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Observation of water dissociation on nanometer-sized FeO islands grown on Pt(1 1 1)

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ABSTRACT

Adsorption and dissociation of water on nanometer-sized FeO islands on Pt(1 1 1) substrate were investigated using scanning tunneling microscopy. It is observed that the adsorbed water molecules may spontaneously dissociate into hydroxyls on the step edges of the FeO(1 1 1) islands, even at 80 K, which can be attributed to the active sites of coordinatively unsaturated Fe atoms at the step edges. These hydroxyls are found to diffuse and form chains on the FeO terrace. The formation of the oxygen vacancy chains on FeO islands indicates that the hydroxyls may desorb from the surface as H_2 and H_2O at room temperature.

1. Introduction

Oxide surface plays an important role in the surface chemistry and heterogeneous catalysis. The chemistry of water on oxide surfaces has received considerable attention [1–6]. Water adsorption on epitaxial films of iron oxides grown on Pt(1 1 1) substrate has been investigated by thermal desorption spectroscopy (TDS), infrared reflection absorption spectroscopy (IRAS) and photoelectron spectroscopy (UPS, XPS) [7–10]. Perfect oxygen-terminated FeO(1 1 1) monolayer films are chemically inert [7–9]. Water molecularly physisorbs through an attractive electrostatic interaction between the oxygen atoms of the adsorbates and the Fe cations located on the second layer. The IRAS measurements show that water is hydrogen bonded at low coverage even at 30 K, and no evidence of isolated water monomers is found. A kinetic analysis determined the isosteric heats of adsorption of $q_{st} = 52\ \mathrm{kJ\ mol^{-1}}$, with a preexponential $\nu = 3 \times 10^{15}\ \mathrm{s^{-1}}$ for the monolayer and $q_{st} = 47\ \mathrm{kJ\ mol^{-1}}$, $\nu = 3 \times 10^{15}\ \mathrm{s^{-1}}$ for the bilayer [9]. On Fe_3O_4(1 1 1) surface exposing both iron and oxygen atoms, initial water adsorption is dissociative. The resulting OH group binds to the iron cations and the H species to the neighboring oxygen sites. As the coverage increases, coadsorbed water molecules bridge the OH and H groups forming a hydronium-ion-like structure OH_3^+–OH [10]. Joseph et al. [7,11] determined the heats of adsorption for the dissociated γ-species (65 kJ $\mathrm{mol^{-1}}$). A recent work by Cutting et al. [12] has demonstrated that the saturation coverage of dissociated water on the Fe_3O_4(1 1 1) surface is limited to the number of surface Fe sites, indicating that the metal sites are the active centers for water dissociation. Using the 'atom-dropping' preparation technique, Parkinson et al. [13] investigated the interaction of Fe^0 atoms with D_2O layers on FeO(1 1 1) and found dissociation products of FeOD and hydroxyl.

Ultra-thin FeO(1 1 1) films can be reduced after exposure to atomic hydrogen at room temperature, leading to the formation of triangularly-shaped oxygen vacancy dislocation loops at specific sites [14,15]. Knudsen et al. [16] observed that water dissociates on the most heavily reduced FeO_x film. The presence of triangular oxygen vacancy dislocation loops was resulted from the reduction of FeO film [14–16], in which the hydroxyls desorb as H_2 and H_2O from the surfaces by either heating the hydroxylated surface to 500 K [14] or increasing the concentration of the hydroxyl to a threshold of 12% ML [16]. Two types of oxygen vacancy dislocation loops were observed [15,16]. The smaller one is always centered at hcp domains with an edge length of approximately five Fe atoms, and the larger one is always centered at the top domains with an edge length of 12 Fe atoms.

Peculiar catalysis of oxide nanoparticles has attracted many concerns, such as gold nanoparticles supported on TiO_2 and nanoparticulated CeO_2 [17]. For the Pt/oxide nanocatalysts, its activity in the preferential oxidation (PROX) reaction at low temperatures could be enhanced by Fe or FeO_x additives [18,19]. The interfacial $CO_{ads} + OH_{ads}$ reaction to produce CO_2 occurred facilely at the Pt–oxide interface at low temperatures [20]. Generally, surface defects strongly influence the surface chemistry of metal oxides. Precisely monoatomic-height step edges at terraces constitute some of the most common defects on the surface. Kim et al. [21] showed that the alcohols dissociate primarily at FeO(1 1 1) step edges. It is found that the step edges are also responsible for the CO oxidation [22]. Similarly, the anatase TiO_2(1 0 1) surface is fairly nonreactive for water dissociated [23]; however, theoretical calculations by Gong et al. [24] showed that both molecular and dissociative H_2O adsorption can occur at the step edge.

