

Supplementary Information

The effect of surface hydrophobicity and hydrophilicity on the ion-ion interaction at water-solid interfaces

Dong Guan,^a Ye Tian,^a Yizhi Song,^a Mengze Zhao,^b Kaihui Liu,^{b,c} Li-Mei Xu,^{a,c,d}
En-Ge Wang,^{a,c,d} and Ying Jiang^{a,c,d*}

^a*International Center for Quantum Materials, School of Physics, Peking University, Beijing 100871, P. R. China.*

^b*State Key Laboratory for Mesoscopic Physics, Frontiers Science Centre for Nano-optoelectronics, School of Physics, Peking University, Beijing 100871, P. R. China.*

^c*Interdisciplinary Institute of Light-Element Quantum Materials and Research Center for Light-Element Advanced Materials, Peking University, Beijing 100871, P. R. China*

^d*Collaborative Innovation Center of Quantum Matter, Beijing 100871, China*

* Corresponding author: yjiang@pku.edu.cn (Y.J.)

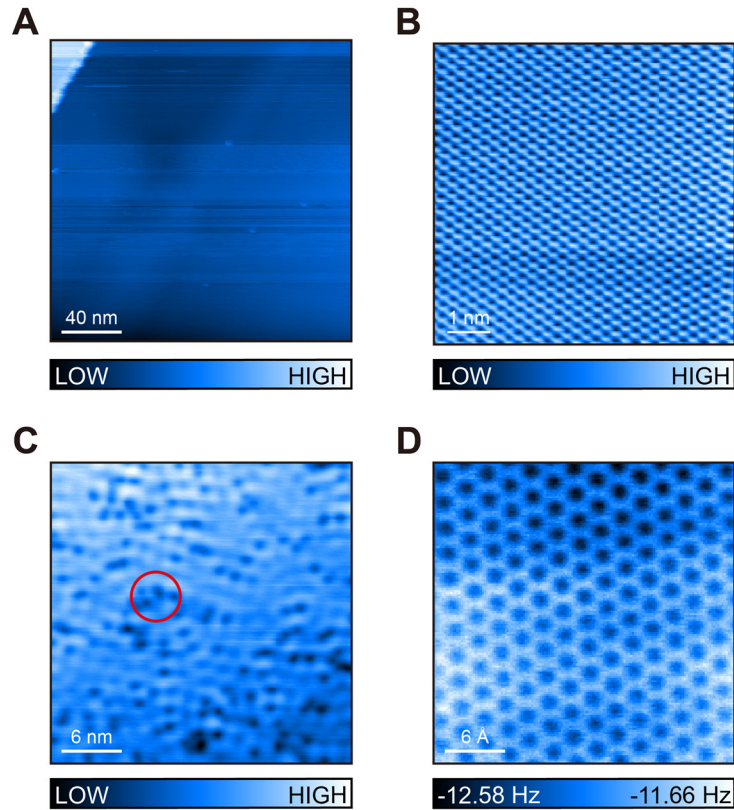


Figure S1. Clean graphite and graphene/Cu(111) sample. (A) STM image of clean graphite surface with a set point of $U_{bias} = 500 \text{ mV}$, $I = 10 \text{ pA}$. (B) Zoom-in STM image for (A) with a set point of $U_{bias} = 50 \text{ mV}$, $I = 50 \text{ pA}$. (C) STM image of clean graphene/Cu(111) surface with a set point of $U_{bias} = 100 \text{ mV}$, $I = 10 \text{ pA}$. The dark areas marked by the red circle are caused by the defects on the Cu(111) surface. (D) Zoom-in constant-height AFM image for (C) with a set point of $U_{bias} = 2 \text{ mV}$, $A = 100 \text{ pm}$. The honeycomb structure of graphene can be clearly seen.

