Transactions of the Materials Research Society of Japan 29 [2] 443-445 (2004)

UHV-STM/STS Studies of Lanthanum Endohedral Metallofullerenes

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We have investigated monolayer and multilayer islands of $La_2@C_{80}$, $La@C_{82}$ and $La_2@C_{72}$ grown on a hydrogen-terminated Si(100)-2x1 surface by ultra-high-vacuum scanning tunneling microscopy/spectroscopy. The observed $La_2@C_{80}$ molecule has a spherical shape, consistent with a recent result by synchrotron X-ray measurements. The energy gap for the $La_2@C_{80}$ multilayer islands is measured to be 1.3-1.5 eV, whereas that for $La@C_{82}$ is 0.5 eV, indicating that the I_h cage of the $La_2@C_{80}$ molecule is highly stabilized by an electron transfer from the encaged La atoms to the cage.. The $La_2@C_{72}$ molecules are observed by STM as ellipsoids, consistent with a recent report by the ^{13}C-NMR structural analysis. The energy gap of the $La_2@C_{72}$ multi-layer islands is measured by STS as 1.0-1.2 eV, suggesting that the C_{72} carbon cage is stabilized by a localized electron transfer from the encaged La atoms to the fused-pentagon area of the fullerene cage.

Key words: UHV-STM, STS, Fullerene, Metallofullerene

1. Introduction

Endohedral metallofullerenes have attracted much attention during the past decade because of their novel structural and electronic solid-state properties [1]. Cage structures of the fullerenes and properties of encapsulated metal atoms of various endohedral metallofullerenes play important roles for determining the electronic properties of endohedral metallofullerenes. Scanning tunneling microscopy is a powerful method to directly image the structures and to obtain information on electronic properties of fullerenes and endohedral metallofullerenes with an atomic resolution. A number of STM studies have previously been performed to characterize fullerenes on various surfaces [2-5]. In this letter, we report structures and electronic properties of the $La_2@C_{80}$, $La@C_{82}$ and $La_2@C_{72}$ molecules in monolayer and multi-layer islands grown on a hydrogen terminated Si(100)-2x1 surface by using an UHV-STM.

2. Experimental

Details of the preparation of the hydrogen terminated Si(100)2x1 (Si(100)2x1-H) surface are described elsewhere [3]. The $La_2@C_{80}$, $La@C_{82}$ and $La_2@C_{72}$ metallofullerenes were prepared by the DC arc discharge method and isolation with high performance liquid chromatography [1,3]. The STM/STS measurements were performed at temperatures between 58 and 100K.

3. Results and Discussion

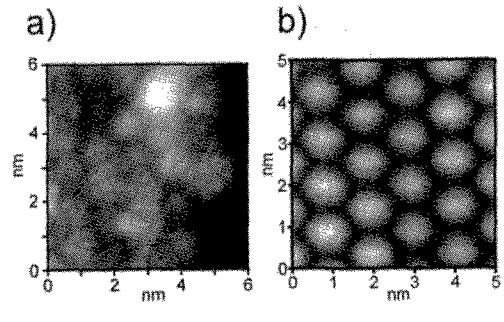

Fig. 1 STM image of (a) a monolayer $La_2@C_{80}$ island and (b) a multi-layer $La_2@C_{80}$ island adsorbed on a Si(100)-2x1-H surface (6nm x 6nm, the sample bias voltage (a) V_s = -1.5 V and the tunneling current I_t = 10 pA, (b) V_s = -2.5 V and tunneling current I_t = 10 pA).

Figure 1(a) shows an STM image of a $La_2@C_{80}$ monolayer island grown on a Si(100)-2x1-H surface. One of the intriguing observations here is that intramolecular structures are clearly observed in the monolayer islands of $La_2@C_{80}$ adsorbed on the Si(100)-2x1-H surface. One can clearly see three or four stripes, two or four leaves-like structures and further complicated patterns, indicating that these metallofullerenes do not rotate freely on the surface.

