# Electronic Transport in Nanoparticle Monolayers Sandwiched Between Graphene Electrodes

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## **Supplementary Information**

## **1. Device Fabrication**

CdSe nanoparticles (NPs) were prepared using cadmium oxide (CdO) and trioctylphosphine selenide (TOPSe) and are initially capped by phosphonates and trioctylphosphine oxide (TOPO). 25.6 mg of CdO (Sigma-Aldrich, 99.99+%), 0.2318 g oleic acid (OA) (Sigma-Aldrich, tech grade 90%), and 4 ml 1-octadecene (Sigma-Aldrich, tech grade 90%) were placed in a three-neck bottle and heated to 240 °C under N<sub>2</sub> for 30 min until a transparent Cd(OA)<sub>2</sub> solution formed. It was cooled to 100 °C and pumped to remove the water generated during the first step. After 20 min, 1 g TOPO (Sigma-Aldrich, tech grade 90%), 1 g 1-hexadecylamine (Sigma-Aldrich, tech grade 90%), and 2 ml 1octadecene were added to this three-neck bottle and pumped for 30 min. The mixture was heated to 305 °C and then 1 ml TOPSe was injected into the solution, and the CdSe NPs grew while this was held at 280 °C for 15 min. TOPSe was made by dissolving a selenium pellet (Sigma-Aldrich) in tri-n-octylphosphine (Strem Chemicals, 97%) and heated to 60 °C, stirring for ~8 hr. The CdSe NP product was then washed once using acetone and twice using ethanol.

The NP ligands were then exchanged to oleates by dissolving the CdSe NPs in 10 ml toluene, mixing in 0.25 g oleic acid, and heating to 100  $^{\circ}$ C under N<sub>2</sub> for 60 min. The final product was washed two more times using ethanol and finally dissolved in hexane. For the run reported below with hexadecylphosphonate ligands, hexadecylphosphonic acid was added instead of oleic acid.

During device fabrication (see Fig. 1a in the main text), after exfoliation of the bottom graphene layer from bulk graphite (Covalent Co.) onto a Si/SiO<sub>2</sub> substrate (300 nm thick thermal oxide layer), this graphene layer was sometimes subdivided into two or three pieces by oxygen plasma etching after patterning a polymethylmethacrylate (PMMA) (495k) mask by electron-beam lithography (EBL); this was done to increase the number of devices. The first pair of drain-source electrodes and the gate electrode were formed on the bottom graphene pieces. All electrodes were thermally deposited Cr/Au with 1 nm/50 nm thickness in the patterned area created by standard EBL techniques. Then the device was put into a small basket held by a micromanipulator. The whole basket was immersed into dimethylsulfoxide (DMSO) and the NP hexane:decane 90:10 solution was drop-cast on top of the liquid surface. Because the oleate-capped NPs dissolve in the hexane: decane solution but not in DMSO, and these two solutions are immiscible with each other, CdSe NPs self-assembled on the liquid interface on top of the denser DMSO, and then formed a monolayer closed-packed film eventually. After 2 hours, the hexane: decane solution evaporated and the devices in the DMSO were slowly lifted up by the micromanipulator. Then, the devices in the basket were allowed to sit overnight in a glove box to allow the remaining DMSO to evaporate. The amount of NP solution used for self-assembly was controlled by using a fine pipette and adjusted to form a monolayer, as determined by the NP coverage seen in parallel experiments conducted on a TEM grid (Fig. S2, below). Small angle x-ray scattering (SAXS) was also

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performed on Si/SiO<sub>2</sub> based NP films to confirm the monolayer structure and core-core distance in plane (Fig. S3, below). The top graphene was first exfoliated onto a PMMA (495k)/polyvinyl alcohol (PVA)/Si substrate. Then the sample was allowed to float on water and the PVA layer dissolved, leaving a graphene/PMMA film floating on the surface. The graphene piece remaining on the PMMA film was then scooped up, flipped over and positioned to overlap with the bottom graphene. To avoid spin coating PMMA on the CdSe NP ML, another PMMA (950K) film was transferred by using the same technique to create an undercut structure and EBL was performed directly on this double layer structure. A second pair of electrodes was then deposited on the top graphene layer by using with the same procedure as for the first pair.

