Dynamics of a Water Nanodrop Through a Holey Graphene Matrix: Role of Surface Functionalization, Capillarity, and Applied Forcing: Supporting Information

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System description

We carefully choose a quasi-2D geometry as described in the previous studies[1] to eliminate the tremendous line tension effect on the observed drop contact angle (θ) and the resulting wetting effects, which are critical to probe the nanodroplet-HGA interactions.

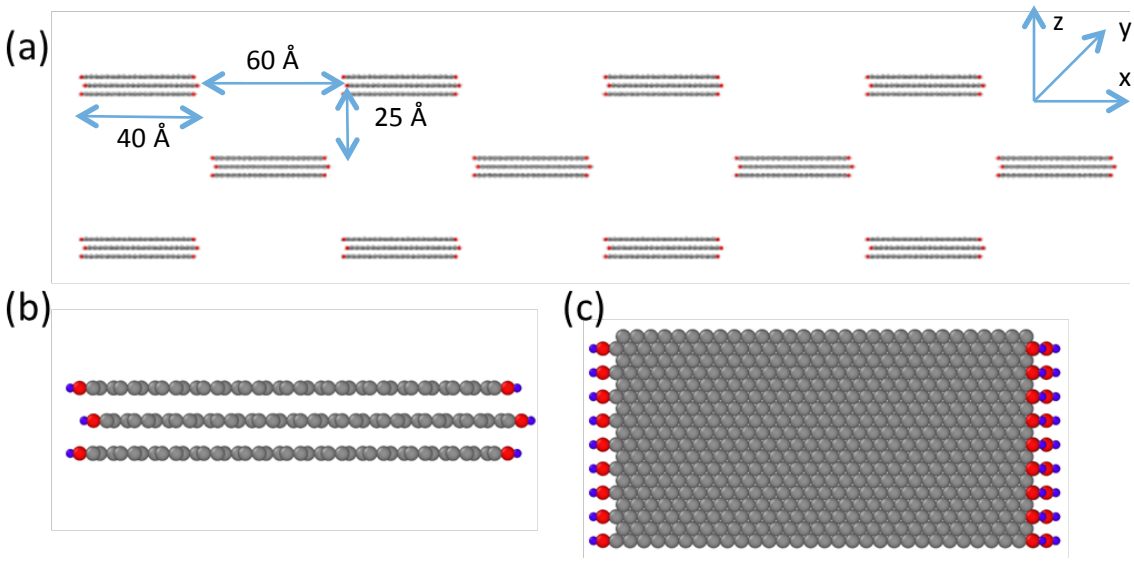

Figure S1. *(a) Side view of the holey graphene matrix with hydroxyl terminations. Magnified (b) side and (c) top view of a representative of holey graphene sheets in between the two holes.*

Accordingly, the simulation box is set as 450 Å in x-axis direction, 20 Å in y-axis direction and 500 Å in z-axis direction. Periodic boundary condition is applied to all directions. Each stack of the graphene matrix (three layers graphene with 40 Å in length and 20 Å in width) represents the graphene sheets in between two holes, and the diameter of the holes are set as 60 Å (see Fig. S1).

The vertical inter-stack separation between two holey graphene stacks is set as 25 Å. The holes (reflected as the lateral ISSs) are created by removing the C atoms; consequently both the edges of the graphene sheets have a zigzag shape ending with hydrogen (-H functionalization) or hydroxyl (-OH functionalization) terminations. The hole diameter and interlayer distance is selected by following the current experimental result, where the hole diameters mostly appear around 5 nm (Ref. 2) and interlayer distance can be tuned in a range of 0.5-7 nm (Ref. 3). Fig. S1 provides a detailed view of the HG matrix.

