Supporting information for "Formation of water layer on graphene surfaces"

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1 Simulation boxes

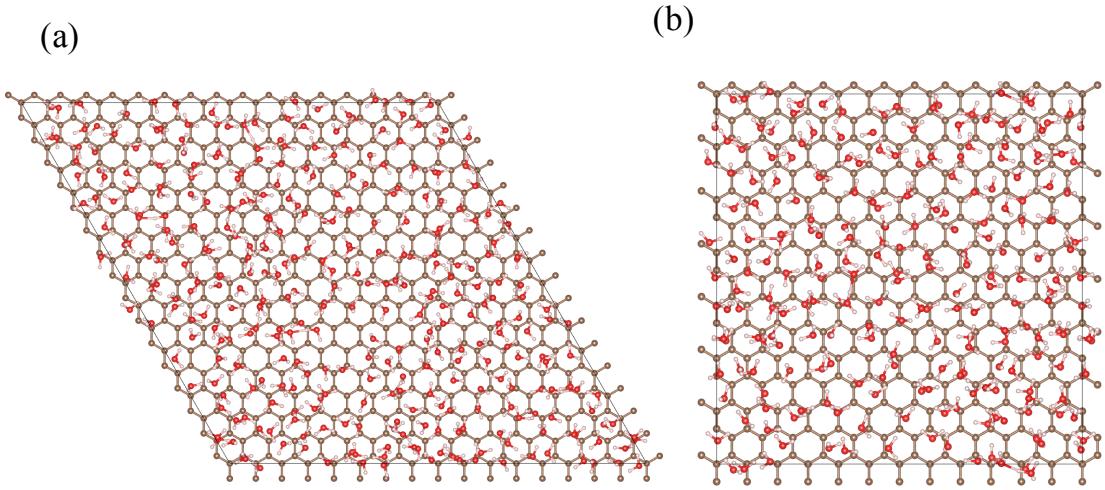

Figure S1: Snapshots of simulations with periodic boundary conditions of (a) (16×16) and (b) (12×7$\sqrt{3}$) graphene supercell box.

In order to examine the effect of the periodic boundaries, we have carried out molecular dynamics simulations by changing the box size of the boundary. Figure S1 shows a top view of simulation snapshots with rhombic and square simulation boxes. We used (16×16)), (24×24), (32×32), (40×40), (48×48), (64×64), (12×7$\sqrt{3}$), (24×14$\sqrt{3}$), (36×21$\sqrt{3}$), and (48×28$\sqrt{3}$) graphene supercells. The number of water molecules in each simulation box is listed in Table S1.

Table S1: Number of water molecules

	(16×16)	(24×24)	(32×32)	(40×40)	(48×48)	(64×64)
$L = 2.13$	320	720	1280	2000	2880	5120
$L = 2.56$	384	864	1536	2400	3456	–
	(12×7$\sqrt{3}$)	(24×14$\sqrt{3}$)	(36×21$\sqrt{3}$)	(48×28$\sqrt{3}$)		
$L = 2.13$	210	840	1890	3360		
$L = 2.56$	252	1008	2268	4032		

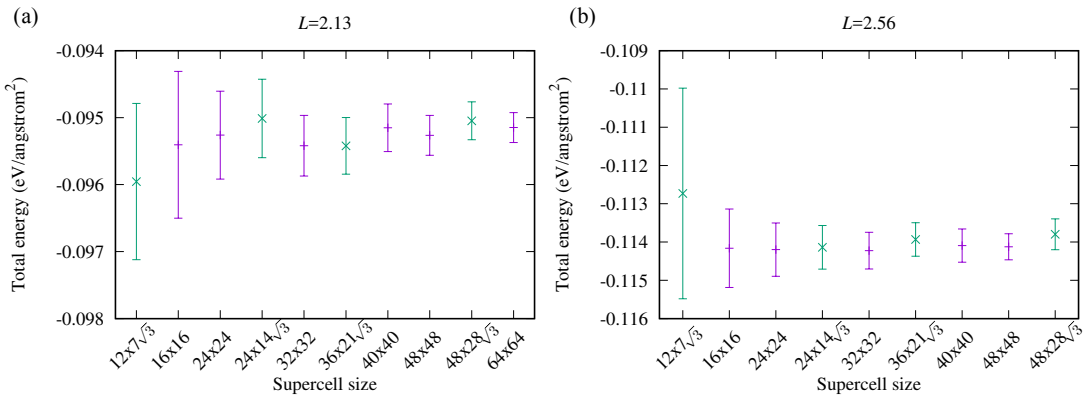

Figure S2: Total energy per area for different simulation boxes.

