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Permalink
https://escholarship.org/uc/item/7zb081bg

Journal
ACS Nano, 7(8)

ISSN
1936-0851

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Publication Date
2013-08-27
Nonmonotonic Size Dependence in the Hole Mobility of Methoxide-Stabilized PbSe Quantum Dot Solids

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ABSTRACT We present a facile procedure to fabricate p-type PbSe-based quantum dot solids with mobilities as large as 0.3 cm^2 V^{-1} s^{-1}. Upon partial ligand exchange of oleate-capped PbSe quantum dots with the methoxide ion, we observe a pronounced red shift in the excitonic transition in conjunction with a large increase in conductivity. We show that there is little correlation between these two phenomena and that the electronic coupling energy in PbSe quantum dot solids is much smaller than often assumed. However, we observe for the first time a nonmonotonic size dependence of the hole mobility, illustrating that coupling can nonetheless be dominant in determining the transport characteristics. We attribute these effects to a decrease in charging energy and interparticle spacing, leading to enhanced electronic coupling on one hand and enhanced dipole interactions on the other hand, which is held responsible for the majority of the red shift.

KEYWORDS: quantum dot solids · electrical transport · optical properties · coupling

Quantum dot solids (QDS) made from PbSe nanoparticles have led to a variety of (opto-)electronic applications ranging from field-effect transistors (FET) and thermoelectrics to photodetectors and solar cells.1,2 Electrical transport in these artificial solids has been well described as a network of spatially and energetically disordered hopping sites, where the mobility is determined by an interplay between electronic coupling, interparticle spacing, charging energy, and energetic polydispersity.3 To increase the conductivity in PbSe QDS, numerous techniques have been developed, employing small cross-linkers such as hydrazine, alkanedithiols, ethylenediamine, thiocyanate, NN-dimethylformamide/tetrafluoroborate, sulfide, dicarboxylic acids, and halogenides.1,4–6

Theoretically, it has been shown that as nanoparticle size is decreased, a fundamental trade-off exists between promoting transport through increased electronic coupling from enhanced wave function overlap and inhibiting transport through increased charging energy from a smaller self-capacitance.7 This trade-off has been suggested as an explanation of nonmonotonic size-dependence of mobility in systems with sufficient electronic coupling, such as electron transport in ethanedithiol (EDT)-capped PbSe QDS.8,9 Here, we observe for the first time a nonmonotonic size-dependence of the hole mobility in QDS, by investigating methoxide-stabilized PbSe nanoparticles. We attribute this behavior to the shorter interparticle spacing, which results in an increase in hole tunneling probabilities and a decrease in charging energy. Typically, ligand exchange with a short cross-linker results in an optical red shift of the S_0 → S_1 transition as well as an enhancement in the field-effect mobility. These processes are usually completed within seconds and therefore difficult to resolve in time.4 Here, we study the shift of these two parameters after ligand exchange with a short cross-linker and its reversal upon exposure to air. Both parameters decay on very different time scales, indicating a lack of correlation between the optical shift and the change in field-effect mobility. We conclude that the induced red shift cannot be primarily due to electronic coupling.

RESULTS

The eight PbSe quantum dot (QD) samples analyzed in this study are characterized...
in terms of size, size distribution, and optical absorption in Figure 1 and show Se\textsubscript{r}Sh transition energies in accordance with previous observations\textsuperscript{10,11}.

To fabricate cross-linked QDS, we apply a 5.0 mM solution of tetrabutylammonium hydroxide (TBA-OH) in methanol to spin-cast thin films. The solution is described by the equilibrium

\[ \text{H}_3\text{C}^-\text{OH} + \text{HO}^- \rightleftharpoons \text{H}_2\text{C}^-\text{O}^- + \text{H}_2\text{O} \]

Following the law of mass action, it is straightforward to show that in a 5 mM solution of TBA-OH in methanol the molar ratio of CH\textsubscript{3}O\textsuperscript{-} to OH\textsuperscript{-} will be 95:1. From here on, we will refer to the capping ligand introduced by this treatment as “methoxide (MeO\textsuperscript{-})”, although the exchange solution contains 1% OH\textsuperscript{-} as an impurity. For more details, the reader is referred to the Supporting Information (SI).

