

Supporting Information for

Conductive Thin Films of Pristine Graphene by Solvent Interface Trapping

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SIMULATION DETAILS

We performed molecular dynamics simulations of adsorption of graphene at water/heptane interface. The Generalized Amber Force Field (GAFF)¹ parameters were used for atomistic models of solvents (see Figure SI1) and graphene. The partial charge distributions for heptane were obtained by performing *ab-initio* calculations using the Gaussian 09 (G09) simulation package³ with 6-31G(d) basis set and B3LYP DFT

method. For water we used TIP3P force field potentials².

$$U_{TOTAL} = \sum_{BONDS} K_r (r - r_{eq})^2 + \sum_{ANGLES} K_\theta (\theta - \theta_{eq})^2 + \sum_{DIHEDRALS} \frac{V_n}{2} [1 + \cos(n\phi - \gamma)] + \sum_{IMPROPER} K_\chi (\chi - \chi_{eq})^2 + \sum_{i < j} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} + \frac{q_i q_j}{\epsilon R_{ij}} \right] \quad (1)$$

The total potential energy of the system consisted of the bonded, bond angle, dihedral angle, improper angle and non-bonded interaction potentials. The interaction parameters for the van der Waals potential between heterogeneous atomic pairs were calculated as the geometric mean of the interaction parameters for each atom. The default AMBER force field weighing coefficients for pair-wise energy and force contributions were used to account for contributions from the van der Waals and electrostatic interactions.

The simulation box was built by using Chem3D⁴, G09, Antechamber⁵ and AMBER2LAMMPS python script that is included with LAMMPS⁶. The G09 input file for the heptane molecule was built in Chem3D, then G09 calculations were performed. The Gaussian output from the calculation was used as an input for Antechamber to determine charges, atom type, bond type, angle and dihedral type assignments.

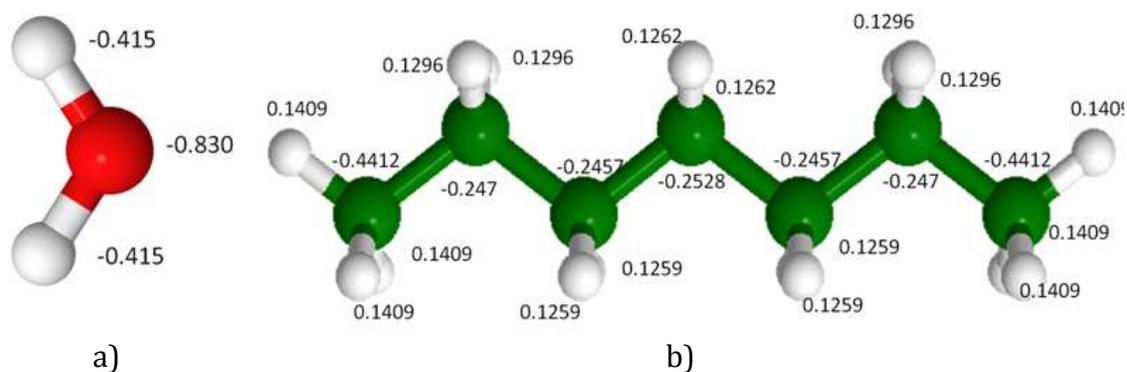


Figure SI1 Partial charge distributions used in simulations of water (a) and heptane (b). The water charges were obtained from Price and Brooks.⁽²⁾ Charges for heptane were obtained by using Mulliken population analysis from *ab initio* calculations with 6-31G(d) basis set and B3LYP DFT method.

The AMBER topology file was created by using LEAP that was included in the Antechamber package. The AMBER topology file was converted into a LAMMPS data file using the python script AMBER2LAMMPS. Using output of the AMBER2LAMMPS script as a template, the solvent molecule was replicated and distributed in the simulation box using in-house code.

