

Dispersion of Metallofullerene Y@C₈₂ on Bare, C₆₀-Modified, and Iodine-Modified Au(111) Surfaces Investigated with ECSTM

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Two-dimensional (2D) assembling behaviors of the endohedral metallofullerene Y@C₈₂ on bare, C₆₀-modified, and iodine-modified Au(111) surfaces have been investigated in 0.1 M HClO₄ solution employing electrochemical scanning tunneling microscopy (ECSTM). The results show that Y@C₈₂ molecules are mobile and aggregate to the terrace edges on bare and C₆₀-modified Au(111) surfaces, but monodispersion of the Y@C₈₂ molecules is achieved on the iodine-modified Au(111) surface. The improvement of Y@C₈₂ dispersion on an iodine-modified gold surface is due to the strong Y@C₈₂–substrate interactions. The modified-substrate method provides an effective strategy to disperse endohedral metallofullerenes.

1. Introduction

Soon after the discovery of buckminsterfullerene by Smalley's group in 1985,¹ the endohedral metallofullerene La@C₆₀ had been found with a mass spectrometry study in the same year.² In 1991, it is again the Smalley group who first macroscopically synthesized and isolated endohedral metallofullerene La@C₈₂.³ Since then there have been dozens of metallofullerenes being isolated with the encaged metal atoms covering group II, group III, and lanthanide metals in the periodic table and the carbon cages ranging from C₆₀ to C₉₄.^{4–8} Among them Y@C₈₂ has attracted special attention due to its relative higher yields and potential applications in many fields such as electronics, physics, quantum computing, and material sciences, etc.

Stimulated by the applications of metallofullerenes, the behavior of metallofullerenes on solid surfaces is highly interesting. It is significantly required in applications to get a well-dispersed metallofullerene adlayer on a metal surface. However, several previous studies^{9–13} have shown that metallofullerene molecules tend to aggregate on the terrace edges of the metal surface. Since the morphology and crystal orientation of a thin film on a solid surface are dominated by both the intermolecular and molecule–substrate interactions,¹⁴ it is believed that well-dispersed metallofullerenes may be achieved through adjusting either the intermolecular interaction or the molecule–substrate interaction. In this article we present a method to assemble a single layer of C₆₀ molecules or iodine atoms on the gold substrate that change the nature of the metal substrate and then affect the Y@C₈₂–substrate interactions. The metallofullerene dispersion property is studied on these modified Au(111) surfaces.

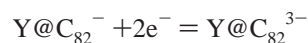
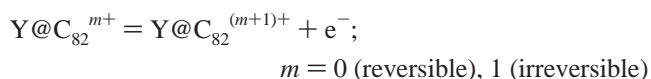
Scanning tunneling microscope (STM) is a powerful method to directly monitor the structures and electronic properties of surfaces with an atomic resolution, and a number of STM studies have been performed to characterize fullerenes and endohedral metallofullerene on metal (Au, Ag, Al, Cu, Ni, Pd) and semiconductor (Si, Ge, GaAs) surfaces.^{9–19} Therefore, the STM technique has been used here to study the dispersion of Y@C₈₂ on bare, C₆₀-modified, and I-modified Au(111) surfaces.

Considering the facts that STM observation of fullerenes in air usually leads to poor resolution and UHV-STM is difficult to handle the modified substrate, we alternatively perform an electrochemical STM study in the HClO₄ solution to explore the dispersion property of Y@C₈₂ molecules.

2. Experimental Section

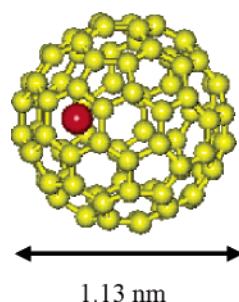
Materials. Metallofullerene Y@C₈₂ was prepared by the traditional Krätschmer–Huffman method²⁰ following by isolation and purification with high-performance liquid chromatography. An aqueous HClO₄ solution was prepared with ultrapure HClO₄ (Kanto Chemical Co.) and ultrapure water (Milli-Q, SP-TOC; ≥18.2 MΩ·cm). Spectroscopy grade benzene from Aldrich was used without further purification. KI and CS₂ were from the Chinese Chemical Co.

