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Perspective: Structure and dynamics of water at surfaces probed by scanning tunneling microscopy and spectroscopy

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The detailed and precise understanding of water-solid interaction largely relies on the development of atomic-scale experimental techniques, among which scanning tunneling microscopy (STM) has proven to be a noteworthy example. In this perspective, we review the recent advances of STM techniques in imaging, spectroscopy, and manipulation of water molecules. We discuss how those newly developed techniques are applied to probe the structure and dynamics of water at solid surfaces with single-molecule and even submolecular resolution, paying particular attention to the ability of accessing the degree of freedom of hydrogen. In the end, we present an outlook on the directions of future STM studies of water-solid interfaces as well as the challenges faced by this field. Some new scanning probe techniques beyond STM are also envisaged. © *2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* [http://dx.doi.org/10.1063/1.4964668]

I. INTRODUCTION

The interaction of water with the surfaces of solid materials is ubiquitous and plays an essential role in a broad spectrum of basic and applied fields, including physics, chemistry, biology, environment, and material sciences.[1–4] The complexity of water at surfaces arises from the delicate interplay between the water-water interaction and the water-surface interaction, which leads to a large variety of different hydrogen-bonding (H-bonding) configurations and phases of water. Therefore, the water structure at surfaces is highly susceptible to the interfacial inhomogeneity and local environments, making the detailed molecular-level understanding indispensible. Conventional methods of investigating interfacial water are mostly based on spectroscopic and diffraction techniques, such as sum-frequency generation (SFG),[5] X-ray diffraction (XRD),[6,7] nuclear magnetic resonance (NMR),[8,9] neutron scattering,[10,11] and so on. However, those techniques suffer from the broadening and averaging effects due to the limitation of spatial resolution, which may easily smear out the subtle details of water-solid interaction.

A promising tool to overcome this difficulty is scanning tunneling microscope (STM), which is able to probe in real space the solid surfaces and the adsorbed molecules with Ångström resolution. To date, STM has been used to image the molecular frontier orbitals[12] and chemical structures[13,14] with submolecular resolution, ranging from small diatomic molecules to organic molecules or even biomolecules.[15,16] In addition to its unprecedented imaging capability, inelastic electron tunneling spectroscopy (IETS) based on STM pushes the vibrational spectroscopy down to the single bond limit.[17,18]

IETS actually endows STM with chemical sensitivity, which is important for molecular identification[19] as well as for studying intra- and inter-molecular interaction in energy space.[20] Besides using the probe tip for a measurement, STM offers the fascinating possibility of atomic manipulation techniques,[21,22] which allows the characterization of molecules at various surfaces under a well-defined environment and in a well-controlled manner. Notably, the chemical bonds of a single molecule can be selectively formed or broken by tunneling electrons.[23–25]

In spite of the advantages as described above, the application of STM techniques to water is not straightforward and easy. The main difficulties lie in the following three aspects. First, the water molecules are linked by H bonds, which are much weaker than the covalent and ionic bonds. It is highly possible that the water molecules can be disturbed by the STM tip during the imaging process and deviate from its original structure. Second, water is a close shell molecule, whose frontier orbitals are located very far away from the Fermi level (E_F). The electrons from the STM tip have little chance to tunnel into the molecular resonance of water, leading to a very poor signal-to-noise ratio. Finally, H atoms are very small and light, so it is very hard to access the internal degree of freedom of water. Those challenges greatly limit the application of STM in water systems until very recently new progresses have been made towards defeating those limitations, which may lead to a potential rise of the STM studies of water at surfaces.

In this perspective, we will put more emphasis on the technical aspects of STM to demonstrate the new capability of STM in probing interfacial water, since the scientific parts of water-solid interaction have been well reviewed and summarized by many excellent articles recently.[3,4,26–28] The article is organized as the following. In Section II, we

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review the recent advances of STM techniques, in terms of real-space imaging, single-molecule vibrational spectroscopy, and atom/molecule manipulation. We will discuss how those newly developed techniques are applied to probe the structure and dynamics of water at solid surfaces with single-molecule and even submolecular resolution, paying particular attention to the ability of accessing the degree of freedom of H. In Section III, we present an outlook on the directions of future STM studies of water-solid interfaces as well as the challenges faced by this field. Some new scanning probe techniques beyond STM are envisaged in Section IV. Finally, a summary is given in Section V.

II. RECENT ADVANCES OF STM TECHNIQUES APPLIED TO WATER/SOLID INTERFACES

A. Real-space imaging

The Ångström spatial resolution of STM allows the real-space imaging of water structure at surfaces with single-molecule precision. This provides an unprecedented opportunity for directly identifying the H-bonding configuration of water, which determines the physical and chemical properties of water/solid interfaces. Since STM usually requires conductive substrates, the majority of work has been focused on various metal surfaces since the beginning of this century. Individual water molecules could be visualized as round-shaped protrusions sitting atop the metal atoms of the substrate.[29–32] The STM images of water monomers did not show any internal structure, mainly due to two reasons. First, the water molecule is a close-shell molecule and its frontier orbitals are located very far away from the E_F. Thus, the water molecule simply acts as an energy barrier for the electrons to tunnel through. Second, the hybridization between the water and conduction electrons of the metal substrates may easily smear out the fine orbital structures of water. Therefore, the spatial orientation of the water molecules cannot be directly distinguished by STM, but have to rely on the density functional theory (DFT) calculations, which revealed a "lying" adsorption configuration, that is, the plane of the water molecule is almost parallel to the metal surface.[32–34]

Since water clustering and wetting on metal surfaces has been summarized in many excellent reviews articles,[3,4,26–28] here we will not go into the details. The current consensus is that there is no general model for water overlayer adsorption. The main factor governing the structure of water nanoclusters and overlayers at metal surfaces is the delicate balance between the water-water H bonding and the water-metal bonding, which leads to immensely rich phases of surface water on Cu(110),[35–37] Ag(111),[38,39] Pd(111),[40,41] Pt(111),[42,43] Ru(0001),[40,41] and Ni(111).[44] Therefore, the wetting behavior of water strongly deviates from the conventional bilayer-ice model, which was originally proposed by Doering and Madey to discuss interfacial water in almost all environments.[45] Furthermore, multilayer ice films on metal surfaces could also be investigated with STM.[46,47] However, the detailed H-bonding structure of those ice films was very difficult to

image due to the insulating nature of ice films thicker than a few layers, only with very limited success on ultrathin ice films (up to three layers).[48]

In recent years, STM studies of water on insulating surfaces have become possible and attracted increasing attention. Such experiments mainly rely on the ability of growing high-quality ultrathin insulating films/islands on metals, among which metal oxides and alkali halides are two ideal candidates.[49–51] Another way to enable the STM studies on bulk insulators is introducing dopants or defects to make the materials conductive.[52–54] Compared with metal surfaces, it is much easier to disturb the water on insulating surfaces due to the poor conductivity of the insulating materials and the prolonged lifetime of the electrons residing in the water molecules. Therefore, small tunneling currents (pA or sub-pA) are ideally needed when scanning water on those surfaces. Furthermore, the insulating films decouple electronically the water from the metal substrates, so it may be possible to image the intrinsic frontier orbitals of water provided that there is enough molecular density of states (DOS) at the proximity of E_F.

