In Situ STM Evidence for Adsorption of Rhodamine B in Solution

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Received: October 15, 2001; In Final Form: December 31, 2001

In situ scanning tunneling microscopy (STM) has been first employed to investigate the adsorption of RB (rhodamine B) on solid surface in solution. An I/Au(111) (iodine-modified Au(111)) surface was used as a substrate for molecular adsorption. In situ STM imaging revealed a highly ordered RB molecular adlayer. A unit cell with parameters of $a = 1.71$ nm and $b = 2.25$ nm was determined. Higher resolution STM images disclosed the structural details of the molecular adlayer. On the basis of STM results, the RB molecule is proposed to adsorb on the I/Au(111) surface by its two diethylamino functional groups in an edge-on orientation. The orientation was related to the molecular degradation.

Introduction

Industrial dyes are becoming one of the largest groups of chemical pollutants and consequently causing significant pollution to groundwater. To control environmental pollution, many treatment technologies have been developed. For example, electrochemical and photoassisted degradations of dye pollutants have proved to be effective methods.[1−3] Photoassisted degradation of several typical dyes was studied on inorganic and metallic crystal surfaces such as TiO_2.[4−10] The understanding of degradation mechanism is an important issue in both fundamental research and industrial application of environmental science. Various possible pathways related to the mechanism were proposed on the basis of the experimental evidences from NMR, ESR, IR, and other characterization techniques.[4−10] As a result, it is known that the prerequisite for degradation reactions occurrence is the adsorption of organic dyes on solid surfaces.[4,5] Furthermore, the adsorption structure of dyes strongly affects the consequent reaction. For example, SRB (sulforhodamine-B) gave different degradation products when it adsorbed on TiO_2 with sulfonate or diethylamino.[4] Therefore, investigating the adsorption of dyes on solid substrate is crucially important to the study of pollutant degradation and of special interest to industrial application.[4−11]

In situ STM has proved to be a powerful tool in the study of electrochemical interfacial and surface science.[12,13] Adsorption of organic molecules on different substrates has been extensively investigated by using STM. Direct and real space information of bonding and coordination of organic molecules with the substrate was obtained.[14−20] In the present study, the adsorption of rhodamine B (RB) has been studied by cyclic voltammetry and in situ STM. RB is a typical dye of rhodamine group. Its degradation was previously studied by UV, ESR, X-ray diffraction, and absorption spectroscopy.[5,21−23] It was found that the degradation process is dependent on bonding and coordination of RB with a solid substrate. Now an Au(111) single crystal is used as a substrate to investigate the adsorption of RB. To avoid strong interaction between RB and the substrate, iodine (I) is modified on the Au(111) surface.[24] Similar to the previous studies of TMPyP, CV, and other organic molecules,[14] RB

molecules, for the first time, are found to form a well ordered two-dimensional adlayer on the I-modified Au(111) in H_2SO_4 solution by electrochemical STM, whereas a disordered structure was observed on a bare Au(111) surface. The individual molecule is clearly resolved. Actually, chemically modified surfaces such as the alkylate sulfonate-modified TiO_2 surface are well used to study molecular adsorption and found to accelerate pollutant degradation.[5] A well-ordered monolayer allows us to investigate the interactions between molecule and substrate, and intermolecules. The extension of the research will give more direct evidences for elucidating the degradation mechanism of RB on other photoactive substrates such as ZnO, CdS, and TiO_2. With the information on RB molecules from high-resolution STM images, an edge-on model is proposed. The proposed model can explain molecular arrangement of RB on the surface. The possibility of RB degradation is discussed with the structural model.

Experimental Section

Single-crystal beads of gold were prepared at the end of Au wires (99.99%) by the method described in previous papers.[18,24] An Au(111) facet formed on the single-crystal bead in an octahedral configuration was used directly for STM experiments. Mechanically polished (111) surfaces were prepared for electrochemical measurements. As a final treatment for exposing well-defined Au (111) surfaces, the single-crystal electrodes were annealed in an oxygen−hydrogen flame and then brought into contact with ultrapure water saturated with hydrogen. Modification of the Au(111) surface with iodine was accomplished by immersing the substrate in 1 mM KI for 3 min.[14] Then, the electrode was rinsed with ultrapure water repeatedly to remove the unadsorbed iodine and transferred to an electrochemical cell with a droplet of ultrapure water to protect the surface from contamination.