STM. 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.²¹ A Au(111) facet on the beads was directly used for STM observation. The adlayer of Y@C₈₂ was prepared by immersing substrate into ~5 μM Y@C₈₂ benzene–CS₂ solution for 2 min, then taking the substrate out and rinsing with ultrapure water. In situ STM observation was carried out with a Nanoscope E STM (Digital Instruments) in HClO₄ solution. Tunneling tips used were prepared by electrochemical etching of a tungsten wire (0.25 mm in diameter) and sealed with transparent nail polish to minimize the Faradaic current. All the STM images shown in this paper were acquired in the constant-current mode. Consulting with the reported electrochemical reductions and oxidations of Y@C₈₂ in dichlorobenzene²²



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the electrode potentials were held in the double-layer region

SCHEME 1: Structure Model of Metallofullerene Y@C₈₂.

(ca. 0.6V) and reported with respect to the RHE (reversible hydrogen electrode) in 0.1 M HClO₄.

3. Results and Discussion

The structure and electronic properties of Y@C₈₂ have been revealed by various types of spectrometries, e.g., ESR, XPS, XRD, UV–vis absorption spectra, etc.^{23–25} As shown in Scheme 1, Y@C₈₂ has a C_{2v} symmetry with the yttrium atom locating along the main C_2 axis of a C₈₂–C_{2v} cage and being off from the cage center about 3.14 Å,²³ which indicates a strong metal–cage interaction. The van der Waals diameter of a single Y@C₈₂ molecule is ca. 1.13 nm.⁶ ESR and theoretical studies reveal that the yttrium atom donates three valence electrons to the C₈₂ cage, i.e., the formal electronic structure is Y³⁺@C₈₂^{3–}.

Figure 1a is a typical STM image of a Y@C₈₂ adlayer on a bare Au(111) surface at 0.62 V, 434.1 pA tunneling current, and a bias of –180 mV. The metallofullerene adlayer shows a stripe structure. Figure 1b is a high-resolution STM image at 0.62 V, which reveals that the stripes are composed of lots of irregularly close-packed Y@C₈₂ clusters along the terrace edges of the Au substrate, and the typical size of the clusters is ca. 8 nm on average. It is believed that the weak Y@C₈₂–Au interaction leads to the Y@C₈₂ molecules being mobile on the Au(111) substrate, and they finally migrate to the terrace edges and aggregate there following absorption. This result is consistent with the UHV–STM study of the Y@C₈₂ adsorbed on a Cu(111) surface, which shows a similar tendency of aggregation on Cu terrace edges.^{10,11} To exclude the possibility that Y@C₈₂ molecules may aggregate to clusters in the benzene–CS₂ solution before their adsorption, we repeated the experiment under very low Y@C₈₂ concentration far below the Y@C₈₂ saturation point. The result shows a similar stripe pattern of Y@C₈₂ clusters, suggesting the aggregation of Y@C₈₂ molecules must occur after the absorption.

Previous UHV–STM studies revealed that the assembling property of fullerenes and metallofullerenes on metal surfaces is determined by the nature of the substrates.^{9,26–28} For example, Tb@C₈₂ molecules are mobile on C₆₀ film but they freeze on the Si(100) 2 × 1 surface;⁹ C₆₀ molecules are mobile on a Cu(111) surface but do not migrate freely on Si(100) and Si(111) surfaces.^{26–28} These studies provide us a clue to overcome the metallofullerene aggregating by changing the substrate nature. We perform a so-called “substrate-induced template” strategy to modify the Au(111) substrate with a layer of external molecules/atoms and hope that the modified metal surface would tune the Y@C₈₂–substrate interaction and then get good dispersion of Y@C₈₂ molecules. In fact, this method has been widely used in fullerene studying for other purposes; for example, Shi et al.⁹ studied the nucleation behavior of Tb@C₈₂ on a C₆₀-modified HOPG surface; Wang et al.¹⁹ used a silver-modified Si surface to improve the surface conductance and got a high-resolution STM image of the Dy@C₈₂ molecule.

