In situ STM Visualization of Fullerene Epitaxial Adlayers on Au(111) Surfaces Prepared by the Transfer of Langmuir Films

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Epitaxial adlayers of fullerenes (C_{60} and C_{60}/C_{70}) on Au(111) surfaces were prepared by the simple transfer of Langmuir films at air-water interface. The structure of the adlayers are essentially same as those prepared by sublimation. The adlayers are stable and reveal no reaction in the whole double layer potential region in 0.1 M perchloric acid.

Fullerenes have offered the increasing attention toward exploration of new physical and chemical properties.[1] Our interest is focused on the preparation and characterization of well-defined epitaxial adlayers of fullerenes on single crystal metal substrates in solutions. The preparation of epitaxial layers of fullerenes based on sublimation in ultra high vacuum (UHV) have been reported.[2] Recently, not only the sophisticated vapor deposition techniques but also simple techniques based on the adsorption from the solution such as self-assembly technique[3] and self-organization induced by the controlled adsorption[4] became popular for the preparation of highly ordered molecular layers. However, in the case of fullerene adlayers on metal surfaces, it would be difficult to form adlayers by means of the adsorption from aqueous or nonaqueous solutions because of the insolubility of fullerenes to water and strong adsorption of organic solvents on metal surfaces. Here, we describe epitaxial adlayers of fullerenes on metal surfaces prepared by the transfer of Langmuir films on air-water interfaces.

The preparation of the fullerene epitaxial adlayers involved the following procedures. C_{60} (Bucky USA, 99.995%) the mixture of C_{60} and C_{70} (TCI Co. Ltd., C_{60}/C_{70} = 4/1) were purchased and used without further purification. The fullerene films on air-water interfaces were prepared using Langmuir trough by means of spreading of benzene solution. Langmuir films on air-water interfaces and Langmuir-Blodgett films of fullerenes have been reported by several groups.[5] The surface pressure has to keep at 10-20 nN/m which can be attributed to the monolayer, after the benzene solution with fullerenes were spreaded. Well-defined bare Au(111) electrodes were prepared in the same manner based on flaming and quenching techniques as described previously.[4] An intact Au(111) surface was immersed into the trough across the films in order to transfer. Then, the electrode was transferred into an in situ STM cell containing 0.1 M perchloric acid. In situ STM measurement carried out a Nanoscope III (Digital Instruments, Santa Barbara, California) with an electrochemically etched W tunneling tip which was sealed with transparent nail polish. All images were collected in the constant current mode.

Figure 1 shows a typical in situ STM image of C_{60} adlayers modified on Au(111) surfaces. It was surprisingly found that the epitaxial adlayers of C_{60} on Au(111) surfaces can be prepared simply transfer from the films on air-water interfaces. Highly ordered molecular layers with a hexagonal-like lattice were are distributed randomly in the adlayers. Similar images for C_{60}/C_{70} mixed adlayers on Au(111) prepared by vapor deposition have been reported.[2b]

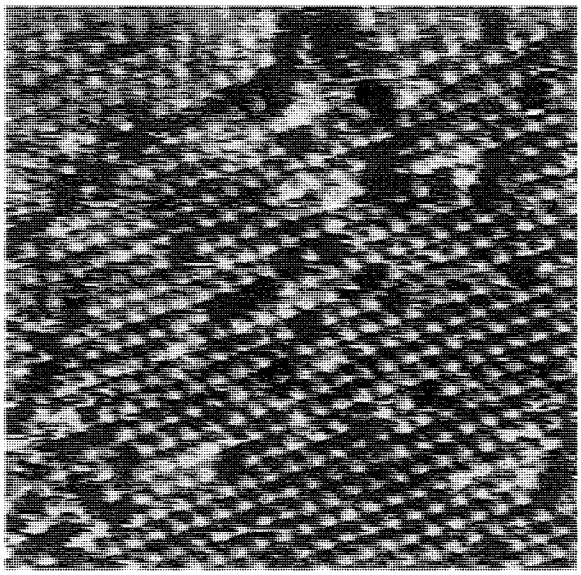

Figure 1. Typical in situ STM image (24.4 nm x 24.4 nm) of C60 epitaxial adlayers on a Au(111) surface in 0.1 M perchloric acid. The image was obtained with a tunneling current of 10 nA. The electrode potentials of the substrate (Es) and the tip (Et) were set at +0.62 V and +0.51 V vs RHE, respectively.

