Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Unexpected Hydrophobicity on Self-Assembled Monolayers Terminated with Two Hydrophilic Hydroxyl Groups

PS1. Literatures of experimental values of contact angles of water droplets on OH-SAMs

Table S1. Literatures of experimental values of contact angles of water droplets on OH-SAMs

Contact angle (°)	Contact angle (°)	Contact angle (°)	Contact angle (°)
(θ^a)<10 [1]	(θ^a)20±2, (θ^r)11±3 [2]	~20 [3]	31.9±3.6 [4]
(θ^a)<15 [5]	(θ^a)25±2, (θ^r)20±2 [6]	22.9±3.0 [7]	32 [8]
(θ^a)10, (θ^r)<10 [9]	(θ^a)28±4, (θ^r)19±4 [10]	24.8±1.5 [11]	(θ^a)~36,(θ^r)~26 [12]
<10 [13]	18±1.7 [14]	25±3 [15]	34±0.9 [16]
(θ^a)<15 [17]	18.1±1.6 [18]	25 [19]	38.2±0.32 [20]
<15 [21]	(θ^a)~20 [22]	25 [23]	44±2 [24]
~0 [25]	16 [26]	25.2±1.6 [27]	4.6±1.6 [28]
17±2.6 [29]	29±3 [30]	12±3 [31]	17 [32]
29.0±0.6 [33]	13.5±0.5 [34]	17.6±1.9 [35]	29.4±1.6 [36]
(θ^a) 16, (θ^r)<5 [37]	19 [38]	31 [39]	

PS2. Snapshots of water covered on $(OH)_2$-SAM at Σ = 2.0 nm^{-2} and 6.5 nm^{-2}

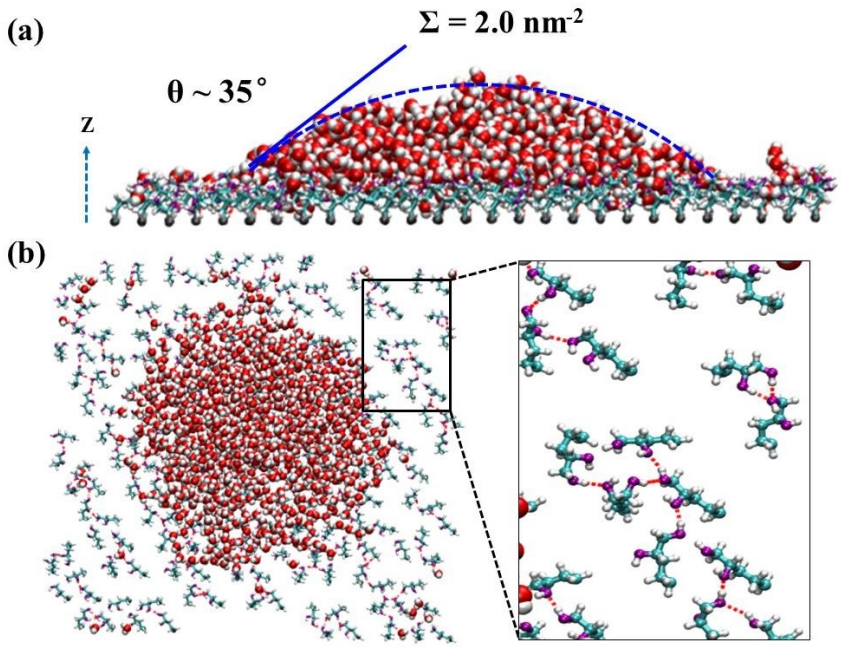

Fig S1. (a) Side view snapshot of water droplet on $(OH)_2$-SAM at Σ = 2.0 nm^{-2}, (b) together with top view and its partial enlargement where OH groups prefer to form localized cyclic H-bonding structures with some exposure of the hydrophobic tails. Atom representations and color settings are as in Fig 1.

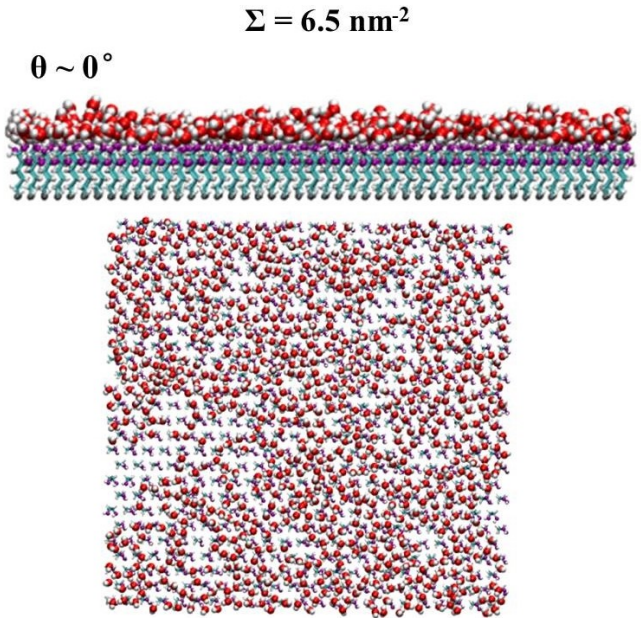

Fig S2. Side view snapshot of water covered on $(OH)_2$-SAM at Σ = 6.5 nm^{-2} together with top view on the bottom. Atom representations and color settings are as in Fig 1.