Exposing a thin film of Pb-oleate-capped PbSe nanoparticles to MeO\textsuperscript{-} leads to instantaneous insolubility of the particle film in nonpolar solvents such as hexanes or chloroform. FT-IR (Figure 2, exemplarily shown for 6.4 nm particles before and after ligand exchange) indicates the change in chemical nature of the ligand shell upon this treatment. The broad band at 3500 cm\textsuperscript{-1} is indicative of an OH-containing species, whereas the band at 1100 cm\textsuperscript{-1} is typical for the methoxide ion. The same species causes the multiple C–H stretching bands at <3000 cm\textsuperscript{-1} and the sharp peak at 1380 cm\textsuperscript{-1}.

In the spectrum of the original Pb-oleate ligand we note two characteristic features of the C\textsuperscript{d}O stretching bands between 1400 and 1500 cm\textsuperscript{-1} (indicating a binding interaction) and the small C\textsuperscript{d}C band at 3010 cm\textsuperscript{-1}. Both features vanish upon treatment with MeO\textsuperscript{-} (the most energetic C–H feature in this spectrum occurs at 2970 cm\textsuperscript{-1}), which we attribute to an at least partial ligand exchange.

The extent of ligand exchange is further validated by X-ray photoelectron spectroscopy (XPS) of the same particle sample in the energy regime of the C 1s level. Where previous studies of Pb-oleate-capped nanoparticle films clearly resolved a COO\textsuperscript{-} feature at 288 eV in XPS, this feature is absent after treatment with MeO\textsuperscript{-} and
supports the conclusion of a partial ligand exchange.4 We note that the C 1s signal cannot be described adequately with a single Gaussian–Lorentzian component but rather requires a second function at higher energy centered at about 286.2 eV. We interpret the first signal with residual hexanes/octane adsorbed by the film and the second signal with the carbon in the methoxide ion. Note that the 1s core level of R₂C—O is expected at 286.4 eV.12

Thin films of all oleate-capped samples have the same Sₓ — Sₓ transition energy as the colloidal sample in tetrachloroethylene. Upon MeO⁻ treatment, all QD samples exhibit a pronounced red shift consistent with results for hydrazine-, ethanedithiol-, or dicarboxylic acid-capped PbSe QDs.1,4,13,14 As demonstrated in Figure 3a the red shift upon ligand exchange increases with decreasing particle size. For the smallest particles (3 nm), the exciton was not measurable in thin films, possibly due to either extremely large exciton shifts or the dominance of Fabry–Pérot cavity modes.7 For more details on these arguments, the reader is referred to the SI. For comparison, we include two reference points for EDT-capped PbSe nanoparticles at a given size in the diagram.4,8 It is apparent that the size-dependence of the shift in Sₓ — Sₓ transition energy upon ligand exchange with MeO⁻ or EDT is very similar for both systems. The shift is found to be highly sensitive to oxidation, to the point that the red shift experiences an oxygen-induced blue shift of equal and opposite magnitude within the first 2 min of exposure to air (Figure 3b). Previous studies using carboxylic acids and PbSe have found similar quick reversals of excitonic red shift upon air exposure.13

We demonstrate the reduction of interparticle spacing upon ligand exchange from Pb(oleate)₂ to Pb(MeO)₂ by a comparative TEM study in Figure 4. Films of initially well-dispersed quantum dots with a mean interparticle spacing of roughly 15 Å undergo a contraction to ~2–3 Å upon exchange with methoxide. We note a similar effect reported in PbSe nanoparticle films where hydrous methanol was used to replace Pb(oleate)₂.15 In that work, partial fusion of nanoparticles was reported upon ligand exchange, which we do not observe with the treatment presented here.

We further investigate the effect of MeO⁻ stabilization on PbSe QDS by field-effect transistor measurements. Initially insulating Pb(Oleate)₂-capped PbSe nanoparticle films become conductive upon methoxide exchange for all samples, with conductivities (σ) as high as 0.05 S cm⁻¹ (d = 6.4 nm). A representative source–drain sweep and transconductance sweep are presented in Figure 5.