The adsorption of water on metal oxide surfaces is more complex than that on metal surfaces, because the water molecules bind not only with the metal cations but also with the oxygen anions, which usually facilitates the dissociation of the water molecule. TiO_2 is an important photocatalytic material, so tremendous efforts have been made to study the adsorption,[53,54] diffusion,[55] and dissociation[56,57] of water molecules on its surfaces. Water monomer adsorbed on the anatase TiO_2(101) was revealed as a "bright-dark-bright" feature at 190 K in the STM images.[54] DFT calculations predicted that the oxygen of water formed a dative bond with a surface Ti_{5c} and the hydrogen formed two weak H bonds with the neighboring bridging oxygen.[54] On the most stable surface, rutile TiO_2(110), it was found that water molecules are situated on the Ti rows and readily dissociated at the oxygen vacancies.[56,57] The RuO_2(110) surface has a very similar structure as TiO_2(110) and has been also extensively used for photocatalytic water splitting. Water monomers adsorbed at the Ru sites and diffused along the Ru rows above 238 K to form dimers.[58] As increasing the temperature to 277 K, the dimer dissociated (deprotonated) into Ru-bound H_3O_2 and bridging hydroxyl species.[58] Isolated water molecules on the Ag(100)-supported MgO films were imaged as bright spheres on top of the Mg cation.[49] Individual water molecules on the SrO-terminated surface of ruthenates appear as bright protrusions between two Sr atoms.[59] Further analysis of the dynamic behavior suggested that the water monomer actually dissociated, resulting in a pair of hydroxyl groups.[59]

Besides the monomers, water clusters and ordered overlayers have also been investigated on various metal oxide surfaces.[50,52,59–62] The water monolayer formed on the Sr_2RuO_4 surface contained a mixture of dissociated OH groups and molecular water, with the OH adsorbed at the Sr–Sr bridge site and the H_2O on top of Sr (Fig. 1).[59] The combination of constant-current STM images with dI/dV mapping provided comprehensive information of water clusters nucleated on the oxidized Cu(111) and revealed a new type of H-bonded cyclic
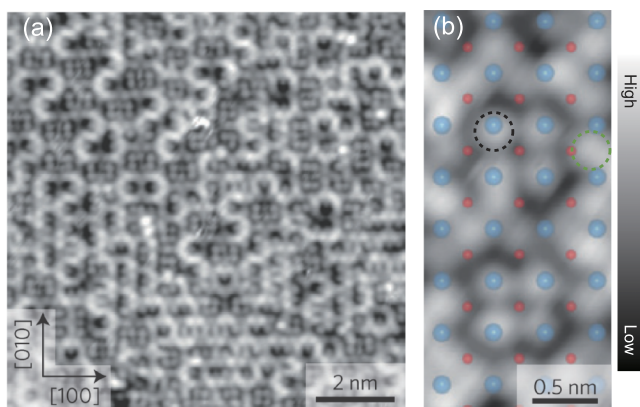
FIG. 1. (a) STM image of monolayer water grown on Sr_2RuO_4 substrate at 160 K. (b) Zoom-in STM image with substrate atoms superimposed. Blue and red spheres denote Sr and O, respectively. The water overlayer is a mixture of dissociated OH groups (dashed green circle) and molecular H_2O (dashed black circle). The OH adsorbed at the Sr–Sr bridge site, while the H_2O was positioned on top of Sr. Set point: V = 500 mV and I = 100 pA (a); V = 400 mV and I = 100 pA (b). Adapted with permission from D. Halwidl *et al.*, Nat. Mater. **15**, 450 (2016). Copyright 2015 Macmillan Publishers Ltd.[59]

water clusters, which interacted with the metal and oxygen sites simultaneously and cooperatively.[61] Water molecules formed large two-dimensional (2D) islands on the bare FeO/Pt(111) surface after annealing to 130 K, while on the hydroxylated FeO surface, water molecules tended to form H bonds with the hydroxyl groups resulting in an ordered ice-like hexameric nanoclusters at 110 K.[60] However, the wetting behavior on the α-Fe_2O_3(0001) is quite different. Water species were observed only on the Fe-terminated Fe_3O_4(111) surface at 235 K, whereas there were no water molecules adsorbed on the O-terminated FeO(111) surface.[52] When the temperature increased to 245 K, the intact water dissociated and regular hydroxyl groups appeared on top of the Fe cations.[52] It is notable that a variety of water overlayer structures formed on the ZnO surface at room temperature

and these structures were actually undergoing a dynamical process.[62]

One big limitation for real-space imaging of water with STM is the inability to resolve the OH directionality of a water molecule, which prohibits the determination of the detailed topology of the H-bonding configuration. Very recently, Guo *et al.* succeeded to achieve the submolecular orbital imaging of water monomers and tetramers on a Au-supported NaCl(001) film, which may defeat the limitation.[51] The key step is using the controllable tip-water coupling to effectively shift the lowest unoccupied (LUMO) and highest occupied (HOMO) molecular orbitals of water towards the E_F. This allows the orbital imaging of water near the zero bias, thus avoiding the instability induced by the excitation of the high-energy tunneling electrons. Based on the orbital imaging, the spatial orientation of the water monomers on the NaCl surface can be determined, which opens up the possibility of identifying the H-bonding directionality and the associated chirality of water tetramers (Fig. 2).[51] Such water tetramers acted as the basic building blocks on the NaCl(001) surface, which were interconnected via a novel bridging mechanism to form bigger water clusters and eventually tetragonal 2D bilayer ice at 77 K.[63] Different from the conventional hexagonal bilayer ice model, such 2D bilayer ice has unusually high density of Bjerrum D-type defects.[63]

