ECSTM study of adsorption of C₆₀, C₇₀, C₈₆ and Y@C₈₂ on Au(111)

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The adsorption of a variety of fullerenes (C₆₀, C₇₀, C₈₆, Y@C₈₂) on Au(111) electrode surfaces was comprehensively investigated in 0.1 M HClO₄ by electrochemical scanning tunneling microscopy (ECSTM). In the ordered C₆₀'s adlayer, C₆₀ molecules formed either ($2\sqrt{3} \times 2\sqrt{3}$) or “in-phase” structure. The high resolution STM image shows that the C₆₀ cage is not simply round but shows a bifurcated feature. The adsorption orientation of C₆₀ on Au(111) is tentatively suggested. In the ordered C₇₀'s adlayer, the perpendicular fullerene molecules are the main adsorption mode and form ($2\sqrt{3} \times 2\sqrt{3}$) structure. However, for C₈₆ and Y@C₈₂, the ordered adlayer could not be obtained on Au(111) under the present condition. These differences may be due to the different molecular shapes and sizes, and the encapsulated metal atom which affects the lattice matches with the substrate. The adsorption of fullerene molecules on Au(111) from disorder to order could be tuned simply by steering the dimensional sizes or shapes of the fullerenes used.

C₆₀, C₇₀, C₈₆, Y@C₈₂, ECSTM, Au(111)

1 Introduction

Since their discovery in 1985 [1, 2], fullerenes have been applied as a new promising material in electronic, optical, catalytic and biochemical applications owing to their novel structures. With various applications, the behavior of fullerenes on solid surfaces is of much interest. Scanning tunneling microscopy (STM) is a powerful method to directly monitor the structures and electronic properties of surfaces with an atomic resolution. STM has been frequently utilized for characterization of the fullerene molecules on metal (Au, Ag, Al, Cu, Ni, Pd) [3–6] and semiconductor surfaces (Si, Ge, GaAs) [3].

C₆₀ is a round ball with a diameter of 7.0 Å, and has a nearest neighbouring distance of 10.04 Å in the bulk (111) plane of the face center cubic (fcc) lattice at 300 K. For the adsorption of C₆₀ on the Au(111) surface, pioneering STM

investigations in ultrahigh vacuum (UHV) by Altman and Colton *et al.* initially led to two suggested structures: ($2\sqrt{3} \times 2\sqrt{3}$) R30° and the “in-phase” (38 × 38) [7–11]. Similar results were obtained on the film prepared by immersing Au(111) into a C₆₀-benzene solution in electrochemical environment using electrochemical scanning tunnelling microscopy (ECSTM) [12]. However, on Ag(111) surface [3, 7–9], STM images show that the C₆₀ monolayer exclusively forms ($2\sqrt{3} \times 2\sqrt{3}$) R30° structure. By contrast, C₆₀ forms (4 × 4) superstructure with respect to Cu(111), which is consistent with its epitaxial relationship [3, 7, 13].

C₇₀ possesses an ellipsoidal shape, with diameters of 7.9 Å along the long axis and 7.0 Å along the short axis. The nearest neighbouring distance of C₇₀ in the bulk phase is measured to be 10.6 Å [14]. Yurov *et al.* investigated the adsorption of C₇₀ on the Cu(111)(1 × 1) surfaces employing STM under UHV conditions [15]. The pure C₇₀ monolayer was found to form the 4 × 4-commensurate structure as a close-packed hexagonal lattice, after a brief annealing at

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approximately 320 °C. The individual C_{70} molecule takes the upright position with the long axis perpendicular to the surface. Zhang *et al.* found the coexistence of standing and lying-down C_{70} molecules on Au(111) with height-shaded molecular resolution STM image, by covering the Au surface with a dichloromethane solution containing fullerene [16]. The distinguishable dark and bright protrusions were seen in the array. Another type of the quasi-hexagonal in-phase packing with the long axis parallel to the surface was found in C_{70} submonolayer deposited at the *n*-tetradecane/ Au(111) interface [17].

Fullerenes with metal atoms encapsulated (endohedral metallofullerenes) are novel forms of fullerene-based materials [18–20]. Shi *et al.* investigated $Tb@C_{82}$ molecules adsorbed on Si(100) 2×1 surface and the C_{60} film with an ultrahigh vacuum scanning tunneling microscope (UHV-STM) [18]. It was found that the $Tb@C_{82}$ molecules were randomly distributed on the surface of Si(100) but form a close-packing monolayer on the C_{60} film. However, on a hydrogen-terminated Si(100)- 2×1 surface, Shinohara *et al.* found in the UHV-STM images that $La@C_{82}$ molecules in the multilayer show the ordered hexagonal close-packing array although $La@C_{82}$ molecules in the monolayer show an disordered adlayer on the surface [20].

