The Effects of Inorganic Surface Treatments on Photogenerated Carrier Mobility and Lifetime in PbSe Quantum Dot Thin Films

E. D. Goodwin^{a,†}, Daniel B. Straus^{a,†}, E. Ashley Gaulding^b, Christopher B. Murray^{a,b}, and Cherie R. Kagan^{a,b,c,}*

[†]equal contribution

^aDepartment of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, United States

^bDepartment of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States

^cDepartment of Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States

* Corresponding author: email kagan@seas.upenn.edu

Abstract

We used flash-photolysis, time-resolved microwave conductivity (TRMC) to probe the carrier mobility and lifetime in PbSe quantum dot (QD) thin films treated with solutions of the metal salts of Na₂Se and PbCl₂. The metal salt treatments tuned the Pb:Se stoichiometry and swept the Fermi energy throughout the QD thin film bandgap. A stoichiometric imbalance favoring excess Se heavily p-doped the QD thin film, shifted the Fermi energy toward the valence band, and yielded the highest TRMC mobility and lifetime. Introducing Pb first compensated the p-doping and shifted the Fermi level through mid-gap, decreasing the TRMC mobility. Further Pb addition created an excess of Pb, n-doped the QD thin film, moved the Fermi level to near the conduction band, and again increased the TRMC mobility. The increase in TRMC mobility as the Fermi energy was shifted toward the band edges by non-stoichiometry is consistent with the QD thin film density of states.

Graphical abstract

Keywords

Time-resolved microwave conductivity; quantum dot; doping; spectroscopy; optoelectronic; lead selenide

Introduction

Colloidal semiconductor quantum dots (QDs) are of current interest for their size, shape, and compositionally tunable electronic, optical, and thermal properties[1–4] as well as the simple and low-cost, solution-based methods available to synthesize QDs and assemble QD thin films. For example, QD thin films have been incorporated as the semiconductor active layer in electronic transistors and circuits [5–9]; optoelectronic solar photovoltaics[10–15], photodetectors[16–19], and light-emitting diodes[20,21]; and thermoelectric devices[22]. To design QDs and QD thin films for integration into devices, the electronic structure and the charge carrier dynamics, namely the carrier mobility and lifetime, of the QDs and QD thin films must be tailored.

The physical and electronic structure of colloidal QD thin films differ from those of bulk semiconductors, presenting both challenges and opportunities. Wet-chemical synthetic methods are typically used to prepare colloidal QDs capped with long, insulating, organic ligands. Solvents are used to isolate the QDs from the growth medium and to assemble thin films of closely-packed QDs separated by these long ligands. To reduce the interparticle spacing and design QD materials for electronic applications, the insulating ligands are replaced with short organic ligands, such as 3-mercaptopropionic acid (MPA)[23,24], or compact inorganic ligands, such as chalcogenides[25], halides[13], or the pseudohalide thiocyanate[26]. The solvents used in post-synthesis purification and in thin film deposition and the ligand exchange process can strip surface atoms[27–29], creating vacancies at the QD surface. Unlike bulk semiconductors with well-defined conduction and valence bands separated by a forbidden energy gap, the density of electronic states for QD thin films is constructed from a high density of quantized conduction and valence band states (or LUMO and HOMO) and localized mid-gap and tail states introduced by vacancies at the QD surface and by interfacial states introduced in electronic devices used to probe carrier transport. These mid-gap electronic states are undesirable and act as traps which inhibit charge carrier transport[5] and limit carrier lifetime[15]. Infilling the QD thin film with an inorganic matrix by atomic layer deposition has been shown to passivate the QD surface and increase the carrier mobility and lifetime[30,31]. Recent introduction of surface chemical modifications have been reported to enrich the QD surface in metal and/or chalcogen or halide ions[27,32–36] that serve to dope the QD thin films and passivate surface traps, controlling the charge carrier type, concentration, mobility, and lifetime. For example, PbSe QD thin films surface-enriched with Se were doped p-type, but the surfaces were unstable and susceptible to oxidation and structural transformation. Subsequent Pb enrichment of the QD surface passivated the unstable Se surface and n-doped the QD films[37]. Similar structural transformations in PbS QD thin films have been reported for S-enriched surfaces [38] or through solvent stripping of surface ligands and atoms[39,40]. Surface passivation has been shown to increase the lifetime of photogenerated carriers[27,41] and doping shifts the Fermi level closer to the conduction or valence band, allowing carriers to populate these higher densities of states, and leads to the higher carrier mobilities reported in field-effect transistor (FET) measurements[5,37].