B. Single-molecule vibrational spectroscopy

Compared with real-space imaging, vibrational spectroscopy of water with STM is premature and much less used, but can offer new insights into the H-bonding configurations, dynamics, and strength, especially the degree of freedom of hydrogen. The vibrational spectroscopy of STM is based on a technique called inelastic electron tunneling spectroscopy (IETS), which was first demonstrated by Jaklevic and Lambe in metal-oxide-metal tunneling junctions.[64] They observed an ~1% increase in the differential tunneling conductance $\frac{dI}{dV}$ at some characteristic voltages V across the junction, which
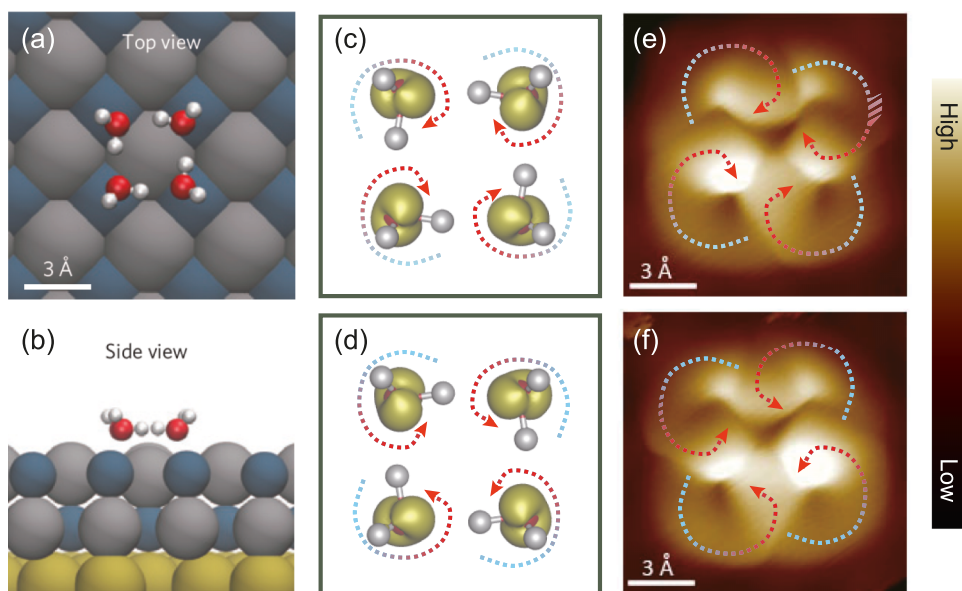

FIG. 2. Top (a) and side (b) views of the calculated adsorption configuration of a water tetramer on the NaCl(001) surface. ((c) and (d)) Calculated HOMO of two chiral tetramers with anticlockwise and clockwise H-bonded loops by plotting isosurfaces of charge densities integrated over 1 eV of the HOMO tail close to E_F. ((e) and (f)) STM images of the two chiral water tetramers. The chirality of the HOMO resembles that of the helical structures as shown in STM images. Set point: V = 10 mV and I = 140 pA. Adapted with permission from J. Guo *et al.*, Nat. Mater. **13**, 184 (2014). Copyright 2014 Macmillan Publishers Ltd.[51]

corresponded to vibrational frequencies of the molecular adsorbates at the oxide/metal interfaces. Tunneling electrons with sufficient energy excited molecular vibrations, thus opening a new inelastic channel paralleling the elastic tunneling current. This new channel would manifest itself more evidently if one takes the derivative of the $\frac{dI}{dV}$ curve. After thirty years, IETS was successfully realized in a STM junction by Stipe *et al.*, which pushed the limit of vibrational spectroscopy to a single molecule level.[17,18]

In the conventional STM-IETS regime, an electron from the STM tip that tunnels into one of the molecular orbitals would be temporarily trapped there with an average lifetime τ, leading to a change of the molecular nuclei position. After the trapped electron escapes eventually to the substrate, the molecule could be left unrelaxed in the excited vibrational state.[65,66] Therefore, basically there are two ways to enhance the IET cross section: either to increase the DOS near the E_F to resonantly enhance the electron-vibration coupling[67] or to increase the lifetime of the electron residing in the molecular resonant state. Unfortunately, both of them have proved extremely difficult for water at surfaces. For one thing, due to the close-shell nature of water, its frontier orbitals are located far away from E_F even in the adsorbed form.[51,68] For the other, the prolonged lifetime of the inelastic electron increases the instability of the molecules on the surfaces,[18] which is particularly true for small molecules like water.

Despite the aforementioned difficulties, pioneering STM-IETS experiments have been performed in various water-related systems. Morgenstern *et al.*[68] obtained the first IETS data for a close packed layer of water adsorbed on a Ag(111) surface at 70 K. It should be noted that a wide HOMO-LUMO gap existed in their system as revealed by Green function calculations, corresponding to the off-resonance IET case. Therefore, the signal-to-noise ratio of IETS features was not good enough to allow the accurate identification of various vibrational modes. In another experiment, Kumagai *et al.*[31] were able to measure the IETS of hydroxyl monomers and clusters, which were dissociated from the water molecules adsorbed on the Cu(110) surface. OH/OD bending and stretching modes can be clearly identified in the IET spectra, which were further used to study the dynamics of the hydroxyl groups. However, the IETS lineshapes were complicated by the structural change of the hydroxyl groups induced by the IET excitation.

The instability of molecules induced by the IET excitation invokes one to think about another spectroscopic method which might be complementary to IETS. Based on the power-law dependence of a single-molecule reaction and the (multiple) vibration-induced enhancement of the reaction,[69] Kawai *et al.*[70] proposed the scheme of action spectroscopy (AS). In a typical STM-AS experiment, the reaction yield Y is measured as a function of sample bias (Fig. 3(a)). The observed AS would possibly show several thresholds related to the vibrational or electronic states responsible for the reaction.[30,71–73] Although limited by the inability to clarify all vibrational modes of a certain molecule and the requirement of an average of multiple measurements due to the intrinsic stochasticity of single-molecule reactions, STM-AS indeed
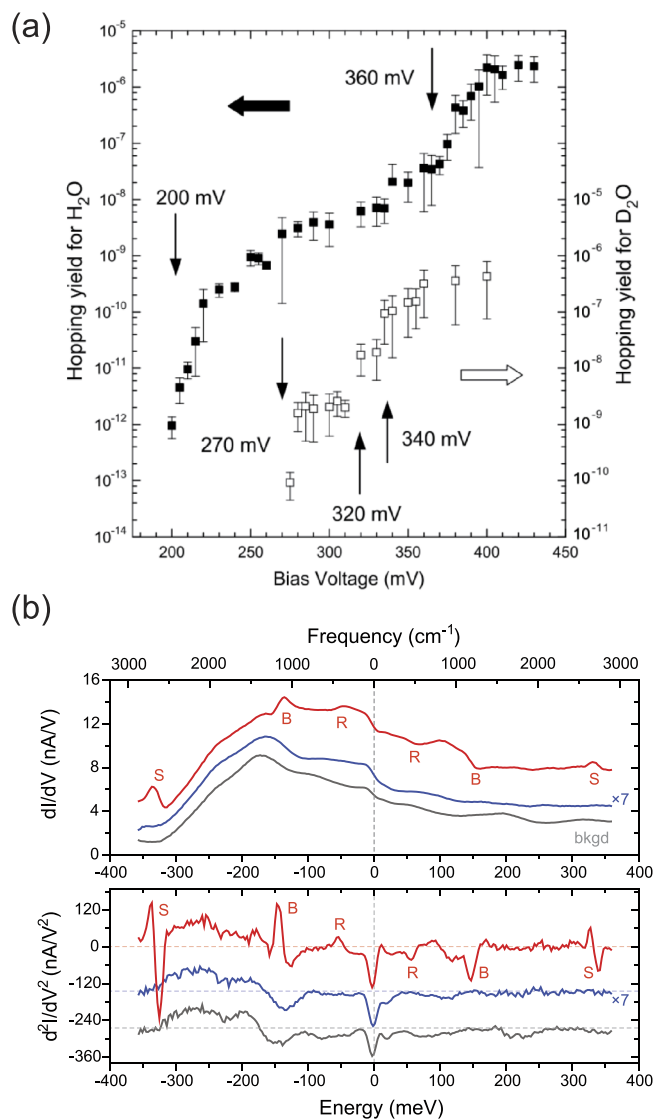