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In this Letter, we studied the effect of the edges of FeO islands on the adsorption behavior of water molecules using scanning tunneling microscopy (STM). The dispersed nanometer-sized FeO islands were grown heteroepitaxially on Pt(1 1 1) substrates. The adsorption behaviors of water on the islands were characterized both at room temperature and at 80 K. The presence of surface hydroxyls and oxygen vacancy chains on the islands after water adsorption indicates that water is dissociative. We suggest that the coordinatively unsaturated Fe atoms were the active centers for water adsorption and dissociation.

2. Experimental details

The STM experiments were performed using a low temperature scanning tunneling microscope (OMICRON, SCALA), in an ultrahigh vacuum (UHV) analysis chamber with a base pressure of $\sim 5 \times 10^{-11}$ mbar. The Pt(1 1 1) single crystal sample was prepared in an UHV preparation chamber with a base pressure of 3×10^{-10} mbar. The Pt(1 1 1) surface was cleaned by cycles of Ar^+ sputtering (1 keV, 20 min) and annealing (flash to 1000 K, 20 min). The FeO islands were prepared by depositing submonolayer of Fe at 150 K with an e-beam evaporator in O_2 partial pressure of 5×10^{-7} mbar. After the vacuum pressure recovered to about 5×10^{-10} mbar, the sample was then annealed to 410 K for 1 min. Water (deuterium depleted, from Sigma–Aldrich) was degassed in several freeze–pump–thaw cycles and introduced into the STM by using a leak value. The water dosing was performed by keeping the sample at room temperature or keeping the sample onto the cryostat of the microscope at 80 K. All STM measurements were performed at 80 K with a constant current mode. A chemically etched tungsten tip was used.

3. Results and discussion

Figure 1a shows the image of nanometer-sized FeO islands dispersed on Pt(1 1 1). Overall, the islands are triangular but with truncated corners. This shape is similar to FeO particles grown on Au(1 1 1) [25]. The size distribution of FeO islands is plotted in Figure 1b. The islands are mainly distributed between 20 and 40 nm^2 in area. The moiré patterned feature in the islands is similar to that in FeO(1 1 1) monolayer on Pt(1 1 1) [26–28]. It is suggested that lattice mismatch between the hexagonal Fe/O-lattice (3.1 Å) and the Pt(1 1 1) substrate (2.78 Å) as well as a small rotation of the Fe/O-lattice relative to the substrate ($\sim 0.6°$) leads to a characteristic moiré patterned structure with ~25 Å periodicity [29]. There are three different domains in the FeO(1 1 1) monolayer, i.e., Fe on top sites (Fe–top), Fe on fcc sites (Fe–fcc), and Fe on hcp sites (Fe–hcp) of Pt(1 1 1) surface [30,29]. The FeO(1 1 1) monolayer consists of a hexagonal Fe-lattice sandwiched in between the Pt(1 1 1) substrate and a hexagonal surface layer of O atoms. As shown in Figure 1c, the atomic resolved image of the Pt(1 1 1) substrate was obtained, which is used to determine the orientation of the islands. It is also noted that there exist dark spots on Pt(1 1 1) substrate between the FeO islands (Figure 1d). These dark spots have quite similar feature as the observation for oxygen atoms on Pt(1 1 1) [31]. Therefore, we assign the dark spots on Pt substrate to the residual oxygen atoms in our sample. The coverage of oxygen is about 0.02 ML. Figure 1e shows a typical atomic resolved image of an FeO island. The centers of the different domains (Fe–top, Fe–fcc, and Fe–hcp) are labeled by circles in the island. The edges of the islands approximately run along $\langle 1\,1\,0 \rangle$ directions. According to the features of the orientations of the island edges and the moiré patterned structure, such islands should adopt the same structure as that for the FeO(1 1 1) monolayer [26–28]. As an example, the atomic model of the FeO island is schematically given in Figure 1f. In the model, the centers of the different domains are correspondingly labeled. We suggest that the edge atoms of the FeO islands are coordinatively unsaturated [22]. In the truncated triangular island, there exist nonequivalent edges, as marked by A and B. In the edge A each outermost Fe atom is bonded with two oxygen atoms (two-fold coordinated Fe atom), while in the edge B each outermost Fe atom is only bonded with one oxygen atom (one-fold coordinated Fe atom). An edge with two-fold coordinated Fe atoms should be energetically more stable than the one with only one-fold coordinated Fe atoms. Therefore, the edge A with a longer lateral length is assigned to two-fold coordinated Fe atoms, and the short edge B to one-fold coordinated Fe atoms. There is some evidence that such coordinatively unsaturated Fe atoms are responsible for the catalytically active sites for CO oxidation [22]. The islands have slightly bright edges, but from the line profile the step edges have almost the same height as the terrace, as shown in Figure 1g.