PbSe QDs are particularly attractive as solar cell materials because of their broad absorption that spans the solar spectrum and the promise of increased power conversion efficiencies through multiple-exciton generation[42,43]. However, the photogenerated charge carrier lifetime is equally as important as mobility to device performance[44]. Flash-photolysis time-resolved microwave conductivity (TRMC) is a technique by which the lifetime and mobility of photogenerated charge carriers can be measured independently of each other and it has been used previously to study the optoelectronic properties of QD thin films[45,46]. Unlike more traditional methods used to determine carrier mobilities, such as FET and time-of-flight (TOF) photoconductivity measurements, TRMC is a contactless measurement. TRMC is therefore not influenced by the properties of metal-semiconductor junctions which may introduce Fermi level pinning, electron-hole recombination, and contact resistance, which have been shown to affect the measured charge carrier dynamics in QD thin films[10,47]. TRMC also differs from these traditional methods because it measures conductivity at zero DC electric field, without a gate field which is applied in FET measurements, and probes a length scale of tens to hundreds of nanometers, so larger scale features like grain boundaries and cracks found across the channel length of FETs or through thick layers needed for TOF measurements have little effect on the results.[48]

In this work, we studied the influences of commonly and recently introduced small-organic and compact, inorganic ligand exchange treatments on the photogenerated charge carrier mobility and lifetime of PbSe QD thin films by TRMC. Electron microscopy, optical absorption, and FET measurements were used to characterize the structural, optical, and electronic properties of the QD films for each ligand treatment. We show that the photogenerated charge carrier mobility depended on the position of the Fermi energy in the semiconductor bandgap and was largest near the band edges, consistent with the trend in FET measurements and with the QD thin film density of states.

Experimental Methods

Synthesis

6 nm PbSe QDs with a first absorption peak at ~1725 nm were synthesized using a previously published method[49] modified to increase yield[50]. In short, 1.78 g of PbO (99.999%), 40 mL of 1-octadecene (90%), and 6 mL of oleic acid (OA) (90%) were heated in a 125 mL 3 neck flask under vacuum on a Schlenk line for 1.5 h to form a lead oleate complex. The flask was then switched to nitrogen and the solution heated to 180 °C. At 180 °C, a solution of 16 mL of 1 M Se (99.999%) in tri-n-octylphosphine (90%) (previously prepared) and 138 µL of diphenylphosphine (98%) (added just beforehand) were rapidly injected into the lead oleate solution. The temperature was then dropped to ~150 °C, held at this temperature for 10 min, and removed from heat to cool. Once cooled to room temperature, the solution was transferred into a Schlenk tube using a cannula and brought into a nitrogen glovebox for purification. The solution was purified by 3 repeated steps of precipitating the QDs with a 2:1 anhydrous butanol:ethanol mixture, centrifugation, and redispersion in anhydrous toluene. The QDs were redispersed in 20 mL of anhydrous hexane for storage. The anhydrous solvents and reagents used in synthesis were all purchased from Sigma-Aldrich.

Before depositing thin films from the QD dispersions, the particles were precipitated with anhydrous isopropanol (Acros) in a 1:3 ratio and centrifuged. The supernatant was discarded and the remaining solvent was evaporated. The QDs were re-dispersed at 10 mg/mL in anhydrous octane (Sigma-Aldrich).

PbSe QD Thin Film Deposition

PbSe QD thin film deposition for optical characterization and FET and TRMC measurements was carried out in a nitrogen-filled glovebox and followed the procedure of Oh *et al*[37]. QD thin films for FETs were assembled on n++ silicon wafers (Silicon Inc.) with a 250 nm thermal oxide layer. 20 nm of Al₂O₃ was deposited by atomic layer deposition (ALD). The oxidized wafers were then cleaned by sonication in ethanol for 5 min and then UV-ozone treated in the nitrogen glovebox for 20-30 min. QD thin films for optical characterization and TRMC measurements were assembled on aluminosilicate float glass (Delta Technologies) that were cleaned by sonication in Hellmanex detergent in water, de-ionized water (3x), 0.1-1.0 M HCl (Fisher), de-ionized water (3x), and ethanol (3x). The aluminosilicate glass surface was coated with a (3-mercaptopropyl)-trimethoxysilane (MPTS, Sigma-Aldrich, 95%) self-assembled monolayer according to modified literature procedures[51]. The MPTS layer prevented

delamination of the QDs during subsequent surface treatment[52]. The PbSe QDs dispersed in octane were spin-cast in the nitrogen glovebox at 800 rpm for 20 s followed by 4000 rpm for 5 s.

