# **Supplementary Information for**

# Spatially resolving density-dependent screening around a single charged atom in graphene

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# **TABLE OF CONTENTS:**

## S1. Methods

- S2. d*I*/d*V* spectroscopy on a calcium atom
- S3. Charge donated to graphene by each calcium atom
- S4. Substrate dielectric constant
- **S5. Simulated local density of states without lifetime correction**
- **S6. Density functional theory**
- S7. Shifted local density of states
- **S8.** Topographic image of calcium atoms
- **S9.** Discrepancies between theory and experiment

## S1. Methods

Graphene samples were grown through chemical vapor deposition (CVD) and were subsequently transferred onto 40 - 100 nm thick hexagonal boron nitride (BN) crystals exfoliated onto SiO<sub>2</sub>/Si wafers (the SiO<sub>2</sub> is 285 nm thick). The Si wafers were heavily doped to serve as electrostatic back-gates for our graphene devices. Graphene was electrically contacted by Ti (10 nm thick)/Au (40 - 50 nm thick) electrodes, and the final devices were cleaned by annealing at 400°C in UHV for several hours before imaging. Calcium (Ca) atoms were deposited onto graphene by thermally heating a calcium getter source (Alvatec and Trace Sciences International) calibrated by a mass spectrometer (SRS Residual Gas Analyzer). Before each deposition the graphene surface was checked using scanning tunneling microscopy (STM) imaging to ensure surface cleanliness. The STM tip was then retracted to avoid contamination of the tip from the Ca getter source. After degassing the getter source, calcium atoms were evaporated directly onto the low temperature (T = 4.8 K) graphene surface.

The scanning tunneling spectroscopy (STS) experiments were performed in an ultra-high vacuum (UHV) Omicron LT-STM at T = 4.8 K using platinum iridium STM tips calibrated against the surface state of an Au(111) crystal. Differential conductance (d*I*/d*V*) was measured using standard lock-in detection of the a.c. tunneling current modulated by a 6 - 10 mV (rms), 500 - 700 Hz signal added to the sample bias ( $V_s$ ). The experiments were repeated with numerous different STM tips on multiple gate-tunable graphene devices for more than 30 calcium atoms. The d*I*/d*V* line profiles in Figs 3d and 4d of the main text were obtained by radially averaging d*I*/d*V* maps such as those in Figs 3a-c and 4a-c of the main text (with the Ca atom as the center) and then correcting for the variation in tip height caused by the constant current feedback loop.

The tunneling parameters for Fig. 1b of the main text are  $V_s = -0.45$  V, I = 2 pA. The initial tunneling parameters for Fig. 2 of the main text are: (a)  $V_s = 0.6$  V, I = 60 pA,  $V_g = -60$  V; (b)  $V_s = 0.6$  V, I = 60 pA,  $V_g = -30$  V; (c)  $V_s = 0.6$  V, I = 60 pA,  $V_g = 30$  V. The tunneling parameters for Fig. 3 of the main text are: (a)  $V_s = 0.28$  V, I = 28 pA,  $V_g = 0$  V; (b)  $V_s = 0.38$  V, I = 38 pA,  $V_g = -30$  V; (c)  $V_s = 0.45$  V, I = 45 pA,  $V_g = -60$  V. The tunneling parameters for Fig. 4

of the main text are: (a)  $V_s = -0.16 \text{ V}$ , I = 17 pA,  $V_g = 5 \text{ V}$ ; (b)  $V_s = -0.22 \text{ V}$ , I = 20 pA,  $V_g = 20 \text{ V}$ ; (c)  $V_s = -0.28 \text{ V}$ , I = 28 pA,  $V_g = 40 \text{ V}$ .

We performed both tight-binding and *ab initio* density functional theory (DFT) calculations to simulate the local density of states (LDOS) of graphene in the presence of an adsorbed Ca atom. For a given value of the chemical potential, we solved the tight-binding Hamiltonian numerically for supercells containing up to 45,000 carbon atoms (corresponding to  $150 \times 150$  graphene primitive cells) and a single calcium adatom using a  $2 \times 2$  k-point grid to sample the Brillouin zone of the supercell. DFT calculations were performed with the ONETEP code (version 4.2.0), using supercells containing up to 6,272 carbon atoms. The Brillouin zone of the supercell was sampled at the  $\Gamma$ -point. We used norm-conserving pseudopotentials with semi-core Ca states, the GGA-PBE functional to describe exchange and correlation, and a basis of atom-centered local orbitals with a radius of 5.3 Å, which are described on a real-space grid corresponding to a plane-wave energy cutoff of 1000 eV and are optimized *in situ* for high accuracy. Simulated dI/dV is proportional to calculated LDOS.

