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Electronic Supplementary Information for:

Graphene Exfoliation using Multidomain Peptides

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General simulation details: All simulations were performed using Gromacs software package (version 2021.4)[1]. For the exfoliation simulations using BEAM molecules, nine identical hexagonal-shape graphene flakes (with diameter approx. 7.5nm) were placed in a vertically-stacked arrangement with the same lateral orientation. Each sheet comprised 1632 atoms (1536 carbon atoms and 96 hydrogen atoms terminating the flake edges). Non-edge carbon atoms were charge neutral, and the edge (under-coordinated) carbon atoms and hydrogen atoms carried a partial charge of 0.115 *e* and -0.115 *e* respectively. The flake at the bottom of the stack was frozen in all three dimensions for mimicking the surface rigidity of graphite at sub-nm depth. The remaining eight flakes were free to move during simulations. ABA stacking was quickly achieved within the first ~50 ps of simulation. The very top graphene flake in the stack was vertically separated (in the *z*-direction) from the remaining eight sheets by a center-to-center distance of ~9.9Å. The introduction of this gap mimics the expected partial expansion of the inter-flake separation at the surface of graphite under experimental ultra-sonication conditions.

Six BEAM molecules were used. For spontaneous insertion simulations, four of the six BEAM molecules were placed around the gap at outside, parallel to the edge of graphene sheets, and the other two were placed at the top of lifted graphene sheet. For pre-insertion simulations, all six peptide domains (P1 or BP7) were placed inside of the gap at the begin of simulations. Ten independent replica simulations, using different (and random selected) initial velocities, were run for a maximum of 150ns for each scenario.

The forcefields used were the CHARMM22* forcefield[2,3], with adaptations for the maleimide group and the F_{10} fatty acid group were taken from previous work[4]. The simulation cell dimensions were set as 22×22×10 nm and 15×15×12 nm for spontaneous-insertion and pre-insertion simulations respectively (description of these herein). The expanded graphene stack system was fully solvated by TIPS3P water[5] molecules in the non-occupied space, resulting in a total number of water molecules of ~152000 and ~82000 respectively. Chloride counter-ions were added to neutralize the positive charge carried by the peptides. Each system was first subjected to a steepest-decent energy minimization with a tolerance of 1000 kJ mol^{-1} nm^{-1}, then a 500 ps equilibration at temperature of 50 K was applied with all non-water atoms fixed in space to allow the water molecules to be equilibrated, such that the waters had especially settled around the BEAMs and in the expanded gap region. For pre-insertion simulations using the BP7 molecules, the smaller size of graphene sheets (with diameter of approx. 4.7nm) were used, and the simulation cell size was correspondingly decreased to 9.9×9.9×9.9 nm.

All simulations were performed in the *NVT* ensemble at 340 K, using the Nose-Hoover thermostat[6,7]. The leap-frog algorithm[8] was used to integrate the equations of motion using a timestep of 1 fs. During the production MD simulations, the system temperature was gradually raised, ramping from 50 K to 340 K in the first 12 ns to minimize artifacts caused by directly simulating systems at an elevated temperature. All runs were of a maximum duration of 150 ns for both pre-insertion and spontaneous-insertion simulations. Long-ranged Lennard-Jones interactions were smoothly tapered to zero from 11-12 Å, and a particle mesh Ewald cutoff of 12 Å was used for long-range electrostatic interactions[9].

BEAM-decorated graphene reunification simulation details: Two identical BEAM-decorated graphene sheets (12 BEAMs per graphene sheet, 6 BEAMs per side) were arranged face-to-face along the z-axis (perpendicular to the graphene plane), where the distance between the two central rings of the graphene sheets was 5.5nm. This meant the closest atom-to-atom vertical distance between the two BEAM-decorated sheet complexes (including the peptides) was around 2.5nm. The complex on the top was defined to have 'surface B' facing towards 'surface A' of the bottom complex. The whole system was placed in an orthogonal simulation cell with dimensions 12×12×12 nm. Approximately 52000 TIPS3P water molecules were added to the simulation cell and chloride ions were added to neutralize the charge carried by the BEAMs. The whole system was subjected to steep-descent energy minimization and a 500ps *NVT* equilibration in which the carbon atoms of the graphene sheets were fixed in space to allow the water and peptides to relax. These carbon atoms were then freed for subsequent steps. All simulations were carried out at 300 K to mimic post-sonication conditions.

To construct the geometries for the umbrella sampling along the reaction coordinate (the vertical inter-sheet distance), steered pulling MD simulations were used in the z-direction, to drag the two complexes closer. The pulling geometry was direction-periodic, with a harmonic force constant imposed during umbrella pulling of 10000 kJ mol^{-1} nm^{-2}, and the pulling rate was 1 Å ns^{-1}. The vector that guided the pulling direction was (0, 0, -1). Positional restraints were applied to the bottom graphene sheet in 3D space during the pulling simulations. The umbrella potentials were applied onto 7 pairs of atoms, the reference group of atoms was formed by the six central ring atoms of the bottom graphene sheet, and the 7 pulled groups of atoms were defined as the central ring atoms of the top graphene sheet, and six corner atoms of the top graphene sheet. Such 7 pairs of pulling groups guaranteed that the orientation of the top graphene sheet could be maintained parallel to the bottom sheet. The cylinder flat-bottom position restraint in the z-direction was applied onto the 7 moving groups. The initial configurations were distributed equally along the reaction coordinate in the z-direction, and were extracted from the 60ns-long pulling trajectory. Those restraints were removed after the steered pulling MD simulations, to allow efficient contact between the two complexes during the umbrella sampling.

