. M.; Hoogland, S.; Lee, A.; Ning, Z.; Fischer, A.; et al. The Donor-Supply Electrode Enhances Performance in Colloidal Quantum Dot Solar Cells. *ACS Nano* **2013**, *7*, 6111–6116.

(14) Kramer, I.; Sargent, E. Colloidal Quantum Dot Photovoltaics: A Path Forward. *ACS Nano* **2011**, *5*, 8506–8514.

(15) Ip, A. H.; Thon, S. M.; Hoogland, S.; Voznyy, O.; Zhitomirsky, D.; Debnath, R.; Levina, L.; Rollny, L. R.; Carey, G. H.; Fischer, A.; et al. Hybrid Passivated Colloidal Quantum Dot Solids. *Nat. Nanotechnol.* **2012**, *7*, 577–582.

(16) Talapin, D. V.; Lee, J.-S.; Kovalenko, M. V.; Shevchenko, E. V. Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications. *Chem. Rev.* **2010**, *110*, 389–458.

(17) Kovalenko, M. V.; Manna, L.; Cabot, A.; Hens, Z.; Talapin, D. V.; Kagan, C. R.; Klimov, X. V. I; Rogach, A. L.; Reiss, P.; Milliron, D. J.; et al. Prospects of Nanoscience with Nanocrystals. *ACS Nano* **2015**, *9*, 1012–1057.

(18) Moreels, I.; Lambert, K.; Smeets, D.; De Muynck, D.; Nollet, T.; Martins, J. C.; Vanhaecke, F.; Vantomme, A.; Delerue, C.; Allan, G.; et al. Size-Dependent Optical Properties of Colloidal PbS Quantum Dots. *ACS Nano* **2009**, *3*, 3023–3030.

(19) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **2003**, *15*, 2854–2860.

(20) Pietryga, J.; Zhuravlev, K.; Whitehead, M.; Klimov, V.; Schaller, R. Evidence for Barrierless Auger Recombination in PbSe Nanocrystals: A Pressure-Dependent Study of Transient Optical Absorption. *Phys. Rev. Lett.* **2008**, *101*, 217401.

(21) Padilha, L. a; Stewart, J. T.; Sandberg, R. L.; Bae, W. K.; Koh, W.-K.; Pietryga, J. M.; Klimov, V. I. Carrier Multiplication in Semiconductor Nanocrystals: Influence of Size, Shape, and Composition. *Acc. Chem. Res.* **2013**, *46*, 1261–1269.

(22) Nootz, G.; Padilha, L. a.; Levina, L.; Sukhovatkin, V.; Webster, S.; Brzozowski, L.; Sargent, E. H.; Hagan, D. J.; Van Stryland, E. W. Size Dependence of Carrier Dynamics and Carrier Multiplication in PbS Quantum Dots. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, 83, 155302.

(23) Sandberg, R. L.; Padilha, L. a; Qazilbash, M. M.; Bae, W. K.; Schaller, R. D.; Pietryga, J. M.; Stevens, M. J.; Baek, B.; Nam, S. W.; Klimov, V. I. Multiexciton Dynamics in Infrared-Emitting Colloidal Nanostructures Probed by a Superconducting Nanowire Single-Photon Detector. *ACS Nano* **2012**, *6*, 9532–9540.

(24) Goldstein, A. N.; Echer, C. M.; Alivisatos, A. P. Melting in Semiconductor Nanocrystals. *Science (Washington, DC, U. S.)* **1992**, 256, 1425–1427.

(25) Zhitomirsky, D.; Kramer, I. J.; Labelle, A. J.; Fischer, A.; Debnath, R.; Pan, J.; Bakr, O. M.; Sargent, E. H. Colloidal Quantum Dot Photovoltaics: The Effect of Polydispersity. *Nano Lett.* **2012**, *12*, 1007–1012.