Figure 3. (a) Size-dependence of the optical shift of the 1Sₓ — 1Sₓ transition in PbSe nanoparticle films on ligand exchange from Pb(oleate)₂ to Pb(MeO)₂ (blue dots) or Pb(ethanedithiolate) (orange crosses). Error bars are standard deviations from three samples. Values for exchange with Pb(ethanedithiolate) were reproduced from ref 4. The dashed line resrepresents simulated optical shifts from dipole–dipole coupling. (b) Vis–IR spectra of the same PbSe sample capped with Pb(oleate)₂ (red dotted line), with Pb(MeO)₂ under argon (blue solid line), and with Pb(MeO)₂ after 2 min in air (green dashed line).

Figure 4. TEM images of monolayers of PbSe nanoparticles capped with Pb(oleate)₂ (a) or Pb(MeO)₂ (b). The insets represent images of the same sample at higher magnifications.

Figure 5. Field-effect transistor characteristics for a 6.4 nm MeO⁻-capped PbSe QDS. (a) Positive drain sweep with 0, 20, 40, and 60 V gate voltages applied. (b) Transfer curve of the same film at 5 V source–drain bias.
The negative slope of the transconductance sweep (Figure 5b), that is, the decrease in drain current upon increased electron injection, is indicative of unipolar hole transport and p-type behavior. We extract the field-effect hole mobilities ($\mu_h$) in the linear regime and derive the hole concentration ($n_h$) via Ohm's law [see SI]. We find $n_h$ to be relatively constant, having a concentration of $(8 \pm 2) \times 10^{17}$ cm$^{-3}$ over the whole size regime studied. 

In Figure 6, we display the size-dependent field-effect hole mobility. For comparison, we plot $\mu_h$ over the same PbSe diameter range as for EDT-capped PbSe QDS taken from ref 8. As explained therein, $\mu_h$ increases monotonically with size. In contrast, for MeO$^-$ capping we find a nonmonotonic size-dependence for the hole mobilities with a maximum at $d = 6.4$ nm, exceeding $\mu_h$ for EDT capping of this particle size by over 1 order of magnitude.

Upon exposing transistors of MeO$^-$-capped PbSe QDS to air, $\mu_h$ is found to decrease slowly over the course of hours and days. We demonstrate this exemplarily for 5.7 nm particles in Figure 7 but note a similar behavior for all sizes. We simultaneously plot the change in $S_e \rightarrow S_h$ transition energy over the same time interval. After an initial red shift due to the ligand exchange, upon air exposure the transition energy gradually blue shifts at a much slower rate, consistent with previous reports.4,14

**DISCUSSION**

The technique presented here provides a facile way to prepare p-type PbSe QDS with large mobilities at high doping levels. This material has potential for application as a thin-film thermoelectric where unipolar transport, large mobilities, and carrier concentrations of $10^{18}$ cm$^{-3}$ are ideal. The preserved quantum confinement and nanostructure with submonolayer wave-length grain sizes hold for additional improvements of the Seebeck coefficient and reduction of thermal conductivity.16,17 We would like to emphasize that the procedure presented here does not involve annealing in air or other less controlled oxidation techniques applied previously.6,18 Rather, the carrier concentration is fixed after brief exposure (~3 s) to the ligand exchange solution. When kept under inert conditions, MeO$^-$-capped PbSe QDS exhibit stability of optical and electrical properties for weeks. In contrast with a similar report on ligand exchange with hydrous methanol, we do not observe significant changes in particle size and morphology.15 We attribute this to the relatively acidic conditions imposed by hydrous methanol, which is known to facilitate the fusion of particles via oriented attachment in lead chalcogenide nanostructures.17 In contrast, the method presented here imposes basic conditions and short exposure times, which minimizes the probability of etching and fusion.

Increased Hole Mobility over EDT Capping and Nonmonotonic Size-Dependence. Transport through a QDS is determined by the interplay between electronic coupling and the activation energy for interparticle hopping.19 We consider three explanations for the greater hole mobilities observed for MeO$^-$ capping vs EDT capping: (1) a decrease of the activation energy due to an increase of the effective static dielectric constant of the ligand matrix, (2) an increase of electronic coupling, and (3) a smaller surface trap state density.