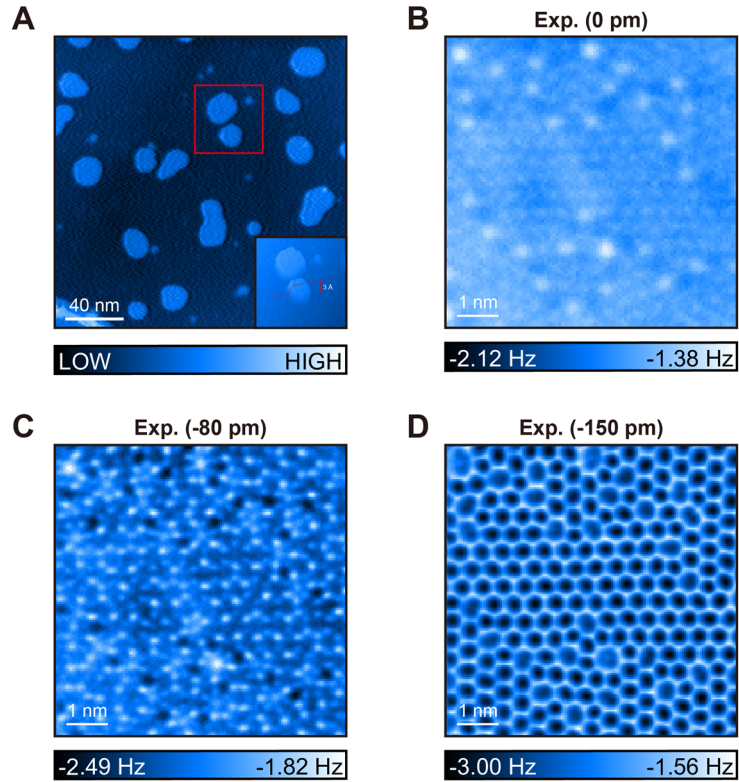


Figure S2. Pure water islands on the graphite surface. (A) Constant-frequency-shift AFM images for pure water islands on the graphite surface with a set point of $\Delta f = -400$ mHz. The zoom-in image for the area marked by the red rectangle shows the height of the pure water island is ~ 3 Å (see inset). (B-D) High-resolution constant-height AFM images for a water island shown in Fig. 1D with different tip heights. We can recognize the domain boundaries consisting of 5,7,8-rings. All the oscillation amplitudes of the experimental images are 200 pm.

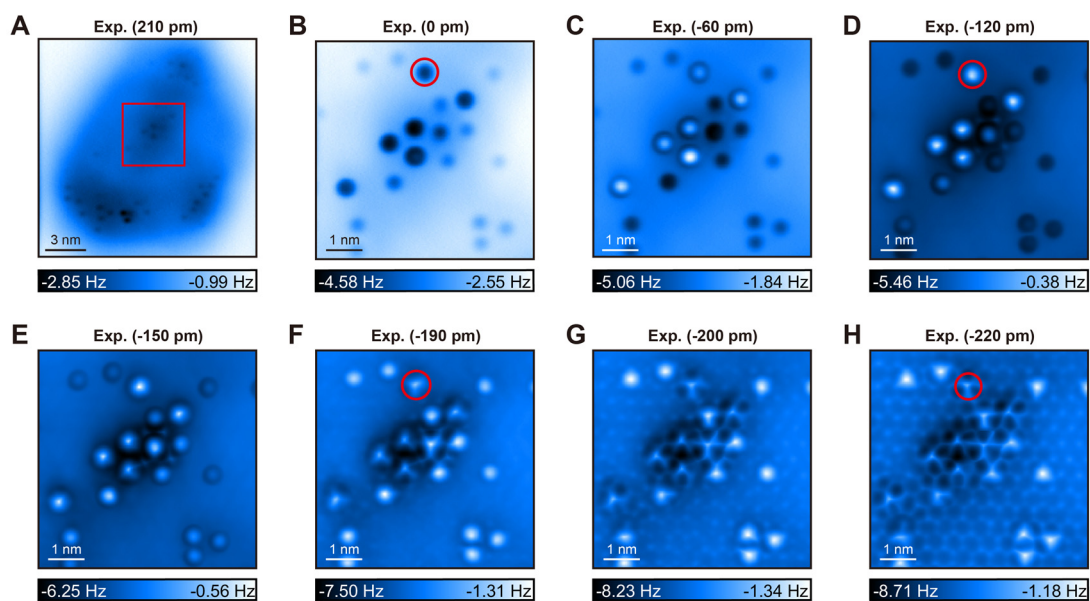


Figure S3. Constant-height AFM images for the K^+ -water island at a relatively high K^+ -water ratio on the graphite sample with different tip heights. (A) Constant-height AFM image of a K^+ -water island with a relatively high K^+ -water ratio. (B-H) are the zoom-in images for the red rectangle marked in (A). The tip heights for (A) and (C-H) are with respect to that for (B), set as 0 pm. The feature of H-up water molecules first shows as black spots (red circle in (B)), then it changes to bright spots (red circle in (D)). When the tip further decreases, it changes to bright triangles (red circle in (F)) and then to bright herringbones (red circle in (H)). The accumulation of K^+ ions leads to the distortion and corrugation of the bilayer water island, thus there are H-up water molecules with different heights and features in one image. All the oscillation amplitudes of the experimental images are 200 pm.