(26) Son, J. S.; Park, K.; Han, M.-K.; Kang, C.; Park, S.-G.; Kim, J.-H.; Kim, W.; Kim, S.-J.; Hyeon, T. Large-Scale Synthesis and Characterization of the Size-Dependent Thermoelectric Properties of Uniformly Sized Bismuth Nanocrystals. *Angew. Chem.* **2011**, *123*, 1399–1402.

(27) Wang, R. Y.; Feser, J. P.; Lee, J.-S.; Talapin, D. V.; Segalman, R.; Majumdar, A. Enhanced Thermopower in PbSe Nanocrystal Quantum Dot Superlattices. *Nano Lett.* **2008**, *8*, 2283–2288.

(28) \overline{Yu} , W. W.; Peng, X. Formation of High-Quality CdS and Other II \pm VI Semiconductor Nanocrystals in Noncoordinating Solvents: Tunable Reactivity of Monomers. *Angew. Chem., Int. Ed.* **2002**, *41*, 2368–2371.

(29) Hines, M. A.; Scholes, G. D. Colloidal PbS Nanocrystals with Size-Tunable Near-Infrared Emission: Observation of Post-Synthesis Self-Narrowing of the Particle Size Distribution. *Adv. Mater.* **2003**, *15*, 1844–1849.

(30) Joo, J.; Na, H.; Yu, T.; Yu, J.; Kim, Y.; Wu, F.; Zhang, J. Z.; Hyeon, T. Generalized and Facile Synthesis of Semiconducting Metal Sulfide Nanocrystals. *J. Am. Chem. Soc.* **2003**, *125*, 11100–11105.

(31) Cao, Y. C.; Wang, J. One-Pot Synthesis of High-Quality Zinc-Blende CdS Nanocrystals. *J. Am. Chem. Soc.* **2004**, *126*, 14336–14337. (32) Yin, Y.; Alivisatos, A. P. Colloidal Nanocrystal Synthesis and the

Organic-Inorganic Interface. Nature 2005, 437, 664-670.

(33) Wang, X.; Zhuang, J.; Peng, Q.; Li, Y. A General Strategy for Nanocrystal Synthesis. *Nature* **2005**, 437, 121–124.

(34) Regulacio, M. D.; Han, M.-Y. Composition-Tunable Alloyed Semiconductor Nanocrystals. *Acc. Chem. Res.* **2010**, *43*, 621–630.

(35) Peng, Z.; Peng, X. Mechanisms of the Shape Evolution of CdSe Nanocrystals. J. Am. Chem. Soc. 2001, 123, 1389–1395.

(36) Zou, Y.; Li, D.; Yang, D. Single Step Synthesis of CdSeS Nanorods with Chemical Composition Gradients. *J. Cryst. Growth* **2010**, *312*, 3406–3409.

(37) Law, M.; Luther, J. M.; Song, Q.; Hughes, B. K.; Perkins, C. L.; Nozik, A. J. Structural, Optical, and Electrical Properties of PbSe Nanocrystal Solids Treated Thermally or with Simple Amines. *J. Am. Chem. Soc.* **2008**, *130*, 5974–5985.

(38) Zarghami, M. H.; Liu, Y.; Gibbs, M.; Gebremichael, E.; Webster, C.; Law, M. P-Type PbSe and PbS Quantum Dot Solids Prepared with Short-Chain Acids and Diacids. *ACS Nano* **2010**, *4*, 2475–2485.

(39) Luther, J. M.; Law, M.; Song, Q.; Perkins, C. L.; Beard, M. C.; Nozik, A. J. Structural, Optical, and Electrical Properties of Self-Assembled Films of PbSe Nanocrystals Treated with 1,2-Ethanedithiol. *ACS Nano* **2008**, *2*, 271–280.

(40) Klem, E. J. D.; MacNeil, D. D.; Cyr, P. W.; Levina, L.; Sargent, E. H. Efficient Solution-Processed Infrared Photovoltaic Cells: Planarized All-Inorganic Bulk Heterojunction Devices via Inter-Quantum-Dot Bridging during Growth from Solution. *Appl. Phys. Lett.* 2007, *90*, 183113.