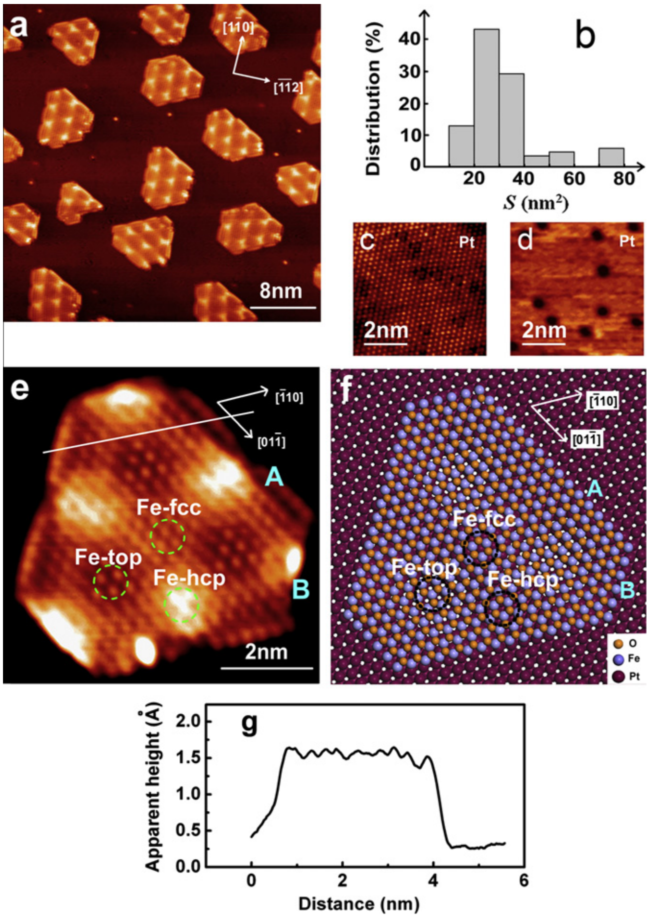

Figure 1. (a) STM image of FeO islands grown on Pt(1 1 1) (acquired at 50 mV and 1.2 nA). (b) Plot of size distribution of FeO islands. (c) Atomic resolved image of the bare Pt(1 1 1) substrate before FeO growth (acquired at 3 mV and 6 nA). (d) Image of Pt(1 1 1) between the FeO islands after FeO growth (acquired at 50 mV and 1.2 nA). (e) Atomic resolved image of an FeO island with two sets of edges A and B (acquired at 20 mV and 2.1 nA). The circles represent the centers of three different domains of Fe on top sites (Fe–top), Fe on fcc sites (Fe–fcc), and Fe on hcp sites (Fe–hcp) of Pt(1 1 1) surface. (f) Ball model (top view) corresponding to the FeO island in (e). (g) Line profile for the label line in (e).