In situ STM measurements were carried out with a Nanoscope-E (Digital Instruments) equipped with a homemade electrochemical cell. All images were acquired in the constant-current mode by using electrochemically etched tungsten tips (0.25 mm in diameter) coated with transparent nail polish.

All of the solutions were prepared with ultrapure H_2SO_4, analytical pure KI, RB (Kanto Chemical Co., Japan), and ultrapure water (Millipore-Q). The electrode potentials are

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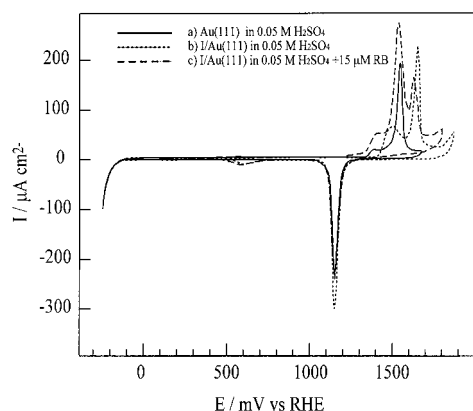
Figure 1. Cyclic voltammograms of (a) bare Au(111), (b) iodine-modified Au(111) in 0.05 H$_2$SO$_4$, and (c) iodine-modified Au(111) in 0.05 H$_2$SO$_4$ + 15 μm RB. The scan rate was 50 mV/s.

reported with respect to a reversible hydrogen electrode (RHE) in 0.05 M H$_2$SO$_4$ solution.

Results and Discussion

Cyclic Voltammetry. Cyclic voltammograms (CVs) for a bare Au(111) and iodine-modified Au(111) electrode in 0.05 M H$_2$SO$_4$ are shown in Figure 1 parts a and b. In Figure 1a, two characteristic peaks at 1.4 and 1.58 V correspond to the two steps of Au(111) surface oxidation. A double layer region involving a small peak at 0.6 V for the surface reconstruction phase transition can be seen. The result is consistent with that reported previously.[25] Figure 1b shows the CV of I-modified Au(111) in 0.05 M H$_2$SO$_4$. Two sharp peaks appear at 1.4 and 1.62 V, respectively, because of the oxidation of iodine adlayer and the Au (111) substrate.[25−27] The featureless voltammogram with small charge current in the potential range between 0 and 1.3 V is associated with the existence of an iodine monolayer on the electrode surface.

Figure 1c shows a CV of I/Au(111) in 0.05 H$_2$SO$_4$ + 15 μm RB. A broad peak appears from 1.2 V, and the other two peaks corresponding to the oxidation of iodine and Au(111) shift positively to 1.58 and 1.64 V. The surface charge associated with two oxidation peaks significantly increases. The CV result implies that some surface processes such as structure change take place in the RB adlayer in this potential region. The change will be investigated by electrochemical STM.

In situ STM. *Structure of the I Adlayer on Au (111).* After immersion of Au(111) in KI solution, the iodine adlayer was observed with ECSTM in 0.05 M H$_2$SO$_4$. The adsorption of I lifts reconstruction of the Au(111) surface, consistent with the previous results.[24,28] An atomic resolution STM image of the I adlayer obtained at 0.4 V is shown in Figure 2. A perfect I adlayer could be resolved. According to the atomic orientation and interatomic distance, the hexagonal ($\sqrt{3} \times \sqrt{3}$)R30° adlayer structure can be deduced. The adlayer of I on Au(111) has been intensively studied with STM, LEED, and other surface characterization methods.[28] As a result, the structure was found to change with applied electrode potentials. An incommensurate centered rectangular $c(p \times \sqrt{3} − R30°)$ structure was defined. In the present study, we have seen the similar incommensurate structure as that obtained previously in HClO$_4$.[24,29]