The activation energy is the sum of the charging energy $E_c$ and the site disorder $\Delta \alpha$. Kang et al. demonstrated that the room-temperature activation energy of PbSe FETs could be well accounted for through nearest-neighbor hopping models, with six nearest neighbors. These models assume two-dimensional transport, as the injected carriers lie in a plane at the gate oxide interface.19 Under this assumption, the site disorder can be approximated from the full-width half-maximum (fwhm) of the $S_e \rightarrow S_h$ transition as

$$\Delta \alpha = 0.43 \text{ fwhm} / (4\sqrt{2} \times \ln x)$$

and the charging energy can be calculated by applying a modified Laikhtman–Wolf model, which takes into account the mutual capacitance of nearest neighbors and the effective dielectric constant of the total medium.
(nanoparticles, ligands, and voids).\textsuperscript{20–22} The full details of these calculations are given in the SI, and it is interesting to note that we arrive at similar values of the charging energy for both the nearest-neighbor calculations and the Laikhtman–Wolf model.

We find the charging energy to be a stronger function of ligand permittivity than interparticle spacing. Assuming the same static dielectric constant of the ligand ($\varepsilon_1$), we calculate comparable values for the charging energy of EDT- and MeO\textsuperscript{-}capped particles, despite the differences in interparticle spacing (2–3 vs 5 Å).\textsuperscript{19} In contrast, large differences in $E_C$ are observed when changing the static dielectric constant. For a 5.7 nm PbSe particle for instance, $E_C$ decreases from 9.3 meV to 2.1 meV upon changing $\varepsilon_1$ from 2.6 (as in Pb(EDT)\textsubscript{2} capping) to 10. Although $\varepsilon_1$ of Pb(MeO)\textsubscript{2} is unknown, we conclude that one possible explanation for the larger mobilities of PbSe films capped with MeO\textsuperscript{-} vs EDT could be a larger static dielectric constant of the ligand.

We now consider increased electronic coupling as the reason for improved transport. As demonstrated in ref 8, the mobility of PbSe nanoparticle films is well described by the Miller–Abrahams expression such that the tunneling rate depends on $\exp(-\beta d)$, where $d$ is the interparticle spacing and $\beta$ is a constant that depends on the carrier effective mass and the height of the tunneling barrier. Since $\beta$ is on the order of 1 Å\textsuperscript{-1}, a change in $d$ from 5 Å to 2–3 Å invokes a significant increase (7–20 times) in the tunneling rate, and we note that the upper end of this range approximately matches the difference in carrier mobility observed for 6.4 nm diameter particles, where mobilities are at their peak.\textsuperscript{9}

Lastly, efficient surface passivation and small trap state densities in PbSe QDS have been shown to result in drastically improved mobilities.\textsuperscript{23} Since methoxide capping of PbSe leads to a larger carrier concentration than capping with EDT, such an effect is unlikely to be responsible for the increased mobility in the present case. Given the low values of charging energy and the large increase in tunneling probabilities, we attribute the improved transport properties predominantly to increased electronic coupling.

Electronic coupling and the activation energy to transport both decrease monotonically with increasing nanoparticle diameter. This is due to the reduction in particle–particle wave function overlap and a growing self-capacitance, respectively.\textsuperscript{7} In many systems, electronic coupling is so small that changes in activation energy are always the limiting factor, and the size–dependent mobilities follow it monotonically. When both parameters are of comparable magnitude, their competition can result in a nonmonotonic size–dependence of the carrier mobility.\textsuperscript{9} For PbSe, this has first been observed by Liu et al. for electrons in EDT-capped nanoparticles.\textsuperscript{5} However, the corresponding hole mobility was seen to increase monotonically with size.

