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Article

Hydration of iodine adsorbed on the Au(111) surface

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A B S T R A C T

The hydration of halogens has been widely researched because of its close relation with the water desalination and biochemical reactions. In this work, by a combination of scanning tunneling microscopy and X-ray photoelectron spectroscopy, we have explored the hydration process of iodine *via* the Eley-Rideal process on the Au(111) surface. Moreover, the hydration process of iodine with the presence of the NiPc self-assembled network as a template has also been investigated, where the stepwise hydration of iodine at room temperature can be visualized on Au(111).

1. Introduction

Halide ion hydrates are ubiquitous in natural and technological environments, and their structures and properties have received considerable attention in many research fields [1–6]. Considering the relevance to water desalination and biochemical processes, the halide-water interactions involved in the hydration process have been widely studied by techniques like mass spectrometry and theoretical calculations at the molecular level, where the halide ions form clusters with the involvement of several water molecules leading to a supermolecule [1,7-10]. Recently, the halide-water interactions in the dissolution process of sodium halides have been demonstrated by scanning tunneling microscopy (STM) on the Au(111) surface, where the formation and desorption of stable halide ion hydrates have been achieved *via* the Langmuir-Hinshelwood (LH) process [11]. Generally, the reactions happening at the gas-solid interface are classified in terms of two proposed mechanisms, i.e., the Eley-Rideal (ER) and the LH processes [12–15]. In the ER process, gas-phase species react directly with the adsorbates, while the LH process occurs between co-adsorbed species on the surface. Our recent research concerning the dissolution of salts verified that in the case of sodium halides, specific interactions exist between surface-confined water molecules and halide ions rather than metal cations, which suggests that the hydration of halide ions on Au(111) can take place through the LH process [11]. Therefore, it would be intriguing to construct a model system without the interference of metal cations to investigate the possibility of halogens hydration independently, which would unravel the mechanism of the interactions between water and halogens on the surface.

In this study, we firstly choose iodine (I_2) and water molecules together with Au(111) and Ag(111) surfaces to construct the model systems. The hydration of iodine on Au(111) has been proved to go through the ER process (*cf.* Scheme 1) at room temperature (RT) by the combination of STM and X-ray photoelectron spectroscopy (XPS), while such a process can hardly take place on Ag(111). Considering the difficulty in quantifying the dosage of pure iodine on bare surfaces during the hydration processes, we tried to measure the amount of iodine by introducing metal-phthalocyanine (MPc) molecules into the system, as the amount of absorbed iodine can be directly reflected by the different ratios of I/MPc in the structural transformations of I-MPc self-assembled structures as reported [16]. Thus, we then introduce nickel-phthalocyanine (NiPc) molecules, whose co-assembled structures with iodine can exhibit the evolution of iodine amount during the stepwise water dosing to confirm the corresponding iodine hydration on the Au(111) surface. From the high-resolution STM imaging, we show the structural transformations among I-NiPc co-assembled structures in response to the water exposure at RT, where the decrease of iodine amount on Au(111) can be detected more obviously. Interestingly, as shown previously in the dissolution process of sodium halide on Au(111), the hydration of halogen can only occur *via* the LH process [11], while the results presented in this study clearly demonstrate that the iodine hydration occurred *via* the ER process without the interference of cations, and the desorption of iodine from the Au(111) surface is achieved by forming the corresponding hydrates (*cf.* Scheme 1).

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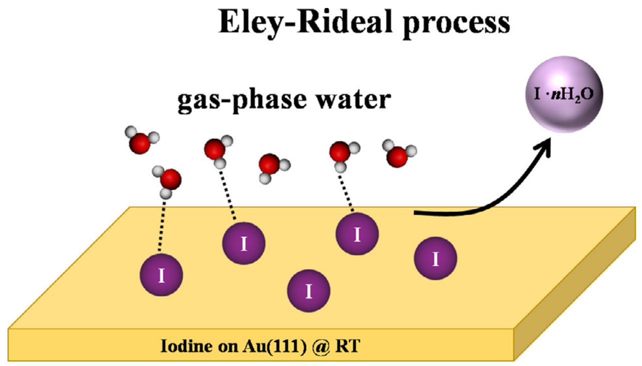

Scheme 1. ***Schematic illustration of the hydration process of iodine adsorbed on Au(111)*** **via** ***the Eley-Rideal process at room temperature.***

