High Carrier Mobility in Single Ultrathin Colloidal Lead Selenide Nanowire Field Effect Transistors

Rion Graham and Dong Yu*

Department of Physics, University of California, Davis, California 95616, United States

ABSTRACT: Ultrathin colloidal lead selenide (PbSe) nanowires with continuous charge transport channels and tunable bandgap provide potential building blocks for solar cells and photodetectors. Here, we demonstrate a room-temperature hole mobility as high as 490 cm²/(V s) in field effect transistors incorporating single colloidal PbSe nanowires with diameters of 6–15 nm, coated with ammonium thiocyanate and a thin SiO₂ layer. A long carrier diffusion length of 4.5 μm is obtained from scanning photocurrent microscopy (SPCM). The mobility is increased further at lower temperature, reaching 740 cm²/(V s) at 139 K.

KEYWORDS: Colloidal, nanowires, mobility, field effect transistors, scanning photocurrent microscopy, carrier diffusion length

Colloidal semiconductor quantum dots (QDs) have great potential for solar energy and photodetector applications.¹ QDs of various sizes, shapes, and chemical compositions can be synthesized inexpensively in large quantities²,³ and are readily dispersed in solution, enabling photovoltaic cell production through roll-by-roll technology, similar to a printing press for newspaper. One major challenge hindering these applications is the poor electric conductivity of the QD films in which charge needs to inefficiently hop between QDs.⁴,⁵ Compared to QDs, colloidal nanorods (NRs) and nanowires (NWs) provide more efficient charge transport channels. Ultrathin colloidal NWs have been synthesized⁶ and exhibit strong quantum confinement effects, just like QDs.⁷⁻⁹ Recently, Alivisatos et al. have demonstrated device-scale perpendicular alignment of colloidal NRs for solar cells.¹⁰ Despite their promising potential, much less work¹¹⁻¹³ has been done to understand the electronic structure and charge transport in colloidal NWs compared to QDs. As a result, their superior conductivity has not yet been demonstrated. The carrier mobilities in colloidal PbSe NWs have been measured in ensemble devices previously to be ~10 cm²/(V s),¹³ which is lower than the recently reported 27 cm²/(V s) mobility in a CdSe QD thin film with short ligands.¹⁴ However, ensemble measurements only provide a lower boundary of the actual mobility due to contact barrier limitations and the fact that not all NWs bridge the electrodes in a device.¹³ By characterizing single NW devices, one can greatly reduce these uncertainties associated with ensemble devices. Single colloidal PbSe NWs have been fabricated by directly growing NWs between electrodes, but a low mobility is extracted, likely due to imperfect contacts and/or poor surface passivation.¹² A much higher mobility of 180 cm²/(V s) has been demonstrated in colloidal PbSe NWs, but with a large diameter of 80 nm.¹⁵ It is not clear if NWs with smaller diameters will maintain a high mobility as surface scattering may substantially reduce the mobility in ultrathin NWs.¹⁶ In addition, the ultrathin channel may be completely depleted, leading to conduction dominated by a space charge limited current.¹⁷ A comprehensive understanding of charge transport in ultrathin colloidal NWs requires an experimental investigation of single NW devices. Nevertheless, detailed experimental results have rarely been reported, partially because of the sensitivity of the colloidal NWs to the harsh fabrication procedure and ambient environment.

Here, we demonstrate a hole mobility as high as 490 cm²/(V s) in single ultrathin colloidal PbSe NW field effect transistors (FETs) measured at room temperature and in air. To passivate the NW surface, we coat the colloidal NWs with a thin layer of SiO₂, which also protects the NWs from being damaged by the lithographic procedures. Devices incorporating single as-grown NWs coated with SiO₂ exhibit an average mobility of 30 cm²/(V s). Furthermore, the postgrowth ligand replacement by ammonium thiocyanate (NH₄SCN) results in better surface passivation and leads to a factor of 10 improvement in conductivity and a high mobility of 490 cm²/(V s). Scanning photocurrent microscopy (SPCM) also supports this enhancement with an increase in carrier diffusion length from 2.5 to 4.5 μm after ligand exchange. The carrier mobility increases at lower temperature, reaching up to 740 cm²/(V s) at 139 K.