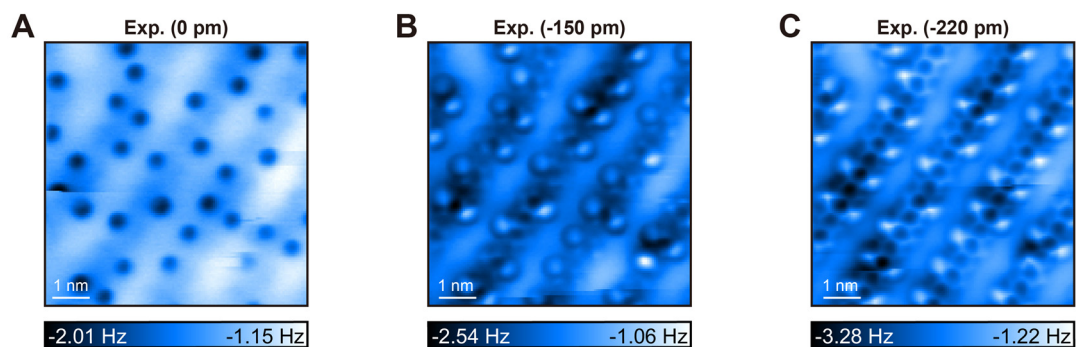


Figure S4. Constant-height AFM images for the K^+ -water island at a relatively high K^+ -water ratio on the graphene/Cu(111) sample with different tip heights. With respect to the tip height for (A) (set as 0 pm), the tip heights for (B, C) are -150 pm and -220 pm, respectively. In these images, we can see that the single chains transform into double chains. All the oscillation amplitudes of the experimental images are 500 pm.

