Nucleation of endohedral metallofullerene Nd@C₈₂ on C₆₀ films

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We have studied the initial stage growth of endohedral metallofullerene Nd@C₈₂ on crystalline C₆₀ films using *in situ* ultrahigh vacuum scanning tunneling microscopy. We find that Nd@C₈₂ molecules aggregate into two-dimensional close-packed configurations. Over 60% of molecules form triangle-shaped trimers with identical orientation with respect to the underlying C₆₀ films. Our observations are attributed to a permanent dipole moment of Nd@C₈₂ molecules. We also use a dipole-dipole interaction model to calculate their binding energy and the result shows that the dipole moments of Nd@C₈₂ molecules will displace off the molecular center while they form trimers. [S0163-1829(98)02728-3]

I. INTRODUCTION

Endohedral metallofullerenes were proposed and produced soon after the discovery of C₆₀.¹⁻⁸ Many experimental results have shown that a group-III metal ($M = \text{Sc, Y, La}$) or lanthanide atom could be attached to a fullerene C₈₂ molecule.¹⁻⁸ X-ray absorption fine-structure (EXAFS) studies on Y@C₈₂ have provided strong evidence that the metal atom is located inside the fullerene cage.⁹ The same conclusion was reached also on the basis of scanning tunneling microscopy (STM) studies, which showed a nearly spherical shape for Y@C₈₂ and Nd@C₈₂ molecules.^{10,11} People also have found evidence that the metal atom donates three electrons to the carbon cage.¹²⁻¹⁵ For example, the synchrotron x-ray diffraction experiment on a powder Y@C₈₂ sample revealed the presence of such a charge transfer from the analysis of the total electron density distribution of an Y@C₈₂ microcrystal.¹⁶ EXAFS and high-resolution transmission microscope measurements showed that the M is displaced significantly from the center,^{9,17} which is supported by theoretical calculations.¹⁸⁻²¹ As a result of the off-center nature of the M atom, a permanent dipole moment for M @C₈₂ is expected.²² This dipole moment may be as large as 4 D and may strongly affect the properties of M @C₈₂ molecules. For example, the intermolecular force of M @C₈₂ is commonly regarded as mainly caused by their dipole moments.²² However, experimentally, there is no direct measurement on the dipole moments.

In this work, we use an ultrahigh vacuum (UHV)-STM to directly image endohedral metallofullerene Nd@C₈₂ molecules and examine their initial stage nucleation behavior on crystalline C₆₀ films. Practically, it is very important to understand the initial stage nucleation to realize thin film and bulk growth. On the other hand, due to the closed-shell electronic structure of C₆₀ molecules, charge transfer between the adsorbed Nd@C₈₂ molecules and the C₆₀ substrate would be greatly minimized. The minimization of charge transfer

between the Nd@C₈₂ and the substrate may keep the intrinsic properties of the Nd@C₈₂ unperturbed, which would be impossible while putting them on a metal surface. We expect that their dipole moments will play more important roles in such a circumstance. As a result, a dipole-dipole intermolecular force may dominate the nucleation behavior of the Nd@C₈₂ molecules. So, this study can also provide some direct information on the dipole moment of Nd@C₈₂.

The remainder of this paper is organized as follows. Section II briefly describes the experimental techniques and procedures. Experimental results are presented in Sec. III. In Sec. IV, we use a dipole-dipole interaction model to interpret the experimental observations. A conclusion is given in Sec. V.

II. EXPERIMENTS

Soot-containing metallofullerenes are produced by the standard arc vaporization method using composite anodes that contain graphite and neodymium oxide. First, graphite powder and Nd₂O₃ in an atomic ratio of Nd/C=0.01 are uniformly mixed with a graphite cement. The mixture is then pressed into a 6-mm-diameter rod under a hydraulic pressure of 3000 kg/cm². After curing at 140 °C for 4 h, the rod is heated to 1100 °C in vacuum for 4 h. The rod is then subjected to a dc discharge as an anode under a He atmosphere of 50 torr. The raw soot is collected and extracted in a Soxhlet extractor using *N,N*-dimethylformamide (DMF) at its boiling temperature for 8 h. After removal of the DMP by evaporation, a black powder is obtained. The soluble fraction is dissolved in toluene and injected into a high-performance liquid chromatography (HPLC). The separations of Nd@C₈₂ samples only need a single-stage HPLC. The injection volume is 1 ml for the C₆₀ preparation column and 4 ml for the 2-(1-pyrenyl) ethyl (PYE) column, and the elution rate is 1 ml per minute. The purity of the Nd@C₈₂ sample prepared in this manner is over 99.9% as verified by desorption chemical ionization (DCI) negative-ion mass spectrometry (Finnigan TSQ7000).