#### 2. Nanoparticle Characterization

a. *NP Absorption*: The UV-visible absorption spectrum of the CdSe NP solution after synthesis is shown in Fig. S1. This shows an absorption peak near 555 nm, which indicates the NPs have core diameters of  $\sim$ 3.5 nm.<sup>[1]</sup>



Fig. S1. UV-visible absorption spectrum of the CdSe NP solution.

b. *TEM*: Fig. S2 shows the TEM image of a CdSe NP ML after it was transferred to a TEM grid, under (a) high and (b) low magnification. This method was used to show the NP coverage was a close-packed monolayer. Fig. S2b shows the TEM image over a larger length scale, which shows large regions of a continuous ML, along with areas where the ML did not transfer well. (This region was purposely chosen so this picture would have contrast between regions with and without a ML.) When the CdSe NP ML

was transferred onto the device structure, optical microscopy was used to confirm that there was film over the entire bottom graphene layer. (If not, the fabrication of that device was stopped).



Fig. S2. TEM image of a CdSe NP monolayer transferred to a TEM grid, in (a) higher and (b) lower magnification. The scale bar in (a) is 100 nm wide. A location with fracture was intentionally chosen for (b) so the ML could be seen through contrast.

c. *Small angle X-ray scattering (SAXS):* The SAXS pattern of a (3.5 nm core diameter) CdSe NP ML transferred onto the SiO<sub>2</sub>/Si substrate is shown in Fig. S3. The position of the (1,1) peak shows an in-plane core-core distance of ~5.8 nm. This image was obtained on the NSLS X9A beamline in the Brookhaven National Laboratory.



Fig. S3. SAXS pattern of CdSe NP ML on a SiO<sub>2</sub>/Si substrate.

#### 3. Additional Fabrication Information and Transport Measurements

A total of 52 device sets were fabricated on separate substrates. In 17 of these, the lower graphene layer was subdivided into two or three pieces by etching, and electrodes were attached to each, leading to a total of 71 potential individual devices from these 52 sets. There were fabrication issues in 31 of these device sets, as determined from visual inspection, including the rolling up of the graphene layer after transfer (in 16 of the device sets), incomplete NP ML coverage over all the graphene regions, and lithography errors relating to the top electrode, such as due as to breakage or shorting. Of the remaining 21 device sets, there were a total of 41 devices, of which 33 were shorted, for reasons given in the main text. Since there was no more than one non-shorted device per set, that device is labeled by its device set number (and called the device number). Transport was characterized in the eight devices. Devices 9, 28, 33, 44, 46, 49, 52 had similar *I-V* shapes and are called (the seven) working devices, and are examined in the main text and here. Device 45 had more of a diode characteristic and was not examined further. Device yield greatly improved in later runs.

Transport in the seven working devices was characterized at room temperature. Device 33 was characterized in Fig. 2 in the main text. Fig. S4a shows the *I-V* curve at zero back gate voltage for device 9. Fig. 4b shows that in this same device there is very little dependence of transport across the bottom graphene layer on the back gate voltage, with  $V_{ds} = 0.2$  V. Varying the back gate voltage never led to zero current in the transport across of any graphene layer measured, including across the top and bottom graphene layers in working devices and the bottom graphene layer in shorted devices and those with fabrication errors, such as a rolled-up top graphene layer.

The resistance across a working device is ~100 M $\Omega$  (~5 nA at 0.5 V). This can be compared to that across a shorted device ~100 k $\Omega$  (~5  $\mu$ A at 0.5 V), and to that across the graphene layers ~8 k $\Omega$  (~25  $\mu$ A at 0.2 V) (which is likely more due to contact resistance than in-plane resistance).

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Fig. S4. (a) I-V characterization across device 9 for zero back gate voltage. (b) Current across the bottom graphene layer, as a function of back gate voltage, with  $V_{ds} = 0.2$  V.

Raman measurements were made with 532 nm laser excitation to determine the level of doping in the graphene in device 49, specifically in regions where there is a top graphene (over the NP ML) but no bottom graphene or a bottom graphene (under the NP ML) and no top graphene, as seen in Fig. S5. The background due to CdSe NP photoluminescence (PL) needed to be removed for the top graphene measurement; for the bottom graphene measurement, the CdSe NPs PL was weak because the device had been exposed to air for several months. For both graphene layers, the G peak shifts to ~1590 cm<sup>-1</sup> from the intrinsic graphene G peak position of ~1584 cm<sup>-1</sup>. Using Ref. [2], this corresponds to doping on the order of  $10^{12}$  cm<sup>-2</sup>. Considering the graphene density of states, this doping level corresponds to a Fermi level shift of ~0.1 - 0.3 eV, so the graphene here is in the heavily doped regime.