PbSe NWs are synthesized following the colloidal method of Murray et al.,¹⁸ isolated through high speed centrifugation (17 000 g), dried under vacuum, and stored in a nitrogen glovebox. Selected area electron diffraction (SAED) shows that the NWs are single crystalline and grow along the (100) direction (Figure 1a), as previously reported.⁶ We have also shown high-
resolution transmission electron microscopic (TEM) images of these NWs in a previous publication. The typical as-grown NWs have diameters of 6–15 nm and lengths of 5–10 μm, confirmed by TEM and atomic force microscopy (AFM). To fabricate single NW devices, NWs are transferred and cleaned inside a N2 glovebox (H2O < 0.1 ppm, O2 < 0.1 ppm). First, as-grown NWs are dispersed in hexane and drop-cast onto a 300 nm SiO2 covered, heavily B-doped Si wafer (Prime grade, University Wafer). The substrate and wires are cleaned of desiccated (dissolved in isopropanol at 90 °C) followed by soaking in anhydrous acetone for 30 min, and dried by gently blowing anhydrous acetone (99.8%, Acros Organics) for 30 min, and finally rinsed with N2. Without this cleaning procedure, the NWs are found to be covered and surrounded by dark films presumably made of organic residues such as oleic acid and trietylphosphine. For those that undergo the ammonium thiocyanate ligand replacement, the NWs are then treated in a 1 wt% solution of ammonium thiocyanate (>99%, Acros Organics) in anhydrous acetone (99.8%, Acros Organics) for 30 min, followed by soaking in anhydrous acetone for 1 min, and dried with N2. Before usage, the ammonium thiocyanate is carefully desiccated (dissolved in isopropanol at 90 °C followed by recrystallization under N2). AFM (Veeco Dimension 3100) shows the deposited and cleaned wires are smooth and confirms the NW diameters are between 6 and 15 nm (Figure 1(b)).

The harsh environment of the electron beam lithography fabrication procedure leads to insulating devices unless a thin SiO2 layer is first deposited on the NWs for protection. To minimize air exposure, the sample is transferred in an airtight container (sealed in N2) to a CHA electron beam evaporator. The air exposure time is within 1 min before an immediate pumping of the CHA chamber. Then, a 30 nm layer of SiO2 is deposited at a rate of 2 Å/s. This layer improves the NW surface passivation, minimizes exposure to oxygen, and serves as a physical barrier to protect the wires during the fabrication process. Individual wires are then located and imaged in a high-resolution FEI 430 NanoSEM. Afterward, a layer of methyl methacrylate (MMA, Microchem) is spin-cast onto the substrate and cured on a hot plate, starting at room temperature and raised at ~25 °C/min to 110 °C, for a total time of 5 min. This is followed by a similar process for poly(methyl methacrylate) (PMMA, Microchem). Ramping the hot plate gradually to a maximum 110 °C is critical for preventing thermal damage to these ultrathin NWs. Devices baked at the normal 180 °C PMMA crystallization temperature or with sudden temperature change do not conduct. Electrodes are then patterned using electron beam lithography (FEI 430 NanoSEM), developed, the SiO2 is etched off at the contacts for 5 s in a 6:1 buffered HF, and metalized with 25/25 nm Cr/Au in the CHA electron beam evaporator, followed by liftoff in acetone (Figure 1c). A typical SEM image of a complete device is shown in Figure 1d.

Electrical measurements are made using a National Instruments data acquisition system and a DL Instruments 1211 current amplifier. SPCM measurements are performed on a system as previously described. Briefly, a diffraction-limited laser spot is raster scanned over a NW FET while reflection and photocurrent are simultaneously measured. A Coherent CW 532 nm laser is used as the illumination source. The beam intensity for SPCM is controlled to be around 100 W/cm². The full width at half-maximum (fwhm) of the laser spot is 830 nm, determined from the photocurrent scan perpendicular to the axis of the NW. Low-temperature measurements are performed in a Lakeshore optical cryostat and the temperature is monitored by a Si diode temperature sensor.