The experimental setup of the *in situ* UHV-STM has been described in our previous publication.¹¹ Briefly, 2–3 ML of C_{60} are deposited on a highly oriented pyrolytic graphite surface to prepare a substrate. Such a thin layer of C_{60} would allow the tunneling current to pass through for STM imaging. Then, endohedral metallofullerene $Nd@C_{82}$ is sublimated onto the substrate by heating a molybdenum crucible containing the $Nd@C_{82}$ sample. The sublimation temperature for $Nd@C_{82}$ varies from 620 to 820 °C in order to achieve different deposition rates. The substrate is always kept at room temperature during deposition. Finally, the sample is transferred without breaking vacuum to the analysis chamber for STM studies. The pressure during scanning is kept below 4×10^{-11} mbar.

The sublimation temperature of $Nd@C_{82}$ is rather higher than that of C_{60} , ~ 450 °C, which agrees with the reported $La@C_{82}$ sample sublimation.²² This fact implies that the cohesive energy of metallofullerene solid is rather higher than that of C_{60} , and, their intermolecular interaction is stronger than a simple van der Waals intermolecular interaction of empty fullerenes. It was suggested that the higher sublimation point of endohedral metallofullerenes is caused by their permanent dipole moment.²²

III. EXPERIMENTAL RESULTS

Figures 1(a) and 1(b) show the deposited $Nd@C_{82}$ molecules on the C_{60} film, where the well-ordered substrate is the C_{60} film and the bright spheres are the adsorbed $Nd@C_{82}$ molecules. Figure 1(b) is a close view of Fig. 1(a). The height of $Nd@C_{82}$ molecules is about 1.2 nm. The diameter of the $Nd@C_{82}$ molecule images is about 2.0 nm, much larger than the theoretical value. This is due to the tip convolution effect of STM scanning. These molecules form two-dimensional close-packed structures on the surface. One can identify monomers, dimers, trimers, and a hexamer, a cluster of six molecules. It is worthwhile to note that all the $Nd@C_{82}$ molecules are registering on top sites of the underlying C_{60} lattice. For a van der Waals interaction system as C_{60} , the threefold hollow sites are energetically favorable to the ad molecules since these sites have three nearest-neighboring coordinates, while the top sites only have one. Thus, the top-layer C_{60} molecules fill the threefold hollow sites of the sublayer to form the close-packed fcc structure. Here, $Nd@C_{82}$ molecules prefer top-site registration, which suggests an interaction other than the simple van der Waals force. We attribute the top-site registration to the dipole moment of the $Nd@C_{82}$ molecules. The $Nd@C_{82}$ may polarize the C_{60} molecule beneath it, so, the dipole-dipole interaction between it and the polarized C_{60} makes the top site a preferred place for the $Nd@C_{82}$ molecule.

Figure 2 is a large area image. There are different layers and islands of the C_{60} substrate in this area. It shows that triangle-shaped trimers are the most prominent structures of $Nd@C_{82}$. Figure 3 is a histogram of cluster size distribution according to the statistical analysis of many STM images. It demonstrates that over 60% of the $Nd@C_{82}$ molecules form trimers. In contrast to the trimer domination in our observation, the cluster size distribution has a maximum at dimer in the case of $Y@C_{82}$ adsorbed on Cu(111) surface.¹⁰ We believe that such a difference is caused by the different nature

(a)

(b)

FIG. 1. STM images of $Nd@C_{82}$ molecules (bright spheres) on a crystalline C_{60} substrate. (b) (below) is a close view of (a) (up). The lattice constant of C_{60} substrate is 1.0 nm, which may serve as a scaling. Tunneling current is 30 pA and bias voltage is 2.0 V (applied to the sample).

of the substrates used and, as a result, the different intermolecular interaction. In our experiment, the $Nd@C_{82}$ molecules are adsorbed on a C_{60} film. The closed-shell electronic structure of C_{60} poses a significant barrier for any charge transfer between the adsorbed $Nd@C_{82}$ molecules and the C_{60} substrate. But in the case of a metal substrate, charge transfer is unavoidable, which has altered the intrinsic properties of the adsorbed molecules. In this context, the dominance of the trimers may simply reflect the dominance of dipole interactions among the $Nd@C_{82}$, because the dipole moments would play more important roles for the intermolecular interaction in the present case.

