Supporting Information for

Nano-scale Hydrophilicity on Metal Surfaces at Room Temperature: Coupling Lattice Constants and Crystal Faces

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PS1. x-y dimensions of all the metal surfaces

The x-y dimensions of all the metals with (100), (110) and (111) are shown in Table S1.

Table S1. x-y dimensions of all the metals with (100), (110) and (111) crystal surfaces.

Metal / Crystal face	Ni	Cu	Pd	Pt	Al	Au	Ag	Pb
100 (nm^2)	9.856×9.856	10.136×10.136	10.114×10.114	10.192×10.192	10.125×10.125	10.200×10.200	9.816×9.816	10.148×10.148
110 (nm^2)	9.856×9.956	9.774×9.727	9.725×9.902	9.800×9.979	9.720×9.737	9.792×9.809	9.816×9.833	9.900×9.800
111 (nm^2)	9.956×9.700	9.983×9.754	9.902×9.529	9.979×9.602	10.023×9.920	10.098×9.994	10.122×10.018	9.800×9.700

PS2. Thickness of first water layer on different metal surfaces

The thickness of first water layer on different metal surfaces, which is defined as the distance from the solid surface to the first valley of the water density distribution profile along z-axis, is shown in Table S2.

Table S2. Thickness of first water layer on different metal surfaces.

metal	Ni	Cu	Pd	Pt	Al	Au	Ag	Pb
Height of first water layer on (100) face (nm)	0.387	0.394	0.436	0.423	0.418	0.409	0.406	0.442
Height of first water layer on (111) face (nm)	0.394	0.396	0.406	0.409	0.417	0.419	0.413	0.457
Height of first water layer on (110) face (nm)	0.367	0.359	0.357	0.426	0.422	0.431	0.422	0.442

PS3. Comparison of number of H bonds formed by first water layer between (100) and (111) crystal faces.

The within-monolayer H bonds and between-droplet-monolayer H bonds of (100) and (111) crystal faces for different metals as illustrated in Figure S1. For (111) crystal faces, we have found that the within-monolayer H bonds are much smaller than that on (100) crystal surfaces, resulting in much larger number of between-droplet-monolayer H bonds. As a result, the water droplet is not found for the (111) surfaces and the water molecules cover the surfaces completely.

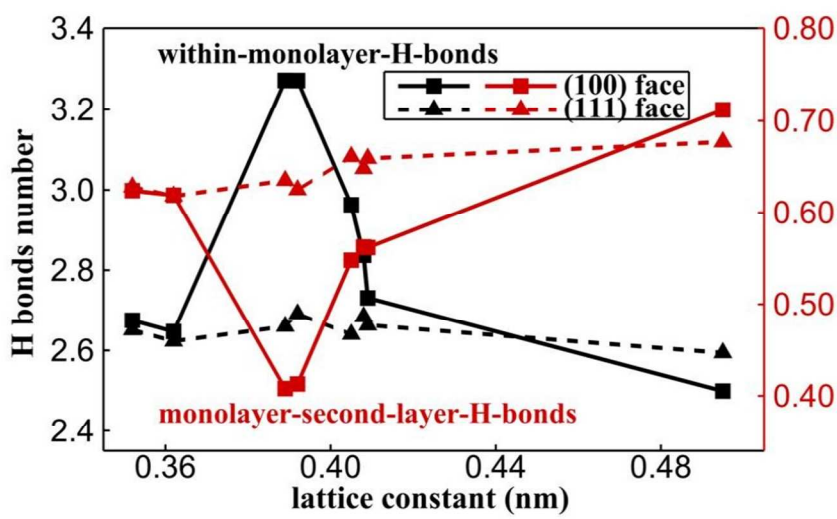

Figure S1. Average number of H bonds formed by a water molecule in first water monolayer with other water molecules in the same monolayer (black), and by a water molecule in first monolayer with water molecules above first monolayer (red) for (100) and (111) crystal faces.

PS4. Test of the force filed we employed

In Table S3, we list the adsorption energy for some typical metal surfaces of our work, without vdW (PBE), and with vdW (optB88-vdW) from the reference.[1] Obviously, the results from our work is close to the adsorption energy without vdW, but lower than the adsorption energy with vdW.