The $La_2@C_{80}$ molecules are adsorbed on the trough between two adjacent dimer rows and are grown into the layer. Since the adsorbed fullerenes cannot rotate in the trough, intramolecular structures are observed in the monolayer islands. Figure 1(b) shows an STM image of a $La_2@C_{80}$ multilayer island grown on a Si(100)-2x1-H surface. The $La_2@C_{80}$ molecules formed a hexagonal close-packed array with a nearest neighbor distance of 1.12-1.14nm and an interlayer spacing of 0.95nm. These nearest neighbor distance and interlayer spacing are in good agreement with the estimated size of $La_2@C_{80}$ from the synchrotron X-ray structural study of $La_2@C_{80}$ [8]. No intramolecular structures are observed in the multilayer islands. This indicates that fullerene molecules start to rotate above the 2nd layer.

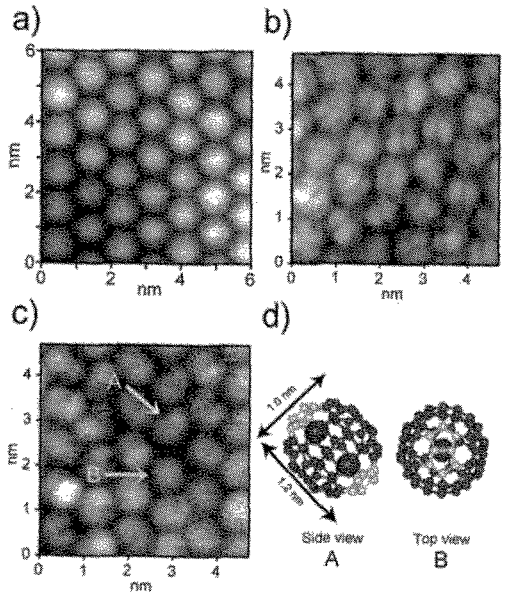

Fig. 2 STM image of the top layer of a multi-layer $La_2@C_{72}$ island grown on a Si(100)-2x1-H surface. (a) Observed at 100 K, V_s = -2.5V, I_t = 30pA and (b) observed at 58 K, V_s = -1.8V, I_t = 30pA (c) observed at 58K, V_s = 2.5V, I_t = 30pA. (d) Calculated D_2 Structure for a $La_2@C_{72}$ molecule (AM1 optimized), showing the side view (A) and the top view (B).

Figure 2(a) shows an STM image of the top layer of a six-layer island of $La_2@C_{72}$ molecules grown on the Si(100)-2x1-H surface at 100K. No intramolecular structures are observed. This indicates that the $La_2@C_{72}$ molecules on the surface of multi-layer islands rotate at 100 K. The $La_2@C_{72}$ molecules show a hexagonal close-packed face with a nearest neighbor distance of 0.9 to 1.17nm. The distribution of the nearest neighbor distance of $La_2@C_{72}$ is fairly wide. The wide distribution is strong evidence that $La_2@C_{72}$ molecule has an ellipsoidal structure as shown in Fig. 2(d).

As the temperature of the sample was gradually lowered from 100K to 58K, the intramolecular structures were observed at 68K. Figure 2(b) and (c) show the STM images of a fifth layer $La_2@C_{72}$ island observed at 58K at the sample biases of -1.8 and 2.5 V, respectively. In Fig. 2(b), intramolecular structures of three or four stripes, two or four leaves-like structures and further complicated patterns are seen, indicating that the adsorption directions of the $La_2@C_{72}$ molecules are random.