Both as-grown PbSe NW devices and ammonium thiocyanate treated NW devices demonstrate nearly linear current–voltage (I–V) characteristics with slight asymmetry between positive and negative drain–source voltages at room temperature. Four-probe measurements confirm a negligible contact resistance of <5% that of the NW resistance for both treated and untreated devices. The transparent contact is consistent with the energy alignment between the Cr work function (4.5 eV) and the valence band of the colloidal PbSe NWs (~4.6 eV). A histogram of conductance measured in 35 devices (Figure 2c) shows the average conductance of treated devices is 10 times that of as-grown devices. The ligand replacement also results in greatly improved device stability. The conductivity of as-grown NW devices decreases substantially over a few days of measurements, while the treated devices maintain their conductivity for over 30 days of measurements and exposure to oxygen.

Application of a negative gate voltage leads to an increased conductivity, implying the wires are p-type (Figure 2a,b)). From the I–V curves at different gate voltage (Vg), we extract the hole field-effect mobility, defined as $μ_{FE} = \left(\frac{L^2}{C_{ox} V_{DS}}\right) \left(\frac{\partial I}{\partial V_g}\right)$, where L is the channel length, $V_{DS}$ is the drain–source voltage, and $C_{ox}$ is the oxide capacitance ($C_{ox} = \left(2πε_0L \right)/\left(\ln(4h/d)\right)$, where h is the oxide thickness). In an as-grown NW device (D1), we obtain $μ_{FE} = 30 \text{ cm}^2/\text{V s}$ and hole concentration $p = 1.3 \times 10^{18} \text{ cm}^{-3}$. These values are 490 cm²/V s and 2.25 × 10¹⁸ cm⁻³ for the ammonium thiocyanate treated device (D2). In D2, the transconductance changes impressively by 2 decades upon 1 V change in $V_g$ across a 300 nm gate oxide. We note the above field-effect mobility is extracted assuming a NW diameter of 10 nm. The exact diameter of the NWs in the FETs cannot be accurately measured because of the SiO2 coating. As the diameters of the colloidal NWs range from 6 to 15 nm, the calculated mobilities can range from 587 to 434 cm²/V s.

The treated NW devices exhibit a greater than 10-fold increase in mobility, indicating a suppression of carrier scattering. Recently, the use of ammonium thiocyanate has led to improved QD thin film mobilities as a result of surface passivation and reduced interdot spacing. We have also

![Figure 1.](image-url)
treated the NWs with hydrazine and ethane-dithiol, respectively, but these treatments are not as effective, presumably due to the greater sensitivity of these chemicals to oxidation. Despite the narrow bandgap of PbSe (0.27 eV for bulk), ambipolar conduction is not seen, likely because the adsorption of oxygen at the NW surface leads to p-doping. A previous report on PbSe NWs also shows a unipolar hole conduction as by coating the PbSe with a high bandgap shell may further improve the FET switching speed.

The elimination of uncertainties associated with ensemble devices in single NW FETs and the improved surface passivation allow for more accurate extraction of carrier mobilities in colloidal ultrathin PbSe NWs. Our best device exhibits a mobility about one-half of the Hall mobility (1000 cm²/(V s)) in bulk PbSe. Considering the underestimation of the mobility from the field effect measurements, the actual mobility in PbSe NWs can be approaching the bulk value. This indicates that surface scattering in NWs with diameters of ~10 nm may not substantially limit their mobility. Further work is necessary to better understand the diameter dependence of the carrier mobility. Generally, the reduction in mobility is attributable to a combination of Coulomb scattering from impurities, surface scattering, and phonon scattering. Phonon scattering plays an important role and will be discussed below in the temperature dependence measurements. Given that we do not intentionally dope the PbSe NWs with impurities, along with the high dielectric constant of PbSe, it is likely that Coulomb scattering does not dominate. It has been reported that ultrathin NWs may have an even higher mobility than the bulk, as doping can be achieved by heterostructures or surface ligands so that no carrier-scattering impurities are required in the NW conduction channels.