We have reported the adsorption of $Y@C_{82}$ on bare, C_{60} -modified and iodine-modified Au(111) in electrochemical environment by electrochemical scanning tunneling microscopy (ECSTM) [21]. The results showed that $Y@C_{82}$ molecules were mobile and aggregated to the terrace edges on bare and C_{60} -modified Au(111), but monodispersion of the $Y@C_{82}$ molecules was achieved on the iodine-modified Au(111) surface via the improvement of the $Y@C_{82}$ -substrate interactions. In this study, we further investigated the adlayers of C_{60} , C_{70} , C_{86} on Au(111) using ECSTM, by immersing the substrate in fullerene-benzene- CS_2 solutions. The obtained results, together with the result of $Y@C_{82}$ adsorbed on Au(111), aim at comprehensively understanding the adsorption of a variety of fullerenes as well as the effect of molecular shapes and sizes, and the encapsulated metal atom to the adsorption of fullerenes. The chemical structures of these fullerene and metallofullerene molecules are shown in Scheme 1.

2 Experimental

2.1 Materials

C_{60} , C_{70} , C_{86} and $Y@C_{82}$ were prepared by the conventional Krätschmer-Huffman method followed by isolation and purification with high-performance liquid chromatography [22]. An aqueous $HClO_4$ solution was prepared with $HClO_4$ (Kanto Chemical Co.) and ultrapure water (Milli-Q, SP-TOC; ≥ 18.2 MQ cm). Spectroscopy grade benzene from Aldrich was used without further purification. CS_2 was

Scheme 1 Chemical structures of (a) C_{60} , (b) C_{70} , (c) C_{86} and $Y@C_{82}$.

from Chinese Chemical Co.

2.2 STM experiments

Single-crystal beads of Au were prepared by the crystallization of a molten ball formed at the end of a pure gold wire in a hydrogen-oxygen flame [23]. An Au(111) facet on a single-crystal bead was directly used for the STM measurements. The adlayers of C_{60} , C_{70} , C_{86} and $Y@C_{82}$ were prepared by immersing the substrate into fullerene-benzene- CS_2 for 1–2 min ($V_{benzene}:V_{CS_2}$: 1:1). The fullerene-adsorbed substrate was taken out and rinsed with ultrapure water. In situ STM observation was carried out with Nanoscope E STM (Digital Instruments) in 0.1 M $HClO_4$. Tunneling tips used were prepared by electrochemical etching of a tungsten wire (0.25 mm in diameter) and sealed with clear nail polish to minimize the occurrence of faradic current. All the STM images shown in this paper were acquired in the constant-current mode. All the electrode potentials are reported with respect to the RHE.

3 Results and discussion

3.1 C₆₀ adlayer

First, we prepared the incomplete C₆₀ monolayer by immersing Au(111) surface into C₆₀-benzene-CS₂ solution containing a small amount of molecules (~0.1 μ M) for 1 min. It has been found that the molecular structure of low-coverage fullerene adlayer on Au(111) is difficult to be observed under ambient conditions. This is perhaps because of the high mobility of C₆₀ molecules together with the external tip scanning on the surface.

However, once the scanned areas are largely filled by C₆₀ molecules with increasing the concentration of C₆₀ in benzene-CS₂ solution, their lateral movement is restricted to allow the acquisition of the STM images. Figure 1(a) shows a typical STM image of C₆₀ monolayer on Au(111) in 0.1 M HClO₄ by immersing Au(111) into ~5 μ M C₆₀-benzene-CS₂ solution for 1 min. Atomically flat terraces were almost completely covered with an ordered adlayer of C₆₀. Spherical bright spots and dark areas correspond to the individual C₆₀ molecule and the molecular defect, respectively. Typical domain sizes range between 5 and 30 nm, often limited by surface defects, domain boundaries and occasional disordered regions.