We exchanged the long oleic acid ligands used to synthesize and disperse the PbSe QDs for short organic and compact inorganic ligands, namely by treatment with 3-mercaptopropionic acid (MPA), Na₂Se, and Na₂Se followed by PbCl₂. For MPA treatment, a 1% MPA (Sigma-Aldrich, 99%) solution in anhydrous methanol (Acros) was deposited on the QD film on the spinner, held for 3 s, dried by spinning at 4000 rpm, and rinsed twice with methanol. For Na₂Se treatment, a 1 mM Na₂Se (Alfa Aesar, 99.8%) solution in methanol was deposited on the QD film on the spinner, held for 10 s, dried by spinning at 4000 rpm, and rinsed twice with methanol. The sequence of QD spin-casting and ligand exchange was carried out an additional two times to form uniform, crack-free QD thin films approximately 50 nm in thickness. The thickness was measured using an atomic force microscope (Asylum). For subsequent PbCl₂ treatment, the three-layer, Na₂Se-treated QD thin films were immersed in 15 mM PbCl₂ (Sigma-Aldrich, 99.999%) in oleylamine on a hotplate at 80 °C for either 1 min, 15 min, 1 h, or 24 h. The QD films were then washed with anhydrous hexane to remove excess oleylamine, and then washed three times with anhydrous isopropanol.

Structural, Optical, and Electrical Characterization

Thinner PbSe QD thin films for TEM characterization were prepared as described above, but by diluting the QD dispersion in octane to ~1 mg/mL and by depositing only a single layer. TEM was performed on a JEOL 2100 microscope operating at 200 keV.

Fourier-transform infrared (FTIR) spectra were taken on a Thermo-Fisher Nicolet 6700 spectrophotometer in transmission mode. The FTIR absorption spectra were normalized using the height of the first excitonic peak from the near-infrared (NIR) absorption spectra of the same QD films. NIR spectra were taken on an Agilent Cary 5000 spectrophotometer at 2 nm spectral bandwidth in transmission mode. NIR measurements reported herein were taken on QD thin films that were encapsulated in the nitrogen glovebox using cover glass and epoxy [27].

Cr (20 nm) and Au (30 nm) top contacts were deposited by thermal evaporation through a shadow mask onto the PbSe QD thin films deposited on Si wafers to make top-contact, bottom-gate FETs. Channel lengths (L) ranged from 50-200 μ m and channel widths (W) ranged from

750-3000 μm with a constant W/L of 15 for all channels. FET measurements were performed in a Karl Suss PM5 probestation mounted in a nitrogen glovebox and measured on an Agilent (now Keysight) 4156C semiconductor parameter analyzer.

Flash-photolysis time-resolved microwave conductivity

Flash-photolysis, time-resolved microwave conductivity (TRMC) measurements were used to perform contactless carrier mobility and lifetime measurements[53–56]. A schematic of the instrument is shown in Figure 3a. X-band (~ 9 GHz) microwaves were generated using a voltage-controlled oscillator (SiversIMA). The output microwave frequency was tuned by voltage from a Keithley 2220-30-1 power supply. Microwaves were passed through an isolator (Pasternack) to prevent back reflection and then through a variable attenuator set to 10 dB (Keysight). A circulator (Pasternack) directed microwaves from the source into a microwave antenna (Penn Engineering), transferring microwaves from coax to a WR90 waveguide connected to a home-built, sealed, resonant microwave cavity [Supporting Information Figure S1]. The resonant microwave cavity was loaded with each sample in the nitrogen-filled glovebox to prevent sample oxidation. 3-5 ns, 532 nm laser pulses were generated by a Continuum MiniLite II Nd:YAG laser and focused through an aperture sealed with aluminosilicate glass into the resonant cavity, expanding to a 7 mm spot diameter at the sample. The circulator directed reflected microwaves into a microwave switch that allowed us to visualize the resonance peak on an HP 8566B spectrum analyzer, or to convert microwave power to voltage on a Keysight 8472B microwave detector. Detected microwave power was amplified through an impedance-matching 25x amplifier (Comlinear CLC-221) and microwave transients were digitized using a Tektronix TDS3054B oscilloscope. To measure the incident microwave power on resonance in the absence of light, the voltage from the microwave detector was recorded on the oscilloscope, and to measure photoinduced microwave transients, a high pass filter with a cutoff frequency of 0.16 Hz was used to cancel the DC offset.