Table 1 Studied Systems

| System | $L_x(\text{\AA})$ | $L_y(\text{\AA})$ | $\langle L_z \rangle (\text{\AA})$ | #Carbon | #Water | #Heptane | Total |
|-----------|-------------------|-------------------|------------------------------------|---------|--------|----------|--------|
| Solvent | 92.1 | 85.08 | 80.97 | 0 | 10000 | 1280 | 59440 |
| 1-Sheet | 92.1 | 85.08 | 81.27 | 348 | 10000 | 1280 | 59872 |
| 2- Sheets | 92.1 | 85.08 | 81.71 | 768 | 10000 | 1280 | 60304 |
| 4- Sheets | 92.1 | 85.08 | 82.58 | 1536 | 10000 | 1280 | 61168 |
| 8- Sheets | 92.1 | 85.08 | 84.20 | 3072 | 10000 | 1280 | 62896 |
| 9- Sheets | 128.94 | 122.3 | 121.29 | 3420 | 41184 | 2576 | 186688 |

Graphene flakes were modeled by G8 coronene-like molecules consisting of eight generations of carbon rings and terminated by the hydrogen (see Figure SI2). The partial charges of the coronene molecule were obtained from the Mulliken population analysis from *ab initio* calculations using G09 with 6-31G(d) basis set and B3LYP DFT method without geometry optimization.

The NPT ensemble simulations were performed using GPU accelerated LAMMPS code⁶
⁷. The equations of motion were integrated by using the velocity Verlet algorithm with a time step 1.0 fs. The system was periodic in x, y and z directions. The standard PPPM⁸

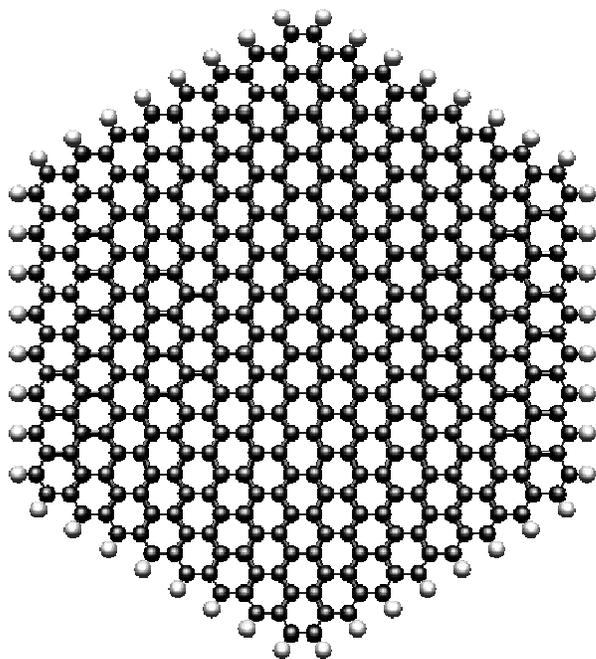


Figure SI2 Generation eight (G8) coronene-like molecule $C_{384}H_{48}$. Carbon atoms are shown in black and hydrogen atoms are colored in light grey.

method with accuracy 1.0×10^{-5} and the near-field cutoff set to 10.0 Å was used to account for contributions from the long-range electrostatic interactions. The graphene

flakes were placed at the interface between two solvents. Solvent molecules were distributed over the volume of the simulation box. The simulation box sizes and the number of atoms in a system are given in Table 1. The system was equilibrated for 3.25 ns to achieve the equilibrium box volume, average system pressure (1 atm) and temperature 300K. A Nose-Hoover thermostat and barostat with relaxation time 0.1 ps and 1.0 ps respectively were used to maintain temperature and pressure in the system. The Nose-Hoover barostat was applied along the z-direction only. During the first 0.25 ns of the equilibration run the location of the atoms belonging to graphene flakes were fixed, and the simulation box was allowed to stabilize, then all constraints were removed. Then NPT simulations were run for 3 ns allowing the system to equilibrate with no constraints. NPT simulations were followed by NVT simulations with a Nose-Hoover thermostat. These simulations lasted 3 ns during which the data were collected (production run). For the 9-sheet system the NPT simulation was run for 6.25 ns and data was collected over the final three ns, no NVT steps were used.