The Au(111) surface was first modified by a layer of C₆₀. Since C₆₀ is a rich π -conjugated molecule and easily polarized,^{9,13} it is hoped that the dipole–dipole intermolecular force and the π -stacking would enhance the Y@C₈₂–substrate interactions and then improve the metallofullerene dispersions. The C₆₀-modified substrate was prepared by immersing the Au(111) into the C₆₀–benzene–CS₂ solution for 1 min. Figure 2a shows a typical STM image of a C₆₀ adlayer on Au(111) in 0.1 M HClO₄ at 0.49 V. The tunneling current is 1.582 nA at a bias of –195 mV. Atomically flat terraces were almost completely covered with a well-ordered adlayer of C₆₀. Spherical bright spots correspond to the individual C₆₀ molecules. Similar with the result reported by Yoshimoto et al. in same conditions,²⁹ the lattices show two domains of A and B which are assigned to be $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ and the so-called “in phase” structures. The observed nearest neighbor distance of the C₆₀ molecules in both domains is 1.0 ± 0.1 nm, which is in accordance with the van der Waals distance of C₆₀ (1.0 nm).

After the confirmation of the ordered C₆₀ adlayer, the C₆₀-modified Au(111) surface was used to assemble Y@C₈₂ molecules by immersing it into the Y@C₈₂–benzene–CS₂ solution for 2 min. Parts b–d of Figure 2 are the typical large-scale and high-resolution STM images of a Y@C₈₂ adlayer on C₆₀/Au(111), with working electrode potentials at 0.27, 0.53, and 0.53 V, respectively. Both the C₆₀ sublayer and the Y@C₈₂ adlayer can be clearly seen from the STM images. It is observed that the Y@C₈₂ dispersion is largely improved compared with that on the bare Au(111) surface. Y@C₈₂ or their clusters locally formed molecular rows as indicated by an arrow in the images.

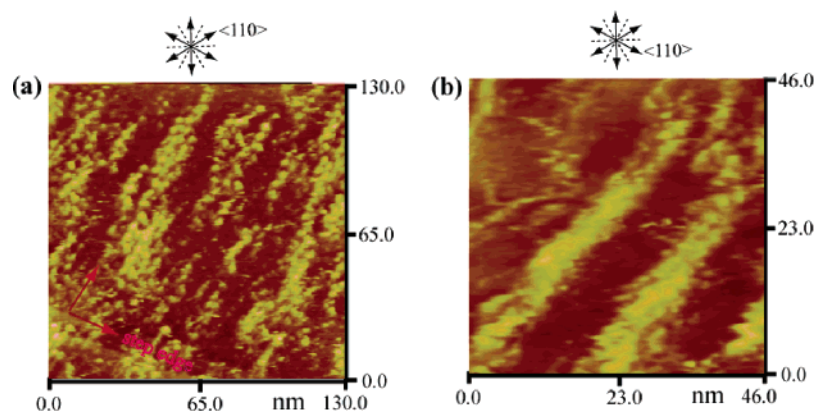


Figure 1. (a) Large-scale STM image of a Y@C₈₂ adlayer on Au(111) in 0.1 M HClO₄ at 0.62 V. The tunneling current is 434.1 pA at a bias of –180 mV. (b) STM image of Y@C₈₂ adlayers on Au(111) in 0.1 M HClO₄ at 0.62 V. The tunneling current is 494.4 pA at a bias of –186 mV.