Following, the sample was exposed to 10 Langmuir water (1.3×10^{-7} mbar for about 100 s) at room temperature. We allowed the sample to be maintained at room temperature for about 6 h with a vacuum pressure of about 5×10^{-11} mbar. Figure 2a shows a typical image of FeO islands. The images were acquired at 80 K. Compared with the as-grown FeO islands (Figure 1a), the

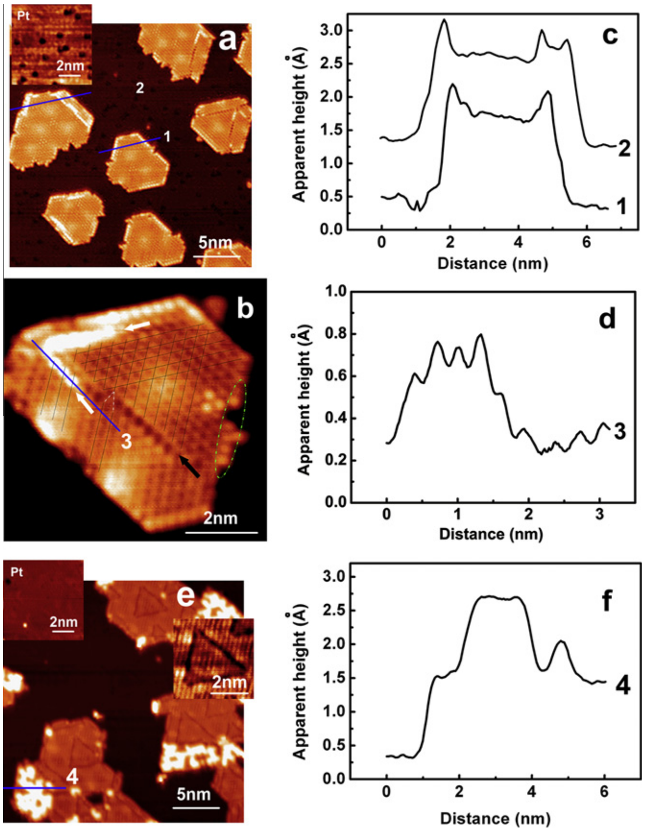

Figure 2. (a) STM image of FeO islands after dosing H_2O (10 Langmuir) at room temperature (acquired at 30 mV and 2.0 nA). The inset shows the Pt(1 1 1) substrate with oxygen coverage of 0.02 ML. (b) Magnified image of a typical island (acquired at 30 mV and 2.0 nA). The superposed grid shows the O lattice, and the white and the dark arrows mark the bright chains and the dark chains, respectively. (c) Line profiles for the lines 1 and 2 marked in (a). Profile 2 is shifted upward by 1 Å for clarity. (d) Line profile for the line 3 marked in (b). (e) Image of the same H_2O dosed sample after annealing at 650 K. The upper left inset shows the image of Pt substrate, and the right inset shows a magnified image of dark triangle on the FeO terrace (20 mV and 2.0 nA). (f) Line profiles for the line marked in (e).

main difference is that there appear some bright protrusions and dark rows inside the FeO islands, and some adsorbates at the island edges. Statistically, the island edges become slightly rough. The feature of Pt(1 1 1) substrate is almost kept unchanged, remaining nearly the same coverage of oxygen, as shown in the inset of Figure 2a. Figure 2b gives a magnified STM image of an island. On the island, it is observed that there exhibit chains of bright protrusions on O lattice both at edge and on terrace (marked by the white arrows) and dark chain (marked by the black arrow). The apparent height is about 1.3 Å for the FeO islands, and the protruded chains are higher than the FeO terrace by about 0.5 Å, as the line profiles given in Figure 2c and d.

Since water desorbs from FeO(1 1 1) around 200 K [7], the molecular water adsorption on the FeO islands for the water-dosed sample at room temperature can be ruled out. The protrusions on FeO islands in Figure 2a may be attributed to the species of dissociative water, most likely hydrogens atop O atoms, forming hydroxyls on FeO islands. Similar bright protrusions and dark rows (or triangles) have been observed in FeO(1 1 1) monolayer film on Pt(1 1 1) after dosing atomic hydrogen [15]. Since H atoms prefer to adsorb and form hydroxyls atop O atoms, the positions of hydroxyls are signature of lattice O sites [15]. It was found that the concentration of surface hydroxyls increases with exposure time of atomic hydrogen at room temperature until a threshold. The well-shaped triangles are assigned to the oxygen vacancy dislocation loops upon heating the hydroxylated surface to 450 K [16], caused by desorption of hydroxyls as H_2 and H_2O [14]. As a result, the remaining O atoms at one side of the oxygen vacancy chain may shift to adjacent hollow sites, forming an edge dislocation. However, the coordinatively saturated Fe atoms in the terrace of FeO(1 1 1) are chemically inert for water dissociation [7–9], therefore the dissociative reaction does not directly happen on the terrace of the FeO islands. The source of hydroxyls should be originated from other mechanisms.

