—Headline—

***In Situ* Electrochemical Scanning Tunneling Microscopy : Adlayers of Organic Molecules**

Kingo ITAYA

Department of Applied Chemistry, Graduate School of Engineering, Tohoku University (Aoba-yama 04, Sendai 980-8579, Japan)

Received January 9, 2001 ; Accepted February 9, 2001

Until recently, there had been only few *in situ* methods available for the structural determination of an electrode surface in solution at the atomic level. Now, several recent investigations have demonstrated scanning tunneling microscopy (STM) to be a powerful new technique for *in situ* characterization, with atomic resolution, of electrode surfaces under potentiostatic control. It has been demonstrated that the *in situ* STM makes it possible to monitor with atomic resolution a wide variety of electrode processes such as the adsorption of inorganic and organic species, the dissolution and deposition of metals and semiconductors. Owing to limitations on space, the focus is on the adsorption of organic molecules such as benzene and related compounds.

Key Words: STM, Single Crystal Electrodes, Organic Adlayers

1 Introduction

Since Binnig and Rohrer invented it in 1981,¹⁾ STM has quickly been established as an invaluable and powerful surface analysis technique with atomic resolution in ultrahigh vacuum (UHV). On the other hand, Sonnenfeld and Hansma demonstrated for the first time in 1986 that STM can be used even in electrolyte solution.²⁾ In 1988, we and other groups proposed a new concept for *in situ* STM using a four-electrode configuration, in which the electrode potentials of the substrate and the tip are independently controlled with respect to a reference electrode.^{3, 4)} The developments in STM operated at solid-electrolyte interfaces under potentiostatic conditions led to its valuation as arguably the premier technique for atomic-level surface structural investigations of electrochemical processes taking place at electrode-electrolyte interfaces. It has been demonstrated that *in situ* STM makes it possible to monitor, under reaction conditions, a wide variety of electrode processes such as the adsorption of inorganic and organic species, the reconstruction of electrode surfaces, the dissolution and deposition of metals and semiconductors. Several review articles on *in situ* STM and related techniques such as *in situ* atomic force microscopy (AFM) have been published.^{3, 4)}

2 Well-defined Electrode Surfaces

As a fundamental basis for all STM studies, electrode-electrolyte interfaces must be prepared reproducibly, and methods must be established to observe these interfaces accurately. Well-defined single crystalline surfaces must be exposed to solution in order to understand surface structure-reactivity relationships on the atomic scale. Efforts have succeeded in producing extremely well-defined, atomically flat surfaces of various electrodes made of noble metals, base metals, and semiconductors without

either oxidation or contamination in solution.⁴⁾

A unique and very convenient way to expose well-defined clean Pt into aqueous solution was proposed by Clavilier in 1980, in which mechanically exposed single crystal Pt was annealed in an oxygen flame and quenched in pure water.⁵⁾ They also established a method of preparing a single crystal Pt electrode by melting a Pt wire in the flame. The so-called flame annealing and quenching method is widely used for other metals such as Au, Rh, Ir, and Pd single crystal electrodes. Figure 1 shows a typical cyclic voltammogram (CV) of the Pt(111) surface in a sulfuric acid solution. Although Clavilier's group and Furuya *et al.* have analyzed the binding sites of hydrogen using systematically prepared stepped surfaces,^{6, 7)} more recent investigations using a CO replacement technique clearly indicate that

Fig. 1 Cyclic voltammogram of Pt(111) in 0.5 M H₂SO₄ at a scan rate of 50 mV/s.

the charges shown in Fig. 1 include a significant contribution of the adsorption and desorption of sulfate/bisulfate.⁸⁾

Nevertheless, direct evidence to support the existence of well-defined surface in solution was demonstrated by us in 1990 using *in situ* STM.⁹⁾ Figure 2a shows our first STM image of a flame-annealed Pt(111) in sulfuric acid solution. The height of each step is ca. 0.23 nm in accord with the monatomic step height of 0.238 nm on the Pt(111) surface. The monatomic steps observed on the surface are usually located on nearly parallel straight lines or form an angle of 60° as expected for the surface with threefold symmetry. The terraces seem to be atomically flat. Later it was shown that the terrace was composed of Pt atoms forming a (1×1) structure as shown in Fig. 2b.¹⁰⁾ On the upper and lower terraces, the Pt(111)-(1×1) structure was clearly discerned at potentials near the hydrogen evolution reaction. The nearest-neighbor spacing and corrugation height were 0.28 nm and 0.03 nm, respectively. Similar atomic images were reported for Au, Rh, Pd and Ir single crystal electrodes prepared by the flame annealing and quenching method.⁴⁾ However, the flame annealing and quenching method cannot be applied for more industrially important less noble metals and semiconductors, because they are heavily oxidized in the flame.