This has recently been explained with different coupling strengths of electrons and holes under the assumption that holes carry a larger effective mass in EDT than electrons.\textsuperscript{9} The fact that MeO\textsuperscript{-}capped PbSe nanoparticle films exhibit a nonmonotonic size–dependence of the hole mobilities (see Figure 6) highlights our conclusion that electronic coupling is significantly improved over EDT capping, in conjunction with a decrease in the activation energy. There may exist a similar increase in electron mobilities as well; however we were not able to measure these values for the moderately doped and unipolar MeO\textsuperscript{-} transistors. We note that a third factor for the observed size–dependence of the mobilities could be a size–dependent trap state density. For example, small, octahedral lead chalcogenide nanoparticles are typically more stable toward oxidation than larger, more cuboctahedral–shaped particles.\textsuperscript{24} The latter type of particles is more likely to possess a large number of surface states for this reason, which may explain the relatively low mobility of the largest PbSe sample in the present work. However, such a size–dependence is not reflected in the carrier concentrations, which are constant over the whole range of particle samples.

Finally, it is noteworthy that despite the seemingly improved electronic coupling for MeO\textsuperscript{-} vs EDT capping, the size–dependence of the optical red shift is very similar for the two systems (Figure 3a). This provides supporting evidence that there is little correlation between the red shift and the degree of electronic coupling in these materials.

**Correlation between Optical Shift and Field–Effect Mobility.**

The origin of this optical shift has previously been attributed to three components: (1) electronic coupling, (2) polarization effects, and (3) transition dipole–transition dipole coupling.\textsuperscript{5,11,12,25–27}

We stress an important difference in the treatment of the dielectric environment between electric and optical problems: Whereas for electric particle–particle interactions the static dielectric constant, that is, the real part of the dielectric function at low frequencies has to be considered, for optical interactions, it is the complex dielectric function at optical frequencies that is most relevant.\textsuperscript{28}

Calculations have shown that a sizable amount of electronic coupling is necessary to overcome the charging energy inherent to QDS and explain the observed mobilities, but the magnitude varied between 10 meV and 8 µeV for the same system depending on the calculation.\textsuperscript{25,29} Strong polarization effects can result from a mismatch of optical dielectric constants at the interface between nanoparticle and ligand; however previous studies have shown such effects to be significantly smaller than the observed shifts.\textsuperscript{25,29} We also find only small shifts (1–5 meV) when applying such calculations to our data. Finally, transition dipole–transition dipole coupling could possibly explain a red shift of similar magnitude for CdS clusters.\textsuperscript{26,30}
In a similar manner, here we explore a classical coupled dipole—dipole model and find that it explains the majority of the observed shift in the MeO$^-$-capped films (dashed line in Figure 3a). In short, we consider the coupling of transition dipoles embedded within a dielectric surrounding defined by the Maxwell—Garnett effective media approximation. While a complete coupled dipole model uses spectrally dependent optical dielectric constants, the version used here is a simplified model that assumes nondispersive properties of both the nanoparticle and ligand. We check this assumption by utilizing the Kramers–Kronig relations to extract optical permittivities from the solution-phase measurements and find that they remain relatively constant (24 ± 1) over the range of optical wavelengths. Complete details of these calculations are given in the SI. We also note that the negligible red shift of the largest particles is far less than expected. This may point to the inadequacy of the various assumptions within the model, such as a constant optical dielectric value, the permittivity of the ligand, the packing fraction of the spheres, the validity of Maxwell—Garnett effective media theory, or the absence of quantum mechanical treatments.

The complete recovery of the original absorption spectrum of oleate-capped QDs upon (1) exchange with MeO$^-$ and (2) exposure to air for 2 min as displayed in Figure 3b has the following implications:

(a) The optical shift is not caused by partial sintering, necking, or ripening as recently put at question since such effects are unlikely to be reversed on brief exposure to air.$^3$

(b) There is little correlation between the optical shift and the field-effect mobility. As demonstrated in Figure 7, the deterioration of $\mu_H$ upon exposure to air happens on a much longer time scale. Where the optical shift has completely vanished after 2 min of air exposure, the mobility decreases by less than 40% in the same time. Notable changes in $\mu_H$ appear after several hours, but at this point the $S_0 \rightarrow S_h$ transition energy of MeO$^-$ and oleate-capped QDS alike have blue-shifted significantly, which is indicative of the formation of an oxide shell.$^{14}$

Hence, our data support the view that electronic coupling is only weakly reflected in the red shift but almost entirely due to transition dipole coupling or polarization effects.