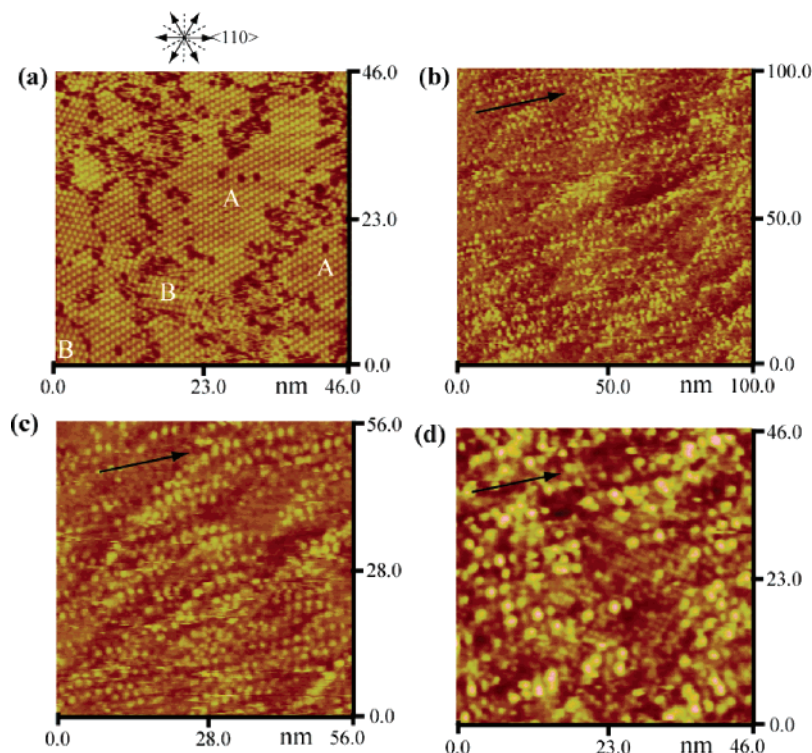


Figure 2. (a) STM image of a C₆₀ adlayer on Au(111) in 0.1 M HClO₄ at 0.49 V. The tunneling current is 1.582 nA at a bias of −195 mV. (b) Large-scale STM image of a Y@C₈₂ adlayer on C₆₀/Au(111) in 0.1 M HClO₄ at 0.27 V. The tunneling current is 2.314 nA at a bias of 142 mV. (c) STM image of a Y@C₈₂ adlayer on C₆₀/Au(111) in 0.1 M HClO₄ at 0.53 V. The tunneling current is 2.314 nA at a bias of −168 mV. (d) STM image of a Y@C₈₂ adlayer on C₆₀/Au(111) in 0.1 M HClO₄ at 0.53 V. The tunneling current is 2.378 nA at a bias of −210 mV.