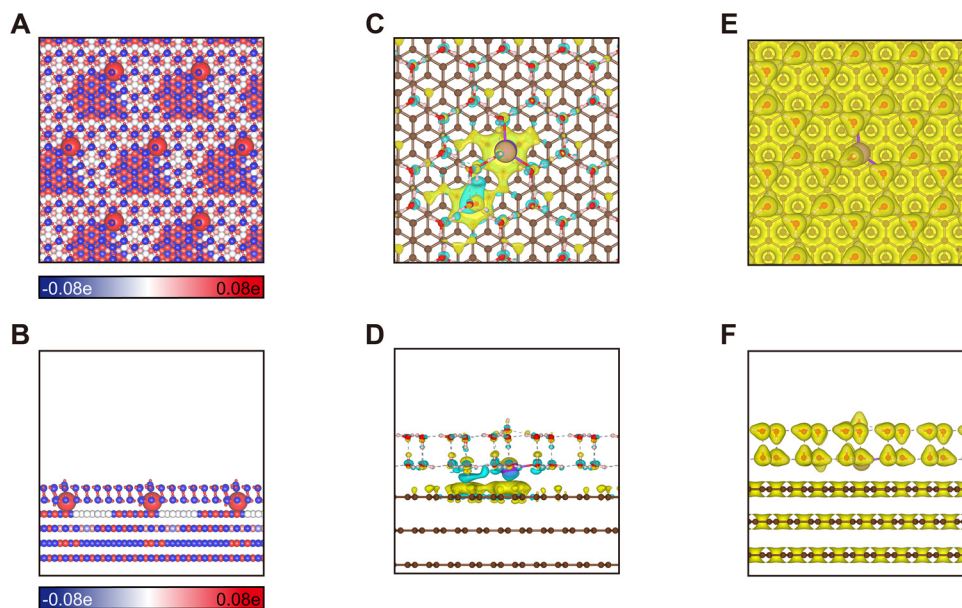


Figure S5. Charge distribution diagrams, the isosurfaces of charge density difference, and total charge density of the K^+ -water island on the graphite sample. (A and B) Charge distribution diagrams of the K^+ -water island on the graphite sample. Atoms are colored by the net charge with a continuous color scale from dark blue (-0.08e, negatively charged) to white (0, electroneutral) to dark red (+0.08 e, positively charged). The maximum/minimum charge of the color bar was set to -0.08 e/+0.08 e to make the top layer of carbon atoms with different net charges more visible. The atoms with a net charge bigger than 0.08 e are colored dark red. The atoms with a net charge smaller than -0.08 e are colored dark blue. For the graphite sample, the top layer carbon atoms are locally charged, and they carry a total charge of -0.526 e for one unit cell. (C, D) The isosurfaces of charge density difference representing charge transfer upon the adsorption of K^+ -water adlayer on the graphite substrate. The yellow and green surfaces are drawn at $0.0005 \text{ e}/\text{\AA}^3$ and $-0.0005 \text{ e}/\text{\AA}^3$, and represent the regions of charge accumulation and charge depletion, respectively. (E, F) The isosurfaces of total charge density of the K^+ -water island on the graphite sample. The yellow isosurfaces are drawn at $0.07 \text{ e}/\text{\AA}^3$.

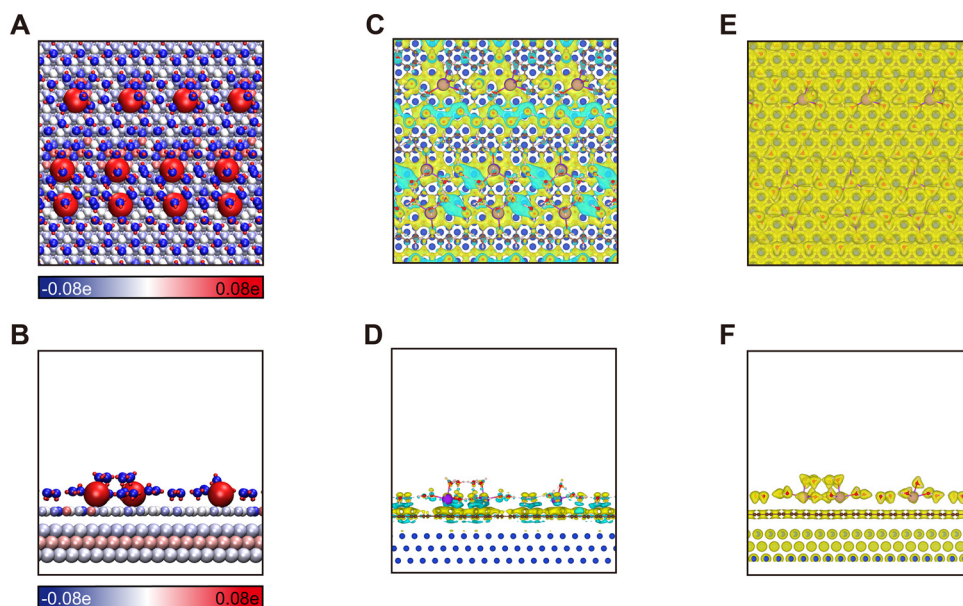


Figure S6. Charge distribution diagrams, the isosurfaces of charge density difference, and total charge density of the K^+ -water island on the graphene/Cu(111) sample. (A and B) Charge distribution diagrams of the K^+ -water island on the graphene/Cu(111) sample. Atoms are colored by the net charge with a continuous color scale from dark blue ($-0.08 e$, negatively charged) to white (0 , electroneutral) to dark red ($+0.08 e$, positively charged). The maximum/minimum charge of the color bar was set to $-0.08 e/+0.08 e$ to make the top layer of carbon atoms with different net charges more visible. The atoms with a net charge bigger than $0.08 e$ are colored dark red. The atoms with a net charge smaller than $-0.08 e$ are colored dark blue. For the graphene/Cu(111) sample, the top layer carbon atoms are averagely charged, and they carry a charge of $-0.663 e$ averaged to each K^+ for one unit cell. It is apparent that the electrostatic interaction between the K^+ -water adlayer with the substrate is stronger for the graphene/Cu(111) than graphite. (C, D) The isosurfaces of charge density difference representing charge transfer upon the adsorption of K^+ -water adlayer on the graphene/Cu(111) substrate. The yellow and green surfaces are drawn at $0.0005 e/\text{\AA}^3$ and $-0.0005 e/\text{\AA}^3$, and represent the regions of charge accumulation and charge depletion, respectively. (E, F) The isosurfaces of total charge density of the K^+ -water island on the graphene/Cu(111) sample. The yellow isosurfaces are drawn at $0.07 e/\text{\AA}^3$.