Number fraction distribution in different water/heptane systems is shown in Figure SI3. In our simulations, the number fraction is obtained by binning the system in the z-axis, with a height of 0.1 Å, and assigning any atoms within this box to their molecule. The number fraction was then calculated by averaging the number of atoms corresponding to water, heptane and graphene to the total number of atoms

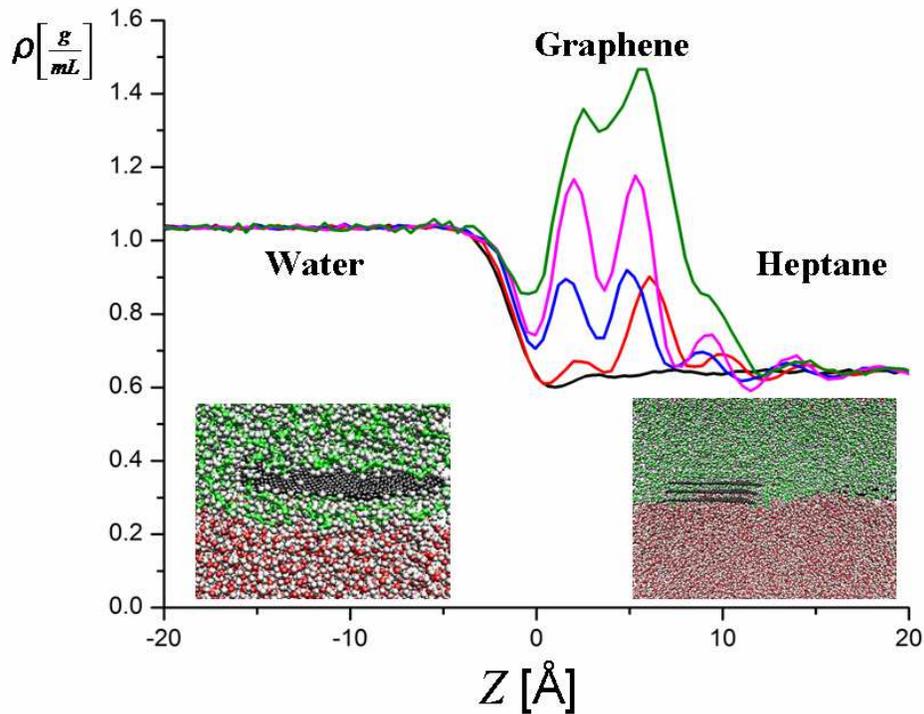


Figure SI3 Density distribution in simulation box along z-axis for water/heptane (black line), water/heptane/graphene flake (red line), water/heptane/2 graphene flakes (blue line), water/heptane/4 graphene flakes (pink line), and water/heptane/8 graphene flakes (green line) systems. Insets show snapshots of the typical system configurations. In all figures hydrogen atoms are shown in light gray, oxygen atoms are colored in red, carbon atoms belonging to graphene and heptane are shown in black and green respectively.

within the box. It follows from this figure that graphene flakes are preferentially located in the heptane phase. For a single flake system there is a heptane layer covering the flake. For multi flake systems we see two well-developed peaks close to the water/heptane

interface with the first peak located closer to the interface than the main peak in the single flake system. These peaks correspond to location of the graphene flake carbon atoms in two flake graphene aggregates. The magnitude of these peaks increases with increasing the number of flakes, which should not be surprising since number of carbon atoms belonging to aggregates increases as well.

We used Weighted Histogram Analysis Method⁹ to calculate the potential of the Mean Force between a graphene flake and water/heptane interface. These simulations were performed at constant temperature and volume (system sizes are listed in Table 2). The constant temperature was maintained by coupling a system to the Nose-Hoover thermostat with relaxation time 0.1 ps. Initially a graphene flake was located at interface between water and heptane and had configuration taken from our NVT simulations.

Table 2 - Systems used in PMF simulations

| System | $L_x(\text{\AA})$ | $L_y(\text{\AA})$ | $L_z(\text{\AA})$ | #Carbon | #Water | #Heptane | Total |
|---------------|-------------------|-------------------|-------------------|----------------|---------------|-----------------|--------------|
| 1-Sheet | 92.1 | 85.08 | 81.27 | 348 | 10000 | 1280 | 59872 |
| 9-Sheets | 128.94 | 122.3 | 121.29 | 3420 | 41184 | 2576 | 186688 |