**Reversal of the Optical Red Shift upon Exposure to Air.** Oxidation of PbSe in air is a multistep process leading to the formation of PbO, Pb(OH)$_2$, and PbSeO$_3$ species.$^4$32 O$_2$ is readily incorporated into the PbSe lattice, resulting in a smaller semiconductor nanoparticle diameter and larger interparticle spacing. This oxidation is rapid in the beginning but slows down considerably as the oxide shell growth proceeds.$^{32,33}$ Water can have a similarly detrimental effect on the structure and chemical nature of PbSe by substitutional incorporation into the lattice and formation of H$_2$Se and Pb(OH)$_2$. For example, Zhang et al. have studied the gradual formation of an amorphous Pb(OH)$_2$ shell onto the surface of PbTe nanoparticles upon exposure to aqueous bases.$^{34}$ Specifically in the case of MeO$^-$-capped nanoparticles, exposure to moisture will lead to the formation of methanol in the ligand sphere. In Figure 8, using the same coupled dipole—dipole model, we consider two different explanations for the rapid reversal of the optical red shift in MeO$^-$-capped PbSe nanoparticles upon exposure to air as displayed in Figure 7: (1) a change in the dielectric environment inflicted by oxidation of the nanoparticle, and (2) a change in nanoparticle diameter due to the oxide shell.

The permittivity of the ligand/void matrix depends upon the permittivities of each of the possible oxidation products and their respective filling fraction. Given the diversity of possible oxidation products, we decided to parametrize the red shift simply in terms of the effective permittivity of the ligand matrix after oxidation. Starting from the permittivity of methanol (~1.8) at optical frequencies, an increase to 9 upon exposure to air would be required to solely explain the red shift reversal. At the same time, we note that increasing quantum confinement and reducing the polarizability volume by the formation of a 0.9 Å thick oxide shell could account for the shift without changing the matrix optical dielectric constant. The realistic
SCHHEEL ET AL. VOL. 7 NO. 8 6774–6781 2013
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anhydrous hexanes/octane. Times on adding anhydrous methanol and one more time with was dissolved in anhydrous toluene. It was washed two more was additionally cooled with an external water bath. While spinning at 2000 rpm, one drop of a filtered hexanes/water, followed by 2-propanol and acetone, blow-dried and were cleaned on using soap scrub and rinsing with distilled to 155 rapidly injected, upon which the solution temperature dropped solution containing the lead precursor was set in an argon phine (DPP) (Aldrich, 98%) was added to the solution. The 2 h. For some particles used in this work, 130 trioctylphosphate (TOP) (Strem Chemicals, >97%) on stirring for (2.2 g) of selenium powder (Aldrich, 99.99%) in 15.0 mL of (1.9 M for the 5.3 nm sample), obtained by dissolving 1.185 g to 155 water, followed by 2-propanol and acetone, blow-dried and hydride concentrations. Description of the dipole ionization methods. Calculation of the ratio between methoxide charging energies calculated by the Laikhtman examination of charging energies calculated by the Laikhtman nearest-neighbor hopping model, (S4) calculation of activation est mobility in methoxide-capped PbSe quantum dots. Figures of (S1) estimation of the size dependence of the static dielectric constant of PbSe, (S2) simulation of charging energies, (S3) compar- on the excitonic shift, and the model predicts the formation of much thicker oxide shells, which would correspond to the significant decline in mobility.

CONCLUSION

We have investigated the correlation between the optical shift of the $S_0 \rightarrow S_n$ transition and the field-effect mobility in methoxide-capped PbSe quantum dot solids. By studying their degradation in air, we find both processes to be weakly correlated, which implies that the actual coupling energy responsible for the observed hole mobilities of up to 0.3 cm$^2$ V$^{-1}$ s$^{-1}$ is much smaller than often assumed. Nonetheless, coupling is found to be competitive with the activation energy to transport, as evident by the nonmonotonic in the size-dependent hole mobilities. On using an effective medium approach, we achieved reasonable agreement between our optical data and the shift predicted due to dipole—dipole interactions upon changing the dielectric environment and interparticle spacing by ligand exchange and oxidation in air.

