Supporting Information

Controlled Chemical Doping of Semiconductor Nanocrystals Using Redox Buffers

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Materials and Methods:

Materials. Bis(cyclopentadienyl)iron, Fc, 99%, and bis(pentamethylcyclopentadienyl)iron, Fc^{*}, 98%, were used as received from Strem. AgNO₃, >99%, ferrocenium hexafluorophosphate, [FeCp₂][PF₆], Fc⁺, 97%, and acetonitrile, anhydrous 99.8%, were used as received from Aldrich. NH₄PF₆, 99.5% (Alfa Aesar), and Bu₄NPF₆, electrochemical grade (Fluka) were without further purification. Reagent grade water used in synthetic preparations was >18 MΩ-cm resistivity (Millipore Type-1). Lead Oxide (PbO, 99.99%), selenium powder (99.99%), oleic acid (OA, tech. grade, 90%), 1-octadecene (ODE, tech. grade, 90%), diphenylphosphine (DPP, 98%), Trioctylphosphine (TOP, 97%), and 1,2-ethanedithiol (EDT, >90%) were purchased from Aldrich and used as received. All other solvents used in synthetic preparations were reagent grade or better and used as received from Aldrich.

Synthesis of decamethylferrocenium hexafluorophosphate, Fc^{*+} . AgNO₃ (250 mg, 1.47 mmol) dissolved in a 2 mL of water was added dropwise to a stirring suspension of decamethylferrocene, Fc^{*}, (507 mg, 1.55 mmol) in 50 mL of a 1:1 acetone:water mixture. The deep green solution which resulted was stirred overnight at room temperature, filtered over celite, and washed twice with 10 mL portions of water. 5 mL of saturated NH₄PF₆ was added dropwise to the filtrate to yield a green precipitate that was isolated by filtration. The isolate was washed twice with 10 mL portions of water and redissolved in 20 mL of acetone. The compound was precipitated from the acetone solution by addition of 50 mL of diethyl ether and isolated by filtration to yield the crude product as a pale green powder. Recrystallization twice from a 2:1 ethanol:acetone solution afforded green plates of [FeCp^{*}₂][PF₆], Fc^{*+}. Yield: 410 mg, 59%. Anal. Calc. for C₂₀H₃₀FePF₆: C, 50.97; H, 6.42. Found: C, 50.98; H, 6.51.

Synthesis and characterization of PbSe nanocrystals. PbSe nanocrystals were synthesized, stored, and handled under an argon atmosphere at all times. The nanocrystal colloids were synthesized using a reported hot-injection procedure¹ with modification. Briefly, 0.54 g of PbO were dissolved in a mixture of 2 mL of OA and 4 mL of ODE. This lead precursor solution was degassed at 100 °C under vacuum for 90 minutes. The selenium precursor solution was prepared by combining 1.185 g of selenium powder and 130 μ L of DPP in 15 mL of TOP. The lead

⁽¹⁾ Steckel, J.S.; Yen, B.K.H.; Oertel, D.C.; Bawendi, M.G. *Journal of the American Chemical Society* **2006**, *128*, 13032-3.

precursor solution was heated to 180 °C and 4.8 mL of the selenium precursor solution was rapidly injected. The reaction solution was rapidly cooled to 155 °C, and nanoparticle growth was abruptly halted after 40 seconds by injecting 10mL of anhydrous, cold hexanes and immersing the reaction vessel in a cold water bath. The resulting nanocrystals were purified by two cycles of precipitation with acetone, isolation by centrifugation, and redispersion in hexanes. The purified nanoparticles were stored under argon as a suspension in hexanes. Optical absorption spectra were taken of particles suspended in carbon tetrachloride (Figure 2b) using a Shimadzu UV-3600 spectrophotometer. Transmission electron micrographs (Figures 2b inset and S2) were acquired with a 200 kV Tecnai G220 S-TWIN electron microscope with a Gatan SC200 CCD camera, and the average particle diameter and size distribution histogram (Figure S3) were calculated using 1536 automated measurements performed with ImageJ software. XPS experiments were performed on a PHI ESCA 5000C X-ray photoelectron spectrometer with an Al target in ultra high vacuum (~10⁻⁹ Torr). Samples of PbSe particles were deposited on Au films, treated with EDT, and then soaked in a bath of 1:1 Fc:Fc⁺ in acetonitrile. They were transferred directly from the glovebox and exposed to air for ~1 minute.