It was reported that at low temperatures a well-ordered bilayer of water can be formed in a hexagonal honeycomb structure on Pt(1 1 1) [32,33]. The water molecules in the lower half bilayer are bonded to the metal and to three neighbors in the upper layer via hydrogen bonds, leaving the upper waters with one unsatisfied hydrogen bond each. The structure of a full bilayer has been determined to be $\sqrt{39} \times \sqrt{39}R16.2^\circ$ by LEED [34,35]. On oxygen precovered Pt(1 1 1) surface, H_2O is dissociative to form a mixed layer of OH and H_2O with $\sqrt{3} \times \sqrt{3}R30^\circ$ and (3×3) structures at about 150 K [36–41]. Water desorbs between 150 and 170 K from a pure water bilayer, while it desorbs around 200 K from the mixed layer of OH and H_2O on an O-covered Pt(1 1 1) surface [42–45]. In the latter case, the proton transfer is important to re-produce water [39,46,47]. However, water does not tend to adsorb at Pt(1 1 1) surface at room temperature [44], thus, the dissociative water may be also restricted on oxygen precovered Pt(1 1 1) for the water-dosed sample at room temperature. Moreover, in our experiment the coverage of the residual oxygen on Pt(1 1 1) is relatively low, with only about 0.02 ML (Figure 1d and the inset in Figure 2a). It is insufficient to form a stable mixed layer of OH/H_2O (or 'OHx') on Pt(1 1 1) [41], especially at room temperature. It is noticed that the coverage of oxygen on Pt(1 1 1) surface is almost unchanged after water was dosed at room temperature in our sample, which indicates that dissociative water on Pt(1 1 1) is, if there were, not a main source for the hydroxyls occurred on FeO islands. Moreover, it also indicates that the diffusion of oxygen on Pt(1 1 1) may not be fast enough (with diffusion barrier of 0.43 eV [31]) to the FeO islands to compensate the deficiency of oxygen when the hydroxyls desorb as H_2 and H_2O from the FeO islands at room temperature. Compared with the coordinatively saturated Fe atoms in the perfect FeO film, the coordinatively unsaturated Fe atoms at the edge may be more active for adsorption and dissociation of water molecules, which is consistent with the observation for alcohol dissociation [21] or CO oxidation [22].

We suggest that the water molecules prefer to adsorb at the edges of the islands and undergo spontaneous dissociation at the coordinatively unsaturated Fe atoms. This process is schematically depicted in Figure 3. A H_2O molecule may initially adsorb at the edge Fe atom site (Figure 3a), and then it spontaneously dissociates into two hydroxyls (Figure 3b). In this mechanism, the number of the coordinatively unsaturated Fe atoms is important since the water dissociation is limited once the unsaturated Fe atoms are exhausted. In the nanometer-sized islands, the ratio of the number of the unsaturated Fe atoms at the step edge to the area of an island can be much large. Knudsen et al. have pointed out that water can dissociate on the corner sites of the dislocation loops (oxygen vacancy sites) [16], on which the Fe atoms are coordinatively unsaturated. In our experiment, since the as-prepared FeO islands have sparse dislocations, we did not observe such phenomenon.

At room temperature, the hydroxyls (or H) may diffuse from the edge into the FeO terrace. It is observed that the hydroxyl protrusions on FeO islands tend to form chains between domains of the moiré patterned structure (Figure 2a and b). This may be due to higher adsorption energy of hydroxyls at these sites. We notice that these sites may be quite related to the formation of dislocation loops in the FeO monolayer. In the work by Metre et al., after the FeO monolayer was exposed to atomic hydrogen and subsequently

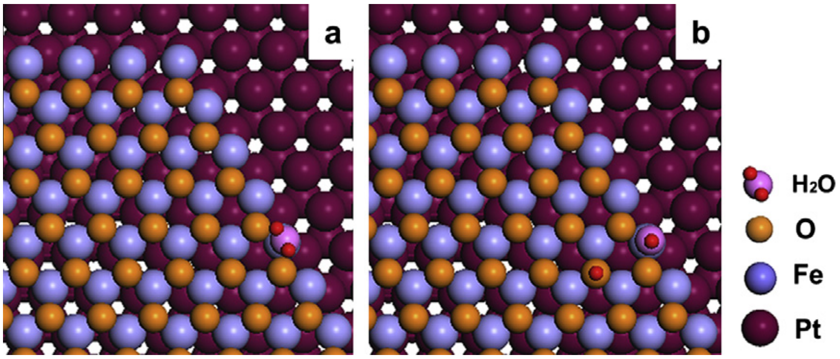

Figure 3. Schematic drawings of (a) H_2O adsorption at coordinatively unsaturated Fe and (b) H_2O dissociation into two hydroxyls.