From the electrochemical point of view, the fullerene adlayers were researched by means of cyclic voltammetry and potential controlled in situ STM. Figure 3 shows typical cyclic voltammograms (CVs) of a bare (dotted line) and a C_{60} modified Au(111) (solid line) electrodes in 0.1M perchloric acid. The features of CV observed in pure electrolyte solution were in good agreement with the data reported in the literature,[4b] indicating that the surface was a well-defined Au(111) free from contamination. On the other hands, a C_{60} modified Au(111) electrode reveals the featureless CV shown as solid line in Figure 3. The decreased double layer capacitance of the modified electrodes obviously proved the modification of C_{60} on Au(111) electrodes. It is worth to note that no redox of fullerene molecules in aqueous media is reported, although the redox activity of fullerenes are well-known in nonaqueous media at low temperature.[6] Exceptionally, Nakashima and co-workers[7] have succeeded in proceeding the redox of fullerene molecules incorporated into the local hydrophobic fields of the bilayer lipid films modified on electrodes. Furthermore, the featureless of CV agrees with the results of in situ STM observation that the adlayers are stable at whole double layer region. The epitaxial adlayers of fullerenes are

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observed at whole double layer potential range (form +0.1 V to extended on the terrace on Au(111) electrodes with many defects. Occasionally, the coexisted domains of two lattices with different rotational angles toward Au lattice were observed. The angles of molecular rows of both domains are 0° or 30° rotated with respect to the direction of underlying Au rows. Observed distances between hexagonal packed C_{60} molecules for both lattices are 1.0 ± 0.05 nm. The commensuracies of lattices can be assigned $2\sqrt{3}$ x $2\sqrt{3}$ and 7 x 7. $2\sqrt{3}$ x $2\sqrt{3}$ lattice seemed to be dominant. These results obviously proved that the structure of the fullerene adlayers prepared by the transfer are regulated under the epitaxial control. Both the same structures of fullerene adlayers on Au(111) surfaces have been reported for the arrays prepared by vapor deposition.[2b] In addition, STM image of C_{60} and C_{70} layers on Au(111) and Au(110) surfaces have been reported by Weaver and co-workers in 1992.[2c]

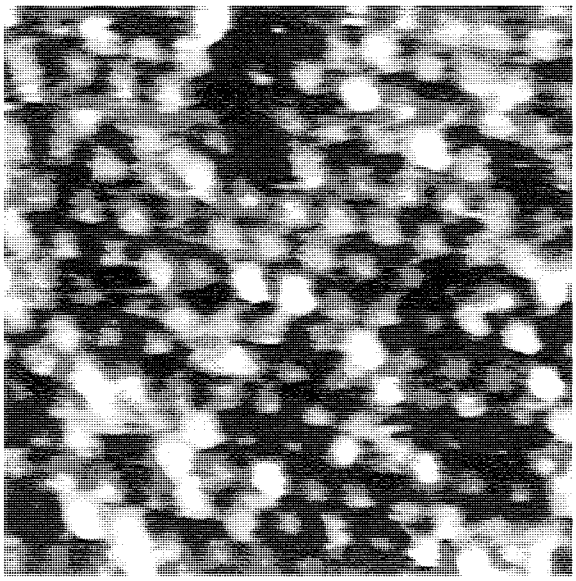

Figure 2. Typical in situ STM image (11.3 nm x 11.3 nm) of C60/C70 (8 : 2) adlayers on a Au(111) surface in 0.1 M perchloric acid. The image was obtained with a tunneling current of 20 nA. The electrode potentials of the substrate (Es) and the tip (Et) were set at +0.27 V and +0.62 V vs RHE, respectively.