We demonstrated that layer-by-layer dissolution occurs on various metals such as Ni, Ag, Co, Pd, and Cu, resulting in the formation of atomically flat terrace-step structures.¹¹⁾ It was also found that the layer-by-layer dissolution occurs on various semiconductors such as Si(111), Si(110), GaAs, and InP.⁴⁾ On the other hand, it was recently reported by Uosaki, *et al.* that the electrodeposition of Pt and Pd proceeded with an epitaxial layer-by-layer growth mode,^{12,13)} suggesting that the electrochemical deposition will be a method for preparing

well-defined surfaces.

3 Adsorption of Aromatic Molecules

The adsorption of organic molecules onto bare electrode surfaces in electrolyte solutions under potential control has long been investigated for elucidating the role of structure and property of adsorbed molecules in electrochemical reactions.¹⁴⁾ Although conventional electrochemical and optical techniques, such as infrared (IR), Raman, and second harmonic generation (SHG) spectroscopy have been extensively applied to the investigation of the molecular adsorption at electrode surfaces in solutions,¹⁴⁾ they usually can provide only averaged information on the molecular orientation and packing within an adlayer. *Ex situ* techniques such as low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), using an ultrahigh vacuum electrochemical (UHV-EC) technique,^{15,16)} have also been extensively employed for generating understanding of the relationship between the adsorbed molecules and the atomic structure of the electrode surfaces. However, *in situ* STM has been well recognized as an important *in situ* method for structural investigation of adsorbed organic molecules on well-defined electrode surfaces in electrolyte solution with atomic resolution.

On the other hand, many reports have described the investigation of the adsorption in UHV of aromatics, such as benzene and its derivatives on Pt, Rh, Ni, Ir, Ru, and Pd, which were performed by using various surface-sensitive techniques such as LEED, AES, and electron energy-loss spectroscopy (EELS). The purpose of those investigations was to evaluate gas phase catalytic reactions, such as hydrogenation, dehydrogenation, and dehydrocyclization.¹⁷⁾ In UHV the (3×3) superlattice of benzene and CO coadsorbed on Rh(111) revealed a well-ordered array of ring-like features associated with adsorbed benzene molecules, whereas CO did not appear in STM images.¹⁸⁾ A more detailed STM study was recently reported by Somorjai *et al.*¹⁹⁾

Nevertheless, we described, for the first time, the adlayer structures of benzene adsorbed on Rh(111) and Pt(111) in HF solutions.²⁰⁾ High-resolution STM images allowed us to determine the packing arrangement and even the internal structure of each benzene molecule in solution.

3.1 Benzene on Rh(111)

Figure 3 shows cyclic voltammograms (CVs) of Rh(111) electrodes in the absence (a) and presence of benzene (b) in 0.01 M HF, respectively. In the absence of benzene, the CV obtained on the well-defined Rh(111) exhibited several highly reversible characteristic peaks. It was noted that the heights and widths of these characteristic peaks depended on the quality of the surface of Rh(111) prepared by the flame-annealing and quenching method.

After the Rh(111) electrode was subjected to the CV measurement in the pure HF solution, the electrode was transferred into a 0.01 M HF solution containing ca. 1 mM benzene. The CV indicated a featureless double-layer region between 0.3 and 0.7 V as shown in Fig. 3b.

Fig. 2 Topographic STM image (a) and atomic resolution image (b) of the flame-annealed Pt(111) in solution.

Fig. 3 Cyclic voltammograms of Rh(111) without (a) and with (b) 1 mM benzene in HF.

The cathodic current commencing at about 0.3 V was considered to be due to simultaneously occurring processes, such as the desorption of adsorbed benzene, the adsorption of hydrogen, and the irreversible hydrogenation of benzene to cyclohexane, according to the previous studies using differential electrochemical mass spectrometry (DEMS).²¹⁾

A well-defined terrace-step structure was easily observed on the well-prepared Rh(111) face. The atomic image of Rh(111)-(1×1) was routinely discerned on the terrace in the pure HF solution. The almost perfectly aligned hexagonal structure can be seen with an atomic distance of 0.27 nm, indicating that the structure of the Rh(111) surface is (1×1).²⁰⁾