(41) Klem, E. J. D.; Shukla, H.; Hinds, S.; MacNeil, D. D.; Levina, L.; Sargent, E. H. Impact of Dithiol Treatment and Air Annealing on the Conductivity, Mobility, and Hole Density in PbS Colloidal Quantum Dot Solids. *Appl. Phys. Lett.* **2008**, *92*, 212105. (42) Tang, J.; Wang, X.; Brzozowski, L.; Barkhouse, D. A. R.; Debnath, R.; Levina, L.; Sargent, E. H. Schottky Quantum Dot Solar Cells Stable in Air under Solar Illumination. *Adv. Mater.* **2010**, *22*, 1398–1402.

(43) Luther, J. M.; Gao, J.; Lloyd, M. T.; Semonin, O. E.; Beard, M. C.; Nozik, A. J. Stability Assessment on a 3% Bilayer PbS/ZnO Quantum Dot Heterojunction Solar Cell. *Adv. Mater.* **2010**, *22*, 3704–3707.

(44) Choi, J. J.; Lim, Y.-F.; Santiago-Berrios, M. B.; Oh, M.; Hyun, B.-R.; Sun, L.; Bartnik, A. C.; Goedhart, A.; Malliaras, G. G.; Abruña, H. D.; et al. PbSe Nanocrystal Excitonic Solar Cells. *Nano Lett.* **2009**, *9*, 3749–3755.

(45) Liu, Y.; Gibbs, M.; Puthussery, J.; Gaik, S.; Ihly, R.; Hillhouse, H. W.; Law, M. Dependence of Carrier Mobility on Nanocrystal Size and Ligand Length in PbSe Nanocrystal Solids. *Nano Lett.* **2010**, *10*, 1960–1969.

(46) Yao, Q.; Arachchige, I. U.; Brock, S. L. Expanding the Repertoire of Chalcogenide Nanocrystal Networks: Ag 2Se Gels and Aerogels by Cation Exchange Reactions. J. Am. Chem. Soc. **2009**, 131, 2800–2801.

(47) Yao, Q.; Brock, S. L. Porous CdTe Nanocrystal Assemblies: Ligation Effects on the Gelation Process and the Properties of Resultant Aerogels. *Inorg. Chem.* **2011**, *50*, 9985–9992.

(48) Mohanan, J. L.; Arachchige, I. U.; Brock, S. L. Porous Semiconductor Chalcogenide Aerogels. *Science* **2005**, *307*, 397–400.

(49) Yu, H.; Bellair, R.; Kannan, R. M.; Brock, S. L. Engineering Strength, Porosity, and Emission Intensity of Nanostructured CdSe Networks by Altering the Building-Block Shape. *J. Am. Chem. Soc.* **2008**, 130, 5054–5055.

(50) Hitihami-Mudiyanselage, A.; Senevirathne, K.; Brock, S. L. Assembly of Phosphide Nanocrystals into Porous Networks: Formation of InP Gels and Aerogels. *ACS Nano* **2013**, *7*, 1163–1170. (51) Rauda, I. E.; Saldarriaga-Lopez, L. C.; Helms, B. A.; Schelhas, L. T.; Membreno, D.; Milliron, D. J.; Tolbert, S. H. Nanoporous Semiconductors Synthesized through Polymer Templating of Ligand-Stripped CdSe Nanocrystals. *Adv. Mater.* **2013**, *25*, 1315–1322.

(52) Rauda, I. E.; Buonsanti, R.; Saldarriaga-lopez, L. C.; Benjauthrit, K.; Schelhas, L. T.; Stefik, M.; Augustyn, V.; Ko, J.; Dunn, B.; Wiesner, U.; et al. General Method for the Synthesis of Hierarchical Nanocrystal-Based Mesoporous Materials. *ACS Nano* **2012**, *6*, 6386–6399.

