

## Two-Dimensional Material Confined Water

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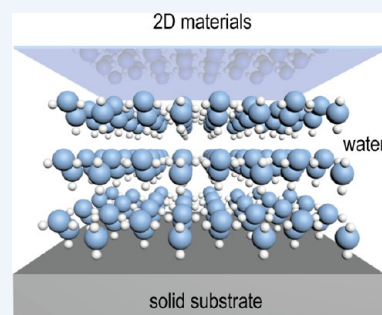
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**CONSPECTUS:** The interface between water and other materials under ambient conditions is of fundamental importance due to its relevance in daily life and a broad range of scientific research. The structural and dynamic properties of water at an interface have been proven to be significantly different than those of bulk water. However, the exact nature of these interfacial water adlayers at ambient conditions is still under debate. Recent scanning probe microscopy (SPM) experiments, where two-dimensional (2D) materials as ultrathin coatings are utilized to assist the visualization of interfacial water adlayers, have made remarkable progress on interfacial water and started to clarify some of these fundamental scientific questions.

In this Account, we review the recently conducted research exploring the properties of confined water between 2D materials and various surfaces under ambient conditions.

Initially, we review the earlier studies of water adsorbed on hydrophilic substrates under ambient conditions in the absence of 2D coating materials, which shows the direct microscopic results. Subsequently, we focus on the studies of water adlayer growth at both hydrophilic and hydrophobic substrates in the presence of 2D coating materials. Ice-like water adlayers confined between hydrophobic graphene and hydrophilic substrates can be directly observed in detail by SPM. It was found that the packing structure of the water adlayer was determined by the hydrophilic substrates, while the orientation of intercalation water domains was directed by the graphene coating. In contrast to hydrophilic substrates, liquid-like nanodroplets confined between hydrophobic graphene and hydrophobic substrates appear close to step edges and atomic-scale surface defects, indicating that atomic-scale surface defects play significant roles in determining the adsorption of water on hydrophobic substrates. In addition, we also review the phenomena of confined water between 2D hydrophilic MoS<sub>2</sub> and the hydrophilic substrate. Finally, we further discuss researchers taking advantage of 2D graphene coatings to stabilize confined water nanodroplets to manipulate nanofluidics through applying an external force by using novel SPM techniques. Moreover, for future technology application purposes, the doping effect of confined water is also discussed.

The use of 2D materials as ultrathin coatings to investigate the properties of confined water under ambient conditions is developing and recognized as a profound approach to gain fundamental knowledge of water. This ideal model system will provide new opportunities in various research fields.



### INTRODUCTION

Water can be found in the bulk form but is also present within confined environments. Confined water at the nanoscale does have different dynamics and structures from that of the bulk water.<sup>1–7</sup> The physical properties and the state of the confined water have been proven to be widely varied depending on the cavity surface and the confinement dimensions, as well as temperature and pressure.<sup>1,2,4–7</sup> Detailed atomic-level understanding of water structures and dynamics in confined environments at ambient conditions is of great importance, not only for improving the knowledge of geological and biological processes but also for the development of advancing technologies.<sup>8,9</sup> Therefore, the study of the chemical and physical properties of confined water is one of the most interesting topics in multidiscipline research.

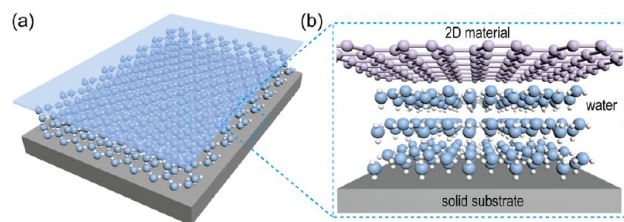
Despite considerable experimental and theoretical work having been done to characterize water structures and dynamics at interfaces,<sup>10–13</sup> the behavior of confined water at the nanoscale under ambient conditions is still not fully understood. The reasons are twofold: first, most knowledge of water

structures at interfaces has been gained at cryogenic temperatures and under ultrahigh-vacuum conditions, which might not be transferable to ambient conditions; second, direct microscopic imaging of wetting dynamics of water confined in nanoscale geometries remains challenging. Recently, the two-dimensional (2D) material graphene has been widely used as an extraordinary coating material owing to its unusual mechanical flexibility, chemical stability, impermeability, high electrical conductivity, etc.<sup>14,15</sup> Through the use of graphene as an ultrathin coating, water thin films confined between various solid substrates and hydrophobic graphene sheets (Figure 1) under ambient conditions have been extensively studied by scanning probe microscopy (SPM). Remarkable progress in understanding the structural and dynamic properties of water on various solid substrates, as well as the effect of graphene coating on water films, has been gained.<sup>16–27</sup>

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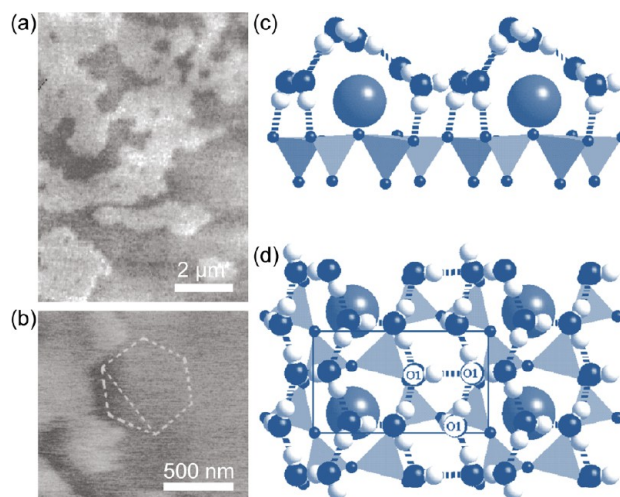
**Figure 1.** (a) Schematics of the water confined between a 2D material and a solid substrate. (b) Zoom-in image showing that the water confined between hydrophobic graphene and the substrate appears ice-like.