General Electrochemical Methods. All electrochemical experiments were conducted using a CH Instruments 600C potentiostat and a high surface area Pt-mesh counter electrode. A silver wire bathed in 0.1 M Bu_4NPF_6 isolated from the working compartment by a porous Vycor frit served as pseudo-reference. All electrochemical experiments were performed using a three-electrode electrochemical cell and all electrode potentials were referenced to the Fc/Fc⁺ redox couple by addition of an internal standard of known redox potential (Fc or Fc^{*}) following each experiment.

Low Temperature Cyclic Voltammetry. For low temperature CV measurements, indium tin oxide (ITO) coated glass pieces, 4 mm × 25 mm, cut from a commercial slide (Aldrich, 8-12 Ω /sq) served as working electrodes and were rinsed with water and acetone prior to use. PbSe nanocrystal films were cast onto the ITO pieces using two cycles of dip-coating from a diluted dispersion of PbSe nanocrystals in hexanes. Following each dip coating cycle, the films were briefly exposed to a 0.1 M solution of EDT in acetonitrile. The EDT treated films were subsequently washed by emersion in pure acetonitrile and dried prior to electrochemical measurements. CV measurements were conducted under argon in a quiescent solution of 0.1 M

Bu₄NPF₆ in acetonitrile and the electrochemical cell was held at -37 ± 3 °C by emersion in a dry ice/acetonitrile bath. Immediately upon immersion of the working electrode into the electrolyte solution, the open circuit potential was recorded as a function of time and reached a stable value within 60 seconds. This value, referenced to the Fc/Fc⁺ redox potential was taken as E_F (Figure 1b and Figure 2a). The CV scan shown in Figure 2a was initiated from the open circuit potential and continued for five cycles without pause.

Preparation of PbSe nanocrystal field-effect transistors. All fabrication and measurement were carried out in an argon glovebox. Patterned gold electrodes were deposited onto p+-doped (<5 mΩ-cm) silicon wafers with 300 nm of gate oxide (Addison Engineering) using standard photolithography techniques. Contacts comprised of a 5 nm titanium adhesion layer, topped with 45 nm of gold. Channel lengths and widths were 20 µm and 800 µm respectively. Nanocrystal thin-films were fabricated via layer-by-layer dip-coating with sequential ligand exchange. Transistor substrates were first dipped by hand into a solution of PbSe nanoparticles suspended in hexane and removed slowly (< 1cm s⁻¹). To effect ligand exchange, the films were then dipped into a solution of 0.1 M EDT in acetonitrile, and finally washed by dipping into pure acetonitrile. The process was repeated several times to build up a smooth thin film (125 ± 20 nm; measured using a Tencor AS500 Profilometer) of nanoparticles.

Measurement of FETs. Electrical measurements were conducted using a Keithley 2636a dual source-meter unit, controlled with a home-built built LabView (National Instruments) program. Substrates were contacted using a home-built probe station enclosed in an argon glovebox. To ensure operation in the linear regime, a low source-drain bias ($V_{DS} = 5V$) was employed compared to the gate voltages swept ($V_{GS} = 0-30$ V), allowing the extraction of linear field-effect mobilities of the injected carriers (μ_{lin}) under the gradual-channel approximation,

$$\left. \frac{\partial I_{DS}}{\partial V_{GS}} \right|_{V_{DS}} = \frac{W C_{OX} V_{DS}}{L} \mu_{lin}$$

where W is the channel width, L is the channel length, I_{DS} is the source-drain current, C_{OX} is the capacitance per unit area of the gate oxide. Consistent with previous studies,² these PbSe quantum dot films exhibit transient decays of current due to trapping of injected carriers. Thus,