After achieving the atomic image of Rh(111)-(1×1), a small amount of 1 mM benzene solution was directly added to the STM cell at 0.45 V. Immediately after the injection of benzene, completely different patterns appeared in STM images. Details of the orientation of benzene in the adlayer are revealed by the high-resolution STM image shown in Fig. 4a. An averaged domain size was about 10×10 nm². It is seen in Fig. 4a that the molecular rows along the direction of arrows A and B cross each other at 90°, and they are always parallel with the close-packed and $\sqrt{3}$ directions of the Rh(111) substrate, respectively. The intermolecular distances along these directions are not equal to each other and were found to

be on the average, 0.8 nm and 0.9 nm, respectively. Based on the orientation of molecular rows and the intermolecular distances, we concluded that the benzene adlayer was composed of rectangular unit cells, namely $c(2\sqrt{3}\times 3)\text{rect}$ ($\theta = 0.17$). The STM image allowed us to determine the internal structure and micro-orientation of each benzene molecule adsorbed on Rh(111). It is clear that each spot is split into two bright spots, forming a characteristic shape of dumbbell for each benzene molecule. It can also be seen in Fig. 4a that the orientation of dumbbell-shaped benzene is not the same for all molecules, but depends on their positions. The dumbbell-shape of the central benzene molecule in the unit cell shown in Fig. 4a is clearly rotated by 60° with respect to the molecules located on the four corners of the unit cell. The molecules on the corners of the unit cell appeared with an identical feature, suggesting that they are situated on an identical binding site. It is also seen that the orientation of these dumbbells is always rotated by 30° with respect to the direction of close-packed rows of the Rh(111) substrate. Figure 4b shows a proposed model for the $c(2\sqrt{3}\times 3)\text{rect}$ structure. All of the adsorbed benzene molecules are assumed to be located on the two-fold bridging sites. The benzene molecule at the center of the unit cell also occupies a two-fold site, but it is rotated by 60° from the orientation of the molecules at the corners. Weiss and Eigler reported three distinct types of STM images for isolated benzene molecules located at three-fold hollow, atop, and bridge sites on Pt(111) at 4 K.²²⁾ They assigned the single bump elongated perpendicularly to the bridge to the bridge-bonded benzene. In Fig. 4a each benzene molecule is seen with the dumbbell shape on Rh(111) and elongated perpendicularly to the bridge. These detailed features can be explained by the model structure shown in Fig. 4b, where two lobes marked by the circles are assumed to be localized to near carbon atoms (1, 2, 6 and 3, 4, 5) bonded across the Rh atoms.

The $c(2\sqrt{3}\times 3)\text{rect}$ structure described above was consistently observed in the potential range between 0.4 and 0.7 V without additional structural transitions. On the other hand, it was found that the adlayer structure changed at negative potentials. A negative potential step from 0.45 to 0.25 V induced a reconstruction in the benzene adlayer from $c(2\sqrt{3}\times 3)\text{rect}$ symmetry to a long-range ordered hexagonal pattern. Such a long-range ordered hexagonal pattern could be seen over almost the entire area of the terrace. The electrode potential of 0.25 V is near the onset potential of the cathodic current as shown in Fig. 3b.

To reveal the internal molecular structure in the hexagonal phase, STM images were acquired under particularly carefully adjusted experimental conditions with minimal thermal drift. Figure 5a shows one of the highest resolution images acquired on the terrace. Compared with the crystal orientation, $[1\bar{1}0]$, determined by the Rh(111)-(1×1) atomic image, it can be seen that all benzene molecules are almost perfectly aligned along three close-packed directions of Rh(111). The molecular rows cross each other at an angle of either 60° or 120° within

Fig. 4 High-resolution STM image of the $c(2\sqrt{3} \times 3)rect$ benzene adlayer at 0.45 V in HF. The tunneling current was 30 nA (a). A space model of the $c(2\sqrt{3} \times 3)rect$ structure is depicted in (b).

an experimental error ($\pm 2^\circ$). The intermolecular distance along these rows was found to be 0.8 nm, which corresponds to 3 times the lattice parameter of Rh(111). Therefore, we conclude that the hexagonal structure is $(3 \times 3)-C_6H_6$ ($\theta = 0.11$) as shown in Fig. 5b. Moreover, a careful examination of the image reveals that each benzene molecule appears as a set of three spots with similar intensities. It can also be seen that a clear dip exists in the center of each triangle with three lobes. In addition, a weaker additional spot with a small corrugation of about 0.02 nm can be seen in the unit cell.