In this Account, we will review recent results exploring and providing understanding of the structures and dynamics of water confined between 2D materials and various substrates at room temperature (RT) by SPM. At first, the studies of water adsorbed onto a hydrophilic substrate under ambient conditions in the absence of 2D material coating are reviewed. Later, we focus on studies of water on hydrophilic and hydrophobic substrates in the presence of a 2D graphene coating. The phenomena of water confined between 2D monolayer MoS<sub>2</sub> and a hydrophilic substrate will also be reviewed. Finally, the doping effects of confined water on graphene, as well as nanomanipulation of the confined water using a SPM tip, are summarized.

## ■ WATER ON HYDROPHILIC SUBSTRATE

For hydrophilic surfaces under ambient conditions, there is always an adsorbed layer of water, which will then dominate the surface behavior.<sup>10,11,13</sup> Hydrophilic mica, a layered aluminosilicate crystal, has been extensively utilized to investigate the properties of thin film water. Beaglehole et al. determined the correlation between the water thickness and relative humidity (RH) at RT through ellipsometry.<sup>28,29</sup> Experimental results clearly show that a thicker water film is fluid-like on mica. A similar conclusion was further confirmed by utilizing infrared spectroscopy (IR).<sup>30</sup> On the other hand, Hu et al. directly visualized a thin water film adsorbed on a mica substrate using scanning polarization force microscopy (SPFM) at ambient conditions.<sup>31–35</sup> By approaching the tip into the contact point on mica surface, they observed molecularly thin island-like structures at RH of 35% (Figure 2a). The structures were metastable and disappeared rapidly due to evaporation. These island-like structures were interpreted as a second layer on a monolayer of water.<sup>10,33</sup> Typical hexagonal shapes can be clearly defined at the boundaries of water layers (Figure 2b), suggesting that the thin water film has an ice-like structure. The axis directions of hexagonal ice-like structures closely correlated with the lattice orientation of the mica substrate confirmed the angular epitaxial relationship between water and the substrate.

Confirmation of these results came from first-principles molecular dynamics (MD) simulations.<sup>36</sup> Odelius et al. found that water formed a fully connected 2D hydrogen-bonded network epitaxial from the mica lattice at monolayer coverage, as shown in Figure 2c,d. All OH groups of the water layer are fully occupied without sticking out from the surface. Simulations indicate that the stable ice-like structure on mica is due to the high surface barriers for water diffusion.



**Figure 2.** Structures of water films on mica substrates under ambient conditions. (a) SPFM image of water structures. Reprinted with permission from ref 33. Copyright 1997 Materials Research Society. (b) The boundaries of the water layer tend to have hexagonal shapes. Reprinted with permission from ref 31. Copyright 1995 American Association for the Advancement of Science. (c) Side and (d) top view of the water molecular structures on mica. Reprinted with permission from ref 36. Copyright 1997 American Physical Society.

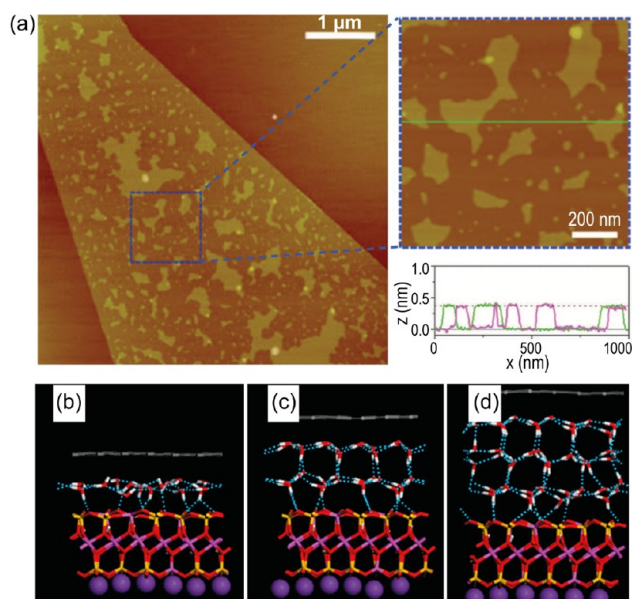
## ■ WATER CONFINED BETWEEN HYDROPHOBIC AND HYDROPHILIC SURFACES

### Water Confined between Graphene and Mica

Although SPFM has been successfully used to study water adlayers on solid substrates at RT,<sup>10,11,31–34</sup> the structure of the water adlayer was not resolved at the molecular level because of the dynamic nature of the water layer and the relative low lateral resolution of SPFM.<sup>31</sup> Atomic force microscopy (AFM) has the ability to characterize the structures of molecules at nanoscale, but its use for imaging water adlayers under ambient conditions remains a challenge. When the AFM tip approaches the surface of the water adlayers under ambient conditions, the strong capillary forces between the tip and the surface will strongly disturb the water adlayers on solid substrates.<sup>37</sup>