⁽²⁾ Liu, Y.; Gibbs, M.; Puthussery, J.; Gaik, S.; Ihly, R.; Hillhouse, H. W.; Law, M. Nano Lett 2010, 10, 1960–1969.

voltages must be swept quickly (0.1 V ms^{-1}) to minimize the influence of trapping and ensure repeatable, history-independent measurements. For transfer curves exhibiting a small degree of nonlinearity, the average of the transconductance was used for mobility extraction. Low-field conductivities were measured grounding the gate and sweeping the source-drain voltage 100mV. Low-field sweeps were found to be free from hysteresis and the current remained stable when held at a single voltage, ruling out the possibility of significant ionic conduction. Contact resistance was measured using the transmission line method³, and was found to be 3% of the channel resistance. Possible reductions in contact resistance are thus negligible compared to the measured increases in conductivity due to doping (0.3% at 1:1 Fc^{*+}:Fc^{*}).

Doping of PbSe nanocrystals. All treatments and preparation were conducted in an argon glovebox. Redox buffer solutions were prepared by combining 5mM stock solutions of decamethylferrocene, Fc^{*}, and decamethylferrocenium hexaflourophosphate, Fc^{*+}, in acetonitrile in the appropriate ratios to achieve the desired redox potential. Nanoparticle films were doped by soaking freshly fabricated PbSe thin-film transistors in the redox buffer solutions, and then washing in pure acetonitrile. Films were soaked for 3-18 hr, with little variation in the properties of transistors for different soaking times. For the determination of electronic properties as a function of soaking time (Figure 5), each transistor was soaked for a given time duration, rinsed in acetonitrile, dried and subjected to field-effect transistor measurements. Following each measurement, the transistor chip was returned to the original redox buffer solution to resume the oxidation reaction. The time values in Figure 5 correspond, therefore, to the cumulative duration over which the film was exposed the redox buffer solution.

³ Sze, S.M. & Ng, K.K. *Physics of Semiconductor Devices, Third Edition*. (John Wiley & Sons Inc.: 2007).

Calculation of Solution Potential and Fermi Level

Redox buffers, which are concentrated solutions of a reversible redox reagent wherein both oxidized and reduced forms are present in a known ratio, define the solution potential as given by the Nernst equation for a one electron process at 298 K,

$$E_{redox} = E^0 + (59.2 \text{ mV}) \log \frac{[\text{Ox}]}{[\text{Red}]}$$

where E^0 is the standard reduction potential of the reagent, corresponding to a solution containing equal concentrations of the oxidized, [Ox], and reduced, [Red], forms of the redox couple.⁴ The solution potential is therefore established by the chemical identity of the redox reagent, which establishes E^0 , and can be easily tuned over a range of at least 180 mV positive and negative of the standard potential by varying the ratio of [Ox] and [Red] in solution.

The electrochemical potential can be equivalently defined relative to vacuum, commonly known as the Fermi level (E_F) for semiconductors. If a solution redox potential is known relative to the standard hydrogen electrode ($E_{redox,SHE}$), the conversion to a vacuum energy scale is stratightforward,

$$E_F = -4.5 eV - eE_{redox,SHE}$$

where e is the elementary charge.⁵

Equivalently, the semiconductor Fermi level can be defined in terms of it's standard potential (E_i , the intrinsic level) and the ratio of it oxidized (p, holes) and reduced (n, electrons) band edge states.

$$E_F = E_i + (59.2 \text{ mV}) \log \frac{[p]}{[n]}$$

⁽⁴⁾ Rigorously, the reaction quotient in the Nernst equation corresponds to activities, which can be safely approximated as concentrations in the limit of the low ionic strengths used in this study.