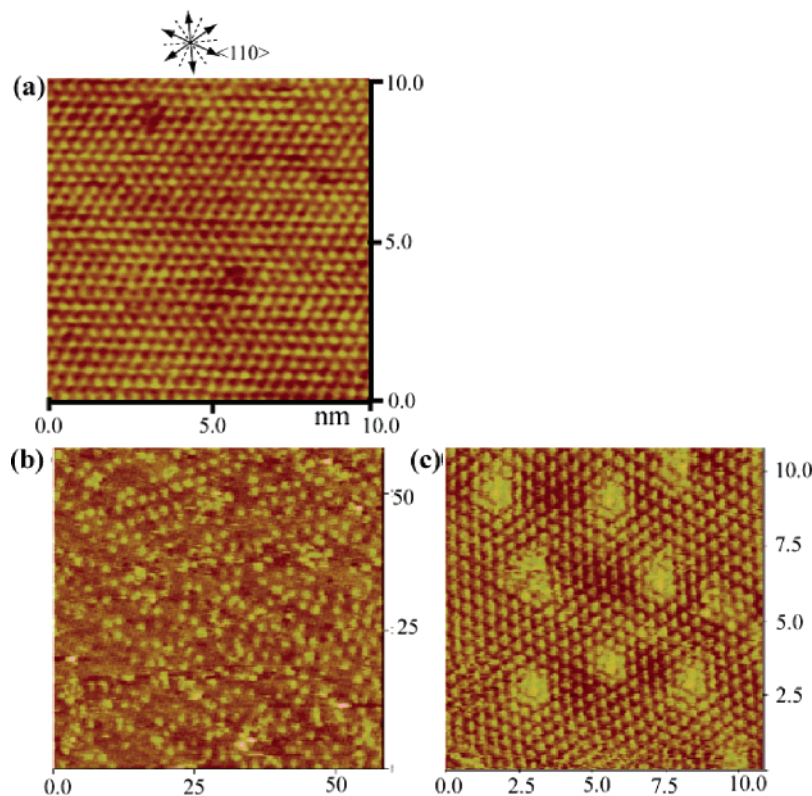


Figure 3. (a) Typical STM image of an iodine adlayer on Au(111) in 0.1 M HClO₄ at 0.6 V. The tunneling current is 6.344 nA at a bias of −72.4 mV. (b) Large-scale STM image of a Y@C₈₂ adlayer on I/Au(111) in 0.1 M HClO₄ at 0.56 V. The tunneling current is 735 pA at a bias of −133 mV. (c) STM images of a Y@C₈₂ adlayer on I/Au(111) in 0.1 M HClO₄ at 0.56 V. The tunneling current is 735 pA at a bias of −128 mV.

However, most of the Y@C₈₂ molecules are still adsorbed as clusters, with the typical size of the clusters at ca. 4 nm on average. Only a small part of individual Y@C₈₂ molecules is randomly distributed on the perfect C₆₀ surface. The high-

resolution STM in Figure 2d reveals that the Y@C₈₂ clusters prefer to locate on the domain boundary of C₆₀ film, which indicates that the Y@C₈₂ molecules are still mobile on the C₆₀ film, as discussed above for the Y@C₈₂ adsorption on the bare

Au(111) surface. In fact, the same tendency had been observed for Tb@C₈₂ adsorption on the C₆₀-modified HOPG surface.⁹ Obviously, though the C₆₀-modified Au(111) surface improves the Y@C₈₂ dispersion largely, it is not good enough to get monodispersion of Y@C₈₂ molecules on the substrate.

The iodine adlayers have been intensively investigated on various single-crystal electrodes, such as Au, Ag, Pt, Rh, and Pd, etc.,^{30–34} using the ex situ LEED (low-energy electron diffraction), in situ STM, and in situ surface X-ray scattering spectrometries. Since Y@C₈₂ is a superatom behaving like the metal Li,^{10,11} and the iodine atom has a large electronegativity, it is expected that the I-modified Au(111) must induce a strong Y@C₈₂–substrate interaction and then improve the dispersion property of Y@C₈₂ molecules further.

The preparation of the I-modified Au(111) surface is essentially the same with that reported by Batina et al.³⁴ Briefly, the Au(111) facet was immersed into 4 mM KI solution for 1 min and taken out. Then the sample was thoroughly rinsed with 0.1 M HClO₄ and transferred into an electrochemical cell for STM study. Figure 3a is a typical STM image of the iodine adlayer on bare Au(111) in 0.1 M HClO₄ at 0.6 V. It can be seen that the surface of the iodine-modified electrode was atomically flat and the well-defined iodine adlayer possesses a “ $c(p\sqrt{3})$ ” structure.³⁴