2. Material and methods

2.1. STM characterization and sample preparation

All the STM experiments were performed in an UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature, fast-scanning "Aarhus-type" STM using electrochemically etched W tips purchased from SPECS [17,18]. A molecular evaporator, a leak valve with a dosing tube, and other standard instrumentation were used for sample preparation. The Au(111) and Ag(111) substrates were prepared by several cycles of 1.5 keV Ar^+ sputtering followed by annealing to 800 K for 15 minutes, resulting in clean and flat terraces separated by monatomic steps. The NiPc molecules (purchased from Tokyo Chemical Industry Co., Ltd., purity > 99%) were loaded into a glass crucible in the molecular evaporator. After a thorough degassing, the molecules were deposited onto the Au(111) substrate by thermal sublimation. The pure deionized water (from Sigma-Aldrich) was loaded in a dosing tube positioned in the preparation chamber and further purified under the vacuum condition by several freeze-thaw cycles to remove remaining impurities [19]. Water molecules were then continuously dosed *in situ* onto the Au(111) surface held at RT through a leak valve at a pressure of $\sim 10^{-3}$ mbar. Iodine (I_2) (purchased from Sigma-Aldrich, purity > 99%) was dosed *in situ* onto the surface through a leak valve at a pressure of $10^{-8} \sim 10^{-7}$ mbar. The sample was thereafter transferred within the UHV chamber to the STM head, where measurements were carried out at ~150 K. All of the STM images were further smoothed to eliminate noises.

2.2. X-ray photoelectron spectroscopy

Photoemission spectroscopy experiments were performed in an UHV chamber at a base pressure of 1×10^{-10} mbar. Iodine 3d XP spectra were acquired with a Phoibos 100 MCD-5 analyzer using a Mg Kα X-ray source. A binding energy of 84.0 eV for Au($4f_{7/2}$) was used for energy calibration. All spectra were recorded with a pass energy of 10 eV.

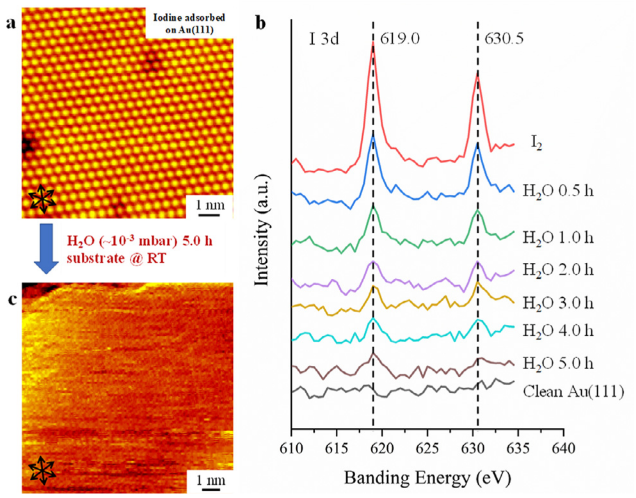

Fig. 1. STM images and XP spectra showing the hydration of iodine on Au(111) *via* the ER process at room temperature. (a) STM image showing the $\sqrt{3} \times \sqrt{3}$ R30° close-packed iodine structure on Au(111). (b) The I 3d XP spectra acquired during the stepwise exposure of the iodine-covered sample to the water environment. I 3d consists of a 3/2 (630.5 eV) and 5/2 (619.0 eV) spin-orbit doublet, and the spectrum of clean Au(111) is provided as a reference. (**c**) STM image showing the clean Au(111) surface after exposing the iodine-covered sample to water for 5 hours at a pressure of $\sim 10^{-3}$ mbar at RT. Scanning conditions: I_t = 0.90 nA, V_t = 1500 mV.