An empty-state image in Fig. 2(c) shows intramolecular structures like broad beans divided into two are observed. Two types of images having an ellipsoidal and a spherical form are observed, which are marked as A and B, respectively, in Fig. 2(c). The image marked as A has a major axis of 1.3 nm and a minor axis of 0.9 nm, and the image marked as B has a diameter of 1.0 nm. The observation is consistent with the wide distribution of the nearest neighbor distance of $La_2@C_{72}$ molecules. A recent ^{13}C

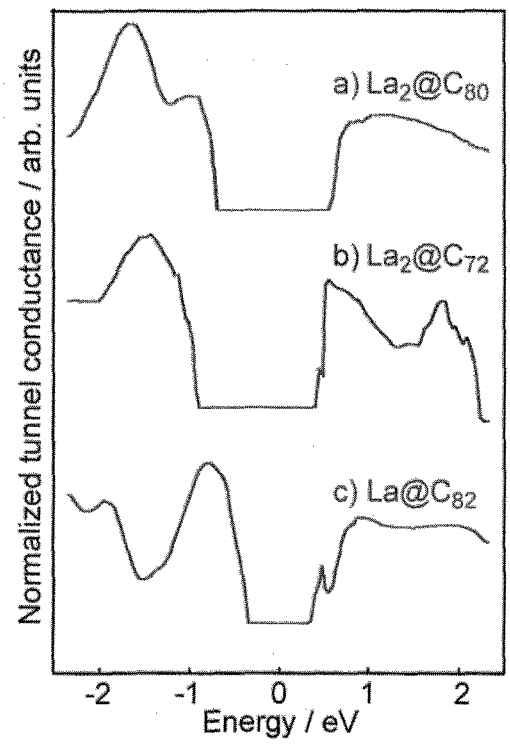

Fig. 3 Normalized tunneling conductance ((dI/dV)/(I/V)) measured at 100K on the multi-layer island of (a) $La_2@C_{80}$, (b) $La@C_{82}$ and (c) $La_2@C_{72}$ grown on the Si(100)-2x1-H surface.

Normalized tunneling conductance in the HOMO-LUMO gap is shown as a constant, since the observed tunneling current is smaller than the observable limit of experiment (0.03pA).

NMR results show the C_{72} carbon cage possesses a non-IPR [6,7] (IPR: Isolated Pentagon Rule) D_2 structure having two fused-pentagons, has an ellipsoidal structure as is shown in Fig. 2(d) [9].

STS was used to analyze the electronic structure of the $La_2@C_{72}$ islands near the Fermi level. Figure 3(a), (b) and (c) show normalized tunneling conductance ((dI/dV)/(I/V)) curves measured at 100K on the multi-layer island of the $La_2@C_{80}$, $La@C_{82}$ and $La_2@C_{72}$ molecules grown on the Si(100)-2x1-H surface, respectively. The HOMO-LUMO gap of the $La@C_{82}$ multi-layer is evaluated as 0.5 eV [3]. The $La@C_{82}$ molecule has the so-called singly occupied molecular orbital. The HOMO-LUMO energy gap of $La@C_{82}$ should therefore be small. The HOMO-LUMO gap of the $La_2@C_{80}$ multi-layer is evaluated as 1.3-1.5eV[3], which is much larger than that of $La@C_{82}$. The presence of the large gap of $La_2@C_{80}$ suggests that the I_h cage is highly stabilized by an electron transfer from the encaged La atoms to the cage [3,8]. The HOMO-LUMO gap of the $La_2@C_{72}$ multi-layer is 1.0-1.2eV, which is much larger than that of $La@C_{82}$ (~0.5eV) [3] but is close to the gap of C_{70} (1.0-1.2eV). Also, the gap is smaller than those of C_{60} (1.5-1.6eV) and $La_2@C_{80}$ (1.3-1.5eV) [3]. This is consistent with the fact that the $La_2@C_{72}$ molecule is fairly stable under ambient conditions, even though the fullerene has a non-IPR structure [9].

Part of this study was performed through Special Coordination Funds for Promoting Science and Technology of the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government.

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(Received October 11, 2003; Accepted February 25, 2004)