On the other hand, flexible graphene allows replication of the topography of a substrate with high precision.<sup>38</sup> Furthermore, graphene is impermeable to standard gases. Thus, it can also conserve the substrate.<sup>39</sup> Recently, the structure of a water adlayer on a mica substrate at RT was determined with an AFM by utilizing hydrophobic graphene as an ultrathin coating material.<sup>16</sup> Xu et al. transferred monolayer graphene onto a mica substrate under humid environments (the number of graphene layers and the confined water were confirmed by Raman spectroscopy<sup>16</sup>). As shown in Figure 3a, atomically flat island-like plateaus up to micrometer scale were observed across all the graphene samples at a RH of 40%. These plateaus were interpreted as the formation of the first water adlayer confined between the graphene coating and the mica substrate. The measured height of the flat plateaus was  $3.7 \pm 0.2$  Å, in good agreement with the thickness of a single puckered bilayer of ice-I<sub>h</sub>. The second ice-like water adlayer starts to appear only after completion of the growth of the first water adlayer. The second water adlayer often appearing preferentially near local defect sites of the mica substrate indicates that surface defects serve as nucleation centers. Subsequent water adlayers adopted a liquid-like form. 2D graphene as a coating material provides





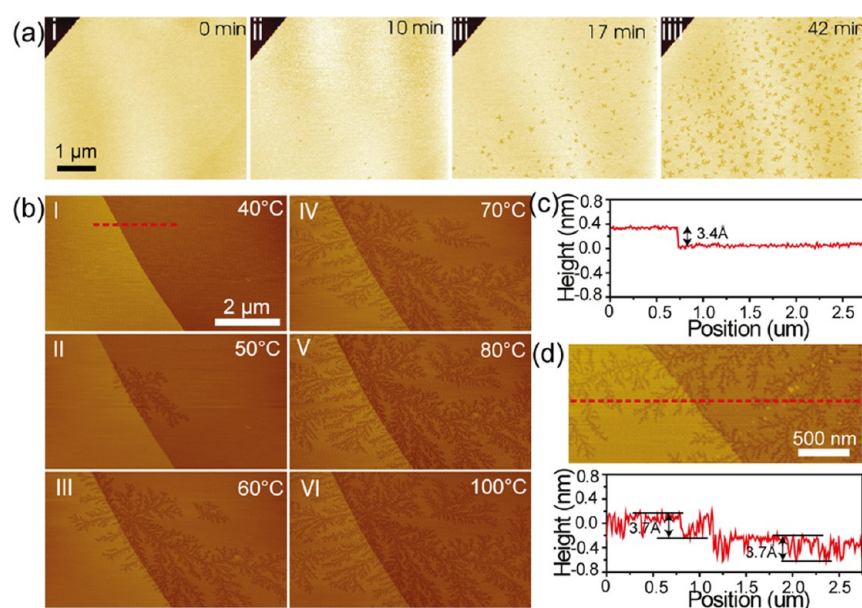
**Figure 3.** Visualization of the water adlayer on mica using graphene as an ultrathin coating. (a) AFM images of a monolayer graphene on mica substrate. The dashed line in height profile image indicates  $z = 3.7 \text{ \AA}$ . Reprinted with permission from ref 16. Copyright 2010 American Association for the Advancement of Science. (b–d) Side view of the monolayer, bilayer, and trilayer ice structures confined between graphene and mica. Reprinted with permission from ref 40. Copyright 2012 American Chemical Society.

an ideal system to explore the growth mechanism of confined molecular films.<sup>17–27</sup>

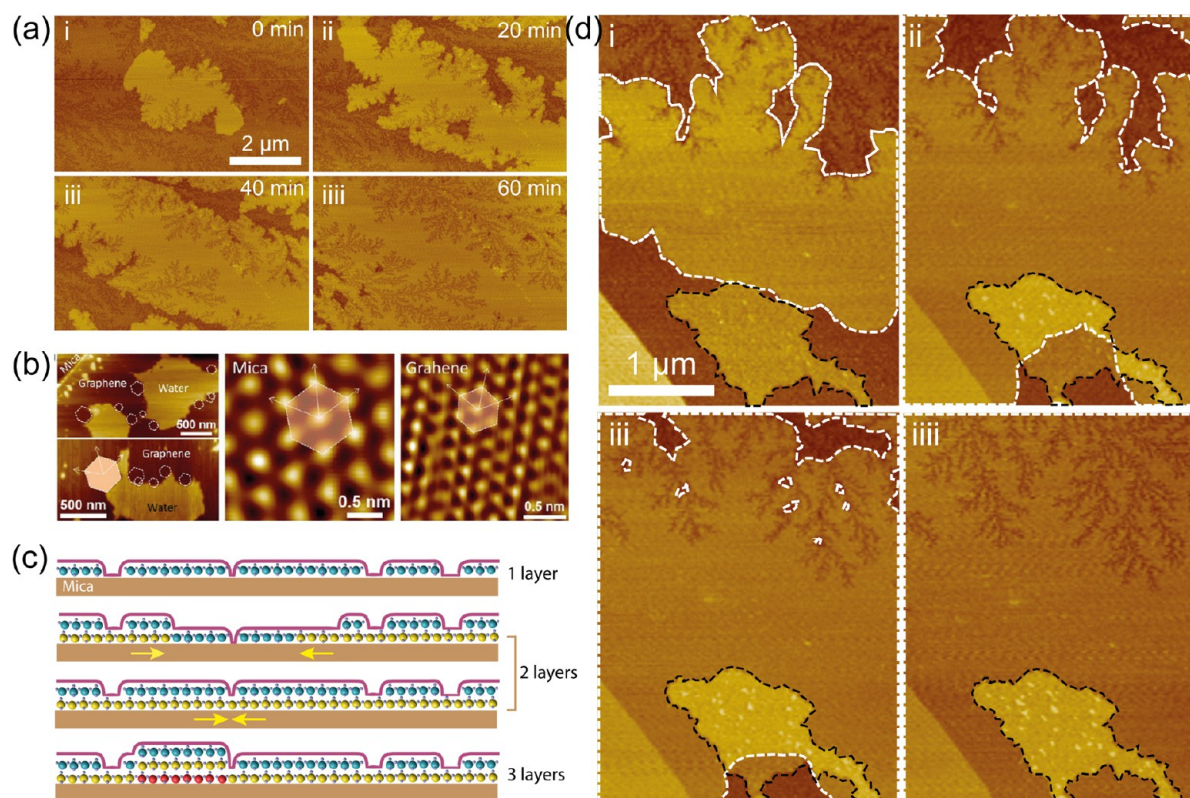
Based on the experimental observations, Li and Zeng performed an *ab initio* MD simulation to further explore the dynamic growth of a confined water film.<sup>40</sup> Two model systems