To investigate the optoelectronic properties, we first measure the photocurrent response time as we turn on and off the illumination for both as-grown and treated devices. A fast response time of <100 µs (limited by the instrument, Figure 3b) is obtained, as compared to many seconds for on-chip grown wires. The fast photoresponse indicates a better passivated NW surface. Photocurrent is sensitive to the polarization of the laser beam with an anisotropy ratio of 0.47 (Figure 3c), which is defined by (I⊥ − I∥)/(I∥ + I⊥), where I⊥ (I∥) is the photocurrent when incident electric field is parallel (perpendicular) to the orientation of the NW. A higher anisotropy ratio is expected given the large dielectric constant of PbSe. The discrepancy is not well understood but may be caused by the reduced dielectric constant in ultrathin NWs and/or scattering of the laser beam. Also, the photocurrent is linear with intensity in the range of this study (<200 W/cm², Figure 3d). At this intensity, we estimate a photoinduced carrier concentration of ~10¹⁷ cm⁻³, smaller than the dark carrier concentration.

We then perform SPCM to analyze the spatially resolved photocurrent in the PbSe NW FETs. Briefly, in SPCM, photocurrent is measured as a function of photoionization position (Figure 3a). SPCM has been used to measure carrier

Figure 2. Electrical characteristics of PbSe NW FETs. (a) I−V curves of a single as-grown PbSe NW device as a function of gate voltage, demonstrating p-type behavior with a mobility of 30 cm²/(V s). (b) I−V curves as a function of Vg for a device treated with ammonium thiocyanate. (Inset) Current at Vg = −0.1 V extracted from the I−V curves in (a) (blue dots) and current as the Vg sweeps at a rate of 100 mV/s (red curve). (c) Histogram of conductance (conductivity) for 35 devices, both untreated (black) and treated (red). Nominal conductivities on the top axis are calculated by assuming all NWs have a diameter of 10 nm and a length of 4 µm. The blue square represents the device in (a), the blue circle the device in (b).
The characteristic length of photocurrent decay \( l_p \) is not likely due to a Schottky electric field near the contact, as the estimated depletion width is small (121 nm for \( D_1 \) and 29 nm for \( D_2 \), using \( \epsilon_r = 173 \) for bulk PbSe, and built-in potential \( V_{bi} = 100 \) meV). Pseudo 1D semiconductors may have a more extended depletion length, but even using a modified expression of the depletion width for thin NWs, \( w_{NW} = d \exp(8\epsilon_r\epsilon_0\muBL/d^2) \), results in depletion lengths similar to the NW diameter. This is because the large relative dielectric constant renders the argument in the exponent small. A reduced effective dielectric constant \( (\epsilon_r^{*} \sim 20) \) in ultrathin PbSe NWs also produces a depletion width much shorter than the measured \( l_p \). As such, the extension of the photocurrent is due to the carrier diffusion. It should be mentioned that we cannot distinguish between exciton diffusion and free carrier diffusion from the experimental results. A high exciton binding energy of \( \sim 200 \) meV has been predicted in \( d = 4 \) nm PbSe NWs because of the reduced screening in the ultrathin NWs. Thus, \( l_p \) is a measure of the minority carrier (electron) or exciton diffusion length. The treated device has a longer diffusion length due to the increased mobility. Further theoretical and experimental work is necessary to distinguish the type of diffusion.

We can calculate the carrier recombination lifetime from the measured diffusion length as \( \tau = qL_p^2/\mu B^2 L \), where the symbols have their usual meanings. If we plug in the hole mobilities obtained from the gate measurements, we can estimate \( \tau \approx 8.3 \) ns for \( D_1 \) and 22.5 ns for \( D_2 \). As we expect that minority carriers (electrons) or excitons have a lower diffusion coefficient, the actual lifetimes can be longer. As a reference, the single exciton recombination lifetime of colloidal PbSe QDs has been measured to be around 1 \( \mu \)s at 80 K. \(^3\) In PbSe NWs, the carrier lifetime has not been measured to our knowledge and is expected to be a strong function of surface passivation. Indeed, the recombination lifetime increases after surface treatment, consistent with the idea that the density of surface states is reduced.