FIG. 3. (a) Action spectra of the lateral hopping of H_2O (filled square) and D_2O (empty square) dimer on Pt(111). Black arrows indicate the vibrational signals, appearing as sudden increase in the spectra. (b) dI/dV and d^2I/dV^2 spectra of a D_2O monomer on NaCl(001)/Au(111) obtained at different tip heights, red curve (−1.2 Å) and blue curve (−0.4 Å). Gray curves (−1.2 Å) were acquired on the NaCl surface (denoted as "bkgd"). The vibrational IET features are denoted as "R" (rotational), "B"(bending), and "S" (stretching). Dashed horizontal lines represent zero levels of the y axes for each curve. The tip heights in (b) are referenced to the gap set with V = 100 mV and I = 50 pA. (a) Adapted with permission from K. Motobayashi *et al.*, Surf. Sci. **602**, 3136 (2008). Copyright 2008 Elsevier;[30] (b) Adapted with permission from J. Guo *et al.*, Science **352**, 321 (2016). Copyright 2016 American Association for the Advancement of Science.[82]

holds complementary aspects when compared with STM-IETS.

First, IETS is commonly believed to be governed by the propensity rule.[67,74,75] Therefore, an opening of new vibrational channels would bring about dispersion and absorption effects in a single channel depending on the real and imaginary part of the Green function as well as interference effects between various channels,[76] complicating the acquired spectra and the extraction of vibrational energies. IETS-AS, on the other hand, is directly related to the vibrational excitation, simplifying the interpretation of the data. Second,

the few % change of the differential conductance in IETS sets very severe requirements on the mechanical stability of the STM system, which could be overcome by multiple measurements with the STM-AS method. So far, STM-AS has been successfully applied to several water-related systems, including selective dissociation of single water molecules on MgO films into different products by various vibrational excitations,[49] identification of the H bonds,[77] and recognition of reaction pathways in H transfer process.[78–81]

In order to enhance the IET cross section for water, Guo *et al.*[82] developed a tip-enhanced STM-IETS technique on the NaCl/Au(111) surface, which involved two key steps. First, the insulating ultrathin NaCl film decoupled water molecules electronically from the Au substrate so the lifetime of the electrons residing in the molecular resonant state was prolonged. Second, the Cl-terminated STM tip was used to tune the relative energy difference between the HOMO of water and E_F via electronic coupling, so the molecular DOS around the E_F was greatly enhanced. The Cl atom was chosen in light of the spatial match between the water HOMO and the Cl p_z orbitals. As a consequence, they were able to acquire near-resonant IETS of single water molecules (Fig. 3(b)). Since the water molecule was essentially confined in the hydrophobic cavity formed by the Cl-tip and the NaCl surface, it could remain stable against the excitation of the inelastic electrons, thus allowing the measurements of high-energy vibrational modes.

Compared with the conventional IETS, the tip-enhanced IETS possesses unprecedentedly high signal-to-noise ratio with the relative conductance change up to 30%. Therefore, it is very easy to assign each spectral feature to different vibrational modes. Furthermore, because of the extraordinary accuracy, it is even possible to determine the H-bond strength from the red-shift of the OH/OD stretching modes.[83] Through H/D isotopic substitution experiments, the impact of nuclear quantum effects (NQEs) on the H-bond strength was revealed at the single bond level.[82] For the next, it would be interesting to see whether the tip-enhanced IETS technique can be generalized to more complex water systems and different surfaces.

C. Atom/molecule manipulation

STM is not only an atomic probe for a measurement but also can artificially manipulate the individual atoms and molecules in a well controlled manner.[21,22,84–86] STM manipulation of water is facilitated by a variety of tip-water interactions (H bond, covalent bond, ionic bond, etc.), the localized electric field of the STM tip, and the excitation of the inelastic tunneling electrons, resulting in water diffusion,[49,87–90] clustering,[35,51,78,87] dissociation,[31,49,89] desorption,[89] and even proton transfer.[78–80,91] Artificial manipulation of water at a single molecule level provides a unique opportunity of studying water-surface and water-water
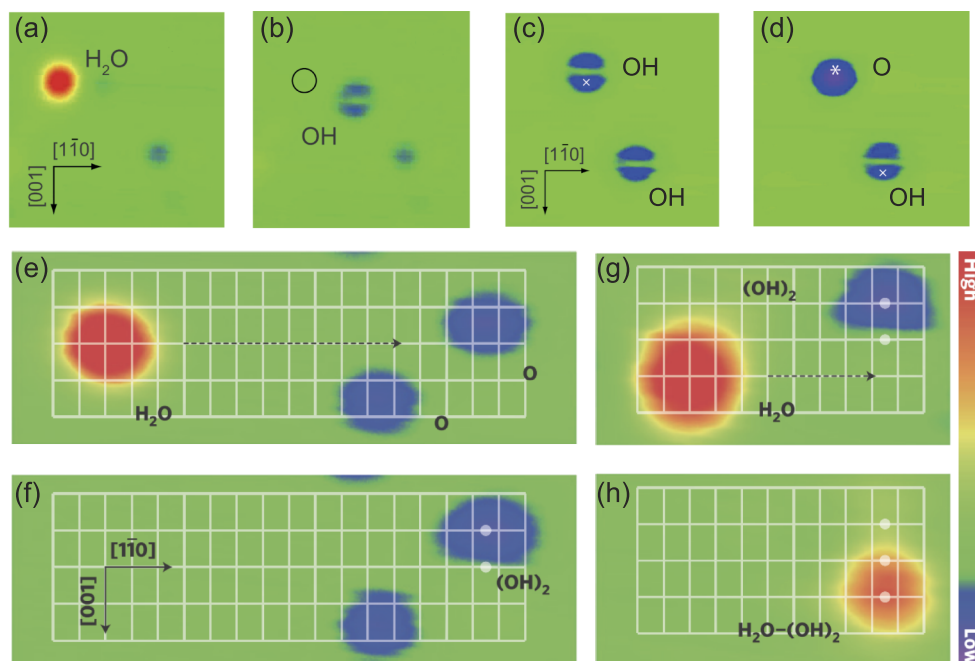