The Y@C₈₂ adlayer is prepared by immersing the I-modified Au(111) surface into Y@C₈₂–benzene–CS₂ solution for 2 min. Figure 3, parts b and c, shows the STM images of Y@C₈₂ adsorbing on an I/Au(111) surface in 0.1 M HClO₄ solution with the working electrode potentials at 0.56 V. The bright protrusions are individual Y@C₈₂ molecules that are randomly distributed on the I-modified surface without any aggregation. Strikingly, even Y@C₈₂ dimers, which were observed to be the major species on the Cu(111) surface by UHV-STM,^{10,11} are rarely found in the current conditions. In a previous experiment of Tb@C₈₂ molecules absorption on a Si(111) surface, Shi et al.⁹ observed a similar monodispersion of Tb@C₈₂ molecules and assigned this result as the strong adsorbates–substrate interactions, so it is the strong Y@C₈₂–substrate interactions that lead to the monodispersion of Y@C₈₂ on the I-modified substrate. Furthermore, it can be observed from the high-resolution STM image of Y@C₈₂/I–Au(111) in Figure 3c that the iodine atoms under the Y@C₈₂ molecules can be seen through the Y@C₈₂ molecules. The “transparent” appearance of the metallofullerenes is attributed to the applied bias voltages at which there is only a weak contribution of the Y@C₈₂ molecular orbitals to the tunneling process. The apparent height of the protrusions in Figure 3, parts b and c, defined as the adlayer distance of the single Y@C₈₂ molecule and iodine, is also measured, and the value is only ca. 0.09 ± 0.02 nm, which is far lower than the physical height of the Y@C₈₂ molecules (1.13 nm). A reasonable explanation for this appearance is that STM images reveal the local electronic density but not a physical height of the molecules.

4. Conclusion

In conclusion, we have studied the dispersion property of metallofullerene Y@C₈₂ on Au(111), C₆₀/Au(111), and I/Au(111) by electrochemistry STM in 0.1 M HClO₄ solution. From bare to C₆₀-modified to iodine-modified Au(111) surfaces, the Y@C₈₂–substrate interactions increase, and the dispersion property of Y@C₈₂ molecules on surfaces improves gradually. Finally the monodispersion of Y@C₈₂ is achieved on the iodine-modified Au(111) surface. The method provides a new scheme to get a monodispersed adlayer of metallofullerenes on sub-

strates, which may in future lead to novel molecular devices or nanomaterials.