⁽⁵⁾ Rajeshwar, K. Fundamentals of Semiconductor Electrochemistry and Photoelectrochemistry. *Encyclopedia of Electrochemistry, Volume 6, Semiconductor Electrodes and Photoelectrochemistry* (2001).

XPS Detection Limit for Dopant Counterions

We calculate the doping detection limit of our XPS measurements by considering the atomic ratio of dopants to lattice atoms,

$$n_{lim} = \left(\frac{V_{NP}}{4a^3}\right) \cdot ff \cdot Lim_{XPS}$$

where n_{lim} is the concentration limit of detection, V_{NP} is the volume of a nanoparticle $(1.4 \times 10^{-19} \text{ cm}^{-3} \text{ for } d = 6.5 \text{ nm})$, *a* is the lattice constant of PbSe (0.612 nm), *ff* is the space filling fraction (assumed to be 0.5 for randomly close packed spheres), and Lim_{XPS} is a liberal estimate of the atomic detection limit (assumed to be 1 part in 1000) of a typical XPS scan. For the assumptions above, the detection limit is calculated as $n_{lim} = 8.7 \times 10^{18} \text{ cm}^{-3}$, or 2.5 dopants per NP, two orders of magnitude higher than the largest level of controlled doping observed in this study. As expected, we thus see no signature of either F or Fe in our measurements (Fig S5), as concentrations of these species in the film are likely well below the threshold limit.



Figure S1. Low temperature, -37 °C, cyclic voltammograms (CVs) of an EDT-treated PbSe nanocrystal solid cast onto an ITO working electrode recorded in quiescent acetonitrile containing 0.1 M Bu₄NPF₆. The direction of scan and potential of scan initiation are indicated with the black arrow. Five CV cycles recorded without pause are shown with switching potentials of -0.62 V (—) and -0.56 V (—)



Figure S2. Representative transmission electron micrographs of PbSe nanocrystal sample from which PbSe thin films were prepared.



Figure S3. Size distribution histogram of PbSe nanocrystal colloids displaying an average size of 6.5 ± 0.3 nm. Automated measurements were performed with ImageJ software.



Figure S4. Average (—) of potentials corresponding to the same absolute value of current, |i|, for the cathodic (—) and anodic (—) waves in Figure 2a. The average potentials estimate an intrinsic potential, E_i , for PbSe nanocrystal solid films of -0.98 ± 0.01 V.



Figure S5. X-ray photoelectron spectra of an EDT-treated PbSe film on Au, soaked in a bath of $Fc^{*+}:Fc^{*}$ in a ratio of 1:1. Clear peaks are present for surface species of Pb and Se of the particles, but any signal for Fe or F, (from Fc^{*+} or PF_6^{-} respectively), are below the threshold of detection (see page S8).



Figure S6. Small field conductivity, σ (— — —), linear field-effect mobility, μ (• • •), and hole majority carrier density, n_h (—), of two PbSe nanocrystal solid films as a function of the time duration of exposure to Fc^{*}/Fc^{*+} doping solutions. The initial points represent untreated films. Both films were exposed to a 5 mM 1:1000 Fc^{*+}:Fc^{*} doping solution in acetonitrile for the first and last time series whereas one was exposed to a 5 mM 1:10 (closed circles) and the other, a 5 mM 1:100 (open squares) Fc^{*+}:Fc^{*} doping solution in between.



Figure S7. Small field conductivity, σ (— — —), linear field effect mobility, μ (= = =), and hole majority carrier density, n_h (—), of a PbSe nanocrystal solid film as a function of the duration of exposure to a 50 μ M Fc⁺ bath.



Figure S8. Small field conductivity, σ (— — —), linear field effect mobility, μ (= =), and hole majority carrier density, n_h (—), of a PbSe nanocrystal solid film as a function of time following exposure to a bath containing Fc^{*+}:Fc^{*} in a ratio of 1:1. The initial point is the untreated device.