flashed to 500 K, triangular dislocation loops were then formed, though there still existed disorderedly some isolated residual hydroxyls on FeO [15,16]. In this process, the formation of dislocation loops should be resulted from desorption of hydroxyl chains as H_2 and H_2O after annealing at a relatively high temperature of 500 K [14], thus leaving oxygen vacancy chains at these sites on FeO. The isolated residual hydroxyls on FeO may have higher desorption energy. In our experiment, the partial oxygen vacancy chains have been observed, as shown in Figure 2b, which indicates that the hydroxyls have already desorbed as H_2 and H_2O even at room temperature. It is noted that the O lattices at both sides of the dark chain are shifted from each other by about half lattice distance, as marked by the superposed grid in Figure 2b. It is in agreement to the process as that described in Ref. [14].

After the measurement, we again annealed the sample at 650 K. The hydroxyl chains disappeared, leaving dark triangles on FeO islands, as shown in Figure 2e. Due to the relatively high annealing temperature, the islands coalesced into larger ones. In this case, there is nearly no oxygen left on the Pt(1 1 1) substrate (the upper inset in Figure 2e). The formation of much bright aggregations on the FeO islands in Figure 2e is attributed to Fe clusters, which is due to lack of oxygen compensation from the surface during annealing, causing the reduction of FeO. The line profile for the bright aggregations is shown in Figure 2f. The apparent height for the bright aggregations is about 2.5 Å, which is in agreement with the monoatomic steps of Fe islands [48].

Figure 4 gives a set of STM images of FeO acquired in-situ within the same area before and after dosing 1 Langmuir H_2O (exposing the sample to water at 1.3×10^{-8} mbar for about 100 s) at 80 K. During water dosing, we retracted the STM tip from the surface by about 5–10 μm to reduce the possible effect that the tip may shadow the water dosing. Overall, the main feature for most of the FeO islands acquired immediately after dosing almost kept unchanged (Figure 4b), which indicates that the FeO islands do not tend to adsorb H_2O on terrace even at 80 K. However, there exhibited some bright spots at the edge of a few islands. The occurred adsorbates at the island edges are then the aggregations of molecular water or the dissociative species. It is noted that the Pt(1 1 1) substrate was covered with disordered submonolayer of adsorbates (inset in Figure 4b). After 1 h, more adsorbates appeared at edges of FeO islands (marked in white circles shown in Figure 4c), which is attributed to the aggregations of the diffusive adsorbates from the Pt(1 1 1) substrate. It was reported that water is adsorbed intact on bare Pt(1 1 1) surface below 180 K, and in the presence of sufficient oxygen, water dissociates to form hydroxyl species above 150 K [49]. However, at temperatures lower than 80 K, water does not dissociate even in the presence of oxygen [38]. By considering our experiment was performed at 80 K, the adsorbates on the Pt(1 1 1) substrate are attributed to molecular water, even though there is oxygen on Pt(1 1 1) with a coverage of about 0.08 ML (inset in Figure 4a). Therefore, the aggregations at the edge of the FeO islands are initially in the form of molecular water.

To trace such water aggregations at the edges of the islands, we acquired atomic resolved images of an island, as shown by the magnified images in Figure 5. The bright protrusions appear at the island edges immediately after dosing H_2O (Figure 5a), and a bright protruded chain (marked by the arrow) even appears on the terrace of the island after 1 h later (Figure 5b). The line profiles of the protrusions are correspondingly shown in Figure 5c and d. The apparent heights of such protrusions are quite similar to those in the experiment performed at room temperature (Figure 2d), typically in the range of 0.3–0.5 Å. A much brighter protrusion occurs at the upper edge of the island (as marked by the larger