PS3. Method to compute the contact angles

The first water layer (0.35nm) above the $(OH)_2$-SAM is not considered. The number densities of water molecules in the droplets are estimated by cuboid lattices with dimensions of 0.05 × 0.05 × 0.6 nm^3. Half of the number density of bulk water is used to estimate that of the vapor-liquid boundary. The contact angles of water droplets are determined by fitting the number density distribution curves of the vapor-liquid boundary to a circle.

PS4. The interaction energies between water molecules outside of the droplets and $(OH)_2$-SAM

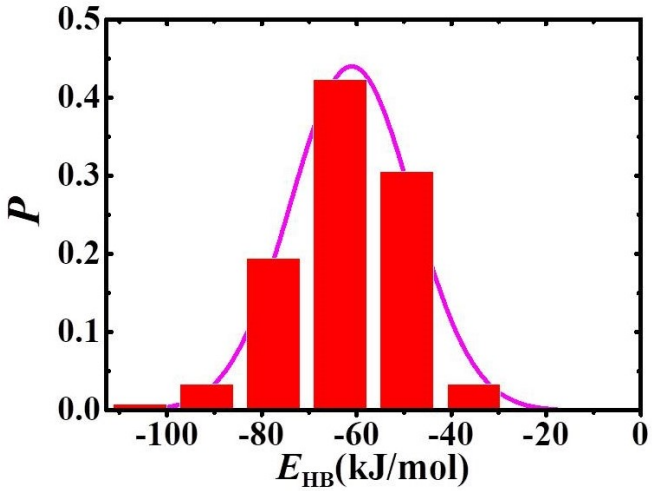

Fig S3. The energies distributions between water molecules and $(OH)_2$-SAM outside of the droplets at Σ = 3.25 nm^{-2}.

PS5. The calculation method of H-bond lifetimes

In this work, the H-bond lifetimes are characterized by the hydrogen bond autocorrelation function

$$C(t) = \frac{\langle h(0)h(t)\rangle}{\langle h(0)h(0)\rangle}$$

where $h(t)$ = 1 if the tagged pair of atoms are continuously bonded from time 0 to time t, and $h(t)$ = 0 otherwise. And $C(t)$ describes the probability a pair of atoms being bonded at time 0 and still bonded at time t.

PS6. The dependence of the contact angle on drop size

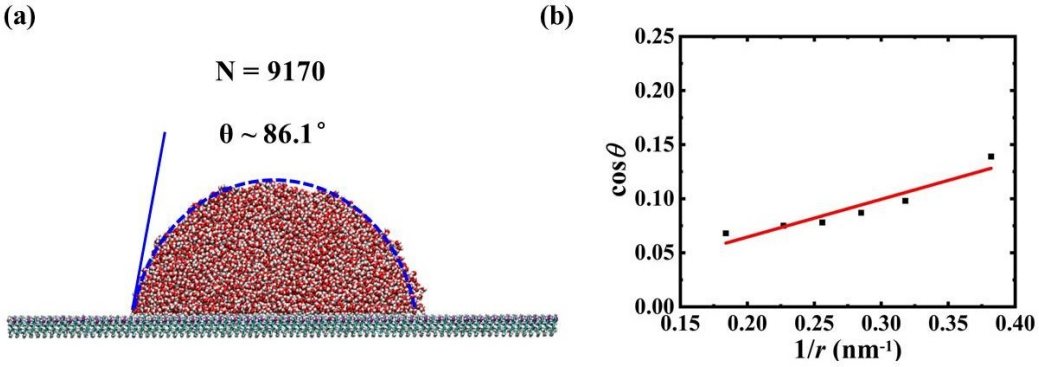

Fig S4. (a) The simulation snapshot of water droplet containing 9170 water molecules (*N* stands for water numbers) with the droplet base radius (*r*) of 5.45 nm at Σ = 4.5 nm^{-2}. Atom representations and color settings are the same as the previous. (b) Cosine of the contact angle θ versus the droplet base curvature 1/*r*.

To analyse the dependence of the contact angle on drop size, we performed MD simulations of water droplets containing 1834, 2751, 3668, 4585, and 9170 water molecules *N* at Σ = 4.5 nm^{-2}, which corresponds to the droplet base radii (*r*) of 3.15 nm, 3.51 nm, 3.91 nm, 4.40 nm, and 5.45 nm, respectively, and the respective contact angles were 84.4°, 85.0°, 85.5°, 85.7°, and 86.1°. The areas of SAMs were also enlarged accordingly to avoid the periodic images of water droplets. Fig S4(b) shows the relationship between the cosine of the contact angle θ and the droplet base curvature 1/*r*, which is consistent with ref. 40. By fitting the relationship between them, we found that the macroscopic contact angle (that for infinitely large droplets, $1/r \rightarrow 0$) was up to ~90°.