FIG. 4. ((a)-(d)) The dissociation of a water molecule on Cu(110) by a STM tip. (a) STM image of a water monomer. Applying a voltage pulse (2 V, 0.5 s) to the water monomer results in the product of OH species imaged as paired depression (b). The black circle (b) denoted the original position of the water monomer. Subsequently, a voltage pulse of 0.9 V was applied over the OH group at the position of the write cross (c) leading to the formation of atomic oxygen appeared as round repression (d). ((e)-(h)) Formation sequence of water-hydroxyl (H_2O–$(OH)_2$) chain by manipulating individual water molecules. The white grid lines indicate the lattice of Cu(110). The water monomer was manipulated by the tip along the dashed arrow towards the O atom (e) leading to the formation of OH dimer (f). Subsequently, another water monomer was pulled along the dashed arrow towards the end of the $(OH)_2$. (g) and the H_2O–$(OH)_2$ chain was constructed (h). All the images are acquired with the same set point: V = 24 mV and I = 500 pA. The sizes of the images are 47×47 Å^2 ((a) and (b)); 42×42 Å^2 ((c) and (d)); 20×58 Å^2 ((e) and (f)); and 20×36 Å^2 ((g) and (h)). ((a)-(d)) Adapted with permission from T. Kumagai *et al.*, Phys. Rev. B **79**, 035423 (2009). Copyright 2009 American Physical Society.[31] ((e)–(h)) Adapted with permission from T. Kumagai *et al.*, Nat. Mater. **11**, 167 (2012). Copyright 2011 Macmillan Publishers Ltd.[80]

interaction under a well-defined environment, which is not possible with any macroscopic spectroscopic and diffraction techniques.

Individual water molecules could be manipulated by the STM tip to construct various water clusters at the low temperature, some of which may also form through self-assembly at a higher temperature.[63] The biggest advantage of assembling water clusters by tip manipulation is that we know for sure how many water molecules are contained in the clusters. For water molecules, the lateral manipulation is more controllable and efficient than the vertical manipulation, which is in clear contrast with the case of a CO molecule.[92] Notably, the gap resistance required for the manipulation is very sensitive to the condition of tip apex and is much larger than that for manipulating atoms on metal surfaces. On the Cu(110) surface, water dimers, trimers, tetramers, and hexamers were reproducibly assembled at 6 K using the lateral manipulation in the "pulling" mode.[35] By manipulating water molecules and atomic oxygen, hydroxyl dimers and water-hydroxyl chains[80] could be reproducibly assembled on Cu(110) (Fig. 4).

The lateral manipulation procedure is also applicable on insulating salt surfaces. Water monomers adsorbed on the NaCl(100) film were easily manipulated to construct water tetramers and bigger clusters.[51] The manipulation becomes more controllable when the tip apex is functionalized with Cl because of the long-range electrostatic interaction between the water and the negatively charged Cl atom on the tip. More excitingly, it is promising that isotopic substitution experiments at the single molecule level can be achieved by

manipulating individual H_2O and D_2O molecules, which are distinguishable by STM-IETS.[82] In this way, it is possible to achieve precise control on the partial deuteration within a single water cluster, which actually provides a perfect platform to study quantum effects of protons in a well-controlled manner.[93]

When electrons tunnel through molecules, the electronic and vibrational excitation induced by the inelastic electrons can be used to manipulate the molecular dynamics.[69,94,95] Water diffusion,[49,88–90] dissociation,[31,49,89] desorption,[89] and restructuring[88,89] have been induced on a variety of metal surfaces and even insulating surfaces by injecting inelastic electrons from the STM tip. It was found that the diffusion of water monomers and clusters was enhanced once the bending and O–H stretching vibrational modes were excited by the tunneling electrons.[49,88–90] When a higher bias voltage (~2 V) was applied, water monomers on the Ru(0001)[89] and Cu(110)[31] dissociated due to the resonant electronic excitation, leaving a hydroxyl group (OH) anchored on the surfaces, which can be further dissociated into atomic oxygen (Fig. 4). In particular, Shin *et al.* found that the dissociation pathway of water monomers on the MgO(001) surface can be controlled by vibrational and electronic excitation, leading to different dissociated products.[49] In addition to water monomers, 3D amorphous ice decomposed and crystallised to form 2D ice clusters when irradiated by high-energy tunneling electrons.[96] The large-scale dissociation of the amorphous ice suggested that the reaction was basically induced by electron injection into the conduction band of ice.[97]
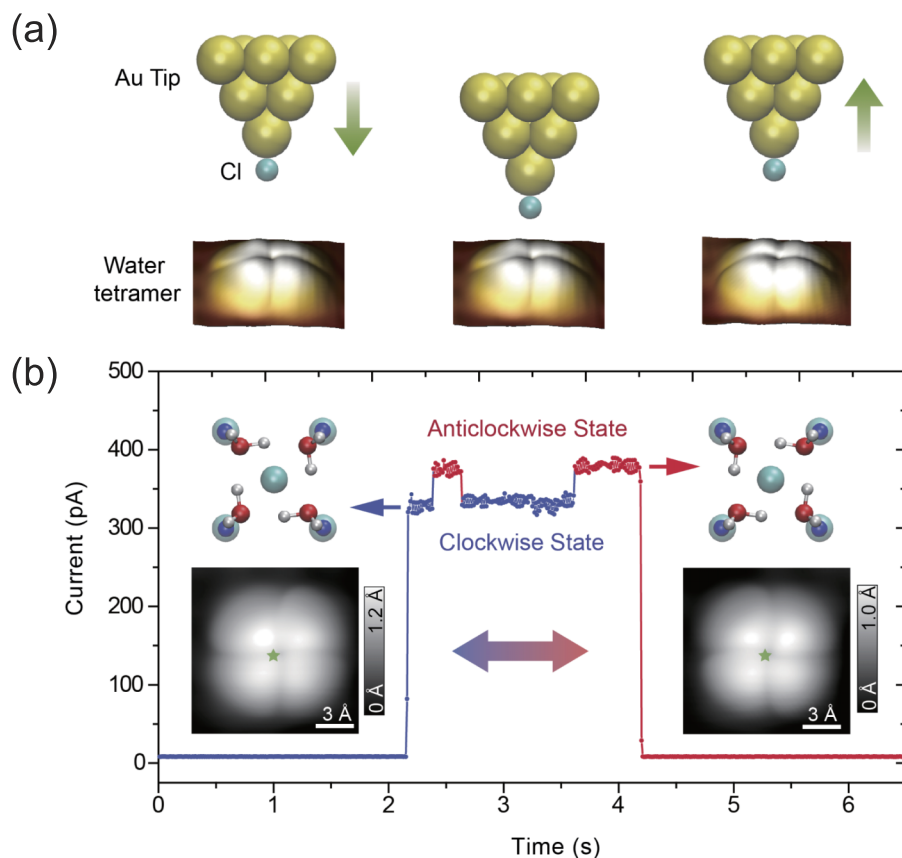