for the mica surface were considered in their simulation: one involves  $\text{K}^+$  ions (the same mica model in the previous simulation<sup>36</sup>), and another has no  $\text{K}^+$  ions. They found that the ice-like water adlayer on the mica surface with  $\text{K}^+$  ions was thermodynamically less stable than the one on the mica surface without  $\text{K}^+$  ions. Furthermore, water on the mica surface with  $\text{K}^+$  ions cannot form a stable second epitaxial adlayer. However, water can form quite stable second and third adlayers on the mica surface without  $\text{K}^+$  ions (Figure 3b–d). Additionally, the stability of the water adlayer structure can be significantly enhanced by introducing a graphene coating. Although Li and Zeng lack confidence in the existence of the third water adlayer, their simulation encourages more researchers to verify whether the third water adlayer can be observed experimentally.

The above works on both experimental and theoretical aspects have presented more structures of the confined water layers at the interface, while more dynamic investigation of water during the growth process will further enrich the understanding of the physical behavior of confined water. Severin et al. reported the *in situ* dynamic process of the confined water film through changing the humidity.<sup>19,20</sup> As shown in Figure 4a, graphene is remarkably flat at a RH of 60% (Figure 4a(i)). When RH was decreased below 4%, small depressions were observed (Figure 4a(ii)). Later, the existing depressions grew into fractals (Figure 4a(iii, iii)). Upon rapid increase of the RH again, the fractal structures disappeared abruptly at  $\sim 50\%$  RH. Therefore, authors concluded that through controlling the environmental humidity, water in such dynamic equilibrium transition between dewetting and rewetting presents fluidic behavior.<sup>19,20</sup> However, the number of water layers in the fractal structures was not discussed. Does this fluidic behavior depend on the number of water layers? Unlike previous humidity dependent experiments,<sup>16,19,31</sup> temperature controlled AFM was recently employed to directly



**Figure 4.** *In situ* visualization of the growth of the fractal structures. (a) AFM images of a graphene on mica substrate imaged during decreasing RH. Reprinted with permission from ref 19. Copyright 2012 American Chemical Society. (b) AFM images of a graphene on mica substrate imaged during increasing temperature from RT to  $100 \text{ }^\circ\text{C}$ . (c) The line profile along the dashed red line marked in panel b(I) revealing a  $3.4 \text{ \AA}$  height step between single and double layer graphene. (d) AFM height image recorded at  $100 \text{ }^\circ\text{C}$ , showing the structure of the fractals. The line profile along the dashed red line provided quantitative depth of the fractals,  $z = 3.7 \text{ \AA}$ . Panels b and d reprinted with permission from ref 41. Copyright 2014 Nature Publishing Group.



**Figure 5.** *In situ* visualization of the growth of the second and the third water adlayers. (a) AFM images showing the growth of the second water adlayer. (b) The boundaries of confined water adlayer tend to have hexagonal shapes, as shown in the larger scan area AFM images (hexagons are drawn for visual reference). Lattice-resolved images of mica substrate and graphene coating are recorded by contact AFM. (c) Schematic diagram showing the water adlayer growth process. The yellow arrows indicate the growth direction of the water adlayer. (d) AFM images of the third water adlayer growth, where the third water adlayer (marked with black dashed line) appears besides the second water adlayer (marked with white dashed line). Panels a, b, and d reprinted with permission from ref 41. Copyright 2014 Nature Publishing Group.

investigate *in situ* dewetting/rewetting dynamics of water confined between graphene and mica.<sup>41,42</sup> AFM images show that small depressions grew into fractal structures when the temperature reached 50 °C. Further increasing the temperature led to the fractal structures growing much faster, while the growth slowed when the temperature reached 80 °C (Figure 4b). This dewetting result through increasing temperature is similar to the observation of fractal growth upon controlling the RH.<sup>19</sup> In order to get the accurate height of the fractal structures, all of the height line profiles were calibrated based on the step height (3.4 Å) between single and double layer graphene (Figure 4c). The measured depth of the fractal structures was  $3.7 \pm 0.2$  Å, in good agreement with the thickness of a single puckered bilayer of ice- $I_h$  (Figure 4d). Therefore, it was argued that the initial aqueous water film confined between graphene and the mica substrate accomplished phase change to rearrange into an ice-like water adlayer after heating to 100 °C.