The theory of time-resolved microwave conductivity has been presented in great detail in several places[54,57]. It is briefly summarized here. The loaded microwave resonant cavity was characterized by the resonance peak [Supporting Information Figure S2], which was measured by sweeping microwaves around the resonant frequency of the loaded, sample-containing cavity.

The resonance curve was normalized by dividing by the reflected power off of resonance (with no microwaves entering the cell), and the resonance peak was fit to the equation

$$R(f) = \frac{R_0 + \left(\frac{2(f-f_0)}{\Delta W}\right)^2}{1 + \left(\frac{2(f-f_0)}{\Delta W}\right)^2} + (mf + b) \quad (1)$$

where f_0 was the resonant frequency (in Hz), ΔW was the full width at half-maximum of the resonance peak, and R_0 was the depth of the normalized peak. The Lorentzian term modeled the microwave resonance peak and the linear term corrected for frequency dependent power variations in the microwave source. The quality factor of the sample-containing cavity was $Q = \frac{f_0}{\Delta W}$, and cavity's response time was $\tau_m = \frac{Q}{\pi f_0}$. Q ranged from 387 to 752 and the response time ranged from 14 to 27 ns.

Pulsed photoexcitation of the sample in the resonant cavity caused a change in the reflected microwave power ΔP . The normalized change in microwave power $\frac{\Delta P}{P_0} = K\Delta G$ where K was the sensitivity factor, G was the conductance, and P_0 was the reflected microwave power in the absence of light. Because a Schottky diode was used to detect microwave power, it needed to be calibrated to ensure the output voltage (V) accurately measured the reflected microwave power, using the equation $P = V^n$ with P being the reflected microwave power. In this experiment, n was 1.42. Because the photoinduced change in voltage produced by the Schottky diode, ΔV , was small compared to V , then $\frac{\Delta P}{P_0} = n \frac{\Delta V}{V_0}$. The sensitivity factor for the microwave cell used in this experiment was

$$K = \frac{Q\left(1 + \frac{1}{\sqrt{R_0}}\right)}{\pi f_0 \epsilon_0 \epsilon_r L \frac{a}{b}} \quad (2)$$

where ϵ_r was the permittivity of the PbSe QD thin film at the resonance frequency, a was the width (0.9 in) and b was the height (0.4 in) of the WR90 waveguide, and L was the length of the resonant cell (9.136 cm). The ϵ_r used in this work was calculated to be 24 by the generalized Penn approximation[10,58,59] and the effective medium approximation[37,60].

The change in conductance

$$\Delta G = \left(\frac{\Delta P}{P_0} \right) \left(\frac{F_I}{K} \right) \quad (3)$$

where F_I was a correction for illuminating only a 7 mm diameter area of the sample, taking into account the electric field cross-section in the microwave cavity[61]. In this work, F_I was 3.19.

The quantum yield-mobility product was

$$\phi \Sigma \mu = \phi(\mu_e + \mu_h) = \frac{\Delta G_{max}}{\frac{a}{b} q I_0 F_A} \quad (4)$$

where q was the fundamental charge, I_0 was the photon flux, and F_A was the fraction of absorbed light (measured at 532 nm using a Thorlabs integrating sphere).

The selection of a resonant cavity significantly increased the measurable signal at the expense of an increased instrumental response time[54]. However, because the cavity response time was determined from the resonance peak, the true mobility was calculated by deconvolving the cavity response time from the measured signal [Supporting Information Figure S3][62].

Results and Discussion

We deposited thin films of 6 nm diameter oleic acid (OA)-capped PbSe QDs by spin-coating and by subsequently treating the QD thin films in solutions of MPA, Na₂Se, and Na₂Se followed by PbCl₂. The MPA ligand was chosen for comparison because it is commonly used in lead chalcogenide QD solar cells[24,63]. Na₂Se and PbCl₂ treatments were chosen because they have been shown to dope PbSe QD thin films p- or n-type, respectively[37]. TEM, FTIR and NIR spectroscopy, and FET measurements were used to structurally, chemically and electronically characterize the thin films studied here.