The SPCM profile is a strong function of gate voltage in the ammonium thiocyanate treated device \( D_3 \) (Figure 5a). In this device, the photocurrent is also highly asymmetric as in \( D_2 \). The photocurrent direction at \( V_g = 0 \) V is consistent with an upward band bending toward the electrode. The band bending indicates that the Fermi level of the PbSe NW is above the

diffusion lengths and local band structures.\(^{27-31}\) Photocurrent spots are localized near the electrodes in our as-grown NW device \( D_1 \) (Figure 4a). The photocurrent as a function of distance from the electrode \( x \) can be fitted by an exponential function \( \left( I = I_0 \exp(-x/L_p) \right) \), giving \( L_p = 2.5 \mu m \) for \( D_1 \). In comparison, the treated device \( D_2 \) shows a more elongated photocurrent spot from which we extract an increased \( L_p = 4.5 \mu m \). The photocurrent profile is highly asymmetric in \( D_2 \), dominated by the photocurrent peak near the right electrode, which is caused by the different contact barrier heights.

The characteristic length of photocurrent decay \( l_p \) is not likely due to a Schottky electric field near the contact, as the estimated depletion width is small (121 nm for \( D_1 \) and 29 nm for \( D_2 \), using \( \epsilon_r = 173 \) for bulk PbSe, and built-in potential \( V_{bi} = 100 \) meV). Pseudo 1D semiconductors may have a more extended depletion length, but even using a modified expression of the depletion width for thin NWs, \( w_{NW} = d \exp(8\epsilon_r\epsilon_0\muBL/d^2) \), results in depletion lengths similar to the NW diameter. This is because the large relative dielectric constant renders the argument in the exponent small. A reduced effective dielectric constant \( (\epsilon_r^{*} \sim 20) \) in ultrathin PbSe NWs also produces a depletion width much shorter than the measured \( l_p \). As such, the extension of the photocurrent is due to the carrier diffusion. It should be mentioned that we cannot distinguish between exciton diffusion and free carrier diffusion from the experimental results. A high exciton binding energy of \( \sim 200 \) meV has been predicted in \( d = 4 \) nm PbSe NWs because of the reduced screening in the ultrathin NWs. Thus, \( l_p \) is a measure of the minority carrier (electron) or exciton diffusion length. The treated device has a longer diffusion length due to the increased mobility. Further theoretical and experimental work is necessary to distinguish the type of diffusion.

We can calculate the carrier recombination lifetime from the measured diffusion length as \( \tau = qL_p^2/\mu B^2 L \), where the symbols have their usual meanings. If we plug in the hole mobilities obtained from the gate measurements, we can estimate \( \tau \approx 8.3 \) ns for \( D_1 \) and 22.5 ns for \( D_2 \). As we expect that minority carriers (electrons) or excitons have a lower diffusion coefficient, the actual lifetimes can be longer. As a reference, the single exciton recombination lifetime of colloidal PbSe QDs has been measured to be around 1 \( \mu \)s at 80 K. \(^3\) In PbSe NWs, the carrier lifetime has not been measured to our knowledge and is expected to be a strong function of surface passivation. Indeed, the recombination lifetime increases after surface treatment, consistent with the idea that the density of surface states is reduced.

The SPCM profile is a strong function of gate voltage in the ammonium thiocyanate treated device \( D_3 \) (Figure 5a). In this device, the photocurrent is also highly asymmetric as in \( D_2 \). The photocurrent direction at \( V_g = 0 \) V is consistent with an upward band bending toward the electrode. The band bending indicates that the Fermi level of the PbSe NW is above the
work function of Cr (4.5 eV). The photocurrent direction is reversed at \( V_g = -1 \) V, indicating a flip of the band bending. At \( V_g = -0.75 \) V, a flat band leads to a negligible photocurrent. From the peak photocurrent as a function of gate voltage (Figure 5b), we calculate the charge separation efficiency, \( \eta_{cc} = I(qF) \), where \( F \) is the absorbed photon flux. \( \eta_{cc} \) increases with \( V_g \) and saturates at \( \sim 100\% \) at \( V_g = 2 \) V (Figure 5b). By increasing the gate voltage, the band bending at the contacts is enhanced, leading to a higher charge separation efficiency. However, the charge separation efficiency is saturated at unity, even as the band bending continues to increase with gate voltage. A near unity \( \eta_{cc} \) implies that the charge separation is significantly faster than the charge recombination at the NW/metal interface.