#### S2. d*I*/d*V* spectroscopy on a calcium atom

Figure S1 shows dI/dV spectra on a calcium (Ca) atom for gate voltage  $V_g = -30$  V (green curve) and +30 V (black curve). The dI/dV spectra resemble dI/dV on bare graphene except are noisier because the STM tunneling current setpoint is very small (I = 0.010 nA) to avoid moving the Ca atom while the tip is directly above it. The dI/dV spectra have no resonances, further supporting our claim that Ca atoms are charge stable within our experimental conditions.

#### S3. Charge donated to graphene by each calcium atom

The charge donated by each Ca atom can be quantitatively assessed by plotting the charge density in graphene against the density of Ca atoms. This data is shown in Fig. S2, in

which charge density *n* is obtained through  $n = E_D^2/\pi(\hbar v_F)^2$ , where  $E_D$  is the Dirac point energy extracted through dI/dV spectroscopy (at back-gate voltage  $V_g = 0$  V) and  $v_F$  is the graphene Fermi velocity. The surface density of Ca atoms is controlled either by the duration of the Ca deposition or by the number of depositions, and is estimated by counting the number of atoms in many different areas. A linear regression line fit to the data points (dashed red line in Fig. S2) yields a charge transfer of  $0.7 \pm 0.2$  electrons for each Ca atom.

## S4. Substrate dielectric constant

The substrate dielectric constant used in our tight binding calculations ( $\epsilon_s = 2.5$ ) is approximated as the average of the vacuum and bulk BN dielectric constants.

## **S5. Simulated local density of states without lifetime correction**

Figure S3 shows the tight-binding-calculated local density of states (LDOS) (i.e. simulated dI/dV without correcting for inelastic tunneling and lifetime effects) plotted as a function of energy for various distances away from the center of a screened Coulomb potential in graphene.

Figure S4 shows the tight-binding-calculated LDOS (i.e. simulated dI/dV without correcting for inelastic tunneling and lifetime effects) plotted as a function of distance for various values of the charge carrier density. The energies are the same as those from the figures in the main text (Figs 3e and 4e).

### **S6.** Density functional theory

Figure S5 shows the LDOS calculated via density functional theory (DFT) plotted as a function of distance from a Ca atom for various values of the charge carrier density. Just like Figs 3e and 4e of the main text, which were calculated via a tight-binding model, the DFT

calculations also show that LDOS decays faster away from a Ca atom for larger magnitudes of the charge carrier density |n|.

#### S7. Shifted local density of states

For energies far from the Dirac point  $(|E - E_D| \gg \hbar v_F/R)$  for Dirac point energy  $E_D$  and distance from impurity *R*), the LDOS at *R* in the presence of a screened Coulomb potential is equal to the LDOS of pristine graphene shifted by the value of the screened Coulomb potential at *R*. Figure S6 shows this behavior for R = 1.3 nm. The red curve is the tight-binding LDOS of graphene at R = 1.3 nm in the presence of a screened Coulomb potential, while the green curve is the LDOS of pristine graphene where the Dirac point has been shifted by the value of the screened Coulomb potential at 1.3 nm. The red and green curves agree for energies much greater than  $\hbar v_F/R \approx 0.5$  eV but do not agree in the vicinity of the Dirac point (as required by the scale invariance of the massless Dirac Hamiltonian).

# **S8.** Topographic image of calcium atoms

As shown in Fig. 1 of the main text and Fig. S7, Ca atoms appear as identical round protrusions on the graphene surface and are surrounded by a dark depression caused by the rearrangement of spectral weight above and below the Dirac point. This is a signature of the graphene screening response to the presence of charged Ca adatoms.