Compared with the dewetting process, the pertinent rewetting process is important for understanding water adsorption on ice-like water and solid substrate to explore the growth mechanism.<sup>41</sup> Island-like plateaus were observed after cooling the sample from 100 °C to RT for about an hour. The isolated island-like plateaus grew independently at low coverage; as the coverage increases, these plateaus merge into extended structures, eventually forming a fully covered water adlayer (Figure 5a). Interestingly, the fractal patterns persisted even during the growth of the island-like plateaus, which further

confirms the solid-like behavior of the first water under the hydrophobic graphene coating.<sup>43</sup> By comparing the molecularly resolved images of the graphene and the mica, it was found that the orientation of the hexagonal shapes of the water adlayer were closely aligned with the lattice orientation of the mica substrate rather than the lattice orientation of the graphene (Figure 5b), which is consistent with the work demonstrated by Kim et al.<sup>23</sup> These observations suggested that the second water adlayer directly grew on the mica substrate (Figure 5c). The measured thickness of the island-like plateaus was  $3.7 \pm 0.2$  Å, again in good agreement with the thickness of a single puckered bilayer of ice- $I_h$ . Two adlayer growth of ice-like water at RT confirmed the previous experimental observations and theoretical predictions.<sup>16,23,40,44–46</sup>

Another important finding during the rewetting process is observing the third ice-like water adlayer.<sup>41</sup> As shown in Figure 5d, two island-like plateaus (marked with black and white dashed lines) meet together. The island-like plateau marked with black dashed line was stacked up forming a third water adlayer.<sup>41</sup> The observation of the third ice-like water adlayer at RT confirmed the previous *ab initio* MD simulations.<sup>40</sup> No ice-like island or plateaus were observed beyond the third water adlayer. Thicker water structures appeared liquid-like (droplet). Although the model of Frank–van der Merwe was employed to describe the growth of the confined water previously,<sup>16</sup> the Stanski–Kratonov model was more appropriate to describe the mechanism of water growth in the temperature-dependent experiment.<sup>41</sup> The growth of the first adlayer (the initial water)



and the second adlayer did follow the model of Frank–van der Merwe. However, after the complete formation of the second water adlayer, the third water adlayer grew continually following the model of Volmer–Weber (the nucleation and coalescence of island-like plateaus) (Figure 5c).

### Water Confined between Graphene and Silicon Dioxide

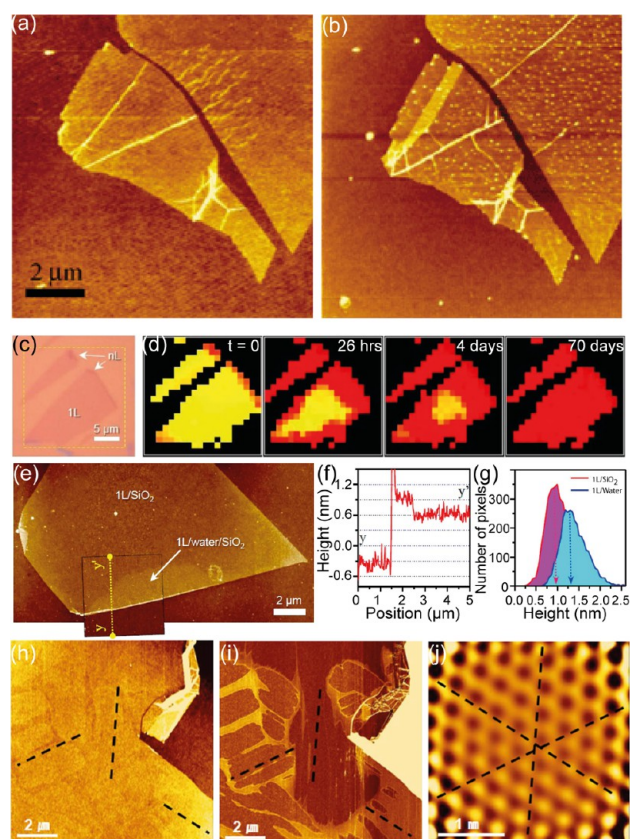
To extend the knowledge for understanding water adsorbed on a hydrophilic amorphous substrate, Lee et al. have investigated water diffusion between graphene and SiO<sub>2</sub> substrates under high humidity conditions by using AFM.<sup>45</sup> The water was found to diffuse into the graphene/SiO<sub>2</sub> interface and formed an ice-like structure up to two layers thick at a RH of over 90%. Furthermore, liquid-like water can then diffuse in, stack on the ice-like adlayer, and evaporate relatively easily in the air, which caused graphene to wrinkle and fold (Figure 6a,b). The water-induced wrinkle formation was found to strongly depend on the hydrophilicity and roughness of the substrate.

A very similar finding was reported by Lee et al.,<sup>27</sup> who immersed the annealed SiO<sub>2</sub> supported graphene in water instead of exposing the sample to high RH. The water diffusing underneath the graphene coating was visualized by Raman spectroscopy in real time (Figure 6c,d). It was found that the diffusion rate of water is as a function of substrate hydrophilicity. AFM measurement confirmed that the thickness of the water adlayer was only  $\sim 3.5$  Å (Figure 6e–g), corresponding to the thickness of a single puckered bilayer of ice-*I<sub>h</sub>*.