Structure of RB on I/Au (111). After we recorded the atomic resolution STM image of iodine adlayer shown in Figure 2, a drop of RB solution was directly injected into the STM cell. The final concentration of RB in the cell was adjusted to ca. 15 μM. After 30 min to achieve adsorption equilibration under
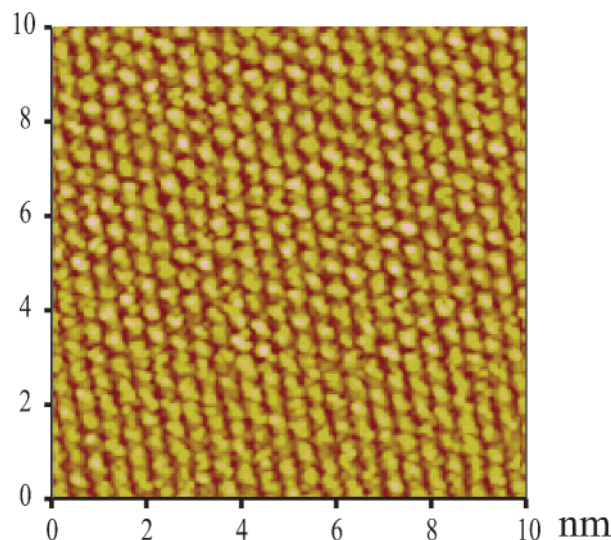

Figure 2. Unfiltered top view of iodine adlayer on Au(111) acquired at 700 mV. The tunneling current was 20 nA. The scanning rate was 9.0 Hz.
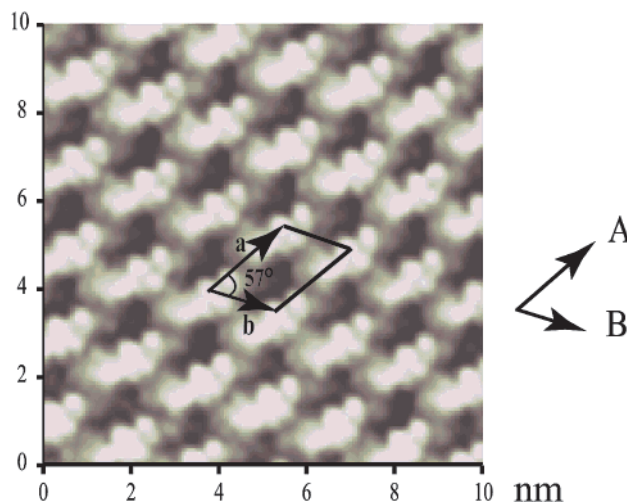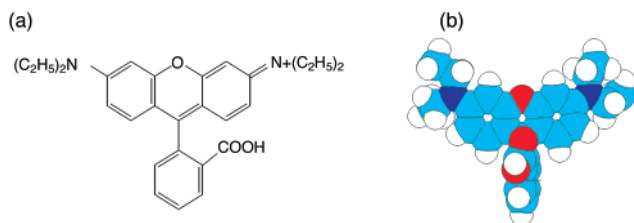

Figure 3. Low-pass filtered STM image of the RB adlayer on I/Au-(111) acquired at 800 mV. The tunneling current was 1.0 nA. The scanning rate was 9.0 Hz. A unit cell with $a = 1.71 \pm 0.02$ nm and $b = 2.25 \pm 0.02$ nm was outlined.

potential control of 0.8 V, the STM observation was conducted. Figure 3 shows a typical high resolution STM image of RB adlayer on I/Au (111) acquired at 0.8 V. It can be seen that a highly ordered two-dimensional adlayer extends over the atomically flat terrace of I/Au(111). The adlayer is nearly free of defects. At the same time, the details of RB molecules can be discerned with the higher resolution image. Each molecule seems to be composed of three side-by-side spots. The molecular rows extend along **A** and **B**, two directions as indicated by arrows in Figure 3. The repeat distances of the adlayer along directions **A** and **B** are measured to be 1.71 ± 0.02 and 2.25 ± 0.02 nm, respectively. The internal angle between directions **A** and **B** is ca. 57 ± 2°. The center line of the molecule appears to tilt at an angle of 5° with respect to the **A** direction. A unit cell for this adlayer is outlined in Figure 3.