#### **S9.** Discrepancies between theory and experiment

Although the LDOS of graphene near a charged impurity has no closed-form expression, we can roughly quantify how quickly dI/dV and the LDOS return to their unperturbed values by fitting the data in Figs 3d and 3e with an exponentially decaying function, i.e.  $A + Be^{-r/\lambda}$ . This allows us to empirically quantify how quickly the dI/dV and LDOS change. The extracted "decay length"  $\lambda$  is an unknown function of the gate voltage  $V_g$ , the probed energy  $|E - E_D|$ , the impurity charge Q, and substrate dielectric constant  $\epsilon_s$ . However, for a fixed  $|E - E_D|$ , Q, and  $\epsilon_s$ , we expect that  $\lambda$  is positively correlated to the Thomas Fermi screening length  $\lambda_{TF}$ . Since  $1/\lambda_{TF}^2$  is directly proportional to  $V_g$ , we elect to plot  $1/\lambda^2$  against  $V_g$  in Fig. S8.

As seen in Fig. S8,  $1/\lambda^2$  increases roughly linearly with increasing  $V_g$ , consistent with the discussion in the main text. Linear fits show that  $1/\lambda^2$  increases by 0.0025 nm<sup>-2</sup>/V for the experimental data and 0.0018 nm<sup>-2</sup>/V for the simulation. Each theoretical curve decays faster than its experimental counterpart with the same gate voltage. This suggests that a new treatment of electron-electron interactions beyond the random phase approximation (RPA) and linear response theory may be required to obtain better agreement between theory and experiment for single charged impurities.



**FIGURE S1.** dI/dV spectroscopy on Ca atom. Green curve:  $V_s = 0.35$  V, I = 0.010 nA,  $V_g = -30$  V. Black curve:  $V_s = 0.35$  V, I = 0.010 nA,  $V_g = 30$  V.



**FIGURE S2.** Charge carrier density vs. calcium atomic density. For  $V_g = 0$  V, with a linear fit (red dashed line) that shows a charge transfer of  $0.7 \pm 0.2$  electrons for each Ca atom.



**FIGURE S3.** Local density of states as a function of energy calculated via a tight-binding model. (a) Tight-binding simulation of p-doped graphene ( $|n| = 2.44 \times 10^{12} \text{ cm}^{-2}$ ) d*I*/d*V* spectra (without inelastic tunneling and lifetime effects) for different distances away from a screened Coulomb potential. (b) Same as (a) for nearly neutral graphene ( $|n| = 1.5 \times 10^{11} \text{ cm}^{-2}$ ). (c) Same as (a) for n-doped graphene ( $|n| = 1.37 \times 10^{12} \text{ cm}^{-2}$ ).



**FIGURE S4.** Local density of states as a function of distance calculated via a tight-binding model. (a) Simulated dI/dV (0.15 eV above the Dirac point, without inelastic and lifetime effects) as a function of distance away from an RPA-screened Coulomb potential on p-doped graphene. (b) Simulated dI/dV (0.08 eV below the Dirac point, without inelastic and lifetime effects) as a function of distance away from an RPA-screened Coulomb potential on n-doped graphene.



**FIGURE S5.** Local density of states as a function of distance calculated via density functional theory. (a) Simulated dI/dV (0.1 eV above the Dirac point) as a function of distance away from a Ca atom on p-doped graphene for different carrier densities. (b) Simulated dI/dV (0.1 eV below the Dirac point) as a function of distance away from a Ca atom on n-doped graphene for different carrier densities.



**FIGURE S6.** Local density of states with and without the screened Coulomb potential. The dotted line is the LDOS of pristine graphene. The red curve is the simulated LDOS of nearly neutral graphene at a distance 1.3 nm away from a screened Coulomb potential. The green curve is the LDOS of pristine graphene shifted by the value of the screened Coulomb potential at 1.3 nm.



**FIGURE S7.** STM topographic image of calcium atoms on graphene/BN. A dark depression is seen in the lower right region.



**FIGURE S8**. Inverse square of the decay length versus gate voltage  $V_g$ . Figures 3d-e in the main text show experimental and theoretical dI/dV as a function of distance from a charged impurity. These experimental and theoretical curves were fit to an exponentially decaying function. The black dots represent the inverse square of the decay length extracted from the experimental curves. The red dots are the same for the theoretical curves.