A total 105 configurations were used in the subsequent umbrella sampling simulations to sample the conformation space covered by the selected reaction coordinate with the same interval of 0.5 Å. Each umbrella sampling window was simulated for 100ns, and the accumulated length of the umbrella sampling simulation was 10.5 μs in total. The Weighted Histogram Analysis Method (WHAM) was used in GROMACS (gmx wham)[10] to calculate the free energy profile along each reaction coordinate, in which the random trajectories bootstrap method was used, with a total number of bootstraps set to 100.

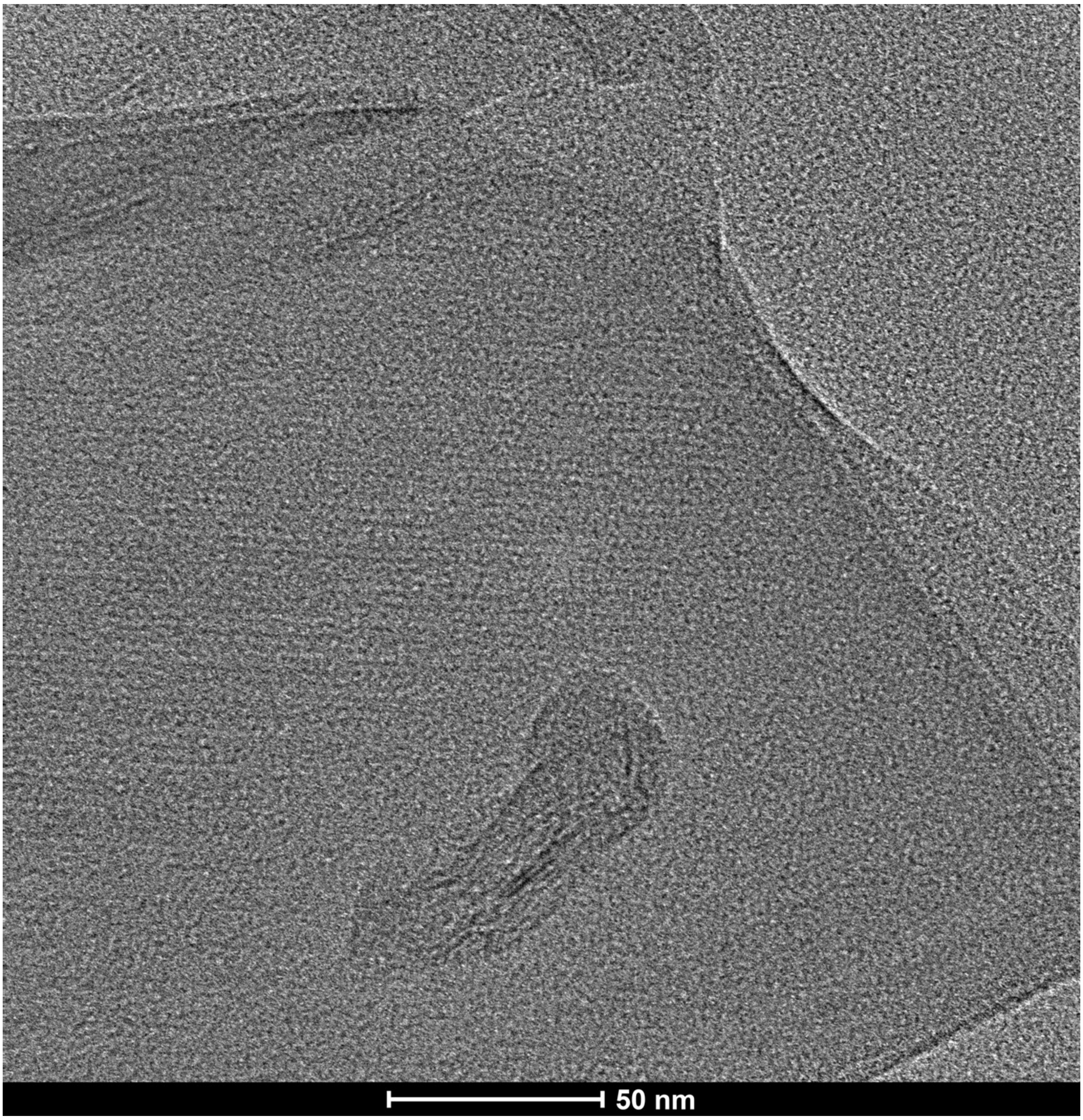

Figure S1. High-resolution TEM image of the BEAM-exfoliated graphene materials.