In Fig. 2, all the trimer triangles are oriented in an identical direction with respect to the C_{60} substrate underneath. In other words, trimers that are located on the same C_{60} terrace

FIG. 2. Large-area STM image of Nd@C_{82} molecules adsorbed on the C_{60} substrate. The inset is the dashed box enclosing area in different contrast. Tunneling current is 30 pA and bias voltage is 2.0 V (applied to the sample).

have the same orientation. This phenomenon may be seen more clearly in Fig. 1(a). The C_{60} substrate in Fig. 1(a) consists of two domains, which misfit with each other by half of a lattice constant along the domain boundary. The trimers on the two domains are oriented in opposite directions. The only distinction between the two domains of Fig. 1(a) is that they are different phases of the $ABCABC\cdots$ stacking structure of the C_{60} film. Hence, the substrate-dependent orientation of the Nd@C_{82} trimers must have resulted from the ABC stacking character of the underlying C_{60} substrate. We will explain this in detail in Sec. IV. Note that the hexamer triangle is orientated opposite to its trimer counterparts on the same terrace. This is always true for all observed hexamers.

All of the STM images presented here have been obtained by using a scanning bias voltage of 2.0 V, with the positive potential applied to the sample. The images are highly reproducible at this bias voltage and the close-packed structures of Nd@C_{82} maintain their configurations. However, once the bias voltage is increased above a critical value, both positive and negative, these close-packed structures will be damaged. The lowest bias voltage to break a dimer is 2.5 V. This

FIG. 3. Histogram of cluster size distribution of Nd@C_{82} molecules.

FIG. 4. Trimers of linear chain configuration (a) and triangle-shape configuration (b). Arrows represent dipole moments of Nd@C_{82} molecules.

phenomenon indicates that the Nd@C_{82} molecules are sensitive to the external electric field applied by the tip. It is known that the electric field around a sharp tip is highly inhomogeneous, and the strongest field is at the apex of the tip. Therefore, reconfiguration will occur once the electric field of the tip is strong enough to overcome the force that binds Nd@C_{82} molecules together. At a typical tip-to-sample distance, 1 nm, the electric field near the tip apex at 2.5-V bias will be over 2.5×10^9 V/m. Supposing that the Nd@C_{82} molecules have a dipole moment of 4 D, the dipole energy in this field is about 180 meV. This value is larger than the estimated cohesive energy of Nd@C_{82} due to mutual dipole interaction, but smaller than a typical covalence bond. Thus, the tip-induced reconfiguration also hints that there is no strong chemical bond between the Nd@C_{82} molecules.

IV. THEORETICAL MODEL

In this section, a simple model of dipole-dipole interaction is used to interpret our experimental observations. Since our STM images show that the Nd@C_{82} molecules have a spherical shape, the simplifying assumption of a rigid spherical cage within which the dipole resides is used.

We first calculate the binding energy of trimers. The calculation shows that a linear chain configuration [as shown in Fig. 4(a)] would be more stable energetically than a triangle-shaped trimer [Fig. 4(b)] if the dipole moment passes through the center of the spherical-shaped Nd@C_{82} molecules. However, only triangle-shaped trimers have been observed experimentally and the linear chain trimers are totally absent in all of our STM images. Hence we suggest that the dipole moment of the Nd@C_{82} molecules may be displaced off the center of the C_{82} cage while they aggregate as trimers.

FIG. 5. Model of Nd@C_{82} molecule with an off-center dipole moment.

FIG. 6. Energy contours of $U(a) - U(b)$ on α - χ domain.

Suppose that the dipole is displaced off the center as sketched in Fig. 5. Here d is the van der Waals diameter of the C_{82} cage and P is the dipole moment. s is the off-center distance of the dipole and r is the length of the dipole. The total dipole-dipole energies of the chain configuration $U(a)$ and the triangular configuration $U(b)$ have been derived as

$$U(a) = -\frac{4u_0}{1-4\alpha^2},$$

$$U(b) = -\frac{3}{2\alpha^2} u_0 \left\{ \frac{\beta}{\beta^2 - \alpha^2} - \frac{1}{\sqrt{\beta^2 + 3\alpha^2}} \right\},$$

where $\alpha = r/2d$, $\chi = s/d$, $\beta = 1 - \sqrt{3}\chi$, and $u_0 = P^2/d^3$. Figure 6 shows the calculated contours of $U(a) - U(b)$ on α - χ domain. The area outside the circle of $s^2 + r^2/4 < d_0^2/4$ has no physical meaning since the dipole only resides inside the C_{82} cage; d_0 is the diameter of the C_{82} cage, which must be less than d . $U(a)$ will become greater than $U(b)$ while the dipole is displaced sufficiently far off center. The onset value of the displacement s that makes a triangular trimer favored over a linear trimer is about $0.012d$, which corresponds to an off-center displacement of $\sim 0.13 \text{ \AA}$. Physically, the dipole is determined by the charge distribution of $Nd@C_{82}$ molecules. When three molecules compose a trimer, the positive