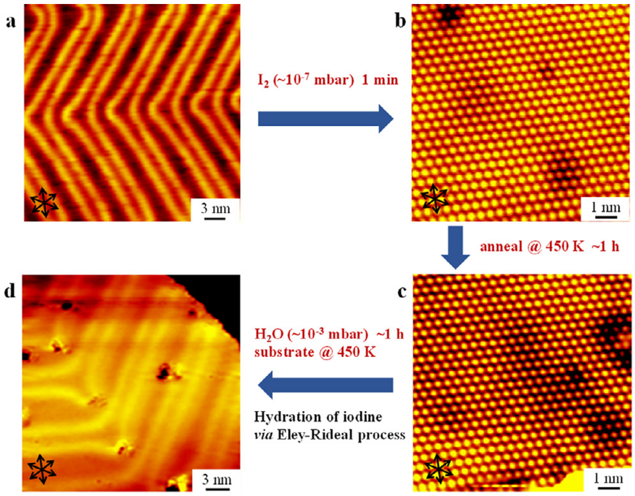

Fig. 2. STM images showing the hydration of iodine on Au(111) *via* the ER process at 450 K. (a-b) Deposition of iodine on Au(111) leads to the $\sqrt{3} \times \sqrt{3}$ R30° close-packed structure of iodine. (b-c) Simply annealing the iodine-covered Au(111) at 450 K under the UHV condition cannot lead to the desorption of iodine. (c-d) Annealing the iodine-covered sample at 450 K in the water atmosphere ($\sim 10^{-3}$ mbar) results in the appearance of the clean Au(111) surface with herringbone reconstruction recovered. Scanning conditions: I_t = 0.70-0.90 nA, V_t = -1700 mV.

3. Results and discussion

Firstly, we directly expose the iodine-covered Au(111) surface to the water environment to explore the possibility of iodine hydration. Iodine and water molecules are introduced into the system by vaporing I_2/H_2O through the corresponding leak valves. Deposition of iodine (I_2) onto the Au(111) surface results in a $\sqrt{3} \times \sqrt{3}$ R30° adlattice structure with atomic iodine resolved as bright dots (Fig. 1a). Besides, XP spectra clearly show the appearance of I 3d peaks (Fig. 1b), confirming the dissociative adsorption of I_2 on Au(111) [20–24]. The measured I $3d_{5/2}$ binding energy of 619.0 eV agrees with the standard spectrum for alkali iodides (I^-) [25]. The herringbone reconstruction of the Au(111) surface is completely lifted due to the relatively strong interaction between iodine and the Au(111) substrate. Thus, iodine is in the ionic form when adsorbed on Au(111) due to the charge transfer with the substrate. Then, by stepwise exposing the iodine-covered sample to the water environment at a pressure of $\sim 10^{-3}$ mbar at RT, surprisingly, the intensities of I 3d peaks gradually decrease and finally disappear in the XP spectra (Fig. 1b), meanwhile the close-packed iodine structures vanish and the clean Au(111) surface is observed in the STM image (Fig. 1c). Further annealing the sample at 450 K leads to the recovery of herringbone reconstruction (Fig. S1). Note that exposing the iodine-covered sample to the water atmosphere at elevated surface temperatures (450 K) directly results in a clean Au(111) surface with herringbone reconstruction recovery, while simply annealing iodine-covered Au(111) at 450 K cannot perturb the adlattice structure of iodine (Fig. 2). As iodine normally des-

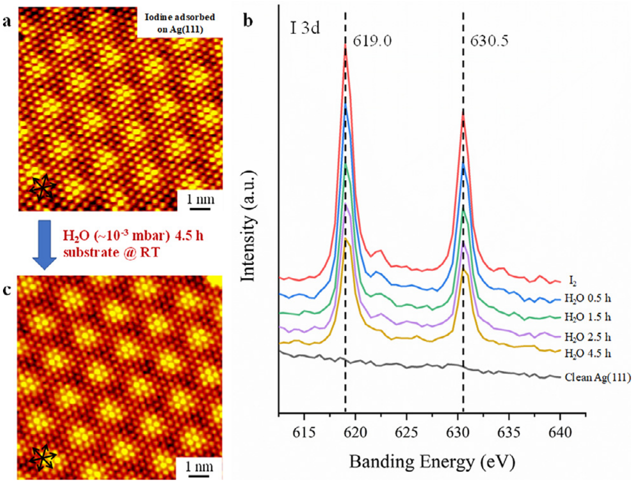

Fig. 3. STM images and XP spectra showing the hardly hydration of iodine on Ag(111) at room temperature. (a) STM image showing the close-packed iodine structure characterized by the Moire pattern on Ag(111). (b) The I 3d XP spectra acquired during the stepwise exposure of the iodine-covered sample to the water environment, and the spectrum of clean Ag(111) is provided as a reference. (**c**) STM image showing the unperturbed iodine structure with the same characteristic of the Moire pattern after exposing the sample to the water environment at a pressure of ~10^{-3} mbar for 4.5 hours at RT. Scanning conditions: I_t = 1.15 nA, V_t = -1000 mV.