One run was conducted with hexadecylphosphonate ligands on the CdSeNPs, instead of oleates. The I-V curve of this device in Fig. S6 suggests tunneling that is qualitatively similar to that seen using oleate ligands, in shape and the magnitude of the current. This is not surprising since both ligands have chains of roughly the same length.



Fig. S6. I-V curve of a sandwich structure with the CdSe NPs capped by hexadecylphosphonate ligands.

## 4. Derivation of the Transport Model

The Bardeen transfer Hamiltonian (BtH) approach is used to derive the tunneling current,<sup>[3,4]</sup> with

$$I = \frac{2\pi e}{\hbar} \sum_{\alpha,\beta} \left| M_{\alpha\beta} \right|^2 \left[ f_B(E_\alpha) - f_T(E_\beta) \right] \delta(E_\alpha - E_\beta), \quad (S1)$$

where  $M_{\alpha\beta}$  is the matrix element for the transition and  $f_{B,T}(E)$  are the Fermi-Dirac distribution functions for the bottom and top graphene. The valley and spin degeneracies for graphene are included when summing over all pairs of states for  $\alpha$  and  $\beta$ . The formula for  $M_{\alpha\beta}$  given by Feenstra et al.<sup>[5]</sup> is used:

$$M_{\alpha\beta} = \frac{\hbar^2 \kappa}{2m^* D} e^{-\kappa d} g_{\omega}(\theta_L, \theta_R) \cdot \frac{1}{A} \int dS e^{i \mathbf{Q} \cdot \mathbf{r}} e^{i \Delta \mathbf{k} \cdot \mathbf{r}}, \quad (S2)$$

where A is the device area,  $m^*$  is the effective mass, D is the interplanar separation in graphite,  $\kappa$  is the decay constant, d is the tunneling distance, and  $g_{\omega}(\theta_L, \theta_R)$  is the angle factor that accounts for the angular mismatch of the top and bottom graphene layers; the surface integral accounts for the momentum difference.

No negative differential resistance effect was observed. Therefore, it is assumed that there are enough disorder centers inside the barrier to effectively compensate the momentum mismatch. Also, for simplicity, we assume the angle mismatch factor  $g_{\omega} \sim 1$ . The fitting procedure shows that these pre-factors have a limited effect on the value of the current across the sandwich and no effect on the shape of the *I-V* curve. In contrast, small changes in the fitting parameters of particular interest, e.g. the effective barrier height  $\Delta$  and width *d*, affect the magnitude and shape of the *I-V* curve significantly. A linearly decreasing barrier is used, instead of the constant barrier and barrier decay constant used in WKB-type transmission probabilities,<sup>[5]</sup> so

$$M(E, V_i) = \frac{\hbar^2 \kappa}{2m^* D} \exp\left(\int_0^d -\sqrt{\frac{2m^*(\Delta - e\frac{V_i}{d}x - E)}{\hbar^2}} dx\right)$$
(S3)

Also, the density of states of graphene near the Dirac point is used to change the sum into an integral. The effective interaction area on the top graphene layer is assumed to be the area of one graphene honeycomb (from which an electron from the bottom graphene can tunnel into), which is  $\frac{3\sqrt{3}}{2}a^2$  for lattice constant *a*. The total tunneling current is then

$$I(V_d) = \frac{2\pi e}{\hbar} A \frac{3\sqrt{3}}{2} a^2 \int_{-\infty}^{\Delta} |M(E, V_i)|^2 [f_B(E) - f_T(E + eV_i)] DoS(E) DoS(E + eV_i) dE,$$
(S4)

where  $DoS(E) = \frac{2|E|}{\pi\hbar^2 v_F^2}$  is the density of states of graphene near the Dirac point and  $f_{B,T}(E) = \frac{1}{\exp\left(\frac{E-\mu_{B,T}}{k_BT}\right)+1}$  is the Fermi-Dirac distribution function at temperature *T* for chemical potential  $\mu_B$  or  $\mu_T$  for the bottom and top graphene layer, respectively.

## 5. Model Fitting Procedure

The magnitude of *I* at a given *V* is very sensitive to the barrier height  $\Delta$  and thickness *d* in the BtH model; the shape of the *I-V* curve is somewhat less so. So, for each device, the locus of points with barrier height  $\Delta$  and thickness *d* that predict the same current as that measured at 0.5 V for that device was determined; this  $\Delta$ -*d* fitting curve is shown in Fig. S7 as the dashed blue curve for each device. Then  $\Delta$  and *d* were determined by optimizing the shape of the *I-V* curve. The results of these fits for the seven working devices are plotted in the inset to Fig. 3b in the main text. The overall model fit results of  $\Delta = 2.88 \pm 0.24$  eV and  $d = 1.89 \pm 0.30$  nm given in the main text are the averages and standard deviations of these fits.