The mixture of fullerens, C_{60} and C_{70} also can be formed epitaxial adlayers by the similar procedure. Figure 2 shows an in situ STM image of C_{60}/C_{70} mixture modified Au(111) surfaces in 0.1 M perchloric acid. The adlayers possess hexagonal lattices as same as C_{60} adlayers. In the array of the mixture, C_{60} and C_{70} molecules can be clearly distinguished as individual dark and brighted protrusions which would be attributed to C_{60} and C_{70} molecules, respectively. C_{70} molecules with standing orientation

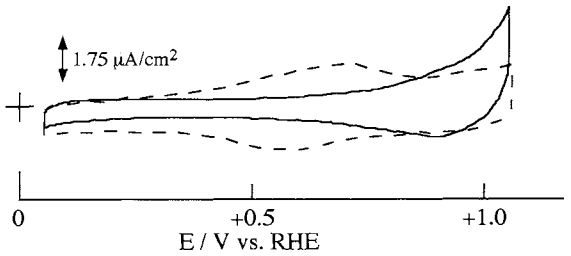

Figure 3. Cyclic voltammograms of unmodified (dotted line) and C60 modified Au(111) electrodes in 0.1 M perchloric acid. The scan rate was 25 mV/s.

+1.1 V vs. RHE) in 0.1 M perchloric acid.

In conclusion, fullerene adlayers prepared by the transfer of Langmuir films are essentially same as the epitaxial adlayers prepared by vapor deposition in UHV. The simple preparation and electrochemical stability encourage us to develop and characterize novel epitaxially modified electrodes of fullerenes.

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References

1 "Fullerene," ed by G. S. Hammond and V. J. Kuck, ACS Symposium Series 481, ACS (1992).

2 a) R. J. Wilson, G. Meijer, D. S. Bethune, R. D. Johnson, D. D. Chambliss, M. S. de Vries, H. E. Hunziker, and H. R. Wendt, *Nature*, **348**, 621 (1990). b) T. Sakurai, X. -D. Wang, Q. K. Xue, Y. Hasegawa, T. Hashizume, and H. Shinohara, *Prog. Surf. Sci.*, **51**, 263 (1996). c) Y. Zhang, X. Gao, and M. J. Weaver, *J. Phys. Chem.*, **96**, 510 (1992).

3 R. G. Nuzzo and D. L. Allara, *J. Am. Chem. Soc.*, **105**, 4481 (1983); I. Taniguchi, S. Yoshimoto, and K. Nishiyama, *Chem. Lett.*, **1997**, 353.

4 a) N. Batina, M. Kunitake, and K. Itaya, *J. Electroanal. Chem.*, **405**, 245 (1996). b) M. Kunitake, U. Akiba, N. Batina, and K. Itaya, *Langmuir*, **13**, 1607 (1997). c) K. Itaya, N. Batina, M. Kunitake, K. Ogaki, Y.–G. Kim, L.–J. Wan, and T. Yamada, ACS Symposium Series 656, Chap. 13 (Solid-Liquid Electrochemical Interface) (1997).

5 Y. Tomioka, M. Ishibashi, H. Kajiyama, and Y. Taniguchi, *Langmuir*, **9**, 32 (1993); M. Yanagida, T. Kuri, and T. Kajiyama, *Chem. Lett.*, **1997**, 911; R. Castillo, S. Ramos and J. Ruiz-Garcia, *J. Phys. Chem.*, **100**, 15235 (1996).

6 Q. Xie, E. P.–Cordero, and L. Echegoyen, *J. Am. Chem. Soc.*, **114**, 3978 (1992).

7 N. Nakashima, T. Kuriyama, T. Tokunaga, H. Murakami, and T. Sagara, *Chem. Lett.*, **1998**, 633.