orbs from the Au(111) surface at temperatures above 670 K [24], the absence of iodine after water exposure at RT has thus attracted our attention. In contrast to the noble Au(111) surface, similar experiments have been carried out on Ag(111) as a control experiment. However, it is found that the iodine structure with the Moire pattern is not perturbed from the STM observations (Fig. 3 and c), while the intensities of I 3d peaks only decrease slightly after water deposition for 4.5 hours as shown in the XP spectra (Fig. 3b), which indicates the stronger interactions between iodine and Ag(111) surface than that of Au(111). It is then rational to speculate that water molecules should facilitate the desorption of iodine from Au(111) by forming the corresponding hydrates. As water molecules can hardly adsorb on the Au(111) surface at RT [26,27], they can only interact with the iodine from the gas phase *via* the ER process (*cf.* Scheme 1). Therefore, by the combination of STM and XPS, we can draw the conclusion that the hydration of iodine is achieved *via* the ER process on the Au(111) surface at RT.

To directly visualize the stepwise changes of iodine dosage on the Au(111) surface, we then introduce the NiPc molecules into the system and utilize their self-assembled structures as a template. It should be noted here that there are no potential hydrogen-bonding sites in NiPc molecules, so that they cannot form water-involved structures on the surface. Deposition of NiPc molecules on the Au(111) substrate leads to the formation of a highly ordered self-assembled structure as shown in Fig. 4a, in which a single NiPc molecule is resolved as a four-lobe pattern with the model superimposed. It can be further identified from the STM image that the NiPc molecules array in parallel on the surface and further self-assemble into a square network structure. Thereafter, we introduce the iodine into the system by stepwise vaporing I_2 through the leak valve at a fixed pressure with a delicate calibration. After dosing iodine (at a vapor pressure of ~10^{-8} mbar for 1 minute) onto the NiPc pre-covered Au(111) surface at RT step by step, the co-assembled structures of NiPc and iodine labelled as **phase 1** and **phase 2** are formed on the surface as shown in Fig. 4b and c respectively, in which the bright spots indicated by white circles are assigned to iodine. Similar to the reported I-MPc co-assembled structures on Au(111) [16], the iodine ions are homogeneously distributed in the self-assembled structure of NiPc molecules. At a low iodine dosage, the iodine ions are located at the center of four NiPc molecules and form **phase 1**. From the STM image with schematic models superimposed (Fig. 4b), the local ratio of I/NiPc in **phase 1** is determined to be 1: 1. With the increasing iodine dosage, **phase 2** is achieved on the surface, where iodine ions are uniformly distributed at both sides of NiPc molecular rows, with the I/NiPc ratio of 3: 1 (Fig. 4c). Further increasing the iodine dosage to a full-monolayer coverage leads to the formation of the extended $\sqrt{3} \times \sqrt{3}$ R30° close-packed structure composed of iodine, which fully covers the former NiPc molecules (Fig. 4d). Subsequently exposing such a sample (held at RT) to the water environment at a pressure of ~10^{-3} mbar