Structural and Optical Characterization of PbSe QD Thin Films

To characterize the interparticle spacing and nanoscale structure, TEM images were taken of OA-capped and MPA, Na₂Se, and Na₂Se and then 1 h PbCl₂-treated PbSe QD thin films (Figure 1a-d). A decrease in interparticle spacing was observed upon ligand treatment, as desired to transform the QD films into electronically active materials. QD thin films treated with MPA (Figure 1b) retained their single particle character and partially transformed from hexagonal to square packing, as reported previously[47]. In contrast, QD films treated with Na₂Se, showed the

onset of epitaxial, oriented attachment of QDs, as has also been previously reported[37]. We note that the degree of oriented attachment increased over time, even as the QD film remained at room temperature in the nitrogen-filled glovebox, representative of the TEM image shown in Figure 1c. QD thin films treated with Na₂Se and then immediately with PbCl₂ (Figure 1d), as exemplified for a 1 h treatment, displayed a small interparticle spacing, without significant epitaxial, oriented attachment, as the Pb and Cl ions passivated surface Se sites and arrested QD fusion[37]. We also note that the added surface Pb sites were passivated by oleylamine and/or Cl atoms during the PbCl₂ treatment, further protecting the QDs from fusion and oxidation.

FTIR measurements were performed on the OA and ligand treated PbSe QD thin films to characterize the removal of the organic capping layer as shown in Figure 1e, highlighting the C-H stretching region. The FTIR absorption spectrum of an OA-capped PbSe QD thin film is included in the inset of Figure 1e. The FTIR spectra before and after ligand treatment showed 86-93% removal of OA ligands by all treatments, as expected and reported previously[24,37], and consistent with the observed decrease in interparticle spacing presented above in TEM images.

Figure 1. (a-d) TEM images and normalized (e) FTIR and (f) NIR absorption spectra of (a) an OA-capped PbSe QD thin film (black) and of PbSe QD thin films treated with (b) MPA (orange), (c) Na₂Se (red), and Na₂Se immediately followed by PbCl₂ for 1 min (green), 15 min (cyan), 1 h (blue), and 24 h (pink). The PbSe QD film shown in (d) was treated for 1 h in PbCl₂ immediately after Na₂Se treatment. Scale bars are 6 nm. (e) Inset: FTIR spectra highlighting the OA-capped PbSe QD thin film (black). Fourier-transform filtering was applied to the NIR absorption spectra to remove the interference pattern

NIR absorption measurements were performed on OA-capped and ligand treated PbSe QD thin films, as shown in Figure 1f. The QD films were allowed to sit for 6 h in the nitrogen atmosphere of the glovebox before measurement to more closely reflect the films measured in TEM above and described below in FET and TRMC measurements. OA-capped PbSe QD thin films displayed a first exciton peak at 1728 nm. The absorption spectrum of Na₂Se-treated QD films showed a 31 meV red shift, caused by QD fusion during the 6 h wait time and the addition of a Se layer to the QD surface. Spectra of QD films treated with PbCl₂ for 1 min, 15 min, 1 h, or 24 h immediately after Na₂Se treatment showed red shifts of 26-29 meV. We note the longer PbCl₂ treatment times were observed to result in a smaller red shift in the QD film absorption resonance, as the PbCl₂ treatment arrested QD fusion caused by the unstable, Se rich surfaces, consistent with the TEM images. The absorption spectrum of PbSe QD thin films treated with MPA showed a red shift of 23 meV compared to that for OA-capped QD films, consistent with the reduced interparticle spacing, noting little to no QD fusion was observed and no ionic layer was added in the MPA treatment.

Electrical Transport Measurements in PbSe QD Field-Effect Transistors

Figure 2. (a) Diagram of a bottom-gate, top-contact FET fabricated from PbSe QD thin films. (b) Transfer curves of PbSe QD thin films treated with MPA (orange), Na₂Se (red), and Na₂Se followed by PbCl₂ for 1 min (green), 15 min (cyan), 1 h (blue), and 24 h (pink). $V_{DS} = -50$ V for QD thin films treated with Na₂Se and Na₂Se followed by PbCl₂ for 1 min and 15 min. $V_{DS} = +50$ V for QD thin films treated with MPA and Na₂Se followed by PbCl₂ for 1 h and 24 h.