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References and Notes

- (1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 165.
- (2) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779.
- (3) Chai, Y.; Guo, T.; Jin, C.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 7564.
- (4) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843.
- (5) Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S. *Nature* **1993**, *366*, 123.
- (6) Takata, M.; Umeda, B.; Nishibori, E.; Sakata, M.; Satio, Y.; Ohno, M.; Shinohara, H. *Nature* **1995**, *377*, 46.
- (7) Park, C.; Wells, B. O.; Dicarolo, J.; Shen, Z. X.; Salem, J. R.; Bethune, D. S.; Yannoni, C. S.; Booth, C.; Bridge, F. *Chem. Phys. Lett.* **1993**, *213*, 196.
- (8) Lin, N.; Ding, J. Q.; Yang, S. H.; Cue, N. *Phys. Lett.* **1996**, *A222*, 190.
- (9) Shi, B. R.; Wang, X. S.; Huang, H. J.; Yang, S. H.; Heil, W.; Cue, N. *J. Phys. Chem. B* **2001**, *105*, 11414.
- (10) Shinohara, H.; Inakuma, M.; Kishida, M.; Yamazaki, S.; Hashizume, T.; Sakurai, T. *J. Phys. Chem.* **1995**, *99*, 13769.
- (11) Hasegawa, Y.; Ling, Y.; Yamazaki, S.; Hashizume, T.; Shinohara, H.; Sakai, A.; Pickering, H. W.; Sakurai, T. *Phys. Rev. B* **1997**, *56*, 6470.
- (12) Sakurai, T.; Wang, X. D.; Xue, Q. K.; Hasegawa, Y.; Hashizume, T.; Shinohara, H. *Prog. Surf. Sci.* **1996**, *51*, 263.
- (13) Lin, N.; Huang, H. J.; Yang, S. H.; Cue, N. *Phys. Rev. B* **1998**, *58*, 2126.
- (14) Guo, S.; Fogarty, D. P.; Nagel, P. M.; Kandel, S. A. *J. Phys. Chem. B* **2004**, *108*, 14074.
- (15) Johansson, M. K. J.; Maxwell, A. J.; Gray, S. M.; Brühwiler, P. A.; Mancini, D. C.; Johansson, L. S. O.; Mårtensson, N. *Phys. Rev. B* **1996**, *54*, 13472.
- (16) Murray, P. W.; Pedersen, M. O.; Laegsgaard, E.; Stensgaard, I.; Besenbacher, F. *Phys. Rev. B* **1997**, *55*, 9360.
- (17) Weckesser, J.; Barth, J. V.; Kern, K. *Phys. Rev. B* **2001**, *64*, 161403.
- (18) Taninaka, A.; Shino, K.; Sugai, T.; Heike, S.; Terada, Y.; Hashizume, T.; Shinohara, H. *Nano Lett.* **2003**, *3*, 337.
- (19) Wang, K. D.; Zhao, J.; Yang, S. F.; Chen, L.; Li, Q. X.; Wang, B.; Yang, S. H.; Yang, J. L.; Hou, J. G.; Zhu, Q. S. *Phys. Rev. Lett.* **2003**, *185504*-1.
- (20) Krätschmer, W.; Fostiropoulos, K.; Lamb, L. D.; Huffman, D. R. *Nature* **1990**, *347*, 354.
- (21) Wan, L.-J.; Shundo, S.; Inukai, J.; Itaya, K. *Langmuir* **2000**, *16*, 2164.
- (22) Suzuki, K.; Oguri, F.; Nakao, Y.; Suzuki, S.; Achiba, Y.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Tetrahedron* **1996**, *52*, 4937.
- (23) Takata, M.; Umeda, B.; Nishibori, E.; Sakata, M.; Saito, Y.; Ohno, M.; Shinohara, H. *Nature* **1995**, *377*, 46.
- (24) Shinohara, H.; Sato, H.; Ohkouchi, M.; Ando, Y. *J. Phys. Chem.* **1992**, *96*, 3571.
- (25) Weaver, J. H.; Chai, Y.; Kroll, G. H.; Jin, C.; Ohno, T. R.; Haufler, R. E.; Guo, T.; Alford, J. M.; Conceicao, J.; Chibante, L. P. F.; Jain, A.; Palmer, G.; Smalley, R. E. *Chem. Phys. Lett.* **1992**, *190*, 460.
- (26) Hashizume, T.; Motai, K.; Wang, X. D.; Shinohara, H.; Saito, Y.; Maruyama, Y.; Ohno, K.; Kawazoe, Y.; Nishina, Y.; Pickering, H. W.; Kuk, Y.; Sakurai, T. *Phys. Rev. Lett.* **1993**, *71*, 2959.
- (27) Hashizume, T.; Wang, X. D.; Nishina, Y.; Shinohara, H.; Saito, Y.; Kuk, Y.; Sakurai, T. *Jpn. J. App. Phys.* **1992**, *31*, L880.
- (28) Shinohara, H.; Hayashi, N.; Sato, H.; Saito, Y.; Wang, X. D.; Hashizume, T.; Sakurai, T. *J. Phys. Chem.* **1993**, *97*, 13438.
- (29) Yoshimoto, S.; Narita, R.; Tsutsumi, E.; Matsumoto, M.; Itaya, K. *Langmuir* **2002**, *18*, 8518.
- (30) Yau, S. L.; Vitus, C. M.; Schart, B. C. *J. Am. Chem. Soc.* **1990**, *112*, 3677.
- (31) Gao, X.; Weaver, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 8544.
- (32) Yamada, T.; Batina, N.; Itaya, K. *J. Phys. Chem.* **1995**, *99*, 8817.
- (33) Sugita, S.; Abe, T.; Itaya, K. *J. Phys. Chem.* **1993**, *97*, 8780.
- (34) Batina, N.; Yamada, T.; Itaya, K. *Langmuir* **1995**, *11*, 4568.