Simulation model

Simulations have been carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software package. Water has been modeled using the Tip4p/2005 model.[4] This model allows accounting for the dipole-dipole interactions between water molecules and the partly charged terminations. Furthermore, in this model, the non-bonded interactions between distinct species (which are water molecules, C atoms, and the functionalization groups) consists of the Lennard–Jones(LJ) 12-6 potential (with a cut off distance of 10 angstroms) and columbic interaction. The parameters are calculated through Lorentz-Berthelot mixing rules[5] and summarized in Table S1. The carbon atoms in the graphene are fixed at their initial position, as there is no significant impact of graphene flexibility on the wetting behavior. Finally, in this model we incorporate the CHARMM36 force field potential file[6] into the LAMMPS for attributing the inner molecular interaction of hydroxyl terminations, which contains C-O and O-H bonds, C-O-H and C-C-O angles, and C-C-O-H dihedral motions. For hydrogen terminations, the C-H bond is set as fixed.

Table S1: *LJ and charge parameters used in the simulations*

Elements	**ε(kcal/mol)**	**σ (Å)**	**q(e)**
C(sp2)	0.0859	3.3997	0
C_{COH}	0.0703	3.55	0.2
H_{COH}	0	0	0.44
O_{COH}	0.155	3.07	-0.64
C_{CH}	0.046	2.985	-0.155
H_{CH}	0.0301	2.42	0.115
H_w	0	0	0.5242
O_w	0.16275	3.16435	-1.0484

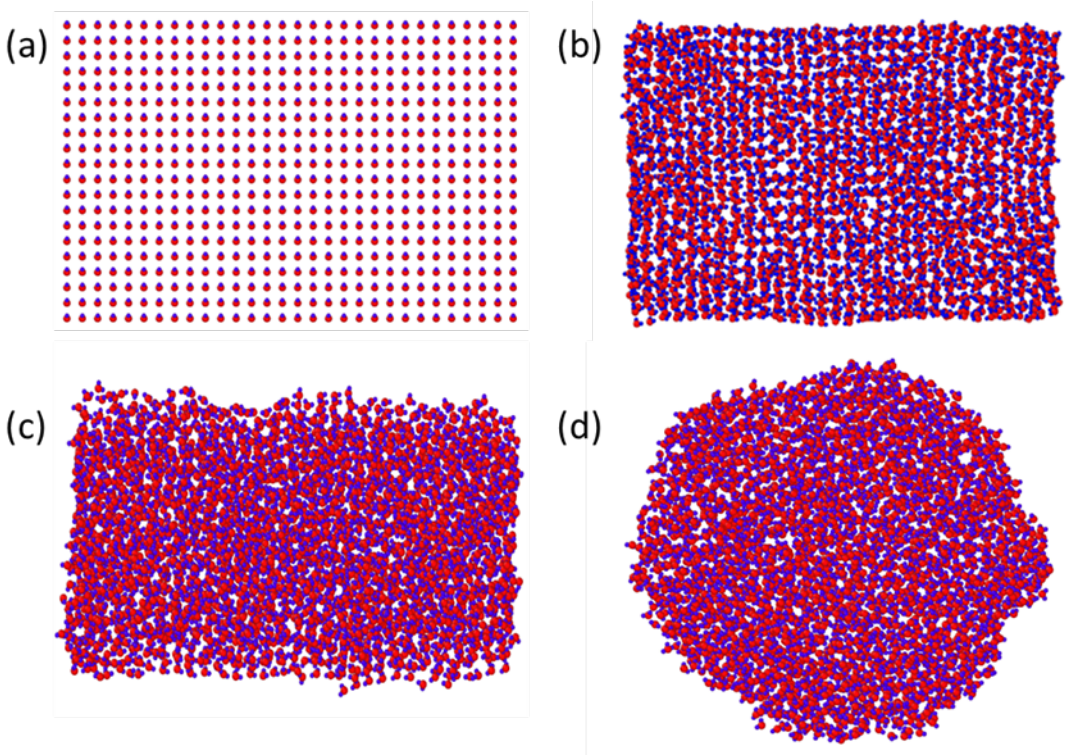

Figure S2. *(a) Side view of 3000 water molecules at their initial position at 0k. (b) 50k. (c) 150k. (d) 300k.*