FIG. 5. (a) Chirality switching of a H_2O tetramer by the manipulation of a Cl-terminated tip. The tetramer stays in the clockwise state (CS) when the tip is far away from the tetramer (gap set with V = 5 mV and I = 5 pA) (left). Reducing the tip height by 230 pm leads to chirality switching (middle). Then lifting the tip back to the initial height leaves the tetramer in the anticlockwise state (AS) (right). (b) AS and CS of the water tetramer could be distinguished in the tunneling current trace as high and low current levels, respectively. Left and right insets: adsorption configuration (upper) and STM images (lower) of CS and AS tetramers, respectively. Set points of the STM images: V = 20 mV and I = 150 pA. The green stars in the STM images denote the tip position where the current trace is acquired. O, H, Au, Cl^- and Na^+ are denoted by red, white, golden, cyan, and blue spheres, respectively. Adapted with permission from X. Meng *et al.*, Nat. Phys. **11**, 235 (2015). Copyright 2015 Macmillan Publishers Ltd.[91]

More recently, STM has shown the possibility of probing and manipulating the proton dynamics within the H-bonded water clusters. Kumagai *et al.*[80] have demonstrated that by assembling a water-hydroxyl chain on a Cu(110) surface, they were able to trigger the sequential proton transfer (H-relay reaction) along the H-bonded chain by vibrational excitation. Moreover, due to the light mass of protons, proton transfer can occur through quantum tunneling.[98–100] The proton tunneling led to the H-bond exchange within a single water dimer on the Cu(110) surface, which was enhanced by the excitation of the intermolecular vibrational mode.[78] Meng *et al.*[91] revealed that the proton tunneling within a water tetramer on a NaCl(001) surface actually involved four protons in concert, corresponding to a many-body tunneling process. This was achieved by monitoring the reversible interconversion of the H-bonding chirality of the water tetramer with a Cl-terminated tip (Fig. 5). It is interesting that such a concerted proton tunneling can be manipulated by engineering the coupling symmetry between the STM tip and the four protons.[91]

Due to its atomically sharp nature, the STM tip is also ideal for defining, changing, and controlling the local environment of the water in a precise way. Gawronski *et al.* employed the electric field of the STM tip to change local potential of the water clusters on Ag(111) and achieved selective control on the water diffusion and H-bond rearrangement within the clusters.[101] Functionalizing the tip with negative ions usually enhances the electrostatic interaction between the protons and the tip, which significantly changes the energy barrier for proton transfer (Fig. 5).[91] In addition to the electrostatic coupling, Guo *et al.* also found that the electronic coupling between the functionalized tip and the frontier orbitals of water substantially changed the distribution of molecular DOS around the E_F, facilitating the orbital imaging and IETS measurement of water molecules[82] as described in Secs. II A and II B. Therefore, it is becoming a new trend to create desirable local environment of water and study its influence on water with properly functionalized tips.

III. PERSPECTIVE ON FUTURE DIRECTIONS

A. Confined water

It is well known that the confined water shows many exotic physical and chemical properties, which are rather distinct from those of the bulk water. Such low-dimensional water determines aspects of various phenomena in materials science, geology, biology, tribology, and nanotechnology. As we already reviewed above, water at surfaces represents an archetypal example of the confined water, which is ideal for STM studies. However, water buried at the interfaces is usually not accessible by STM. Recently, the water confined between the ultrathin 2D materials and various solid surfaces has attracted extensive attention and opens up the possibility of probing the water confined at solid/solid interfaces with STM.[102–105] The 2D layers coated on the surface water is so thin that any geometric and electronic corrugation of the underlying water layer is easily reflected on top of the 2D

layers. Those 2D layers also act as protecting layers, enabling stable STM measurements even at ambient conditions.

The water adlayer growth at both hydrophilic and hydrophobic substrates in the presence of 2D coating materials has been successfully realized, but the water structure is yet to be determined.[102–104] In particular, water confined between the graphene and mica surface forms nanodroplets at room temperature.[103] This provides an exciting chance to probe the liquid-like water and manipulate nanofluidics by STM. It is even possible to confine the water in between the hydrophobic graphene layers.[105] Such a hydrophobic confinement applies a high pressure to the water, leading to the formation of a close packed square ice structure,[105] which resembles the high-pressure tetragonal phase of bulk water. Very recently, single water molecule and water dimmer have been encapsulated into the single fullerenes, yielding a 3D confinement of water.[106,107] Those water-contained fullerenes can be easily prepared on the surfaces and are quite inert to harsh environments, thus providing an ideal platform for studying the intrinsic properties of water and H bonds.

Another interesting system is water confined in the nanopores of the covalent organic framework (COF) and metal organic framework (MOF) on metal surfaces.[108,109] Those nanopores in MOF or COF provide 2D lateral confinements to water. The advantage of the MOF and COF is that the size of the nanopores is adjustable by a self-assembly technique. It would be interesting to study how the size of the lateral confinement affects the water structure and dynamics. Hydrophobic and hydrophilic confinements can be selectively achieved by functionalizing the molecules with proper chemical groups. In addition to the lateral confinement, the vertical confinement can be implemented by approaching the STM tip to the water confined in the nanopores. The interaction between the water and the tip is also tunable by functionalizing the tip apex with different atoms or molecules.[51,82,91] The cavity formed by the nanopores and the STM junction is sizeable, which may allow the well-controlled "high-pressure" experiments of water/ice[110] with a STM setup.