METHODS

Synthesis of PbSe Nanoparticles. PbSe nanocrystals were synthesized by slightly modifying previously reported procedures. All manipulations were carried out in a dry and oxygen-free envi- ronment. Specific amounts and times for individual particle sizes are reported in Table 1.

Lead(II) oxide (Aldrich, 99.999%) was mixed with oleic acid (Aldrich, 90%) and 1-octadecene (ODE) (Aldrich, 90%) in a three- necked flask with a temperature control center flask, reflux condenser, and septum and heated under vacuum to 100°C for at least 90 min, by which a colorless solution was obtained.

For the synthesis of 3.0 nm nanoparticles, we followed the procedure developed by Ma et al. A solution of 68 μL of bis- trimethylsilyl)selenium (in 3.0 mL of ODE) was used as the selenium precursor. The reaction temperature was 130°C.

For all other particles, we used a 1.0 M TOP-Se solution (1.9 M for the 5.3 nm sample), obtained by dissolving 1.185 g (2.2 g) of selenium powder (Aldrich, 99.99%) in 15.0 mL of trioctylphosphine (TOP) (Strem Chemicals, >97%) on stirring for 2 h. For some particles used in this work, 130 μL of diphenylphos- phine (DPP) (Aldrich, 98%) was added to the solution. The solution containing the lead precursor was set in an argon atmosphere and heated to 180°C. The TOP-Se solution was rapidly injected, upon which the solution temperature dropped to 155–160°C, and the heater was switched off.

For all particles after the desired reaction time had passed, 10 mL of cold hexanes was carefully injected, and the solution was additionally cooled with an external water bath.

The nanocrystals were precipitated by the addition of anhy- drous ethanol, the suspension was centrifuged for 5 min at 4500 rpm, followed by 2-propanol and acetone, blow-dried and plasma-cleaned for 5 min, and mounted onto a spin-coater. While spinning at 2000 rpm, one drop of a filtered hexanes/ octane (9:1) solution of nanoparticles (roughly 10 mg/mL) was drop-cast onto the substrate, followed by 30 μL of a filtered 5 mM solution of tetrabutylammonium hydroxide in methanol, three consecutive drops of methanol to spin-off excess ligand, and, finally, three consecutive drops of hexanes to wash off the olate. This procedure was repeated until a thickness of roughly 50 nm was reached as determined from ellipsometry.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Description of characterization methods. Calculation of the ratio between methoxide and hydroxide concentrations. Description of the dipole—dipole model, calculation of the charging energy, description of the Kramer–Kronig transform, and simulation and Fabry–Perot modes in thin films of 3.0 PbSe quantum dots. Figures of (S1) estimation of the size dependence of the static dielectric constant of PbSe, (S2) simulation of charging energies, (S3) compar- on the excitonic shift, and the model predicts the formation of much thicker oxide shells, which would correspond to the significant decline in mobility.

Acknowledgment. Nanoparticle synthesis and characterization, ligand exchange, sample preparation, and transport measurements were funded by the Self-Assembly of Organic/ Inorganic Nanocomposite Materials program (Grant DE-AC02- 05CH11231 to A.P.A), photoelectron spectroscopy experiments were carried out within the Helios Solar Energy Research Center, and FT-IR spectroscopy was performed as a User Project at the Molecular Foundry, Lawrence Berkeley National Laboratory, all of which are supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. M.S. would like to thank the Alexander von Humboldt Foundation for a Feodor Lynen Fellowship. David K. Brit is acknowledged for providing the 5.3 nm nanoparticle sample and Waqas Khalid for fabricating the FET substrates used in this work.

TABLE 1. Specific Amounts and Times for Individual Particle Size Fractions of PbSe QDs

| particle size/nm | PbO mg | oleic acid mL | ODE mL | TOP-Se mL | reaction time/s | DPP added?
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REFERENCES AND NOTES