To confirm the charge carrier type and relative carrier concentration of ligand treated PbSe QD thin films, thin films were integrated into FETs to form the semiconducting channel layer [Figure 2a]. Transfer curves of the devices are shown in Figure 2b. Na₂Se-treated QD films became degenerately, p-doped by the introduction of excess Se, consistent with the Fermi level shifting towards the valence band. Successive PbCl₂ treatment after Na₂Se treatment added Pb ions to the QD surface, shifted the stoichiometric imbalance towards excess Pb, and moved the Fermi level towards the conduction band. Pb addition first compensated the Se p-doping at short 1 min and 15 min treatment times and then increasingly n-doped the devices with longer 1 h and 24 h treatment times. In contrast, MPA-treated PbSe QD thin films were highly resistive and showed ambipolar, predominantly n-type transport. These FET characteristics reproduced reports of similarly treated PbSe QD thin films[37,47].

Flash-Photolysis, Time-Resolved Microwave Conductivity

To characterize the photogenerated charge carrier mobility and lifetime, the treated QD films were probed in a home-built, flash-photolysis, time-resolved microwave conductivity (TRMC) measurement apparatus [Figure 3a]. Example photoconductance (ΔG) transients of the

Figure 3. (a) Diagram of the home-built, TRMC setup showing the VCO: voltage controlled oscillator (microwave source), I: isolator, At: 10dB attenuator, C: microwave circulator, microwave switch, spectrum analyzer, D: microwave power detector, A: amplifier, HP: high pass filter, S: oscilloscope, and computer. Also shown is the laser (532 nm) and optics for controlling and delivering the light to the sample. WP: rotating half wave plate, P: polarizer, BD: beam dump, FS: UV-fused silica window, and P M: power meter. (b) Example photoconductance transients of PbSe QD thin films treated with Na₂Se (red) and Na₂Se followed by PbCl₂ for 1 min (green), 15 min (cyan), 1 h (blue), and 24 h (pink). Inset: Photoconductance transient of MPA (orange) treated PbSe QD thin film. Dashed lines show fits (see text for details).

treated QD films are shown in Figure 3b for the largest excitation intensity, as this data showed the best signal-to-noise ratio. The Na₂Se-treated QD film showed the largest ΔG , noting the sample was allowed to fuse in the nitrogen atmosphere of the glovebox prior to measurement. The impact of QD fusion on the TRMC measurements will be discussed below. As Pb was added by successive PbCl₂ treatments for times of 1 min and 15 min, ΔG decreased. For longer 1 h and 24 h PbCl₂ treatment times, an increase in ΔG was observed. MPA-treated QD thin films displayed the smallest ΔG and is highlighted in the inset of Figure 3b.

Figure 4a shows the product of the quantum yield for charge generation and the sum of the electron and hole mobilities, $\Phi\Sigma\mu$, for the treated PbSe QD thin films as measured by TRMC. Since the quantum yield for carrier generation has a maximum value of unity, the data presents a lower bound for charge carrier mobility, in convention with previous reports[46,64]. We note and will discuss below that as shown in Supporting Information Figure S4, $\Phi\Sigma\mu$ does not saturate even at the lowest photoexcitation density used in this work (~ 0.5 photoexcitations/QD), consistent with a quantum yield that is less than unity and with true carrier mobilities that are greater than what is reported here. The decrease in $\Phi\Sigma\mu$ with increasing photoexcitation density is consistent with higher order recombination that occurred on timescales faster than the 14-27 ns

Figure 4. (a) $\Phi\Sigma\mu$ product at the lowest photoexcitation density in PbSe QD thin films treated with MPA (orange), Na₂Se (red), Na₂Se followed by PbCl₂ for 1 min (green), 15 min (cyan), 1 h (blue), and 24 h (pink). (b) Photogenerated charge carrier lifetimes from nonlinear least-squares fits of the photoconductance transient data to: the sum of three exponential decay functions for MPA, Na₂Se, and Na₂Se followed by 1 min PbCl₂-treated (black, red, and blue showing lifetimes on the order of 100 ns, 1 μ s, and 10 μ s, respectively) and single exponential decay functions for Na₂Se followed by 15 min, 1 h and 24 h PbCl₂-treated PbSe QD thin films. Error bars are one standard deviation.

response time of the microwave resonance cavity[45,46], as discussed in further detail below.