The image in Figure 3 is the first STM evidence for RB adsorption on a solid surface in solution. The internal structure details revealed in the image can supply direct information of bonding and coordination of the RB molecule with the substrate. From the chemical structure, there are mainly three possible structures of RB molecules adsorbed on the electrode, as

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SCHEME 1:   Three Possible Adsorption Structures of RB on Electrode Surface, (a) Flat-On, (b) End-On, and (c) Edge-On

(a)

(b)

(c)

Electrolyte

Electrode
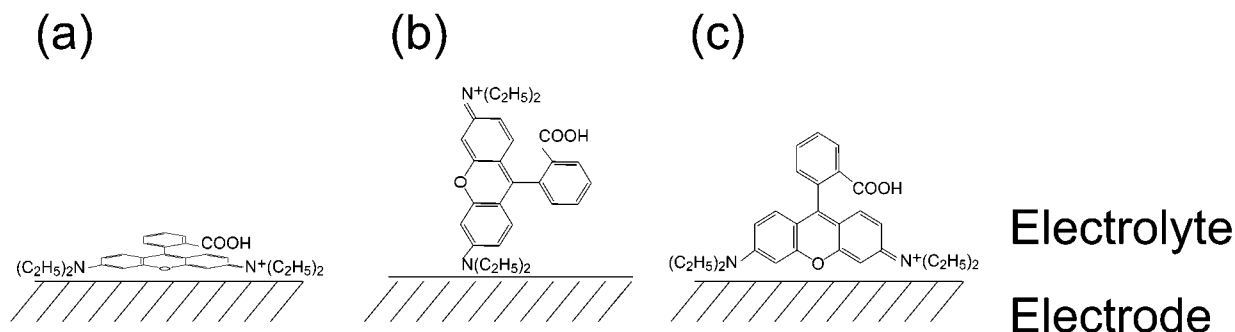
SCHEME 2:   (a) Chemical Structure and (b) Space Filling Structure of a RB Molecule

SCHEME 3:   Proposed Structural Model for a RB Adlayer, (a) Top View and (b) Side View