Although the structure proposed here is basically the same as that proposed previously, based on the LEED, EELS¹⁷⁾ and STM¹⁸⁾ studies in UHV, for the adlayer of coadsorbed benzene and CO on Rh(111), two CO molecules thought to be located at the three-fold hollow sites in the unit cell are omitted in Fig. 5b. Each benzene molecule is assumed to bond at the three-fold hollow site. The coadsorption of CO was unlikely to take place in the solution. Instead of CO, water molecules or hydronium cations might be coadsorbed near the uncoordinated three-fold hollow sites to stabilize the (3×3) structure, their function being similar to that of the coadsorbed CO. The weak small spots seen in Fig. 5a might be due to such coadsorbed water molecules or hydronium cations. It is important to note that all these features of the STM image for the (3×3) adlayer observed at 0.25 V are essentially identical to those found for the coadsorbed benzene and CO adlayer on Rh(111) in UHV reported by

Fig. 5 High-resolution STM image of the (3×3) benzene adlayers at 0.25 V. The tunneling current was 20 nA (a). A space model of the (3×3) structure is depicted in (b). Each small circle between two Rh atoms represents a brighter protrusion in the STM image.

Ohtani *et al.*¹⁸⁾ They also found the weaker spot, which was attributed to the coadsorbed CO or artifacts caused by asymmetric tips.¹⁸⁾

The structures and registries of chemisorbed benzene on Rh(111) have been thoroughly scrutinized by the surface-sensitive techniques, such as LEED, EELS, and angle-resolved photoemission spectroscopy in UHV.¹⁷⁾ These previous studies revealed various structures for benzene, including well-known structures such as $c(2\sqrt{3} \times 4)rect$ and (3×3) , depending on whether CO was present unintentionally or intentionally in the UHV chambers. Although it has been repeatedly demonstrated that the adlayer structures of benzene on Rh and Pt were greatly affected by the presence of CO in the adlayer, the structure of the pure benzene adlayer has not yet been fully understood. Neuber *et al.* recently reported that a completely new structure with a $(\sqrt{19} \times \sqrt{19})R 23.4^\circ$ symmetry appeared for the pure benzene adsorption on Rh(111) under cleaner UHV conditions in the absence of CO, and the previously known structures of $c(2\sqrt{3} \times 4)rect$ and (3×3) were found to appear upon admission of CO.²³⁾

However, it was found in our study that the anodic peak due to the oxidation of CO was hardly detectable in CV even after a prolonged STM experiment for several hours in an air-saturated HF solution. We strongly believe that the adlayer structures found in HF solution described above did not result from contamination with CO.

It is extremely important to recognize that in the previous study of the adsorbed benzene on Rh(111) in UHV,²³⁾ one of the structures of the pure benzene adlayer was attributed to the $c(2\sqrt{3}\times 3)rect$ structure, which was found in solution as described above. This result strongly suggests that the existence of water molecule on top of the benzene adlayer plays a minor role in determining the structure of benzene.

3. 2 Naphthalene on Rh(111)

After the atomic resolution was achieved with Rh(111), a saturated naphthalene solution was added to the STM cell. A high-resolution image acquired in an ordered domain is shown in Fig. 6a. An averaged domain size was about $20\times 20\text{ nm}^2$. The STM image allowed us to determine the internal structure and orientation of each naphthalene molecule.²⁴⁾ The elongated features along the longer molecular axis (C_2) were discerned for each molecule. In addition, the images of some molecules clearly show a two-ring structure expected from the molecular model. It can also be seen that naphthalene molecules are perfectly aligned with a regular micro-orientation along the molecular rows.

According to the results described above, the unit cell can be defined as a $(3\sqrt{3}\times 3\sqrt{3})R30^\circ$ symmetry as shown in Fig. 6b.²⁴⁾ It is now clear that all naphthalene molecules align their C_2 axes along the close-packed directions of Rh substrate. The molecules aligned along the $\langle 112 \rangle$ direction, which is the so-called $\sqrt{3}$ direction, have the same orientation. The spacing between two adjacent molecules along the $\sqrt{3}$ direction is measured to be 1.4 nm, which is three times the $\sqrt{3}$ spacing. In our model structure shown in Fig. 6b two carbon atoms at the 9- and 10-positions are assumed to be attached directly to a Rh atom. It is noteworthy that this structure is identical to that previously proposed from LEED results by UHV workers.²⁵⁾ If one recalls the identical results for benzene adsorbed on Rh(111) in UHV and in HF solution as described above, the results obtained with naphthalene further support the predominant adsorbate-substrate interaction for hydrophobic molecules and the minor role of water molecules.

