Graphene nanogaps for the directed assembly of single-nanoparticle devices

Electronic Supplementary Information

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1 The Simmons Model

A trapezoidal tunnel barrier between a Left (L) and Right (R) electrode, separated by a distance $d$ and an electrical bias $V$. Here, L and R are of the same material and at zero bias $\phi_L = \phi_R$.

An expression for the current density $j$ flowing through a trapezoidal tunnel barrier of width $d = x_2 - x_1$ between two biased electrodes was derived by Simmons:

$$j = e \frac{4 \pi m}{h^3} \int_{0}^{\infty} d\epsilon [f_L(\epsilon) - f_R(\epsilon)] \int_{0}^{\epsilon} d\epsilon_x T(\epsilon_x)$$

where $m$ is the electron mass, $f_{L,R}(\epsilon) = (e^{-(\epsilon - \mu_{L,R})/k_B T} + 1)^{-1}$ is the Fermi energy of the left and right leads, respectively, dependent on their chemical potential $\mu_{L,R}$, and $T(\epsilon_x)$ describes the transmission probability of an electron of energy $\epsilon_x$ through the tunnel barrier in the $x$-direction. An expression for $T(\epsilon_x)$ can be found by using the Wentzel-Kramers-Brillouin (WKB) approximation:

$$T(\epsilon_x) = e^{-\beta \int_{x_1}^{x_2} dx \sqrt{\phi(x) - \epsilon_x}}$$

where $\beta = 2 \frac{\sqrt{m \phi}}{h}$ and $\phi$. If the work functions of the left and right leads are not equal, but change linearly from $\phi_L$ at $x_1$ to $\phi_R$ at $x_2$ as the a voltage $V$ is applied symmetrically across the junction then we can write:

$$\phi_{L,R} = (1 \pm \alpha)\phi'$$

where $\phi' = \frac{\phi_L - \phi_R}{2}$ is the average barrier height and $\alpha = \frac{\phi_L - \phi_R}{\phi_L + \phi_R}$ is an asymmetry factor, which are used for simplified fitting. Different analytical expressions for the integral $\int_{x_1}^{x_2} dx \sqrt{\phi(x) - \epsilon_x}$ can be found depending on the relative magnitudes of $\phi_L$, $\phi_R$ and $\epsilon_x$:²
if $\Phi_{L,R} < \epsilon_x < \Phi_{R,L}$: 

$$\int_{x_1}^{x_2} dx \sqrt{\Phi(x) - \epsilon_x} = \frac{2}{3} \left( \Phi_{R,L} - \epsilon_x \right)^{3/2}$$  \hspace{1cm} (S4)

else $\epsilon_x < \Phi_{L}, \Phi_{R}$: 

$$\int_{x_1}^{x_2} dx \sqrt{\Phi(x) - \epsilon_x} = \frac{2}{3} \left( \Phi_{R} - \epsilon_x \right)^{3/2} - \frac{2}{3} \left( \Phi_{L} - \epsilon_x \right)^{3/2}$$  \hspace{1cm} (S5)

In the low temperature limit where $k_B T << \mu_L, \mu_R, \Phi(x)$ the Fermi distribution becomes a step function and (S1) becomes:

$$j = e \frac{4\pi m}{h^3} \int_{\mu_L}^{\mu_R} d\epsilon \int_0^\epsilon d\epsilon_x T(\epsilon_x)$$  \hspace{1cm} (S6)

In order to fit (S6) to the measured current $I$ we must multiply it by the cross sectional area $A'$ of the junction such that $I = A' j$. However, $A'$ is not independent of other variables such as the effective electron mass and so is incorporated into a prefactor $A = e \frac{4\pi m}{h^3} A'$. Current-voltage data can then be fitted to the model to (S7) to find $\Phi' [eV]$, $\alpha$, $d$ [m] and $A$ [eV$^{-2}$].

$$I = A \int_{\mu_L}^{\mu_R} d\epsilon \int_0^\epsilon d\epsilon_x T(\epsilon_x)$$  \hspace{1cm} (S7)

2 The Orthodox Model

Electron transport through a mesoscopic island separated by two tunnel barriers is well described by the classical ‘orthodox’ theory of correlated electron tunneling. 3–5 This model does not consider any discreteness of the energy spectrum of the island. This is a particularly good approximation for metals where level spacing is negligible. The orthodox theory can be extended to consider the presence of quantised energy levels provided that $k_B T$ is much greater than the intrinsic width of these levels, details of which can be found in 6,7, but this will not be considered here.