2 Energy per area

In order to evaluate the effect of the periodic boundary condition, we compare the total energies for difference sizes of simulations boxes. Indeed, the use of small simulation boxes gives rise to the mismatch between graphene lattice and the water structure that may manifest configurational errors. Figure S2 shows the total energy per area for different simulation boxes. Except for (12x14), the average value of total energy is almost the same, meaning that the effect of water interactions across simulations boxes is enough small.

3 Clustered and Layered structures

To evaluate the stability of the double layer structure, we have carried our simulations with different initial configurations of water molecules. Figure S3 (a) shows a snapshot of the simulations, where a water droplet is placed on graphene surfaces. For the other initial configuration, water molecules are put as a double layer on the surface as shown in Fig. S3 (b). In our simulations, both structures are stable and are not transformed into each other at room temperature. However, by comparing their total energies, as shown in Fig. S2 (c), it turns out that the layered structure is more stable. We presume that the nanocluster formation is metastable.

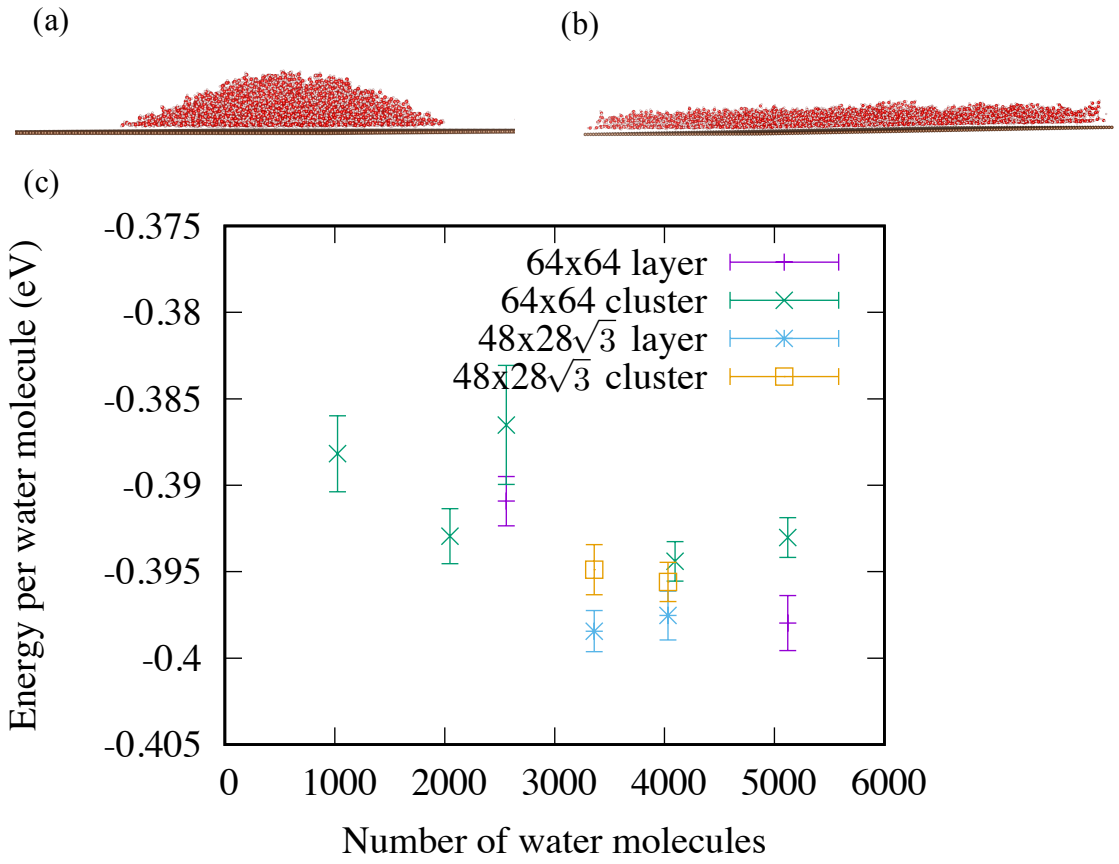

Figure S3: (a,b) Snapshots of MD simulations with the boundary condition of a (64x64) graphene supercell. Initial configurations of water molecules are (a) a nanocluster on graphene and (b) a layered structure. (c) Total energies per water molecule as a function of the number of water molecules for each initial condition.