To further understand the intercalation pathways of water film diffusion between graphene and SiO<sub>2</sub> substrate, Kim et al. performed contact mode AFM on water diffusion experiments.<sup>23</sup> As shown in Figure 6h, bulging regions on the graphene were caused by water intercalation. Additionally, an AFM based friction image (Figure 6i) clearly demonstrated lower friction contrast on the graphene because of the lubricant properties of subsurface intercalation water.<sup>47</sup> By comparison of the AFM topographic images and the lattice direction of graphene (Figure 6j), the diffusion direction of water was demonstrated to follow the direction of the hydrophobic graphene instead of the hydrophilic SiO<sub>2</sub> substrate.

### WATER CONFINED BETWEEN TWO HYDROPHOBIC SURFACES

The structural studies of water adlayers on hydrophilic surfaces at ambient conditions have already been extensively investigated through the water dewetting/rewetting process.<sup>10,16,31,35</sup> However, the experimental investigations of water on hydrophobic surfaces at a microscopic level are still lacking because of the weak surface adsorption of water on a hydrophobic substrate. Cao et al. utilized graphene sheets to investigate the structures of adsorbed water on three distinct hydrophobic substrates: H-terminated Si(111), graphite, and trimethylchlorosilane (TMCS)-functionalized mica.<sup>18</sup> Liquid-like nanodroplets (10–100 nm) can be easily observed at step edges and surface defects with the help of graphene coating (Figure 7a–c). Similarly to the hydrophilic mica surface, surface defects and step edges promote the water nucleation on the surface.<sup>19,20,31</sup> The sizes and the density of nanodroplets were dependent on RH. By choosing Au(111) substrate with graphene coating, Cao et al. observed water clusters mainly at the gold steps (Figure 7d) using scanning tunneling microscopy (STM).<sup>25</sup> It was argued that the water clusters had initially adsorbed to the gold step edges under ambient conditions similar to the

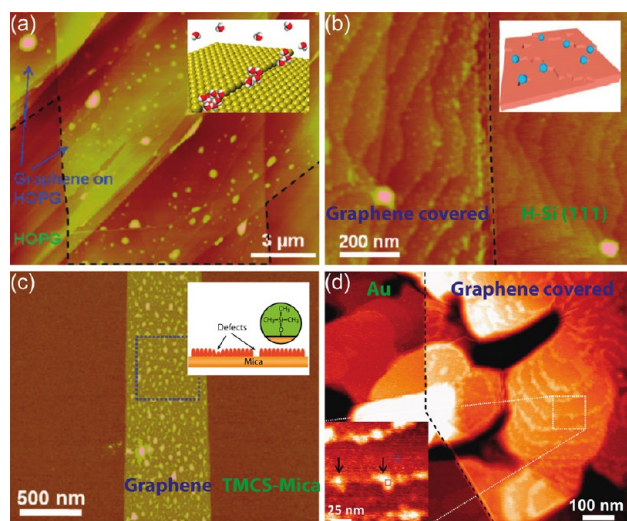


**Figure 6.** Water diffusion between graphene and SiO<sub>2</sub> substrate. (a, b) AFM images of a monolayer graphene deposited on SiO<sub>2</sub> substrate before and after exposure to high humidity ( $\sim 90\%$ ). (c) Optical image of monolayer graphene deposited on SiO<sub>2</sub> substrate. (d) The  $\omega_G$  Raman maps obtained from the region in the dashed square marked in panel c for varying immersion time. (e) AFM image of graphene on SiO<sub>2</sub> substrate after 14 h submersion following thermal annealing at 400 °C for 8 h. (f) The line profile along the  $y$ – $y'$  line marked in panel e. (g) Height histograms for the regions marked with the black square in panel e. (h) AFM height image and (i) corresponding friction image of graphene on SiO<sub>2</sub> substrate under high RH of 60%. (j) Lattice-resolved image of graphene. Black dashed lines marked on panels h and i indicate the directions of water strip patterns, while black dashed lines marked in j show the graphene zigzag directions. Panels a and b reprinted with permission from ref 45. Copyright 2012 Springer Science and Business Media. Panels c–g reprinted with permission from ref 27. Copyright 2014 American Chemical Society. Panels h–j reprinted with permission from ref 23. Copyright 2013 Nature Publishing Group.

previous AFM studies. One can conclude that surface defects and step edges may determine water adsorption on hydrophobic surfaces.

### WATER CONFINED BETWEEN TWO HYDROPHILIC SURFACES

So far, we discussed that hydrophobic graphene was used as an ideal coating to investigate the substrate effect on water condensation. One can expect that the hydrophobicity of coating materials may also influence water condensation. It will be very interesting to use a hydrophilic surface as a coating to investigate confined water between two hydrophilic surfaces. Although confined water between two hydrophilic mica surfaces was studied by surface forces apparatus, no molecular structures of the confined water films could be obtained due to