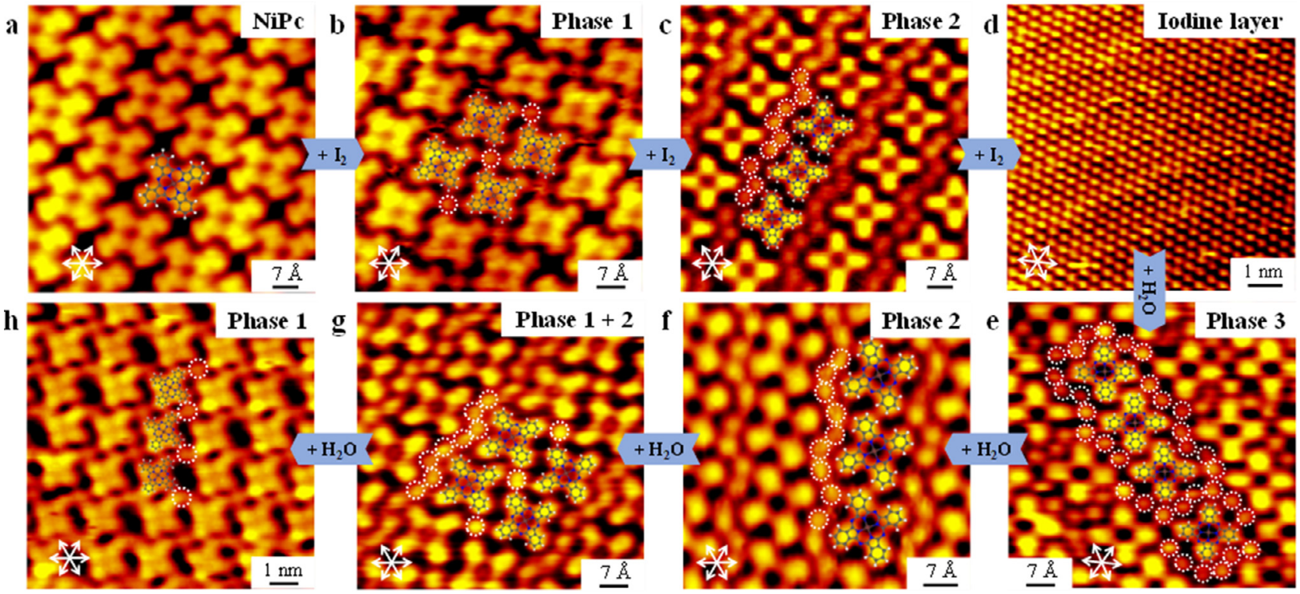

Fig. 4. STM images showing the structural transformations of I-NiPc co-assembled structures in response to the dosage of iodine/water on Au(111) at room temperature. (a) Self-assembled structure of NiPc molecules. (b-d) The stepwise structural transformations by increasing the dosage of iodine onto the NiPc pre-covered surface. (e-h) The structural transformations responsive to an increasing water dosage onto the I-NiPc co-assembled structures, implying a stepwise hydration of iodine on Au(111) *via* the ER process. Iodine ions in the I-NiPc co-assembled structures are indicated by white circles. The schematic models of NiPc molecules are partially superimposed on the STM images. H: white; C: gray; N: blue; Ni: dark red. Scanning conditions: I_t = 0.70-0.90 nA, V_t = 1200 mV.

step by step, we have successively achieved the reappearance of various I-NiPc co-assembled structures with the structural transformation from **phase 3** through **phase 2** to **phase 1** (Fig. 4e-h), which clearly shows the decrease of adsorbed iodine during this process. After exposing the sample (Fig. 4d) to the water environment for 20 minutes, the I-NiPc co-assembled structure labelled as **phase 3** appears on the surface, where some NiPc molecules are surrounded by multiple iodine ions as an enclosure. From the STM image with schematic models superimposed (Fig. 4e), it can be identified that the ratio of I/NiPc in **phase 3** is 4.25: 1. With the following water dosage, the I-NiPc co-assembled structure goes through **phase 2** (Fig. 4f, with a I/NiPc ratio of ~ 3: 1), then transforms to a nonperiodic I-NiPc structure randomly mixed by **phase 1** and **phase 2** (Fig. 4g, labelled as **phase 1 + 2**), and finally ends at **phase 1** (Fig. 4h, with a I/NiPc ratio of ~ 1: 1). By applying the NiPc network as a template on Au(111), the changes of iodine dosage can be quantified by the I/NiPc ratio in the periodic co-assembled structures during the process of iodine/water deposition. After further exposing the **phase 1** pre-covered surface to the water environment at a pressure of $\sim 10^{-3}$ mbar for 2 hours, **phase 1** remains unchanged. That is because these iodine ions are stabilized by four NiPc molecules at the hydrogen-rich harbors through electrostatic interactions, leading to the difficulty in the thorough hydration. From the above process, we directly visualize the stepwise hydration of iodine on the Au(111) surface. At this point, we can finally draw the conclusion that the hydration of iodine, that is, the formation and desorption of iodine hydrates from the surface, is achieved *via* the ER process at RT on Au(111).

4. Conclusion

In this study, the halide-water interactions on the Au(111) surface have been investigated by combining STM and XPS, which shows that the hydration of iodine adsorbed on Au(111) is achieved at RT *via* the ER mechanism. During the hydration process, the desorption of iodine from the Au(111) surface is realized at RT by forming the stable iodine hydrates, which provides the possibility for further studies on the halide ion hydrates. The strategy shows the potential to be extended to other halogens (e.g., Cl, Br) systems, which would further provide a clean and efficient way to remove halogen byproducts from the Au(111) surface during the dehalogenative reactions in the field of on-surface synthesis.

Declaration of Competing Interest

The authors declared that they have no conflicts of interest in this work.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fmre.2021.10.005.

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