Table S3. Adsorption energy of our work, without vdW (PBE), and with vdW (optB88-vdW) for some typical metal surfaces. The values of PBE and optB88-vdW are from the reference.[1]

	Au(111)	Cu(111)	Ag(111)	Pd(111)	Pt(111)	Al(111)
Our work (kJ/mol)	-18.39	-19.47	-16.60	-20.84	-23.88	-15.35
PBE (kJ/mol)	-11.81	-16.03	-13.15	-23.33	-20.83	-18.43
optB88-vdW (kJ/mol)	-26.98	-30.62	-26.98	-40.61	-38.69	-28.99

The work[2] reported that the pentagon structure on Cu(110) surface is favored over other structures because it maximizes the water-metal bonding while maintaining a strong hydrogen-bonding network. To verify this phenomenon, we perform the new molecular dynamics simulation of 1062 water molecules with the thickness of 0.8 nm water film on Cu(110) surface at 100 K. Then after the equilibrium of 8 ns simulation, we check the structures of first layer of the water on Cu(110) surface. In Fig. S2(a), we have found a mixture of 5-, 6-membered rings of water molecules during our simulation time, which is quite favorable with the previous work.[2] The local pentagon structures illustrate the force field we employed could reproduce some of the known structures on Cu(110) surface.

The work[3] showed that the wetting structure on Pt(111) with T < 115K is a mixture of 5-, 6-, and 7-membered rings of water molecules. Then we perform a new molecular dynamics simulation of 1230 water molecules with the thickness of 0.8 nm water film on Pt(111) surface at 100 K to explore whether the mixture of 5-, 6-, and 7-membered rings of water molecules could exist. After the equilibrium of 8 ns simulation, we can see that a mixture of 5-, 6-, and 7-membered rings will be stable at the Pt(111) surface, as shown in Fig. S2(b), favorable with the previous work.[3] This result shows that the force field we employed could be used to predict the known structure of water on metals.

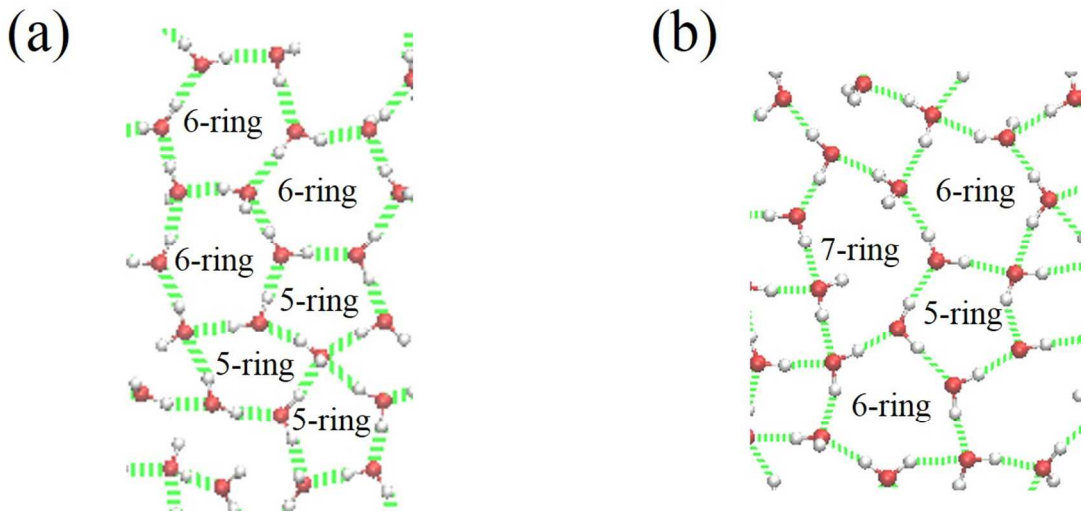

Figure S2. Top views of the water structure of a mixture of (a) 5- and 6-membered rings of water molecules and H bonds network on Cu(110) surface, and (b) 5-, 6-, and 7-membered rings of water molecules and the H bonds network on Pt(111) surface.

REFERENCES

(1) Carrasco, J.; Klimeš, J.; Michaelides, A. The Role of van der Waals Forces in Water Adsorption on Metals. *J. Chem. Phys.* **2013,** *138*, 024708.
(2) Carrasco, J.; Michaelides, A.; Forster, M.; Haq, S.; Raval, R.; Hodgson, A. A One-dimensional Ice Structure Built from Pentagons. *Nat. Mater.* **2009,** *8*, 427-431.
(3) Nie, S.; Feibelman, P. J.; Bartelt, N. C.; Thürmer, K. Pentagons and Heptagons in the First Water Layer on Pt(111). *Phys. Rev. Lett.* **2010,** *105*, 026102.