(53) Rivest, J. B.; Buonsanti, R.; Pick, T. E.; Zhu, L.; Lim, E.; Clavero, C.; Schaible, E.; Helms, B. A.; Milliron, D. J. Evolution of Ordered Metal Chalcogenide Architectures through Chemical Transformations. *J. Am. Chem. Soc.* **2013**, *135*, 7446–7449.

(54) Buonsanti, R.; Pick, T. E.; Krins, N.; Richardson, T. J.; Helms, B. A.; Milliron, D. J. Assembly of Ligand-Stripped Nanocrystals into Precisely Controlled Mesoporous Architectures. *Nano Lett.* **2012**, *12*, 3872–3877.

(55) Warren, S. C.; Messina, L. C.; Slaughter, L. S.; Kamperman, M.; Zhou, Q.; Gruner, S. M.; DiSalvo, F. J.; Wiesner, U. Ordered Mesoporous Materials from Metal Nanoparticle-Block Copolymer Self-Assembly. *Science* **2008**, *320*, 1748–1752.

(56) Corma, A.; Atienzar, P.; García, H.; Chane-Ching, J.-Y. Hierarchically Mesostructured Doped CeO2 with Potential for Solar-Cell Use. *Nat. Mater.* **2004**, *3*, 394–397.

(57) Ba, J.; Polleux, J.; Antonietti, M.; Niederberger, M. Non-Aqueous Synthesis of Tin Oxide Nanocrystals and Their Assembly into Ordered Porous Mesostructures. *Adv. Mater.* **2005**, *17*, 2509–2512.

(58) Brezesinski, T.; Wang, J.; Polleux, J.; Dunn, B.; Tolbert, S. H. Templated Nanocrystal-Based Porous TiO2 Films for next-Generation Electrochemical Capacitors. J. Am. Chem. Soc. 2009, 131, 1802–1809.

(59) Szeifert, J. M.; Feckl, J. M.; Fattakhova-Rohlfing, D.; Liu, Y.; Kalousek, V.; Rathousky, J.; Bein, T. Ultrasmall Titania Nanocrystals and Their Direct Assembly into Mesoporous Structures Showing Fast Lithium Insertion. *J. Am. Chem. Soc.* **2010**, *132*, 12605–12611.

(60) Stefik, M.; Wang, S.; Hovden, R.; Sai, H.; Tate, M. W.; Muller, D. a.; Steiner, U.; Gruner, S. M.; Wiesner, U. Networked and Chiral Nanocomposites from ABC Triblock Terpolymer Coassembly with

Transition Metal Oxide Nanoparticles. J. Mater. Chem. 2012, 22, 1078–1087.

(61) Papadas, I. T.; Vamvasakis, I.; Tamiolakis, I.; Armatas, G. S. Templated Self-Assembly of Colloidal Nanocrystals into Three-Dimensional Mesoscopic Structures: A Perspective on Synthesis and Catalytic Prospects. *Chem. Mater.* **2016**, *28*, 2886–2896.

(62) Dong, A.; Ye, X.; Chen, J.; Kang, Y.; Gordon, T.; Kikkawa, J. M.; Murray, C. B. A Generalized Ligand-Exchange Strategy Enabling Sequential Surface Functionalization of Colloidal Nanocrystals. *J. Am. Chem. Soc.* **2011**, *133*, 998–1006.

(63) Rosen, E. L.; Buonsanti, R.; Llordes, A.; Sawvel, A. M.; Milliron, D. J.; Helms, B. A. Exceptionally Mild Reactive Stripping of Native Ligands from Nanocrystal Surfaces by Using Meerwein's Salt. *Angew. Chem., Int. Ed.* **2012**, *51*, 684–689.