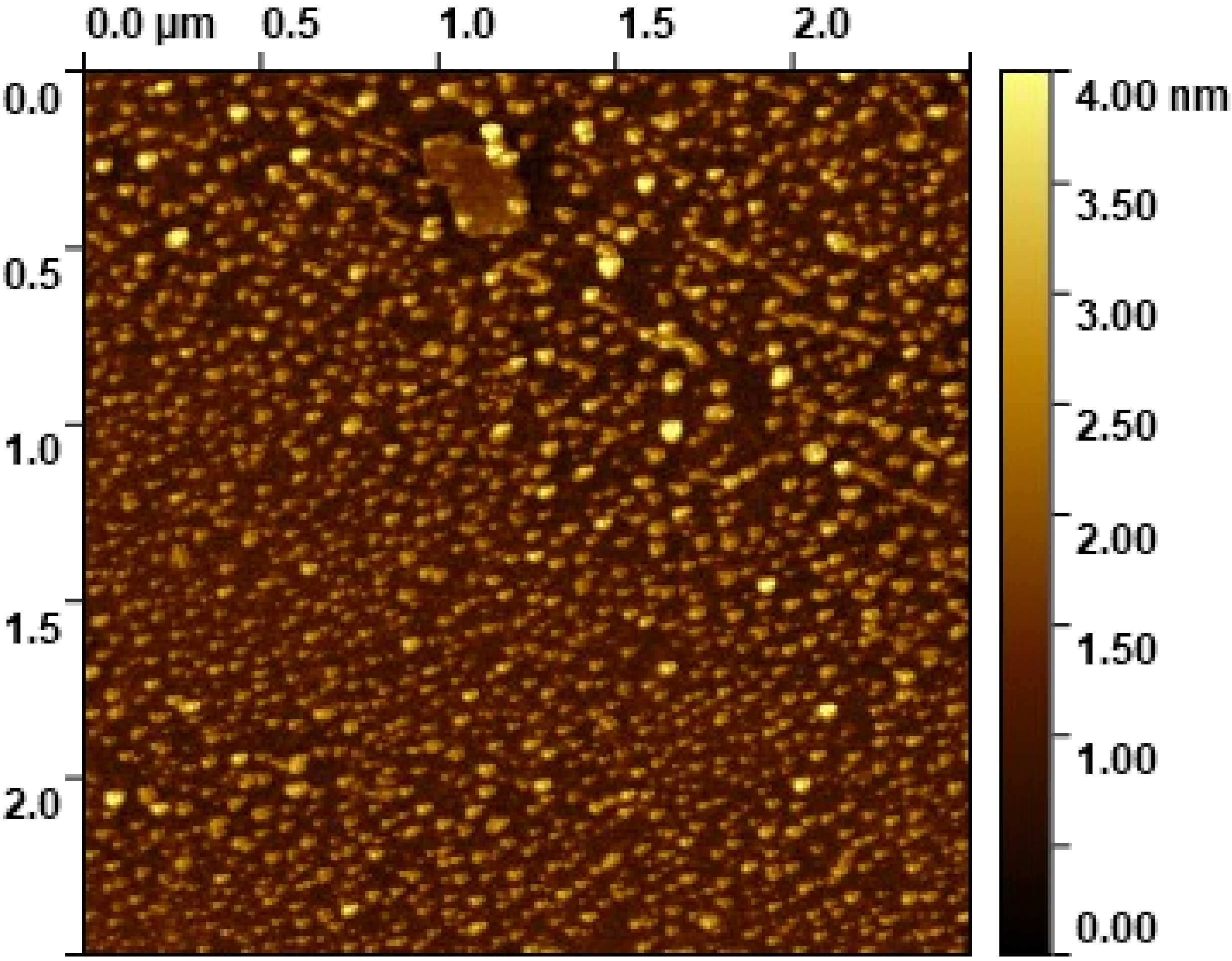

Figure S2. Zoomed in AFM image of the BEAM-exfoliated graphene sheets.

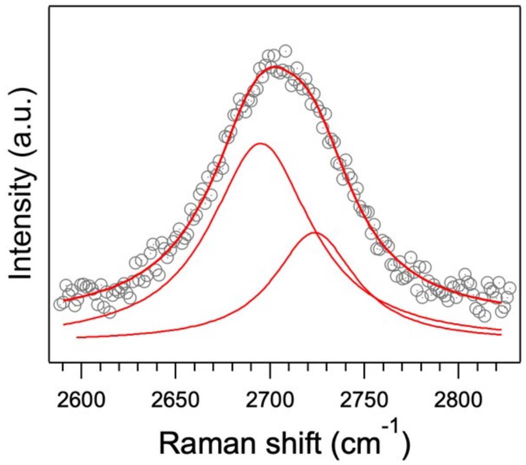

Figure S3. Lorentzian lineshape analysis of the graphene 2D band for the BEAM exfoliated graphene sheets. The 2D peak can be deconvoluted into two Lorentzian peaks, as expected for few (less than 5) layers of graphene.[11]

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