In WHAM simulations the z-coordinate of the center of mass of the graphene flake or multi flake aggregate with z-coordinate of the center of mass z^{gr} was tethered to z^* by harmonic springs

$$U_{spring} = \frac{K_{spring}^{(1)}}{2} (z_{cm}^{gr} - z^*)^2 \quad (2)$$

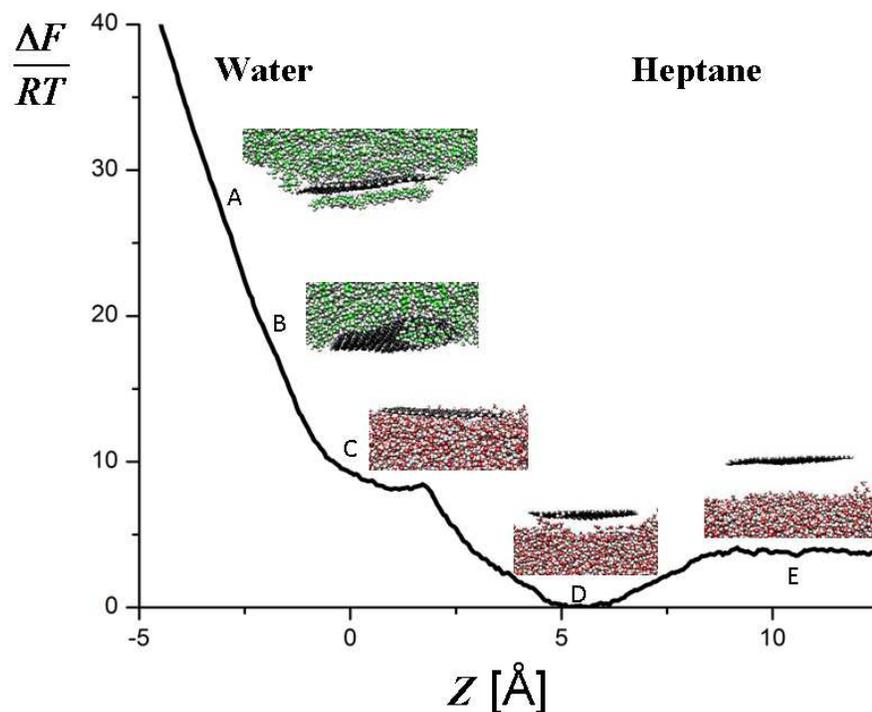


Figure SI4 Potential of the mean force for single graphene flake system. Insets show typical configuration of the graphene flakes. The solvent in which graphene flake is pulled in is transparent.

where the value of the spring constant is $K_{spring}^{(1)} = 250 \text{Kcal/mole}/\text{\AA}^2$. To prevent the solvent interface from moving with the graphene we have tethered the z-coordinate of the center of mass of water molecules z^w at its initial location z_0 . The value of the tethering spring constant was set to $K_{spring}^{(w)} = 750 \text{Kcal/mole}/\text{\AA}^2$. During these simulation runs we varied location of the tethering point z^* of the graphene flake or multi flake aggregate with increment $\Delta z^* = \pm 0.1 \text{\AA}$ until $z^* = \pm 12 \text{\AA}$ is reached in water and heptane phases. For each location of the tethered point the system was equilibrated for a 0.1 ns. The equilibration step was followed by the production run lasting 0.3 ns during which we calculated the distribution of the center of mass location of graphene flake for WHAM calculations of the potential of the mean force.

Figure SI4 shows the potential of the mean-force for single flake system. There is a shallow local minimum at water/heptane. The main minimum is located at about 5.5 Å. The potential saturates when the graphene flake is covered by approximately two layers of the heptane molecules on both sides. Note that the potential of the mean force increases faster with moving a flake into the water phase than into the heptane phase. Therefore the graphene has higher affinity to heptane than to the water. Furthermore graphene flake moves its solvation heptane layer into a water phase deforming the water/heptane interface (see Inset in Figure SI4). □

SI Experimental Details

To prepare graphene films a typical procedure is as follows: 2 mg of bulk pristine graphite was first put into a 20 mL glass scintillation vial. 5.0 mL of n-heptane (Fisher Scientific, HPLC grade) was then added and the system was briefly bath sonicated to break up any large particles. It was then tip sonicated for 15 minutes at 40% power to exfoliate the graphite and disperse it into the heptane. After the sonication, 5 mL of water was added and the system was bath sonicated again briefly to help move the graphene sheets to the interface. The mixture was then tip sonicated with the tip right above the main liquid-liquid interface a second time for 15 minutes at 40% power to further exfoliate the graphene sheets and to distribute the sheets about the interface. After the second tip sonication, the system may be shaken to create emulsion spheres, which upon coalescence generate a film that climbs the walls of the vial, or a slide inserted into the system. This film is very metallic looking.