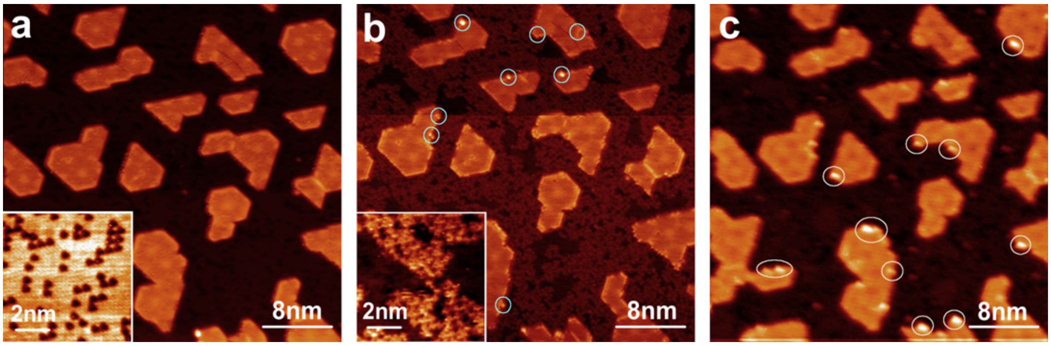

Figure 4. A set of STM images acquired within the same area at 80 K, (a) as-grown sample before dosing H_2O (inset shows the Pt substrate with residual oxygen coverage of 0.08 ML), (b) acquired immediately after dosing 1 Langmuir H_2O in-situ, and (c) acquired after 1 h by holding the H_2O dosed sample at a pressure of 5×10^{-11} mbar and at 80 K (acquired at 0.2 V and 1.5 nA). The feature changes are marked by circles in (b) and (c).

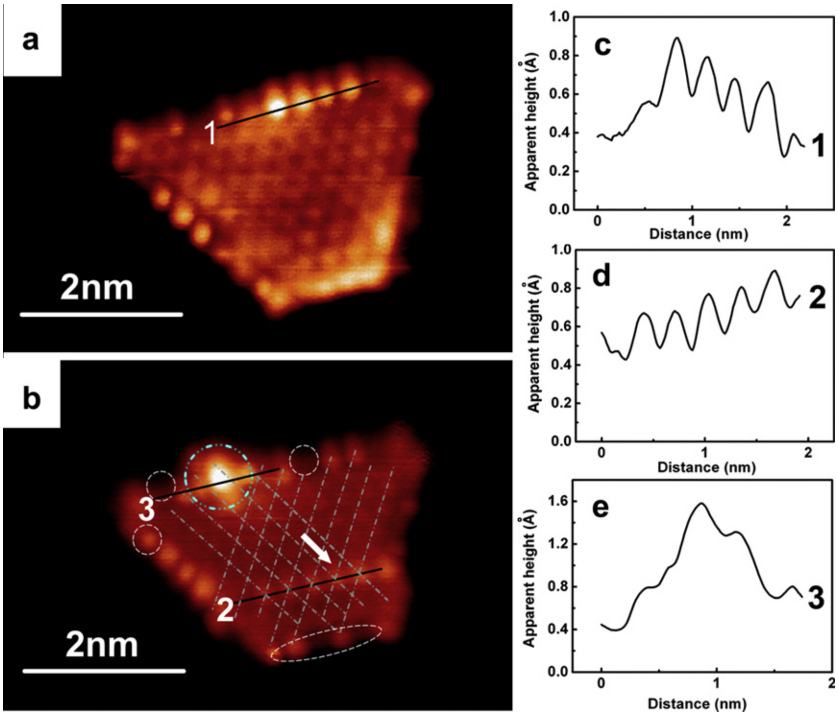

Figure 5. (a) STM image of an FeO island acquired immediately after H_2O dosing (acquired at 50 mV and 3.0 nA). (b) STM image acquired after 1 h later (60 mV and 2.5 nA), measured in-situ at 80 K. (c–e) Line profiles of the lines 1, 2, and 3 marked in (a) and (b), correspondingly.

circle in Figure 5b, and its line profile is shown in Figure 5e), which thus can be most likely attributed to the water molecule(s) from the water adsorbates from the Pt surface. It is also observed that some protrusions appear or disappear at some sites of the step edges by comparing Figure 5a and b (marked by the small circles and the ellipse).