Figure 1(b) shows the typical high-resolution STM image

of C₆₀ monolayer on Au(111) where the stripe in bottom right is due to the mobility of C₆₀. Each C₆₀ molecule is more clearly recognized as a round bright spot. Some missing C₆₀ molecules lead to the molecular defects on Au(111) as indicated by the white arrows. The measured corrugation height of the round bright spot is ~0.09 nm (Figure 1(c)), which is much smaller than the diameters of C₆₀. Such a reduced apparent height is related to the electronic structure of the adsorbed C₆₀ molecules [17]. In Figure 1(b), two different domains α and β , despite with the similar hexagonal pattern, could be revealed by careful observation and analysis. The molecular rows in domains α and β cross each other at the boundary at an angle of 150° within an experimental error of $\pm 3^\circ$. A precise comparison between the domains and the underlying Au(111)-(1 $\times$ 1) lattice reveals that molecular rows in domains α and β are in parallel with $\langle 121 \rangle$ and $\langle 110 \rangle$ directions of Au(111), respectively. In both types of domains, the nearest neighbour molecular distance is estimated to be 1.0 ± 0.1 nm. This value matches with the nearest neighbouring distance of C₆₀ in the bulk phase at 10.04 Å, suggesting the good commensurate between C₆₀ and Au(111) lattice. Based on these measurements further in combination with the previous reports [8–12], one may identify an oblique experimental unit cell of $(2\sqrt{3} \times 2\sqrt{3}) R30^\circ$ for domain α and an “in-phase” struc-

Figure 1 STM images of C₆₀ adlayers on Au(111) in 0.1 M HClO₄. (a) Scan size, 50 nm $\times$ 50 nm, I_t (tunneling current)=1.582 nA, E_{bias} (sample bias)=−195 mV; (b) scan size, 10 nm $\times$ 10 nm, I_t =1.757 nA, E_{bias} =−145 mV; (c) cross section diagram corresponding to the line in (b); (d) scan size, 9 nm $\times$ 9 nm, I_t =501.9 pA, E_{bias} =−218 mV; (e) tentatively suggested adsorption orientation of C₆₀ on Au(111).

ture for domain β .

To understand the adsorbed orientation of C_{60} molecules on Au(111), more high-resolution STM images of C_{60} monolayer on Au(111) were recorded as shown in Figure 1(d). It shows C_{60} cage is not simply round but shows a bifurcated feature. Its inset clearly shows the details of such morphology. This acquired bifurcated structures of C_{60} molecules under the electrochemical environment are similar to that of C_{60} - C_{60} on Au(111) in ultrahigh vacuum [24]. According to the model for C_{60} - C_{60} on Au(111) provided by Itaya *et al.*, a corresponding adsorption orientation of C_{60} on Au(111) is suggested in Figure 1(e). The result in Figure 1(d) also indicates that the rotational movement of C_{60} is hindered at enough high coverage at room temperature and the electronic structure of the cage could be observed by STM in the electrochemical environment.

3.2 C_{70} adlayer

Similar studies have been carried out for the adsorption of C_{70} on Au(111) in aqueous $HClO_4$ solution. Figure 2(a) shows a typical large-scale STM image of the C_{70} adlayer on Au(111) in 0.1 M $HClO_4$, which is prepared by immersing Au(111) into benzene- CS_2 solution containing a large amount of fullerene molecules ($\sim 10 \mu M$) for 1 min. At high coverage, excessive C_{70} molecules are irregularly packed on Au(111) and appear as the line structure perpendicular to the Au(111) step edges, indicating the preferential direction of C_{70} film growth along the $\langle 121 \rangle$ direction of gold [17]. The continual scanning for a while at lower tip-surface distance could not move these fullerene molecules. It indicates the molecule-substrate interaction between C_{70} and Au(111) substrate may be strong [25].

A further reduction in the coverage could result in the growth of the ordered adlayer of C_{70} molecules that extended on the atomically flat gold terraces ($\sim 3 \mu m$). Figure 2(b) shows a representative STM image of C_{70} adlayer on Au(111). Typical domain sizes range between 10 nm and 35 nm. Figure 2(c) shows a typical high-resolution STM

image of C_{70} molecules on Au(111). The spherical protrusion corresponds to the individual C_{70} molecule and does not show the presence of intramolecular structures at various bias voltages. It indicates that C_{70} molecules take an upright position with the long axis perpendicular to the surface and continue to rotate along their long axis [15]. The molecular rows in most domains are essentially parallel with the $\sqrt{3}$ direction. The nearest-neighbour intermolecular distance is measured to be 1.0 ± 0.1 nm. The value matches with the nearest neighbouring distance of C_{70} in the bulk phase at 10.6 Å. It suggests the good commensurate between upright C_{70} and Au(111) lattice similar to that between C_{60} and the substrate. Based on the measurements, the $(2\sqrt{3} \times 2\sqrt{3}) R30^\circ$ could be identified, which is the same as the case for C_{60} .