3. 3 Benzoic acid and terephthalic acid on Pt(111)

To elucidate the effect of molecular structures on the packing arrangement, adlayer structures of benzoic acid (BA) and terephthalic acid (TA) were investigated on a well-defined Pt(111).²⁶⁾ It will be shown that TA molecules formed long range ordered adlattices, whereas BA produced a disordered structure. Surprisingly, it was found that TA formed highly ordered adlayers on Pt(111). An averaged domain size was about $20\times 20\text{ nm}^2$. Figure 7a displays a high-resolution STM image, from which the internal structure of TA molecules can be discerned. With the aid of the closed-packing directions of Pt(111) as shown by the arrows, one identifies two orthogonally intersected molecular rows of I and II in parallel with the close-packed and $\sqrt{3}$ directions of the Pt(111) substrate, respectively. The intermolecular distances of ca. 1.1 and 0.96 nm along these two directions can be interpreted as the unit vectors of 4 and $2\sqrt{3}$, respectively. This structure is thus characterized as $c(2\sqrt{3}\times 4)rect$, $\theta = 0.125$,

Fig. 6 High-resolution STM image of naphthalene on Rh (111) at 0.3 V in HF. The tunneling current was 10 nA (a). A space model of the $(3\sqrt{3}\times 3\sqrt{3})R30^\circ$ structure is depicted in (b).

Fig. 7 High-resolution STM image of terephthalic acid on Pt (111) at 0.4 V in HClO_4 . The tunneling current was 10 nA. A ball model is depicted in (b). The arrows indicate the close-packed directions of the Pt(111) substrate.

and the rectangular unit cell is outlined in Fig. 7a.

The STM image leads to a structural model of TA on Pt(111) as shown in Fig. 7b. TA molecules are assigned

to 2-fold bridge sites with all oxygen atoms in the -COOH groups residing near the bridge sites. The two -COOH groups at the para-positions of the TA molecule have exactly the same coordination environment with the Pt substrate. In fact, a bulk crystal of TA has a layered structure,²⁷⁾ and the molecular arrangement within each layer is very similar to that presented in Fig. 7b. As intermolecular hydrogen bonding is crucial to the layer-type packing, it is anticipated that similar intermolecular interaction exists in the overlayer of TA. The 0.24 nm spacing between two oxygen atoms of two neighboring -COOH groups appears to be optimal for the formation of OH-O hydrogen bonding. If this view is valid, adsorbed TA molecules should not be deprotonated unlike BA molecules adsorbed on Pt(111). It is expected that the -COOH groups are stabilized by the intermolecular H-bonding.

It was demonstrated that molecular structure is critical in forming ordered adlayers at a well-defined Pt(111) electrode. Molecules of higher symmetry such as TA formed the characteristic ordered structures of $c(2\sqrt{3}\times 4)rect$, whereas the adlayer of BA was mostly disordered.²⁶⁾ The adlayer of TA formed a $c(2\sqrt{3}\times 4)rect$ structure, which was thought to be stabilized by the hydrogen bonding between adjacent -COOH groups, forming molecular chains along the $\sqrt{3}$ direction.

3. 4 *p*-Xylene on Rh(111)

The results described above for TA prompted us to investigate adlayer structures of para-substituted benzene derivatives to understand further the effect of intermolecular interactions on the formation of ordered adlayers.²⁸⁾ Somorjai and his co-workers reported results of an STM study of the adsorption of *p*-xylene on Rh(111) at room temperature in UHV.²⁹⁾ They observed that there were many areas of the monolayer where the *p*-xylene molecules were disordered and that the ordered domain size was only about 7 nm. However, their results strongly encouraged us to investigate the adsorption of *p*-xylene on Rh(111) in aqueous solution. It was also of our great interest to compare the adlayers of *p*-xylene formed on Rh(111) in solution and in UHV.

Details of the orientation of *p*-xylene molecules in the adlayer are seen in the high-resolution STM image shown in Fig. 8a. An averaged domain size was about $20\times 20\text{ nm}^2$. Each molecule appeared as an elongated shape due to the existence of two methyl groups at the para-position of the benzene ring. All molecules are oriented with their long axis along the $\sqrt{3}$ direction. It is clearly seen that the *p*-xylene molecules are adsorbed horizontally on the Rh(111) surface. The set of three spots for each molecule are attributed to the two methyl groups and the benzene ring as expected from a theoretical calculation.³⁰⁾

A precise comparison between the image of Fig. 8a and that of Rh(111)-(1 $\times$ 1) revealed that the two molecular rows along the directions of A and B cross each other at $90\pm 1.5^\circ$. The intermolecular distances are $0.98 (\pm 0.02)$ and $1.04 (\pm 0.02)$ nm along the directions of A and B, respectively. The rectangular lattice spaces of $2\sqrt{3}$ and 4 on Rh(111) (0.268 nm) correspond to 0.93