The BtH model does not predict the correct curve shape for barrier widths *d* larger than 2.5 nm, as is illustrated for one such barrier in Fig. 3a in the main text. Barrier heights  $\Delta$  exceeding the work function of graphene, 4.5 eV, were rejected in the fitting procedure because the top of the barrier would then be in the vacuum.

This procedure gives a local optimization  $\Delta$ -*d* space, as was confirmed by leastsquare fitting of the model curves in  $\Delta$ -*d* space for  $0.5 \times$  and  $2 \times$  the current measured at 0.5 V. Moreover, this procedure gives a global optimization in  $\Delta$ -*d* space, as was confirmed by least-squares fitting of the model over a grid of points in  $\Delta$ -*d* space. Although a best curve can be found along this constant-current curve, nearby points along the curve give nearly as good fits. Consequently, the reported best fit for each device is taken as the point (the squares in Figs. S7 and S8, which are also given in the inset to Fig. 3b in the main text) in the curve halfway between points with  $1.5 \times$  this minimum least squares deviation (the solid red curve defines this range). The final results are relatively insensitive to the exact details of this procedure, giving barrier heights and widths consistent to ~0.2 eV and ~0.1 nm; this is less than the run-to-run variations. The overall uncertainty in measurement is that due this model fitting uncertainty, the deviation among best fits for the experimental results for the seven devices, and the systematic uncertainty in the BtH model itself and the parameters used in this model.



Fig. S7. The  $\Delta$ -*d* fitting curves (dashed blue curves) for the measured current densities at 0.5 V for each device. The model best fits are shown (squares), along with the ranges of  $\Delta$ -*d* fitting parameters along these curves that give a fit least squares standard deviation within 50% of each best fit (solid red curves).

For comparison, the model fits using the Simmons model<sup>[6]</sup> are shown in Fig. S8, along with the BtH model fits (from Fig. S7 and the inset to Fig. 3b in the main text); the BtH model is appropriate for the 2D graphene electrodes, while the Simmons model assumes 3D electrodes. The Simmons model consistently predicts lower barrier heights and wider barrier widths.



Fig. S8. The  $\Delta$ -*d* model parameters providing the best fits for the BtH model for the seven devices (squares), as is also shown in Fig. S7 and the inset to Fig. 3b in the main text, along with the best fit parameters for the Simmons model.

## 6. Photocurrent Calculation

The extinction coefficient of CdSe NPs at the first exciton absorption peak given by <sup>[1]</sup> is scaled to the 532 nm laser wavelength by using the UV-visible absorption spectrum, and is used in the photoconductivity modeling. According to <sup>[1]</sup>, the absorbance A at the first exciton peak can be written as

$$A = \varepsilon C L$$
, (S5)

where  $\varepsilon \approx 5857 (D_{NP}/\text{nm})^{2.65} \frac{\text{L}}{\text{mol}} \text{cm}$  is the extinction coefficient of CdSe NPs with diameter  $D_{NP}$ , *C* is the molar concentration (mol/L) of the NPs, *L* is the path length (cm) of the laser beam. The path length here for the monolayer NP film is  $\sim D_{NP}$  and the molar concentration can be written as

$$C = \frac{\eta}{N_A \times \frac{1}{4} \pi a_{cc}^2 D_{NP}}, \quad (S6)$$

where  $\eta = \frac{\pi}{2\sqrt{3}}$  is the packing density of a 2D hexagonal lattice and the core-core distance  $a_{cc} = 5.8$  nm; this distance is larger than the NP diameter according to the SAXS data in Fig. S3, which is reasonable because of the ligands on the NP core. After using Fig. S1 to account for the detuning of the laser from the exciton peak, the fraction of light absorbed by the CdSe NP monolayer is ~0.18% at 532 nm.

Assuming 100% quantum efficiency of converting absorbed photons to excitons, the created photocurrent is

$$I = \frac{P}{h_{\lambda}^{c}} (1 - 10^{-A}) \sim 7.0 \text{ nA.} \quad (S7)$$

This is much larger than the measured photocurrent given in the text, ~0.8 nA, so most of the excitons recombine due to the ligand barrier.

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