Table 1 reports the maximum $\Phi\Sigma\mu$ for the differently treated PbSe QD thin films, calculated at the lowest photoexcitation density. MPA-treated QD films exhibited the lowest mobility of the QD films presented in this work, with a mobility similar to another report of TRMC mobility on compact organic ligand treated PbSe QD thin films[45] and consistent with the greater interparticle spacing and the lack of intentional doping. Ligand exchange with the inorganic Na_2Se salt increased the carrier mobility, consistent with the observed QD fusion and heavy p-doping introduced by excess Se. As the Se-rich QD thin films were treated with PbCl_2 , a lower mobility was observed after 1 min and further after 15 min. PbCl_2 treatment arrested QD fusion and the addition of surface Pb compensated the p-doping, shifting the Fermi level from the valence band toward mid-gap. Further PbCl_2 treatment for 1 h n-doped the QD thin films and increased the carrier mobility. No further increase in mobility was seen upon longer PbCl_2 treatment times of 24 h. As greater amounts of Pb^{2+} was added to the surface, the Fermi level

Ligand Treatment	$\Phi\Sigma\mu$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	f_1	τ_1 (ns)	f_2	τ_2 (μs)	f_3	τ_3 (μs)
MPA	0.14 ± 0.02	0.54 ± 0.03	365 ± 86	0.22 ± 0.02	4.1 ± 1.7	0.23 ± 0.01	38.5 ± 6.4
Na_2Se	2.57 ± 0.23	0.674 ± 0.005	252 ± 2	0.137 ± 0.003	2.76 ± 0.07	0.190 ± 0.003	26.68 ± 0.03
$\text{Na}_2\text{Se} + \text{PbCl}_2$ 1 min	1.29 ± 0.14	$0.908 \pm .004$	97 ± 3	0.061 ± 0.003	1.50 ± 0.06	0.030 ± 0.001	19.1 ± 1.1
$\text{Na}_2\text{Se} + \text{PbCl}_2$ 15 min	0.092 ± 0.011	--	66 ± 8	--	--	--	--
$\text{Na}_2\text{Se} + \text{PbCl}_2$ 1 h	0.544 ± 0.026	--	50 ± 1	--	--	--	--
$\text{Na}_2\text{Se} + \text{PbCl}_2$ 24 h	0.547 ± 0.057	--	47 ± 3	--	--	--	--

Table 1. Summary of the Quantum Yield-Mobility Products ($\Phi\Sigma\mu$) and the Carrier Lifetimes (τ) Extracted from TRMC Transients of Ligand Exchanged PbSe QD Thin Films. $\Phi\Sigma\mu$ shown was calculated at the lowest photoexcitation density.

was swept through the QD thin film density of states, from the valence band, through mid-gap, toward the conduction band.

Figure 5. Photogenerated charge carrier lifetimes from nonlinear least-squares fits of photoconductance transient data to the sum of three exponential decay functions for Na_2Se (red), and Na_2Se followed by 1 min PbCl_2 (green) treatments and to a single exponential decay function for Na_2Se followed by PbCl_2 treatment for 15 min (cyan), 1 h (blue) and 24 h (pink) of PbSe QD thin films. Lifetimes on the order of 100 ns are shown in (a), 1 μs in (b), and 10 μs in (c). Error bars are one standard deviation.

treated films were consistent with reported spectroscopic measurements of carrier lifetime in PbSe QD thin films. A TRMC study by Gao *et al.*[45] reported a half-amplitude lifetime of tens of nanoseconds for 6 nm ethanedithiol (EDT) treated PbSe QD thin films with a long-lived component in the transient that extended to μs [45]. Transient absorption measurements of MPA-

The ΔG transients in Figure 3b show that the lifetimes for MPA, Na_2Se , and Na_2Se followed by 1 min PbCl_2 -treated QD films persisted for tens of μs through multi-exponential decay processes and the transients were fit to a sum of three exponential decays. The QD films treated with PbCl_2 for 15 min, 1 h, and 24 h showed ΔG transients that decayed by a single exponential process on faster hundreds of ns timescales and were fit to a single exponential decay. Figure 4b and Table 1 summarize the charge carrier lifetimes extracted from the TRMC data shown in Figure 3b. The normalized fit amplitudes f_i corresponding to the lifetimes τ_i in Table 1 show the decrease in f_2 and f_3 in the Na_2Se followed by 1 min PbCl_2 treated films in comparison to the Na_2Se treated films, showing the progression from multi-exponential to single exponential decay processes.

The long tens of μs lifetimes in MPA, Na_2Se , and Na_2Se followed by 1 min PbCl_2 -

treated PbS QD thin films reported carrier lifetimes of 31 μs and even longer 93 μs lifetimes for EDT treated particles [24].