Fig. 8 High-resolution STM image of *p*-xylene on Rh(111) at 0.3 V in 0.01 M HF. The tunneling current was 3 nA (a). The arrows indicate the close-packed directions of Rh(111). Two repeating cells were superimposed by thicker solid and dashed lines, respectively. The arrows marked A, B, a, and b indicate the directions of the molecular rows. A structural model is depicted in (b).

and 1.07 nm, respectively, which are almost identical to the experimental values for the rectangular cell drawn by dashed lines. Consequently, we conclude that the adsorbed *p*-xylene molecules form a $c(2\sqrt{3}\times 4)rect$ structure on Rh(111). Note that coincidentally, the same structure was found for the adsorbed TA on Pt(111) as described above. More accurately, the unit cell should be denoted as $\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$, which is shown by the thicker solid lines in Fig. 8. According to this notation, we expect that the unit cell has an angle of 81.8° and that the intermolecular distance is 0.71 nm for both sides. We carefully measured intermolecular distances along the directions marked a and b, yielding 0.70-0.73 nm. The experimental values agree with the calculated value (0.71 nm).

On the basis of these detailed results, we proposed that the *p*-xylene adlayer has the so-called $c(2\sqrt{3}\times 4)rect$ cell or the $\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$ unit cell, whose models are illustrated in Fig. 8b. Periodical units of the two cells are shown by dashed lines and solid lines, respectively. Although it was recently reported that computationally calculated images exhibited little dependence on the binding site on a rhodium cluster,³⁰⁾ the aromatic ring is tentatively assumed to be located on the two-fold bridge site, as in the case of TA on Pt(111). The long axis of each molecule is aligned along the $\sqrt{3}$ direction. Two neighboring methyl groups have a face-to-face configuration

along the $\sqrt{3}$ direction. In the case of TA, it was concluded that the -COOH groups are stabilized by intermolecular hydrogen bonding, which subsequently forms the $c(2\sqrt{3}\times 4)rect$ ordered structure. Because the methyl groups of the two neighboring *p*-xylene face each other to form the $c(2\sqrt{3}\times 4)rect$ structure, some attractive interactions between the neighboring methyl groups must be taken into account to explain this face-to-face configuration. It is well known that there is a hyperconjugation between the methyl group and the aromatic ring. This type of interaction might extend through the neighboring methyl groups. A molecular orbital calculation seems to be needed for the evaluation of these intermolecular interactions.

It is important to discuss the fact that Somorjai and co-workers reported a rhomboid as a unit cell with an angle of 80° and the sides of 0.84 and 0.69 ± 0.05 nm for the *p*-xylene adlayer prepared on Rh(111) in UHV.²⁹⁾ As described above, we observed that the sides of the unit cell (0.70–0.73 nm) for the adlayer formed on the Rh(111) surface in solution are equal in length within the experimental error. In general, the structure of an adlayer formed on electrodes in solution is not necessarily the same as that formed in UHV. However, it has been demonstrated that adlayer structures of aromatic molecules such as benzene and naphthalene on Rh(111) in HF solution are almost identical to those formed in UHV as described above. From our results, one might expect that the structure of the adlayer of *p*-xylene would be the same in UHV and in solution. A further detailed investigation seems to be needed to elucidate the structure of *p*-xylene on Rh(111) in UHV.

3. 5 Other molecules

It is noteworthy that we disclosed a novel property of iodine-modified electrodes for the adsorption of organic molecules.^{31–35)} It was found, for the first time, that a water soluble porphyrine, 5, 10, 15, 20-tetrakis(*N*-methylpyridinium-4-yl)-21H, 23H-porphyrine (TMPyP), formed highly-ordered molecular arrays via self-ordering on the iodine-modified Au(111) electrode in HClO₄ solution.^{31, 32, 34)} We demonstrated that I-Au(111) electrode is one of the most promising substrates for the investigation of organic molecules in solution. Indeed, we discovered this electrode, with great generality, to be suitable on which to form highly-ordered adlayers not only TMPyP but also various other molecules such as crystal violet.³²⁾ It was also demonstrated in our previous papers that various iodine-modified metal electrodes such as Ag(111),³³⁾ and Pt(100)³⁵⁾ can also be employed as a substrate on which to investigate the adsorption of organic molecules.