B. Water hydration

Hydration is of relevance for a wide range of fields and systems, including electrochemistry, biological environments, and atmospheric aerosols. So far the information on microscopic structures of hydrates mainly comes from the theoretical simulations,[111,112] while the molecular-level experimental studies are very scarce. Based on the ability to probe water at surfaces with STM, it is possible to further explore the hydration interaction between water molecules and other adsorbates on surfaces. Many interesting fundamental issues about hydration can be directly addressed with single-molecule precision, such as the solvation of salts,[112–114] the nature and range of the ion-water interaction,[115] the H-bonding dynamics of the hydration shell,[116] hydrophobic hydration,[117] and the impact of external electric fields on hydrations.[118] This is a relatively new field for STM community. In the following, we propose several possible systems for future studies.

Salt surface provides an unprecedented opportunity for studying the ion hydration. Previous works show that it is possible to pull out individual cations and anions from the surface by the STM tip.[91,119] Thus, it is foreseeing that ion hydration clusters can be formed by artificially manipulating individual water molecules and ions on the salt surfaces. This capability is particularly useful to clarify the microscopic structure of the hydration shell and the mechanism of ionic-specific effects. The effect of the ions on the H-bonding dynamics of the surrounding water can be also addressed based on such a manipulation method. Along this line, ion hydration can be studied in a well-controlled manner and in great details, which may provide new perspective to the initial stage of salt melting,[111–113] water desalination,[120] and the selectivity of ion channel.[121]

For molecular hydration, the choice of the substrates is very critical. It is desirable to choose the hydrophobic surfaces to minimize the interaction between the water and the surfaces. Meanwhile, the hybridization between the substrates and the molecules should be as small as possible to preserve the electronic structure and the chemical structure of the molecules. In light of those requirements, graphene and Au surfaces might be two good candidates. In addition, these two surfaces are both inert to the ambient environment, making them compatible to the standard preparation procedure of large molecules on the surfaces by a spin-coating method or a pulse injection method.[122,123] One noteworthy example of the molecular hydration is the protein hydration.[124] STM should be ideal in identifying the hydration sites and tracking the protein dynamics during the stepwise hydration process at a single-molecule level by tip manipulation. Combined with *ab initio* simulations, it may shed new lights on the competition between the water-water interaction and water-protein interaction, which plays an important role in many biochemical processes including protein folding,[125,126] enzyme function,[127] and molecular recognition.[128]

C. Nuclear quantum effects

The complexity of water largely arises from the nuclear quantum effects (NQEs) in terms of tunneling and zero-point motion, due to the light mass of H nuclei (proton). The NQEs play important roles in the structure, dynamics, and macroscopic properties of water.[4,110,129–131] Despite enormous theoretical efforts on pursuing proper treatment of the nuclear motion at a quantum-mechanical level, accurate and quantitative description of NQEs has proven experimentally challenging for decades. The main difficulty lies in that the quantum states of H nuclei are extremely sensitive to the coupling with local environments, leading to significant broadening and averaging effects when using conventional spectroscopic or diffraction techniques.[98,132–134] Therefore, it would be ideal to address the NQEs at a single molecule level.

One way to probe the NQEs with STM is locating in real space the position of protons within the H-bonded network, such that the motion of the protons can be tracked. This requires the ability to access the internal degree of freedom of water molecule, which is quite challenging.

Although the studies towards this direction are very limited, some substantial progresses have been made in recent years. Not only the single proton tunneling and sequential proton tunneling were visualized,[78,80,81] but the direct evidence has been also obtained for the concerted proton tunneling in a water tetramer on a NaCl(001) surface by monitoring the H-bonding chirality switching.[91] It was subsequently found by rotational spectroscopy that such a concerted proton tunneling can even occur in the water hexamer prism.[135] The other way to detect the NQEs is using vibrational modes of water as the sensitive probes in energy space.[82] The anharmonic zero-point motion of the H nuclei can change the H-bonding strength,[136] leading to the shift of the vibrational frequency. The contribution of the NQEs is usually evaluated by performing isotopic substitution experiments.[82,134,135] Using single-molecule vibrational spectroscopy based on STM-IETS, we have recently extracted quantitatively the quantum component of a single H bond and unraveled the influence of polar environment on the NQEs.[82]

STM studies of the NQEs in water are still at the very beginning. There are many important issues yet to be solved. For instance, it would be interesting to explore how the confinement affects the NQEs. It was recently found that a single water molecule confined inside a hexagonally shaped channel of the gemstone beryl exhibited a new quantum state, which smeared out the positions of the H atoms into a pair of corrugated rings due to the quantum tunneling.[137] It also remains a question what would happen if the NQEs are entangled with the correlation effects, as stepping further from the single water clusters to larger ones or more extended H-bonded network.[91,138,139] Since the NQEs are very sensitive to the temperature, the temperature dependence of NQEs also needs systematic studies in a large range of temperature. In addition, the detection by STM can easily destroy the quantum coherence of the nuclear quantum states due to the scattering of the tunneling electrons. How to achieve coherent detection with STM is an even more challenging issue.

IV. CHALLENGES AND NEW POSSIBILITIES

A. Determination of the detailed topology of the H-bonded network

Although STM has proven to be powerful for identifying the microscopic structure of water adsorbed on solid surfaces with single-molecule or even submolecular resolution, the determination of the detailed topology of the H-bonded network is still not straightforward. The reason is that STM mainly probes the local DOS near the E_F (molecular frontier orbitals), which is not easily related to the chemical structure of molecules. It has been shown that the spatial orientation of single water molecules on the surfaces can be deduced from orbital imaging,[51] but this strategy is not viable for complicated H-bonded network and needs to reply on sophisticated STM simulations. In addition, STM experiments usually require conductive substrates or atomically thin insulating layers, which greatly limits the application of STM in water science.

Recent advances in qPlus-based noncontact atomic force microscopy (nc-AFM) show the ability to achieve superior resolution in real space.[140–146] The high stiffness and high quality factor of the tuning fork allow the probe to access the short-range forces with a very low detection noise level, which yields the unprecedented atomic resolution within a single molecule. Different from STM, nc-AFM is sensitive to the total density of electrons, which is closely correlated with the nuclei. Therefore, nc-AFM can directly image the chemical structure of single molecules,[140] charge distribution within a single polar molecule,[144] and even the internal structure of metal clusters.[145] Strikingly, nc-AFM is also applicable to H-bonded systems and even multilayer ice.[146] The H-bonding skeletons of molecular assemblies could be directly imaged,[143] although the origin of those H-bond like features is still under debate.

When applying nc-AFM to water systems, there exist two main challenges. First, H bonds are much weaker and more flexible than covalent or ionic bonds, so the water structure may be easily disturbed by the tip-water interaction. This problem becomes more serious considering that the submolecular resolution of nc-AFM is only achieved at the very small tip-molecule separation where the short-range force dominates.[147] This difficulty might be overcome by using flexible tip termination (such as CO) which is more prone to relax than the water molecule. Second, the water molecule has a strong dipole moment, so the electric fields within the H-bonded water network can be highly inhomogeneous. In such a case, the imaging mechanism becomes more complicated than that of weakly polar molecules, in light of the important role of electrostatic force.[148–150] However, this might be a good chance to map out the electrostatic potential of water using ion-functionalized tips.