(64) Doris, S. E.; Lynch, J. J.; Li, C.; Wills, A. W.; Urban, J. J.; Helms, B. A. Mechanistic Insight into the Formation of Cationic Naked Nanocrystals Generated under Equilibrium Control. *J. Am. Chem. Soc.* **2014**, *136*, 15702–15710.

(65) Nag, A.; Kovalenko, M. V.; Lee, J.; Liu, W.; Spokoyny, B.; Talapin, D. V. Metal-Free Inorganic Ligands for Colloidal Nanocrystals: S2-, HS-, Se2-, HSe-, Te2-, HTe-, OH-, and NH2- as Surface Ligands. J. Am. Chem. Soc. **2011**, 133, 10612–10620.

(66) Kirsch, B. L.; Chen, X.; Richman, E. K.; Gupta, V.; Tolbert, S. H. Probing the Effects of Nanoscale Architecture on the Mechanical Properties of Hexagonal Silica/polymer Composite Thin Films. *Adv. Funct. Mater.* **2005**, *15*, 1319–1327.

(67) Debnath, R.; Bakr, O.; Sargent, E. H. Solution-Processed Colloidal Quantum Dot Photovoltaics: A Perspective. *Energy Environ. Sci.* **2011**, *4*, 4870–4881.

(68) Nordell, K. J.; Boatman, E. M.; Lisensky, G. C. A Safer, Easier, Faster Synthesis for CdSe Quantum Dot Nanocrystals. *J. Chem. Educ.* **2005**, *82*, 1697.

(69) Neo, D. C. J.; Cheng, C.; Stranks, S. D.; Fairclough, S. M.; Kim, J. S.; Kirkland, A. I.; Smith, J. M.; Snaith, H. J.; Assender, H. E.; Watt, A. A. R. Influence of Shell Thickness and Surface Passivation on PbS/CdS Core/Shell Colloidal Quantum Dot Solar Cells. *Chem. Mater.* **2014**, *26*, 4004–4013.

(70) Regan, W.; Alem, N.; Alemán, B.; Geng, B.; Girit, Ç.; Maserati, L.; Wang, F.; Crommie, M.; Zettl, A. A Direct Transfer of Layer-Area Graphene. *Appl. Phys. Lett.* **2010**, *96*, 113102.

(71) Baklanov, M. R.; Mogilnikov, K. P.; Polovinkin, V. G.; Dultsev, F. N. Determination of Pore Size Distribution in Thin Films by Ellipsometric Porosimetry. J. Vac. Sci. Technol., B: Microelectron. Process. Phenom. 2000, 18, 1385.

(72) Smilgies, D. Research Papers Scherrer Grain-Size Analysis Adapted to Grazing- Incidence Scattering with Area Detectors Research Papers. *J. Appl. Crystallogr.* **2009**, *42*, 1030–1034.

(73) Dirin, D. N.; Dreyfuss, S.; Bodnarchuk, M. I.; Nedelcu, G.; Papagiorgis, P.; Itskos, G.; Kovalenko, M. V. Lead Halide Perovskites and Other Metal Halide Complexes As Inorganic Capping Ligands for Colloidal Nanocrystals. J. Am. Chem. Soc. **2014**, *136*, 6550–6553.

(74) Efros, A.; Rosen, M. The Electronic Structure of Semiconductor Nanocrystals 1. *Annu. Rev. Mater. Sci.* **2000**, *30*, 475–521.

(75) Ekimov, A. I.; Hache, M. C.; Schanne-Klein, M. C.; Ricard, D.; Flytzanis, C.; Kudryavtsev, I. A.; Yazeva, T. V.; Rodina, A. V.; Efros, A. L. Absorption and Intensity-Dependent Photoluminescence Measurements on CdSe Quantum Dots: Assignment of the First Electronic Transitions. J. Opt. Soc. Am. B **1993**, *10*, 100–107.