Since physisorbed molecular water and hydroxyl may exist on FeO at 80 K [7,9,16], it is difficult to directly determine the exact species of the adsorbates in the STM images. However, it is noticed that the protruded chain on the terrace of the FeO is quite similar to those occurred on the terrace of the sample at room temperature (Figure 2a). Such similarity may suggest that these chains have the same origin, i.e., the hydroxyl chains from the dissociative water at the island edges, which thus indicates that water may spontaneously dissociate at the step edges even at 80 K.

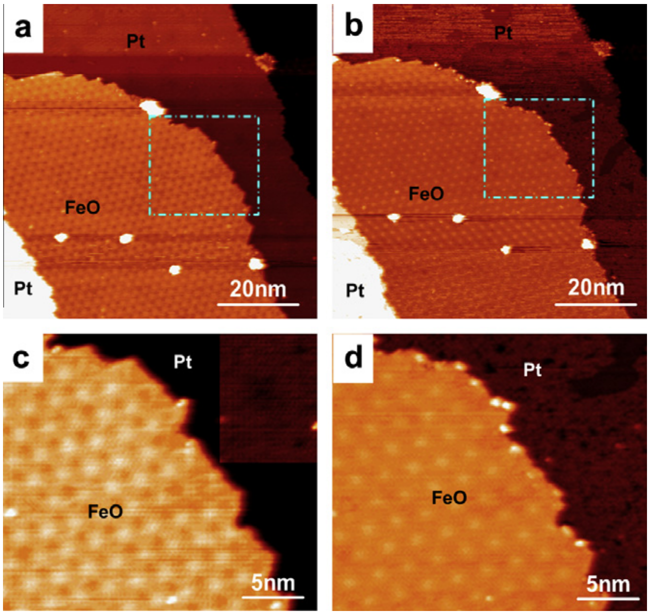

Figure 6. STM images of (a) before and (b) after H_2O dosed sample at 80 K in-situ, and (c) and (d) corresponding magnified images with marked area in (a) and (b). Images in (b) and (d) were acquired after 1 h later for 1 Langmuir H_2O dosed sample. Acquired at 60 mV and 0.2 nA.

As a further confirmation, we prepared another sample with larger FeO islands, which was annealed at 900 K. Figure 6 shows the results for a larger FeO island (typical lateral size of about 60 nm) performed with 1 Langmuir water dosing, acquitted within the same area in-situ measurement at 80 K. With almost one monolayer of water adsorbed on the Pt(1 1 1) substrate, we only observed a few adsorbates at the edges of this large FeO island. From the size and height of the protrusions, it seems that these adsorbates are nondissociated water molecules. The feature inside the island nearly keeps unchanged. Further comparison with the results from the small FeO islands seems to suggest that the island size is also another factor for water dissociation on FeO islands. In the large island, the ratio of the number of the coordinatively unsaturated Fe atoms at the step edges to the island area becomes small. In this case, only a small amount of hydroxyls can be produced and the feature of the island may not be obviously affected.

4. Conclusions

In conclusion, we have observed spontaneous dissociation of water into hydroxyls on the nano-sized FeO/Pt(1 1 1) islands, with typical size of 5–10 nm. We found that after dosing water at room temperature there exhibited bright protrusions and dark rows on the terrace of the FeO islands. The bright protrusions were attributed to the hydroxyls, and the dark rows were attributed to the oxygen vacancies because of further desorption of hydroxyls as H_2 and H_2O. The hydroxyls totally desorbed and left well-shaped oxygen vacancy triangular loops on the FeO islands after the water-dosed sample was further annealed at 650 K. The presence of surface hydroxyls and oxygen vacancies on the terrace of

FeO suggests that the water adsorbates may dissociate on the nano-sized FeO islands. The experimental results obtained at 80 K show that molecular water may adsorb at the step edges of the FeO islands, which may undergo spontaneous dissociation even at 80 K. The STM images revealed that the hydroxyls were diffusive and formed hydroxyl chain on the FeO islands as a function of time. We suggest that the outermost Fe atoms of the islands are coordinatively unsaturated. Such coordinatively unsaturated Fe atoms act as the reaction centers for the water dissociation. On larger FeO islands, say, with lateral size of about 60 nm, the feature inside the islands was not obviously affected after exposure to water. It suggests that the ratio of the number of coordinatively unsaturated Fe atoms to the area of an island plays an important role.

Acknowledgements

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