Figure S2 shows an equivalent 2-terminal RC circuit model that the orthodox theory describes. The tunnel rates $\Gamma_{L,R}^{+,-}$ capture the rate at which electrons are added to/taken off the island from to/from the left/right electrodes, as indicated by the arrows. We can describe the associated addition/subtraction energies with each added/removed electron starting from an initial state of $n$ electrons on the island as:

$$\Delta E_L^+(n) = U(n + 1) - U(n) + \eta eV_b$$  \hspace{1cm} (S8)

$$\Delta E_L^-(n) = U(n) - U(n - 1) + \eta eV_b$$  \hspace{1cm} (S9)

$$\Delta E_R^+(n) = U(n + 1) - U(n) - (1 - \eta)eV_b$$  \hspace{1cm} (S10)
Figure S2: A circuit diagram representing the orthodox model. Each tunnel barrier is represented by a RC circuit and electrons tunnel from (-)/to (+) the Left/Right electrodes at rate $\Gamma$. The central island has a residual fractional charge $Q_0$.

$$\Delta E_R^-(n) = U(n) - U(n-1) - (1 - \eta)eV_b \quad (S11)$$

Where $U(n)$ is the total energy of the island with $n$ electrons, $V_b$ is the bias voltage and $\eta$ is the fraction of the voltage dropped over the left tunnel barrier. Within the limits of the model we can equivalently express these in electrostatic terms:

$$\Delta E_L^\pm(n) = \Delta U^\pm(n) \pm \frac{eC_R}{C_L + C_R} V_b \quad (S12)$$
$$\Delta E_R^\pm(n) = \Delta U^\pm(n) \mp \frac{eC_L}{C_L + C_R} V_b \quad (S13)$$
$$\Delta U^\pm(n) = \frac{(Q \pm e)^2}{2(C_L + C_R)} - \frac{Q^2}{2(C_L + C_R)} \quad (S14)$$

Where $Q = (ne - Q_0)$ is the total charge of the island before the electron tunnels and $Q_0$ is the fractional charge ($|Q_0| < e/2$) present on the island at zero bias. We can then write:

$$\Delta E_L^\pm(n) = \frac{e}{C_L + C_R} \left( \frac{e}{2} \pm (ne - Q_0) + C_R V_b \right) \quad (S15)$$
$$\Delta E_R^\pm(n) = \frac{e}{C_L + C_R} \left( \frac{e}{2} \pm (ne - Q_0) - C_L V_b \right) \quad (S16)$$

The tunnelling rates across the left-side and right-side barriers can be obtained from a golden rule calculation$^3$:

$$\Gamma_{L,R}^\pm(n) = \frac{1}{R_{L,R}e^2} \left( \frac{-\Delta E_{L,R}^\pm(n)}{1 - \exp(\Delta E_{L,R}^\pm(n)/k_BT)} \right) \quad (S17)$$
Where any dependence of $\Gamma_{L,R}^\pm$ on $n$ itself has been neglected. The current through the island at a given bias voltage is then given by:

$$I(V_b) = e \sum_{n=-\infty}^{\infty} \sigma(n) \left[ \Gamma_R^+(n) - \Gamma_R^-(n) \right] = e \sum_{n=-\infty}^{\infty} \sigma(n) \left[ \Gamma_L^-(n) - \Gamma_L^+(n) \right]$$  \hspace{1cm} (S18)

Here, $\sigma(n)$ describes the ensemble distribution of the number of electrons on the island: the probability that any one value of $n$ electrons are on the island. Finding $\sigma(n)$ requires noting that the net probability for making a transition between any two adjacent states is zero under a steady state, giving:

$$\sigma(n) \left[ \Gamma_R^+(n) + \Gamma_R^-(n) \right] = \sigma(n+1) \left[ \Gamma_L^-(n+1) + \Gamma_L^+(n+1) \right]$$  \hspace{1cm} (S19)

and by implementing the normalisation condition $\sum_{n=-\infty}^{\infty} \sigma(n) = 1$. Thus, we can solve for $\sigma(n)$ and thereby $I(V_b)$ numerically.

We can extend this theory to include the influence of a gate electrode at voltage $V_g$ connected to the island by a capacitor $C_G$ by modifying (S15) and (S16) to:

$$\Delta E_L^\pm(n) = \frac{e}{C_{\Sigma}} \left( \frac{e}{2} \pm \left( (ne - Q_0) + C_R V_b - C_G V_g \right) \right)$$ \hspace{1cm} (S20)

$$\Delta E_R^\pm(n) = \frac{e}{C_{\Sigma}} \left( \frac{e}{2} \pm \left( (ne - Q_0) - (C_L + C_G) V_b - C_G V_g \right) \right)$$ \hspace{1cm} (S21)

where $C_{\Sigma} = C_L + C_R + C_G$. From here the derivation of the current follows the same process as above.