Performing simulation

All simulations are performed on a canonical ensemble (NVT) with temperature controlled by a Nose´–Hoover thermostat at 300 K. The time step is 1 fs. The simulations start by equilibrating water drops significantly away from the HG matrix. This will ensure that we consider the interaction between a water nanodrop and a HG (and not "bulk-water"-nanoporous-graphene interaction). In Fig. S2, we show the equilibration process. 3000 water molecules (this number of water molecules leads to a drop of 6.5 nm diameter) transfer from solid phase to liquid phase by when the system temperature is increased from 1K to 300K in 50K increments. All the intermediate temperatures are held constant for 50 ps and the final 300K is kept constant for 200 ps to ensure that the equilibrium phase has been achieved.

Post equilibrium, a force (~Kcal/mol- Å) is applied to every individual water molecule in the drop in order to make the drop permeate across the HGA (a representative snapshot is shown in Fig. S3). We use a large simulation box as compared to the water droplet size to ensure that the drop is not affected by its neighbors. As a result, only a small area (140 × 20 $Å^2$, see Fig. S3) of the matrix interacts with water and we use this area information to convert the applied force to a pressure (for the present dimensions, where *F* and pressure are linearly related, F=1 kcal/mol Å is equivalent to a pressure of 22 GPa), which helps the results to tally better with the experiments.

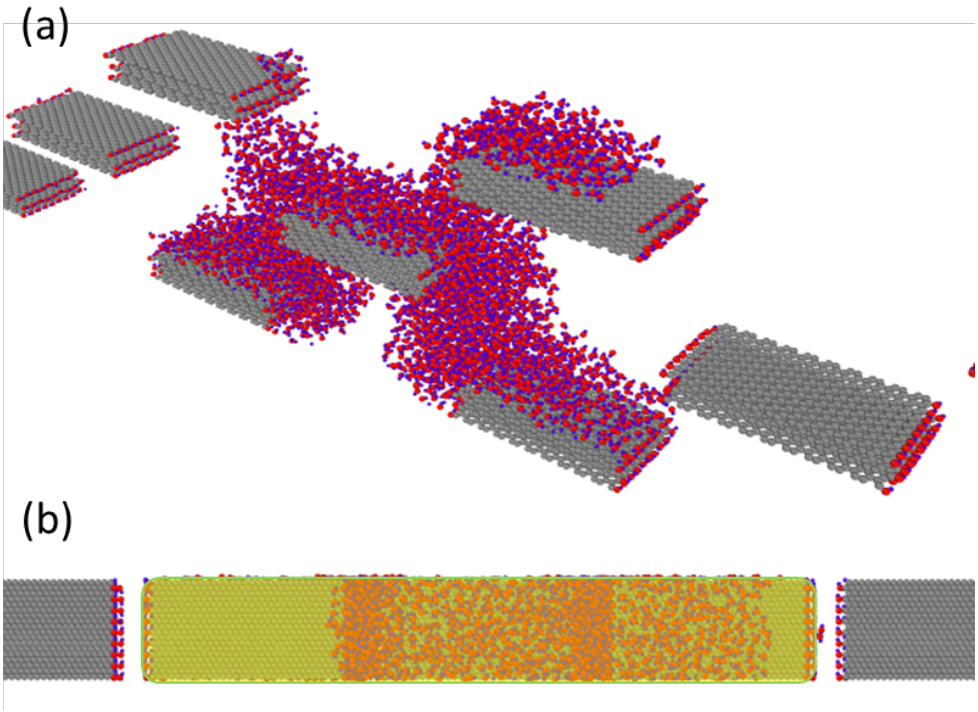

Figure S3. *(a) Perspective view of the water molecules permeating the holey graphene matrix at 300k. (b) Top view of the matrix with the equivalent pressure calculation zone highlighted.*

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