schematically illustrated in Scheme 1. The three possible structures are that (a) the molecular plane is parallel to the substrate in a flat-on orientation, (b) the molecule is standing on the surface by one diethylamino functional group, forming an end-on orientation, and (c) the molecule is standing on the surface by its two diethylamino ($-N(C_2H_5)_2$) functional groups in an edge-on orientation. The most possible structural model for the RB molecular adlayer will be proposed by comparing the three possibilities with acquired STM images. First, an important feature of the structure of RB from the space-filling model shown in Scheme 2 optimized with Chem3D is that two major planes formed by the benzoic acid and the xanthene intersect each other with an angle of near 90°. This feature has been found in the crystal structure of other compounds of the rhodamine group, such as rhodamine 6G and lactone form of RB.[30,31] If the molecule adsorbed on the iodine-modified Au(111) surface in a "flat on" orientation, a triangle, or a "T"-shaped appearance should be expected in STM images. For example, if the RB molecule is adsorbed on I/Au(111) with a COOH group sticking on the surface but with the other extended aromatic plane laying parallel to and elevated off the I/Au(111) surface, a "T"-shaped configuration for the molecule should be seen in the high resolution STM image. However, only the images such as Figure 3 with the feature of three side-by-side spots were observed in the present potential region. On the second possibility shown in Scheme 1b, the RB molecule interacts with the substrate by one diethylamino group in an end-on orientation. In this case, a RB molecule should appear in one bright spot in the STM image, rather than three side-by-side spots. Compared with the two structures, the edge-on structure shown in Scheme 1c is the most reasonable one. In this configuration, the theoretical length of the RB molecule is ca. 1.7 nm, and the width of the benzoic acid group from the oxygen atom to the opposite hydrogen atom is ca. 0.6 nm. The measured sizes for a RB molecule in the STM image of Figure 3 are consistent with the length and width from the theoretical chemical structure. On the basis of the present STM observation, a tentative structural model for RB adsorption on iodine-modified Au(111) is proposed in Scheme 3. The intermolecular distances accord with the unit cell outlined in the STM image.
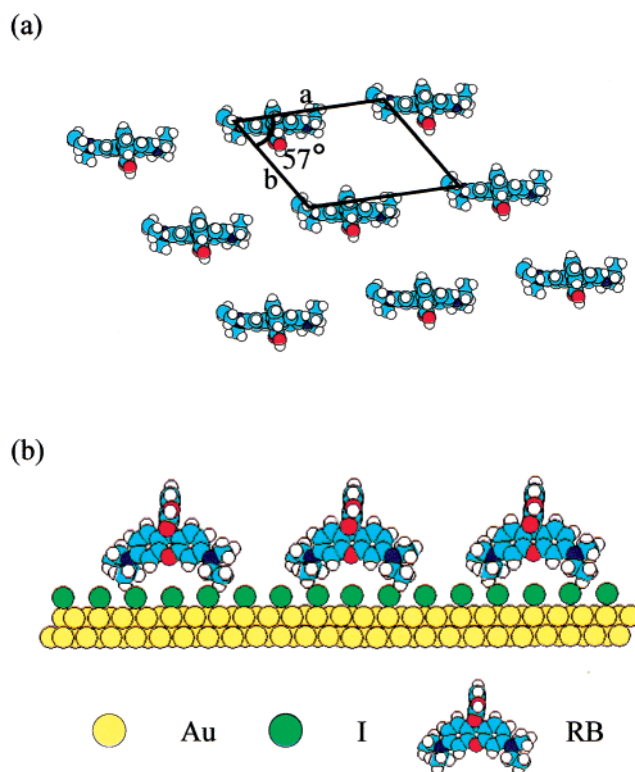
The two diethylateamino groups of RB are assumed to interact with the I/Au(111) surface and organize a well-ordered RB adlayer.

In a visible light irradiation experiment in aqueous TiO₂ dispersions, the RB molecules were proposed to degrade from their ethyl groups.[5] The deethylation was assumed in a stepwise manner, i.e., ethyl groups were decomposed one by one. In the proposed model shown in Scheme 3, RB molecules adsorb on the I/Au(111) surface with the ethyl groups. The electron transfer between these ethyl groups and the substrate is easier than other functional groups if a degradation reaction takes place. Thus, the degradation of the molecule should first start from these groups. However, it is obvious that the TiO₂ substrate should be used for the study of RB degradation, and other straightforward experimental techniques such as IR must be applied to obtain further structural information.

Upon obtaining high-resolution STM image of the RB adlayer, the potential was scanned positively and negatively in the increment of 10 mV. In the potential range from 0.6 to 1.1 V, RB molecules exhibited nearly the same configuration as

that in Figure 3, whereas the unit cell parameter of the adlayer varied a little. This potential dependent adlayer structure transformation is due to the incommensurate iodine adlayer, which shows a $c(p \times \sqrt{3} - 30°)$ structure.[24] At the potential more positive than 1.2 V, the STM image became noisy, which was attributed to a structural variation on RB or partial iodine adlayer oxidation. The result is consistent with the CV of Figure 1. However, further studies by using different techniques such as capacitance measurement and in situ IR are needed to understand the nature of RB adlayer at positive potential region.

Conclusion

In summary, the adsorption of RB on I/Au(111) is first studied with EC−STM. A direct evidence for the adsorbed structure is obtained from high resolution STM images. An ordered RB adlayer is resolved, and an edge-on adsorption structure is proposed. The diethylamino groups of a RB molecule directly bind with the I/Au(111) surface. The degradation of the molecule would be start from the diethylamino groups. The present study demonstrates that electrochemical STM can be used in environmental science to clarify the adsorption of organic pollutants.

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