3.3 C_{86} adlayer

C_{86} is a larger fullerene molecule. Few investigations of C_{86} , especially by STM, have been reported. In this study, molecularly resolved images of C_{86} on Au(111) were provided. Figure 3(a) shows a large-scale STM image of C_{86} adlayer on Au(111) in 0.1 M $HClO_4$ which is prepared by immersing Au(111) into $\sim 5 \mu M$ C_{86} -benzene- CS_2 solution for 1 min. C_{86} molecules appear as the bright spots and are irregularly packed on Au(111) with very local ordered structure. The high resolution STM image in Figure 3(b) shows that while there are some semi-hexagonal structures visible, the overall ordering is much less evident for the monolayer. One significant and interesting observation of the adsorption structure is that individual C_{86} molecules are not imaged uniformly in topography, suggesting that there are several types of C_{86} adsorption modes coexisting on the gold surface, and they are not completely spherical. In contrast to C_{60} and C_{70} , further increase or reduction of the surface coverage by changing the concentration of C_{86} in benzene- CS_2 could not get the ordered C_{86} adlayer on Au(111). It is possible that the increased size (C_{86} has a van der

Figure 2 STM images of C_{70} adlayers on Au(111) in 0.1 M $HClO_4$. (a) Scan size, 50 nm $\times$ 50 nm, $I_t = 751.7$ pA, $E_{bias} = -117$ mV; (b) scan size, 50 nm $\times$ 50 nm; $I_t = 880.4$ pA, $E_{bias} = -232$ mV; (c) scan size, 6 nm $\times$ 6 nm; $I_t = 880.4$ pA, $E_{bias} = -232$ mV.

Figure 3 STM images of C_{86} adlayers on Au(111) in 0.1 M $HClO_4$. (a) Scan size, 50 nm $\times$ 50 nm, $I_t = 3.0$ nA, $E_{bias} = -195$ mV; (b) scan size, 10 nm $\times$ 10 nm, $I_t = 3.197$ nA, $E_{bias} = -175$ mV.

Waals radius roughly 15% larger than C_{60} [25]) and asymmetry of the fullerene cage disfavor commensurate binding.

3.4 $Y@C_{82}$ adlayer

As a comparison, the adsorption of $Y@C_{82}$ adlayer on bare Au(111) is also described here [21]. Figure 4 shows a typical STM image of $Y@C_{82}$ adlayer on a bare Au(111) which is prepared by immersing Au(111) surface into $\sim 5 \mu M$ $Y@C_{82}$ -benzene- CS_2 solution for 2 min. The metallofullerene adlayer shows a stripe structure which is composed of a large number of irregularly close-packed $Y@C_{82}$ along the terrace edges of the Au substrate. The possible reason is that the weak $Y@C_{82}$ -Au interaction leads to the $Y@C_{82}$ molecules being mobile on the Au(111), and they finally migrate to the terrace edges and aggregate there

Figure 4 STM image of the $Y@C_{82}$ adlayer on Au(111) in 0.1 M $HClO_4$. Scan size, 130 nm $\times$ 130 nm; $I_t = 402.8$ pA, $E_{bias} = -186$ mV.

following absorption. Similar to C_{86} , further increase or reduction of the surface coverage could not get the ordered $Y@C_{82}$ adlayer on Au(111). This may be related to the increased size of the fullerene cage as well as the encapsulated metal.

According to the STM observation previously described, all fullerene molecules appear as a bright spot. One possible reason to explain these similarities is that fullerene molecules have similar π -conjugated molecular structures composed of five and six carbon rings. It is noteworthy that the adsorption of C_{60} , C_{70} , C_{86} and $Y@C_{82}$ on electrode surfaces are very different. This may be due to different molecular shapes and sizes, and the encapsulated metal atom. The adsorption of fullerene molecules on Au(111) from disorder to order could be tuned simply by steering the dimensional sizes or shapes of the fullerenes used.

4 Conclusions

A variety of fullerenes (C_{60} , C_{70} , C_{86} , $Y@C_{82}$) have been studied on Au(111) electrode surfaces in 0.1 M $HClO_4$ using electrochemical scanning tunneling microscopy. The adlayers of fullerene were formed on electrode surfaces in benzene- CS_2 solution, and the adsorbed structures were characterized by high-resolution STM images. High-resolution STM images reveal that C_{60} molecules formed either $(2\sqrt{3} \times 2\sqrt{3})$ or "in-phase" structure, and C_{60} cage is not simply round but shows a bifurcated feature. In the ordered C_{70} 's adlayer, the perpendicular fullerene molecules are the main adsorption mode and form $(2\sqrt{3} \times 2\sqrt{3})$. In the C_{86} 's adlayer, the local ordering is less evident for the monolayer, possibly because of larger misfit between the larger size of C_{86} and Au(111) lattice. $Y@C_{82}$ formed the disordered adlayer on Au(111) surface, which may be due to the increased size of fullerene cage and encapsulated metal atom. The adsorption of fullerene molecules on Au(111) from disorder to order could be tuned simply by steering the dimensional sizes or shapes of the fullerenes used. It is hoped that the obtained result will facilitate the understanding of the adsorption of fullerenes on the surface.

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