Finally, we perform temperature dependent charge transport measurements of the colloidal PbSe NW FET treated by ammonium thiocyanate (device D3). At 79 K, the \( I-V \) curves are much more asymmetric than at 300 K (Figure 6a). The suppression of current at positive bias voltage is due to the asymmetric contact barrier heights, also observed in the SPCM (Figure 5a). At room temperature, the asymmetry is not obvious because the thermal activation is sufficient to overcome the contact barrier height. In addition, the intrinsic current fluctuation observed at room temperature is greatly reduced at 79 K. We associate this with a “freezing out” of trap-sites, that is, thermal energy is too small to lead to trapping/detrapping of charge carriers. From the \( I-V \) curves at different gate voltages, we extract the hole mobility as a function of temperature (Figure 6b). As temperature is decreased, the hole mobility first increases from 300 cm\(^2\)/Vs at 300 K to a maximum of 740 cm\(^2\)/Vs at 139 K and then decreases to 410 cm\(^2\)/Vs at 79 K. The mobility increase with decreasing temperature is due to reduced phonon scattering, consistent with bulk PbSe behavior. It has been reported that the bulk mobility increases by a factor of 10 upon cooling from 300 to 100 K.\(^{55}\) The reduction in the measured mobility below 139 K is likely caused by the charge blocking contact barrier, which is more pronounced at lower temperature.

At a fixed bias \( (V_g = -0.1 \) V), the current largely increases with temperature (Figure 6c). From the slope, we can extract the effective activation energy to be \( E_a = 90 \) meV at \( V_g = 0 \) V and \( E_a = 60 \) meV at \( V_g = -5 \) V. This effective activation energy reflects both the change of carrier mobility and carrier concentration as a function of temperature. The smaller \( E_a \) at negative \( V_g \) is consistent with the valence band edge shifting closer to the Fermi level. Surprisingly, we find that the current curve at \( V_g = 0 \) shows a dip at \( \sim 160 \) K (observed in all five devices measured). For \( V_g = -5 \) V, the dip at 160 K vanishes. In order to investigate the cause of the current dip, we measure current at fixed \( V_g \) while sweeping the gate voltage (Figure 6d). We notice a sudden shift in threshold gate voltage \( (V_g) \) from +1 V to -1 V at 160 K, which results in a reduction in current at \( V_g = 0 \) V. At \( V_g = -5 \) V, there is not much change in current, consistent with the disappearance of the dip. While further investigations are necessary to clarify the mechanism of this interesting behavior, the dip is most likely related to surface traps, which can significantly influence the gate threshold.

In summary, we have successfully fabricated FETs incorporating single ultrathin colloidal PbSe NWs treated by ammonium thiocyanate and demonstrated a record-high hole mobility of 490 cm\(^2\)/Vs at room temperature. The carrier diffusion length is measured to be 4.5 \( \mu m \) and a close-to-unity charge separation efficiency at the metal contact has been achieved. Carrier mobility increases at lower temperature and peaks at 740 cm\(^2\)/Vs at 139 K. A shift in gate threshold voltage has also been observed at 160 K. The demonstrated high carrier mobilities in ultrathin colloidal NWs encourage the optoelectronic applications of these materials in devices such as photodetectors and solar cells. The study identifies that surface passivation is key to improving performance of such devices. This work also provides a method for fabricating high quality, air-stable single colloidal NW FETs and opens up new exciting opportunities for understanding charge transport in low dimensional colloidal semiconductors.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: yu@physics.ucdavis.edu.*

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the U.C. Davis Startup Fund. We thank P. A. Baeza and I. Arslan for assistance with TEM. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

**REFERENCES**


(33) The flux is calculated by integrating the Gaussian shape of the laser beam over the NW, giving $F = (\pi r^2)^{1/2} (P \Delta \nu)/(\eta h \nu)$, where $P$ is the total laser power, $\alpha = 10^{5}$ cm$^{-1}$ is the absorption coefficient of PbSe at 532 nm, $r$ is the radius of the NW, $h \nu$ is the photon energy, and $\sigma$ is the standard deviation.