### 3 Thermally Broadened Peaks

From Beenakker,\(^7\) in the classical limit of $h \Gamma, \Delta E \ll k_B T \ll e^2/CE$ the line-shape of the Coulomb blockade resonances is given by:

$$G/G_{max} \approx \cosh^{-2} \left( \frac{\beta e|V_g - V_0|}{2.5k_B T} \right)$$ \hspace{1cm} (S22)

where $\beta$ is the capacitive coupling to the gate, $V_g$ is the gate voltage and $V_0$ is the voltage at which the resonance is centred.

### 4 Electric Field Calculations

The electric field distribution in our graphene devices was modelled using the finite element method in COMSOL Multiphysics 5.5 using the electric currents interface from the AC/DC physics module which computes electric fields and
Figure S3: Schematics of the geometries used for electric field calculations for:
(a) A 2 nm graphene nanogap with a floating buried gate, (b) a single graphene
electrode trapping against a buried gate and (c) a 20 nm gold electrode trapping
against a buried gate.

potential distributions for conducting media where inductive effects can be ne-
eglected. The model was solved in the frequency domain at $\omega = 1 \text{ MHz}$. In this
interface Poisson’s equation is expressed as:

$$\nabla \cdot \mathbf{J} = Q = -\frac{\partial \rho}{\partial t} \quad (S23)$$

$$\mathbf{J} = \sigma \mathbf{E} + j\omega \mathbf{D} \quad (S24)$$

$$\mathbf{E} = -\nabla \varphi \quad (S25)$$

The simulation domain was built as shown in Figure S3a. The citrate so-
lution was assumed to have a permittivity of 80 and was found to have a con-
ductivity of $600 \mu\text{S cm}^{-1}$. The HfO$_2$ was assigned a permittivity of 13$^8$ and a
negligible conductivity. Dirichlet boundary conditions of $\varphi = 0.75$ and $\varphi = 0$
were set on the left and right vertices of the graphene layer at the edges of the
simulation domain, respectively. The buried gate electrode was assigned a
‘floating potential’ boundary condition. All other external boundaries were set
to an insulating Neumann boundary condition $\mathbf{n} \cdot \mathbf{J} = 0$. At the graphene layer
a dielectric shielding boundary condition was used whereby:

$$\mathbf{n} \cdot (\mathbf{J}_1 - \mathbf{J}_2) = -\nabla_T \cdot d_s d((\sigma + j\omega\varepsilon_0\varepsilon_r)\nabla_T \varphi) \quad (S26)$$

where $\mathbf{n}$ is the normal vector, $\mathbf{J}_{1,2}$ are the current densities on either side
of the boundary, $\nabla_T$ is the tangential differential, $d_s$ is the thickness of the
boundary which was set as 1 nm. We used $\varepsilon_r = 6.9^9$ and set the conductivity
as $\sigma = e\mu_c n_{2D}(\varphi(x))$, where $\mu_c$ is the electron mobility in graphene ($2.5 \times 10^4$
$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)$^{10}$ and $n_{2D}$ is the surface charge concentration per unit area. This
was defined according to the analytical expression presented by Barik et al.$^{11}$

$$n_{2D}(\varphi(x)) = \frac{2 \Gamma(2)}{\pi} \left( \frac{k_BT}{\hbar \nu_F} \right)^2 \left[ \mathcal{F}_1\left(\frac{e\varphi(x)}{k_BT}\right) - \mathcal{F}_1\left(\frac{-e\varphi(x)}{k_BT}\right) \right] \quad (S27)$$
where $\nu_F$ is the Fermi velocity ($10^6$ ms$^{-1}$ in graphene), $\varphi(x)$ is the electric potential at position $x$ in the graphene layer and $F_1$ is the Fermi-Dirac integral of order 1:

$$F_j = \frac{1}{\Gamma(j + 1)} \int_0^\infty \frac{e^d}{e^{\epsilon + \eta} + 1}$$

where $\eta = \pm k_B T$ and $\Gamma(n) = (n - 1)!$. $n_{2D}(x)$ was calculated in MATLAB using the algorithm published by Wang and Lundstrom,\textsuperscript{12} which was then used by COMSOL in a self-consistent calculation for $\varphi$.

The calculations for a single graphene electrode trapping against a local gate electrode were configured in much the same way, except that the gate electrode was assigned a Dirichlet boundary condition of $\varphi = V_g = 0.75$ and the left electrode was removed. This is shown in Figure S3b. For the gold electrode a 20 nm high, rounded geometry was used, and the potential difference was again applied between the buried gate and the right electrode as shown in Figure S3c. The gold was assigned a conductivity of $4.6 \times 10^7$ S cm$^{-1}$\textsuperscript{13} and a permittivity of 1.

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