PS7. The effects of other water models and another force field on the contact angles

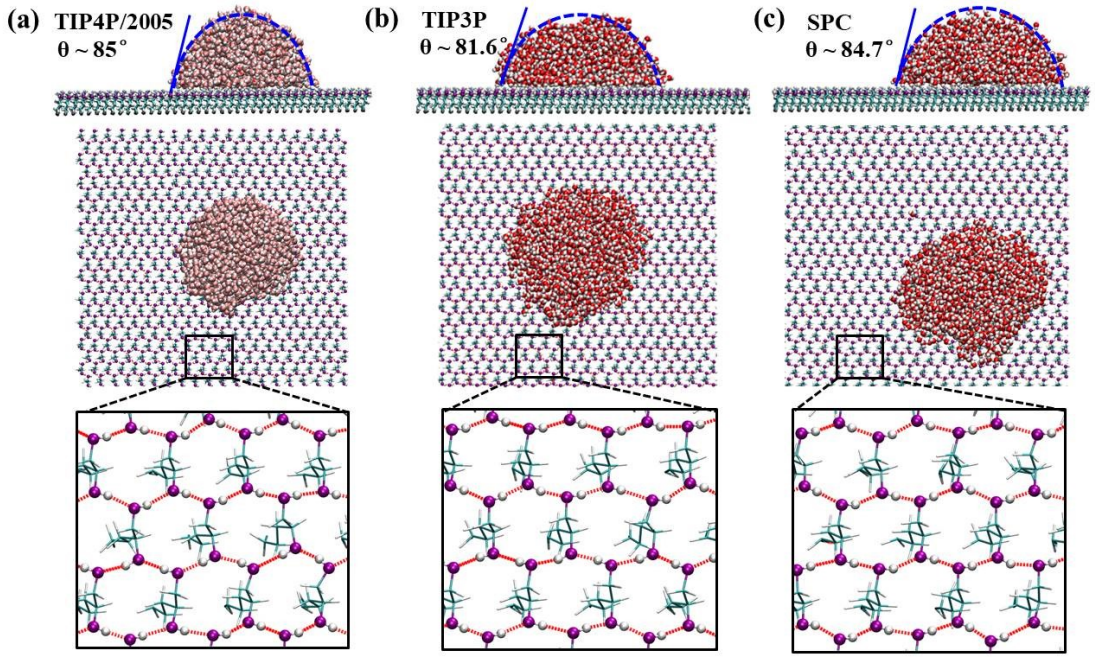

Fig S5. The representative snapshots of water droplets on $(OH)_2$-SAM for different water models, i.e., (a) TIP4P/2005, (b) TIP3P, (c) SPC at Σ = 4.5 nm^{-2}. Atom representations and color settings are the same as the previous.

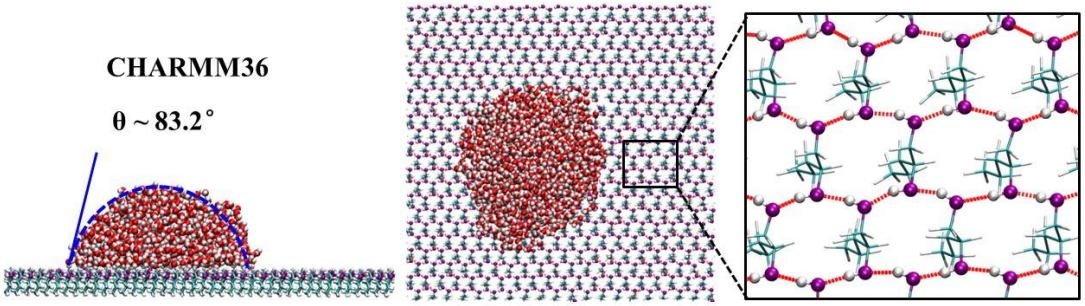

Fig S6. The representative snapshots of water droplets on $(OH)_2$-SAM for CHARMM36 force field at Σ = 4.5 nm^{-2}. Atom representations and color settings are the same as the previous.

To investigate the effects of other water models and another force field on the contact angles, we performed MD simulations of other water models (TIP4P/2005,[41] TIP3P,[42] and SPC[43]) and another force field (CHARMM36[44]) at the packing density of 4.5 nm^{-2}. The simulation results were shown in Fig S5 and S6, respectively. It was noticed that these corresponding calculated contact angles (i.e., 85°, 81.6°, 84.7°, and 83.2°) were very close to 82° in the main text, indicating that our conclusions will not be affected by changes in other water models and other force fields.

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