To transfer the film, using the method above, but before the water dried under the

graphene layer, the slide was dipped into a beaker of water. The film detached from the slide and floated on the top of the water. Depending on the substrate, the film was transferred by either putting it under the water and lifting the film onto it, or pushing the substrate under while near the film.

Using a Renishaw 2000 Raman Spectrometer, we analyzed the 2D peak of the graphene in the film. This shows us how many layers of graphene make up the film:

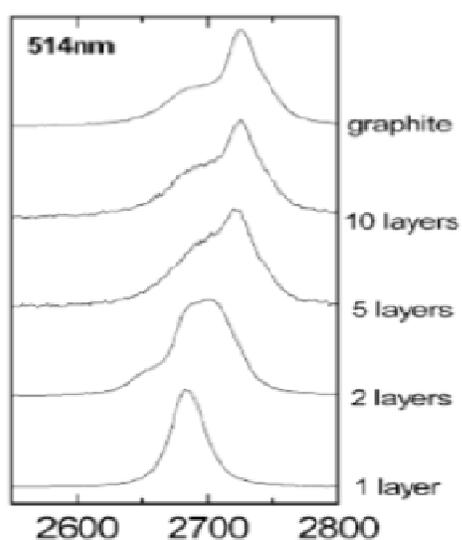


Figure SI5. Evolution of Raman spectra at 514 nm with the number of layers.¹⁰

Transparency was determined using a Cary 5000 UV-VIS-NIR Spectrophotometer. The film was created using the above method with graphite (Asbury Carbons grade 2299). The slide with the film on it was then taken out of the vial to dry, with some aggregation of the film occurring as the heptane evaporated.

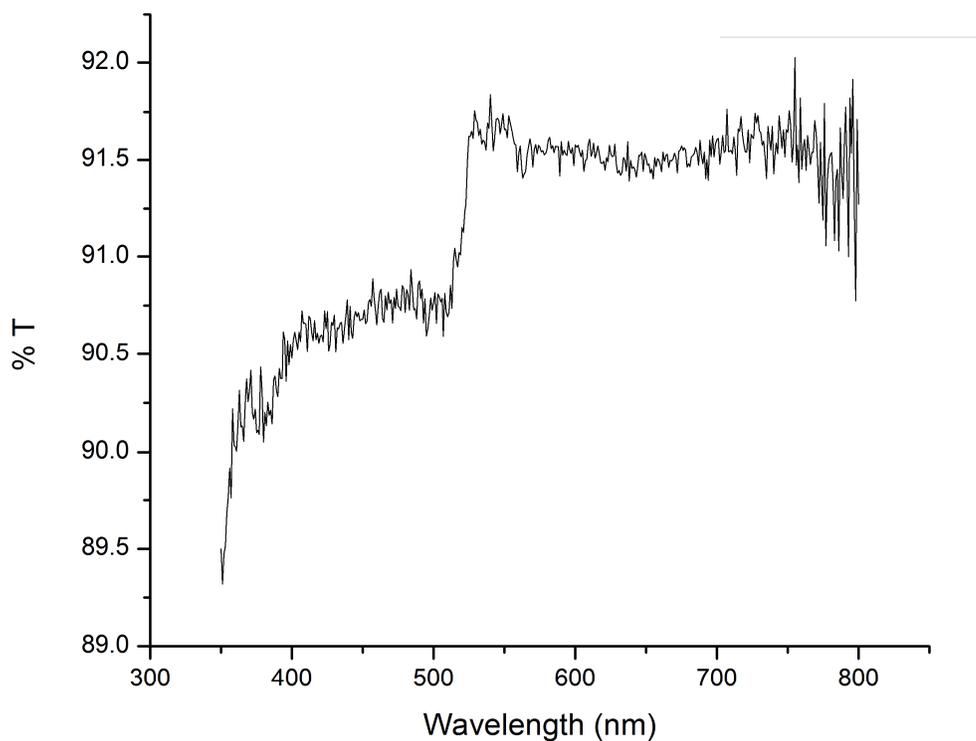


Figure SI6: UV-VIS spectrum of the glass slide used as a substrate for our films.

FESEM images were obtained using a JEOL JSM 6335F FESEM.

TEM images were obtained using a Tecnai T12 TEM, we were able to confirm the average size of the sheets, as well as determine the percent coverage of the film through image analysis to be 82%. An example of a TEM image used to determine surface coverage is shown in SI7.