B. Ultrafast H-bonding dynamics

The bandwidth of the STM electronics is usually limited to MHz range. However, the time scale of H-bonding dynamics in water such as proton transfer, bond-formation and breaking, and energy relaxation is typically within picosecond (ps) or even femtosecond (fs) range. Therefore, with STM one can only probe the initial states and the final states, without any information of the intermediate or transition states. Combining STM with ultra-fast laser is expected to achieve both Ångström spatial resolution and femtosecond temporal resolution simultaneously.[151,152] In such a setup, two laser pulses with a time delay are focused into the STM junction, exciting the molecules on the surface one after the other. The excitation of the molecule will induce a transient change of the tunneling current. If the molecule excited by the first pulse does not relax to the ground state at the moment when the second pulse arrives, the second pulse cannot induce a current change. Changing the delay between the two laser pulses thus leads to a variation of the average tunneling current, which could be readily measured by the slow STM electronics. Therefore, the temporal resolution is only limited by the width of the laser pulse.

The application of laser-combined STM has been successfully demonstrated on semiconductor surfaces, focusing on the charge carrier dynamics and spin relaxation dynamics.[151,152] Applying such a technique to water systems needs further improvement of the signal-to-noise ratio and ensuring the stability of water molecules under the laser illumination. In addition, the thermal disturbance of the laser on the STM tip is an intractable issue. In the last decade, some research groups have made solid progresses towards eliminating or attenuating the laser-induced thermal effects, including the use of the shaken-pulse-pair method,[153] pulse-picking method,[152] THz pulse probe,[154] high-repetition rate of laser, and so on. The laser-combined STM is particularly useful to study the H-bonding dynamics of interfacial and confined water, which are susceptible to the coupling with the local environments. It is predictable that the laser-STM will become a powerful tool in the near future for investigating various ultrafast dynamics processes at the single molecule level, which may reshape our current knowledge of water/solid interfaces.

C. Non-perturbative scanning probe technique

An intrinsic problem of scanning probe microscopes (SPMs) is that all the probes inevitably induce perturbation to the water structure, due to the excitation of the tunneling electrons and the tip-water interacting forces. In addition, high-resolution STM/AFM measurements usually require ultrahigh vacuum (UHV) conditions and low temperatures, otherwise the imaging would become unstable and very difficult to understand. Those limitations make SPM fall short when compared with the conventional spectroscopic methods such as optical spectroscopy, neutron scattering, and nuclear magnetic resonance (NMR). Recently, an emerging SPM technique, which employs the nitrogen-vacancy (NV) center as the scanning probe (NV-SPM), shows great potential to overcome those limitations and may become an ideal non-perturbative tool for the study of interfacial water systems under ambient conditions.

NV defect centers naturally existing in diamond serve as nanoscale magnetometers because of its atomic size and proximity to diamond surface (<10 nm). Its lone-pair electrons result in a triplet ground state, whose spin state can be polarized by laser excitation and readout by spin-dependent fluorescence. Long-coherence time (0.1–1 ms)[155] makes such solid-state quantum sensors stable at ambient conditions and easy to be coherently manipulated by a microwave pulse sequence. Unknown target spins and magnetic field could be sensed by a single NV center through magnetic dipole interaction, which allows the detection of weak signals such as spin fluctuations of protons in water at a probe-sample distance of 5–20 nm.[156,157] Meanwhile, the power of excitation/readout laser is as low as several tens of microwatt, so the laser-heating effect is negligible. Therefore, NV-SPM is almost non-invasive to the water structure during the imaging.

In addition, NV-SPM is compatible with both low-temperature UHV environment[158] and ambient conditions. The diamond host of the NV center is quite inert to the harsh environments and the coherence time of NV center changes very small over a large range of temperature (4–300 K).[159]

Therefore, the NV-based magnetometry is not only suitable for probing single water molecules and clusters under UHV and low temperature but is also free of the disturbances and thermal fluctuations of atmospheric environment at room temperature, thus allowing the detection of thermal dynamics of small ensemble (10^3–10^4) of protons.[156] Therefore, this new technique is very promising to bridge the gap between the UHV and the realistic conditions.

Finally, NV-SPM is able to conduct NMR spectroscopy at nanoscale or even a single molecule level. Similar to RF pulse-based technology ubiquitously applied in conventional NMR experiments, modified elaborate microwave pulse sequence endows NV-SPM with a variety of spectroscopic technologies with a high resolution (∼10 kHz) and a large bandwidth (DC to ∼3 GHz).[160,161] For example, intramolecular proton magnetic resonance of a single water molecule could be resolved by an extremely proximal NV center or by the quantum state transference through reporter spin[162] near the target molecule; proton correlations[163] and molecular dynamics[164] could be analyzed from relaxation/dephasing spectroscopy mapping with nanoscale spatial resolution.

V. SUMMARY

Since the beginning of this century, STM has been extensively applied to investigate the water at solid surfaces, including the most studied metal surfaces and the less understood insulating or semiconducting surfaces. Besides the real-space imaging technique, the vibrational spectroscopy and the atom/molecule manipulation techniques have gained substantial advances and started to show great power in the STM studies of interfacial water. The most exciting advance in this field probably lies in the ability of accessing the degree of freedom of H nuclei, such as discerning the O–H directionality, tracking the proton transfer within the H-bonded network, and probing the nuclear quantum effects of protons. So far, most of the water/solid systems studied by STM are still somewhat too simple and idealized. Now it is the time to apply STM techniques to more complex and realistic water-related systems, such as confined water, bulk ice, multilayer water, and water hydration systems, which will definitely continue to create surprises in the years to come.

Furthermore, it is also necessary to introduce new SPM techniques to overcome the intrinsic limitations of the STM. First, qPlus-based nc-AFM is able to reveal the detailed topology of H-bonded network on both metallic and insulating substrates in real space, which may make the structure determination much easier and more direct. Second, the combination of STM with ultra-fast laser technique is expected to improve the temporal resolution of STM to ps or fs, thus enabling the investigation of various ultrafast H-bonding dynamics processes at the single molecule level. Third, the SPM based on NV-center magnetometry shows great potential to become a non-perturbative tool for studying the interfacial water under ambient conditions, through probing the proton spin with nanoscale precision. We are confident

in that those new scanning probe techniques will open up new avenues for the research of interfacial water, which may refresh on our current understanding of water-solid interactions.

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