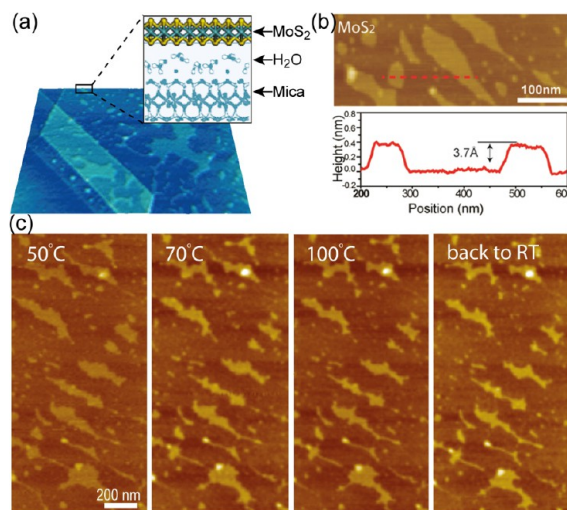


**Figure 7.** Adsorbed water structures under ambient conditions on a hydrophobic substrate. (a) AFM height image of graphene coating on HOPG surface. The inset image shows that there are water nanodroplets that mainly located along the step edges of the HOPG surface. (b) AFM height image of graphene covering on H-terminated Si(111) surface. The inset image shows that there are water nanodroplets that located along edges. (c) AFM height image of graphene coating on TMCS-functionalized mica. The inset image shows the surface of TMCS-functionalized mica. (d) STM topographic image of graphene coating on the Au(111) surface. The inset is a zoom-in of three steps with droplet-like water clusters. Panels a–c reprinted with permission from ref 18. Copyright 2011 American Chemical Society. Panel d reprinted with permission from ref 25. Copyright 2012 American Chemical Society.

the difficulty of controlling the space of two mica surfaces.<sup>10</sup> On the other hand, flexible monolayer MoS<sub>2</sub>, a prototypical transition metal dichalcogenide material, is hydrophilic. This offers another opportunity for observing water confined between two hydrophilic surfaces.<sup>41</sup> As shown in Figure 8a, temperature controlled AFM again was employed to study the structures of water confined between MoS<sub>2</sub> and mica, as well as the related dynamic process. Island-like water plateaus with height of  $3.7 \pm 0.2$  Å between MoS<sub>2</sub> and mica were observed, indicating that the water adlayers confined between the mica substrate and MoS<sub>2</sub> are also ice-like (Figure 8b). No obvious changes were observed during the dewetting/rewetting process (Figure 8c). This observation indicated that water diffusion could only present at the graphene/mica interface. It is most likely due to two reasons: (i) polar water molecules can form bonds to atoms on both mica and MoS<sub>2</sub> crystals; then the water adlayers would be easily trapped between MoS<sub>2</sub> and mica; (ii) the adhesion force between hydrophilic MoS<sub>2</sub> surface and hydrophilic mica substrate was stronger than that between hydrophobic graphene surface and hydrophilic substrate, which can narrow the space between MoS<sub>2</sub> and mica.

### ■ NANOMANIPULATION OF CONFINED WATER AND DOPING EFFECT OF CONFINED WATER ON GRAPHENE COATING

Without a 2D material coating, the water adlayers on a hydrophilic substrate can be easily disturbed using an AFM tip at RT.<sup>34</sup> Therefore, manipulation of water at RT is a great challenge. In the presence of a 2D graphene coating, individual confined water can be easily visualized and manipulated