In this section, we briefly describe only the adlayer of TMPyP formed on an iodine-modified Au(111). The experimental procedure was rather simple. A well-defined Au(111) surface prepared by the flame-annealing and quenching method was immersed into 1 mM KI solution for several minutes and then thoroughly rinsed with 0.1 M HClO₄ solution. The iodine modified electrode, thus prepared, was installed in an electrochemical cell containing a TMPyP solution for *in situ* STM measurements.

Molecular orientations, packing arrangements and even internal molecular structures of the adsorbed TMPyP molecules can be seen in high-resolution STM images. A typical STM image is presented in Fig. 9. The high-resolution image directly demonstrates that the flat-lying TMPyP molecule can be recognized in the images as a square with four additional bright spots. The shape of the observed features in the image clearly corresponds to the chemical structure of TMPyP molecule. The characteristic four bright spots located at the four corners of a square correspond to the pyridinium units of TMPyP. The center to center distance between the bright spots was found to be 1.3 nm measured diagonally, which is nearly equal to the distance between two diagonally located pyridinium units. In addition to the internal structure, the STM image shown in Fig. 9 reveals details of the symmetry and the packing arrangement. Although the TMPyP molecules adsorbed directly on Au(111) could be seen by STM, the adsorbed molecules did not form ordered adlayers.³⁴⁾ Disordered adlayers formed on bare Au(111) suggest that strong interactions including chemical bonds between the Au substrate and the organic molecules prevented self-ordering processes from occurring, which must involve surface diffusion of the adsorbed molecules. The surface diffusion of the molecules adsorbed on bare Au was found to be very slow. Relatively weak van der Waals type interactions between the hydrophobic iodine adlayer and the organic molecules could be the key factor promoting self-ordering processes on the I-Au(111) substrate.

Finally, it should be noted that organosulfur compounds adsorbed on metal electrodes have been investigated most extensively using STM. Recent articles are useful for finding the literature on STM studies of various organosulfur molecules.^{36–39)}

Fig. 9 High-resolution STM image of TMPyP on an I-modified Au(111) in HClO₄. The tunneling current was 4 nA (a). The chemical structure of TMPyP is shown in (b).

4 Conclusion

The methods for exposing well-defined electrode surfaces in solution were reviewed. The flame-annealing and quenching method can be applied to Au, Pt, Rh, Pd, and Ir single crystal electrodes. It was pointed out that the electrochemical etching method produced atomically flat terrace-step structures of various metals such as Ni, Ag, Co, Pd, and Cu. The adlayer structure of benzene on Rh(111) was also described in detail; it was found to be dependent on the electrode potential. The (3×3) structure found on Rh(111) in the cathodic potential range is almost identical to that found in UHV for the coadsorbed benzene and CO. The molecular shape of naphthalene and packing arrangement could be clearly discerned by *in situ* STM. The unit cell of the naphthalene adlayer on Rh(111) can be defined as a $(3\sqrt{3} \times 3\sqrt{3})R 30^\circ$ symmetry. It was also shown that terephthalic acid and *p*-xylene form highly-ordered adlayers on Pt(111) and Rh(111), respectively. It was briefly shown that the iodine-modified electrodes are suitable for producing highly-ordered adlayers of various organic molecules. TMPyP forms highly-ordered adlayers on iodine modified-Au(111). It is clearly demonstrated that *in situ* STM allows us to determine interfacial structures with atomic resolution. It is certain that *in situ* STM will continue to be the premier technique for atomic-level surface structural investigations of electrochemical processes taking place at electrode-electrolyte interfaces.

Acknowledgement

This work was supported by a Grant-in-Aid for Science Research (A) (No. 12305055) from the Ministry of Education, Science, Sports and Culture, Japan.