(76) Wolcott, A.; Doyeux, V.; Nelson, C. a.; Gearba, R.; Lei, K. W.; Yager, K. G.; Dolocan, A. D.; Williams, K.; Nguyen, D.; Zhu, X. Y. Anomalously Large Polarization Effect Responsible for Excitonic Red Shifts in PbSe Quantum Dot Solids. *J. Phys. Chem. Lett.* **2011**, *2*, 795– 800.

(77) Foos, E. E. The Complex Interaction of Spectroscopic Shifts and Electronic Properties in Semiconductor Nanocrystal Films. *J. Phys. Chem. Lett.* **2013**, *4*, 625–632.

(78) Leatherdale, C.; Bawendi, M. Observation of Solvatochromism in CdSe Colloidal Quantum Dots. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2001**, *63*, 1–6. (79) Chan, E. M.; Xu, C.; Mao, A. W.; Han, G.; Owen, J. S.; Cohen, B. E.; Milliron, D. J. Reproducible, High-Throughput Synthesis of Colloidal Nanocrystals for Optimization in Multidimensional Parameter Space. *Nano Lett.* **2010**, *10*, 1874–1885.

(80) Lambert, K.; De Geyter, B.; Moreels, I.; Hens, Z. PbTelCdTe CorelShell Particles by Cation Exchange, a HR-TEM Study. *Chem. Mater.* **2009**, *21*, 778–780.

(81) Ghosh Chaudhuri, R.; Paria, S. Core/shell Nanoparticles: Classes, Properties, Synthesis Mechanisms, Characterization, and Applications. *Chem. Rev.* **2012**, *112*, 2373–2433.

(82) Zhang, J.; Yang, Q.; Cao, H.; Ratcliffe, C. I.; Kingston, D.; Chen, Q. Y.; Ouyang, J.; Wu, X.; Leek, D. M.; Riehle, F. S.; et al. Bright Gradient-Alloyed CdSe X S 1– X Quantum Dots Exhibiting Cyan-Blue Emission. *Chem. Mater.* **2016**, *28*, 618–625.

(83) Li, H.; Zanella, M.; Genovese, A.; Povia, M.; Falqui, A.; Giannini, C.; Manna, L. Sequential Cation Exchange in Nanocrystals: Preservation of Crystal Phase and Formation of Metastable Phases. *Nano Lett.* **2011**, *11*, 4964–4970.

(84) Lechner, R. T.; Fritz-Popovski, G.; Yarema, M.; Heiss, W.; Hoell, A.; Schülli, T. U.; Primetzhofer, D.; Eibelhuber, M.; Paris, O. Crystal Phase Transitions in the Shell of PbS/CdS Core/Shell Nanocrystals Influences Photoluminescence Intensity. *Chem. Mater.* **2014**, *26*, 5914–5922.

(85) Manna, L.; Scher, E. C.; Alivisatos, A. P. Synthesis of Soluble and Processable Rod-, Arrow-, Teardrop-, and Tetrapod-Shaped CdSe Nanocrystals. J. Am. Chem. Soc. 2000, 122, 12700–12706.

(86) Manna, L.; Milliron, D. J.; Meisel, A.; Scher, E. C.; Alivisatos, A. P. Controlled Growth of Tetrapod-Branched Inorganic Nanocrystals. *Nat. Mater.* **2003**, *2*, 382–385.

(87) Goris, B.; Van Huis, M. A.; Bals, S.S.; Zandbergen, H. W.; Manna, L.; Van Tendeloo, G. Thermally Induced Structural and Morphological Changes of CdSe/CdS Octapods. *Small* **2012**, *8*, 937– 942.

(88) Groeneveld, E.; Witteman, L.; Lefferts, M.; Ke, X.; Bals, S.; Van Tendeloo, G.; de Mello Donega, C. Tailoring ZnSe-CdSe Colloidal Quantum Dots via Cation Exchange: From Core/Shell to Alloy Nanocrystals. *ACS Nano* **2013**, *7*, 7913–7930.