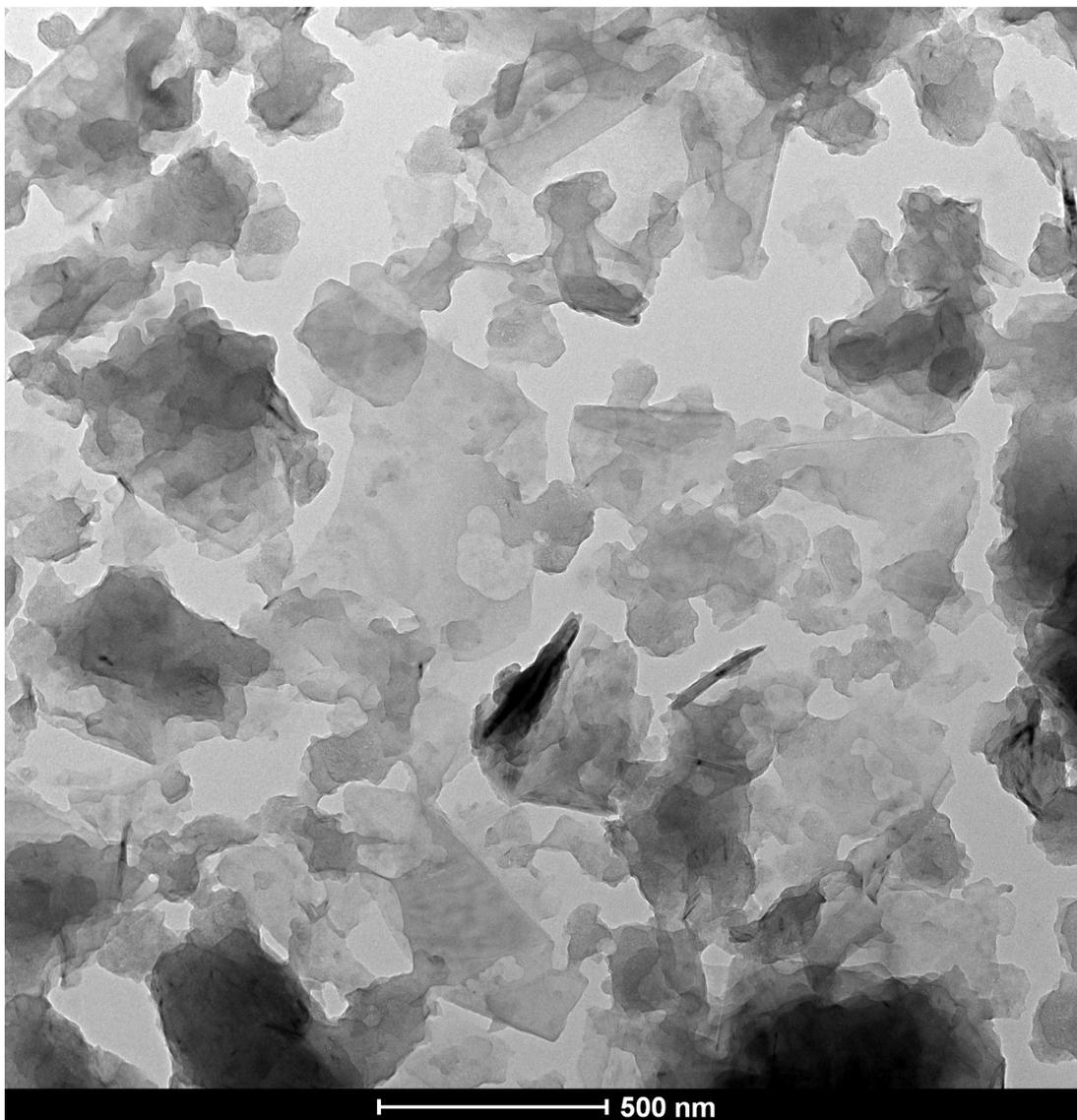


Figure S17. TEM image of typical graphene film.

A typical conductivity measurement was made as follows: a graphene film was formed on a glass slide with graphite (Asbury Carbons grade 3243) using the above methods. Four strips of copper tape were placed on the film with 1 cm spaces in between to form a 4-point probe. The conductivity was then measured using a Keithly Model 2420 SourceMeter.

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