References

- 1) H.-J. Guntherodt and R. Wiesendanger (Eds.), *Scanning Tunneling Microscopy I*, Springer-Verlag, Berlin (1991).
- 2) R. Sonnenfeld and P. K. Hansma, *Science*, **232**, 211 (1986).
- 3) A. A. Gewirth and B. K. Niece, *Chem. Rev.*, **97**, 1129 (1997).
- 4) K. Itaya, *Prog. Surf. Sci.*, **58**, 121 (1998).
- 5) J. Clavilier, R. Faure, G. Guinet, and R. Durand, *J. Electroanal. Chem.*, **107**, 205 (1980).
- 6) J. Clavilier, A. Rodes, K. El. Achi, and M. A. Zamakhchari, *J. Chim. Phys.*, **88**, 1291 (1991).
- 7) N. Furuya and S. Koide, *Surf. Sci.*, **220**, 18 (1989).
- 8) J. M. Feliu, J. M. Orts, R. Gomez, A. Aldaz, and J. Clavilier, *J. Electroanal. Chem.*, **372**, 265 (1994).
- 9) K. Itaya, S. Sugawara, K. Sashikata, and N. Furuya, *J. Vac. Sci. Technol.*, **A8**, 515 (1990).
- 10) S. Tanaka, S.-L. Yau, and K. Itaya, *J. Electroanal. Chem.*, **396**, 125 (1995).
- 11) K. Itaya, *Interfacial Electrochemistry-Theory, Experiment, and Applications* (Ed. A. Wieckowski), Marcel Dekker, New York, p.187 (1999).
- 12) K. Uosaki, S. Ye, H. Naohara, Y. Oda, T. Haba, and T. Kondo, *J. Phys. Chem. B*, **101**, 7566 (1997).
- 13) H. Naohara, S. Ye, and K. Uosaki, *J. Phys. Chem. B*, **102**, 4366 (1998).
- 14) J. Lipkowski and P. N. Ross (Eds.), *Adsorption of Molecules at Metal Electrodes*, VCH Publishers, New York (1992).
- 15) A. T. Hubbard, *Chem. Rev.*, **88**, 633 (1988).
- 16) M. P. Soriaga, *Prog. Surf. Sci.*, **39**, 325 (1992).
- 17) G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, John Wiley & Sons Inc., New York (1994).
- 18) H. Ohtani, R. J. Wilson, S. Chiang, and C. M. Mate, *Phys. Rev. Lett.*, **60**, 2398 (1988).
- 19) H. A. Yoon, M. Salmeron, and G. A. Somorjai, *Surf. Sci.*, **373**, 30 (1997).
- 20) S.-L. Yau, Y.-G. Kim, and K. Itaya, *J. Am. Chem. Soc.*, **118**, 7795 (1996).
- 21) H. Baltruschat and U. Schmiemann, *Ber. Bunsenges. Phys. Chem.*, **97**, 452 (1993).
- 22) P. S. Weiss and D. M. Eigler, *Phys. Rev. Lett.*, **71**, 3139 (1993).
- 23) M. Neuber, F. Schneider, C. Zubragel, and M. Neumann, *J. Phys. Chem.*, **99**, 9160 (1995).
- 24) S.-L. Yau, Y.-G. Kim, and K. Itaya, *J. Phys. Chem. B*, **101**, 3547 (1997).
- 25) R. F. Lin, R. J. Koestner, M. A. Van Hove, and G. A. Somorjai, *Surf. Sci.*, **134**, 161 (1983).
- 26) Y.-G. Kim, S.-L. Yau, and K. Itaya, *Langmuir*, **15**, 7810 (1999).
- 27) M. Bailey and C. J. Brown, *Acta Crystallogr.*, **22**, 387 (1967).
- 28) K. Suto, M. Wakisaka, M. Yamagishi, L.-J. Wan, J. Inukai, and K. Itaya, *Langmuir*, **16**, 9368 (2000).
- 29) P.D. Cernota, H. A. Yoon, M. Salmeron, and G. A. Somorjai, *Surf. Sci.*, **415**, 351 (1998).
- 30) D. N. Futaba and S. Chiang, *Surf. Sci.*, **448**, L 175 (2000).
- 31) M. Kunitake, N. Batina, and K. Itaya, *Langmuir*, **11**, 2337 (1995).
- 32) N. Batina, M. Kunitake, and K. Itaya, *J. Electroanal. Chem.*, **405**, 245 (1996).
- 33) K. Ogaki, N. Batina, M. Kunitake, and K. Itaya, *J. Phys. Chem.*, **100**, 7185 (1996).
- 34) M. Kunitake, U. Akiba, N. Batina, and K. Itaya, *Langmuir*, **13**, 1607 (1997).
- 35) K. Sashikata, T. Sugata, M. Sugimasa, and K. Itaya, *Langmuir*, **14**, 2896 (1998).
- 36) G. E. Poirier, *Chem. Rev.*, **97**, 1117 (1997) and references therein.
- 37) L.-J. Wan, M. Terashima, H. Noda, and M. Osawa, *J. Phys. Chem. B*, **104**, 3563 (2000).
- 38) S. Yoshimoto, N. Hirakawa, K. Nishiyama, and I. Taniguchi, *Langmuir*, **16**, 4399 (2000).
- 39) B. Ohtani, A. Shintani, and K. Uosaki, *J. Am. Chem. Soc.*, **121**, 6515 (1999).