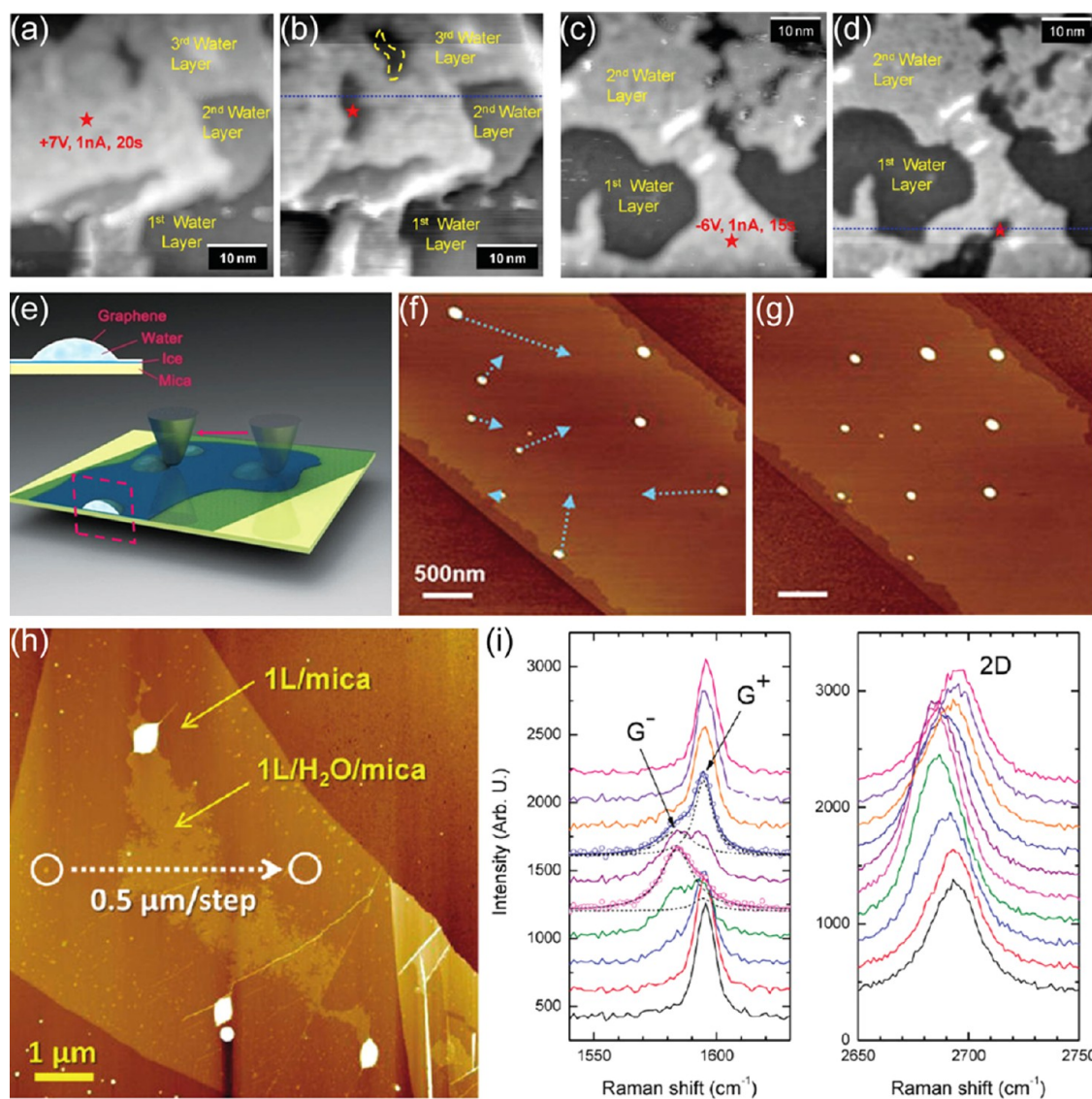


**Figure 8.** Structures and dynamics of a water adlayer confined between MoS<sub>2</sub> and mica. (a) Schematic representation showing the sandwich structure of MoS<sub>2</sub>/water/mica. (b) AFM image and height line-profile (along the red dashed line marked on the AFM image) of a monolayer MoS<sub>2</sub> on mica substrate under ambient conditions. (c) *In situ* AFM images of the confined water adlayer between MoS<sub>2</sub> and mica during heating and cooling processes. Reprinted with permission from ref 41. Copyright 2014 Nature Publishing Group.

simultaneously by standard SPM nanolithography techniques. He et al. attempted to manipulate the water layers by utilizing a STM tip.<sup>21</sup> As shown in Figure 9a–d, pinholes could be created in the second and third water layers by alternating polarity of sample bias. Under positive/negative bias, the tunneling electrons can transfer through graphene and directly interact with water to disturb the water layers. Interestingly, the first adlayer of water could not be manipulated because the ice-like first adlayer can strongly bind to substrate, which is consistent with the previous AFM study.<sup>16</sup> More recently, Cheng et al. applied an AFM tip to confined water for single droplet manipulation (Figure 9e).<sup>24</sup> With the assistance of a graphene coating and a very stable ice-like lubricant monolayer, these individual water nanodroplets can be manipulated in a controlled manner (Figure 9f,g).

Beyond confined water structures between graphene and mica substrate, the effects of confined water on the graphene coating are also investigated.<sup>22,25,27,42,48</sup> Shim et al. showed that the freshly cleaved mica substrate could induce hole-doping on graphene by permanent charge transfer.<sup>22</sup> However, an ultrathin interfacial water film of  $\sim 4$  Å thickness (Figure 9h) can effectively suppress the induced charge doping to a high degree visualized by Raman spectroscopy measurements (Figure 9i). Cao et al. reported the use of STM to characterize the local doping effects of the confined water clusters between bilayer graphene and Au(111) substrate.<sup>25</sup> The electron doping is closely associated with the sites of water clusters. In the meantime, the increasing size of the water cluster can further enhance the doping effect on graphene, which is in good agreement with the recent scanning Kelvin probe microscopy and Raman spectroscopy measurements.<sup>22,27,42,48</sup> The results in these studies will benefit control of the carrier densities of graphene and its electronic properties for future device applications.





**Figure 9.** Manipulation of water confined between graphene and a mica substrate. (a, b) STM images of the third water layer before and after manipulation by applying a positive sample bias. (c, d) STM images of the second water layer before and after manipulation by applying a negative sample bias. The red star markers on STM images indicate the position where the tip was centered. (e) Schematic diagram showing the manipulation of a water droplet using an AFM probe. Inset image shows the sandwich structure of graphene/nanodroplet/mica. (f, g) The disordered nanodroplets are rearranged with a multistep translation. The blue dashed arrows represent the pathway of the tip. (h) AFM image of graphene on a mica substrate. (i) A series of Raman spectra (G and 2D band) of graphene on mica substrate along the dashed arrow in panel h. Panels a–d reprinted with permission from ref 21. Copyright 2012 American Chemical Society. Panels e–g reprinted with permission from ref 24. Copyright 2014 American Chemical Society. Panels h and i reprinted with permission from ref 22. Copyright 2012 American Chemical Society.

## CONCLUSION AND OUTLOOK

The progress in an essential understanding of the structures and dynamics of the confined water at RT has been rapidly developed in the past few years. This Account reviewed the recent progress on water confined between 2D materials and various solid substrates. The approach of using graphene as an ultrathin coating has been recognized as an efficient method to study the structural and dynamic properties of confined water through such ideal model systems under ambient conditions. Those important findings in relation to the structure of water confined between graphene and solid substrate have been obtained; however, there remain many unresolved challenges such as the use of other methods (e.g., optical Raman, IR) to define the chemical structures of confined water and controlling the structures and dynamics of confined water and then using

these findings to improve the technological process. The examples given in this Account demonstrate that graphene and other 2D materials can create the nanoscopic confined space for investigating other confined liquids, which will lead to further discoveries and applications.

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## Notes

The authors declare no competing financial interest.

## Biographies

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