Figure 5 shows the dependence of carrier lifetime on photoexcitation density. For Na_2Se -treated QD films the lifetime increased at larger photoexcitation densities for all calculated lifetimes. We hypothesize that this increase in lifetime arose from greater trap filling at larger photoexcitation densities and therefore the charge carrier decay in the Na_2Se -treated PbSe QD films was dominated by trap-assisted recombination on the timescales probed by TRMC. No change in lifetime was observed for the 1 min PbCl_2 -treated QD films with increasing photoexcitation density. In contrast, the lifetime for Na_2Se followed by 15 min, 1 h, and 24 h PbCl_2 treatments of the QD films decreased with increasing photoexcitation density. This decrease suggests that the charge carrier decays were largely dominated by bimolecular or higher-order recombination processes such as Auger recombination, and lifetimes were reported for excitation densities greater than a few per quantum dot to study the influence of these processes on lifetime. In addition, the photoinduced change in conductivity $\Delta\sigma = q(\mu_e + \mu_h)\Delta N$, assuming unimolecular charge carrier kinetics, should scale linearly with the number of photoexcitations/QD. $\Phi\Sigma\mu$, however, decreased with increasing photoexcitation density [Supporting Information Figure S4], consistent with higher order recombination processes that reduce the quantum yield for charges measured in TRMC [65–67]. The lifetimes for MPA-treated QD films did not show a clear trend with increasing photoexcitation density because of the large error in the low signal-to-noise data of these highly resistive thin films [Supporting Information Figure S5].

We note that the TRMC signals were convolved with the 3-5 ns laser pulse width, the nanosecond response of the electronic circuitry, and the cavity response time of 14 to 27 ns [Supporting Information Figure S3]. We deconvolved the cavity response time from the measured signal because it had the largest impact. Dynamics occurring on timescales shorter than several nanoseconds cannot be detected using the TRMC apparatus. The low TRMC mobilities measured for Na_2Se followed by 1 h and 24 h PbCl_2 -treated QD films may be limited by charge trapping or decay within the TRMC instrument response time. Notably, the TRMC mobilities are smaller than the $25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ mobilities reported for Na_2S exchanged PbSe QD thin films studied by time-resolved terahertz spectroscopy (TRTS)[68]. The same study also

reported carrier lifetimes for Na₂S exchanged PbSe QD thin films of ~1 ns or less, much shorter than the 200-27,000 ns lifetimes we report here for Na₂Se exchanged PbSe QD thin films. TRTS offers a complementary technique that detects mobility and lifetime on a picosecond timescale; however, it does not reach the several nano- to- microsecond timescale that are probed in TRMC measurements. We attribute the discrepancy in lifetimes to the fact that the two measurements probe different carrier dynamics occurring on different timescales. We note that the timescales measured in TRMC are of particular interest to photovoltaic applications as it is on those timescales that charge transport and collection occurs[24].

The degree of epitaxial, oriented attachment between PbSe QDs in thin films affected the red shift observed in NIR absorption measurements [Supporting Information Figure S6] and the measured TRMC carrier mobility [Supporting Information Figure S7], regardless of whether the QD thin film was enriched in Se or Pb. For example, PbSe QD thin films treated with Na₂Se and measured within 30 minutes of fabrication showed a TRMC mobility of 1.17 cm² V⁻¹ s⁻¹. However, films stored in a nitrogen glovebox and measured 2-6 h after fabrication had a mobility of 2.57 cm² V⁻¹ s⁻¹ that was consistent over this storage time. To see how fusion would affect the mobility of subsequently PbCl₂-treated films, Na₂Se-treated PbSe QD thin films were left to sit for 24 h in the nitrogen glovebox to allow for epitaxially oriented attachment prior to a 1 h PbCl₂ treatment. These films showed an increase in TRMC mobility to 0.69 cm² V⁻¹ s⁻¹ compared to 0.54 cm² V⁻¹ s⁻¹ for films that were immediately treated with PbCl₂ for 1 h after Na₂Se treatment.

Conclusion

We used TRMC measurements to study the evolution in carrier dynamics in PbSe QD thin films as we enriched the QD surface in Se and Pb through treatments with inorganic Na₂Se and PbCl₂ salts and swept the Fermi energy through the QD thin film density of states. Se-rich films were highly p-doped and demonstrated high carrier mobility and long lifetime. As increasing amounts of Pb were added to the surface of the QDs, the mobility first decreased as the Fermi level moved near mid-gap, and then increased again as QD films were n-doped and the Fermi level approached the conduction band. Future experiments will explore the origin of the recombination processes leading to the long lifetimes seen for Se-enriched in comparison to the shorter lifetimes of Pb-enriched QD thin films.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5