FIG. 7. Off-center located dipoles of $Nd@C_{82}$ molecules in a trimer. FIG. 8. Top view of two oppositely orientated $Nd@C_{82}$ trimers on a C_{60} substrate. Both the top-layer and sublayer C_{60} molecules are drawn.

charge of one molecule may attract the negative charge of another molecule, as shown in Fig. 7, so the dipole may be off the molecular center.

The triangle-arranged dipole picture of trimers can give a sound explanation to the ordered orientation of the trimers. Figure 8 is a diagram illustrating the top view of two trimers adsorbed on the C_{60} substrate, where one points up and another, down. Due to the ABC stacking nature of the C_{60} lattice, the two trimers are distinct physically because the center of the up-pointing trimer is above a hollow site of the second-layer C_{60} and down-pointing one, an occupied site. Assuming that both the top-layer and the second-layer C_{60} are polarized by the adsorbed $Nd@C_{82}$ trimers, the trimer interactions with the top-layer C_{60} are identical for the two orientations, giving the same contribution. While the second-layer C_{60} molecules have different geometry for the two orientations, the polarization of the second-layer C_{60} will be different also. Thus, only the energetically favored orientation is observed.

The ordered orientation of trimers may also explain the phenomenon that hexamer triangles are always orientated opposite to the trimer triangles on the same C_{60} terrace. As sketched in Fig. 9, where the empty spheres are molecules of

FIG. 9. Illustrations of two hexamers developed from trimers. (a) will lead to more frustrations to the cluster than (b).

a trimer, a hexamer triangle is formed by adding three molecules (shown as gray sphere in the figure) to the trimer. Basically there are two ways to add them: (a) attaching the three molecules as an edge of the hexamer triangle and (b) attaching them to the three sides of the trimer triangle. (a) will lead to a hexamer triangle of the same orientation as the trimer, while (b) flips the orientation of the hexamer triangle. Both of them will raise the frustration of the cluster on account of the dipole-dipole interaction. However, the frustration of (a) is more prominent than that of (b). So, (b) is an energetically favored structure.

V. CONCLUSION

We have investigated the initial stage nucleation of endohedral metallofullerene Nd@C₈₂ on a substrate of crystalline C₆₀ film. Nd@C₈₂ molecules form close-packed configurations on the substrate, and they register on top sites of

the C₆₀ lattice. Over 60% of the molecules tend to aggregate as triangular trimers, and all trimers located on the same C₆₀ terrace point in the same direction. Considering the inert electronic character of the C₆₀ substrate, we suggest that the nucleation behavior of Nd@C₈₂ may be ascribed to its permanent dipole moment. A theoretical model based on dipole-dipole interactions provides a reasonable interpretation of the experimental results. The model also suggests that the dipole moment does not pass through the center of the C₈₂ cage while Nd@C₈₂ form trimers. The off-center displacement is ~ 0.13 Å.

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¹J. R. Heath, S. C. O'Brien, Q. Zhang, Y. Liu, R. F. Curl, H. W. Kroto, F. K. Tittel, and R. E. Smalley, *J. Am. Chem. Soc.* **107**, 7779 (1985).

²Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J. M. Alford, and R. E. Smalley, *J. Phys. Chem.* **95**, 7564 (1991).

³R. D. Johnson, M. S. De Vries, J. Salem, D. S. Bethune, and C. S. Yannoni, *Nature (London)* **355**, 239 (1992).

⁴J. H. Weaver, Y. Chai, G. H. Kroll, C. Jin, T. R. Ohno, R. E. Haufler, T. Guo, J. M. Alford, G. Palmer, and R. E. Smalley, *Chem. Phys. Lett.* **190**, 460 (1992).

⁵H. Shinohara, H. Sato, M. Ohkohchi, Y. Ando, T. Kodama, T. Shida, T. Kato, and Y. Saito, *Nature (London)* **357**, 52 (1992).

⁶J. Q. Ding and S. H. Yang, *Angew. Chem. Int. Ed. Engl.* **35**, 2234 (1996).

⁷J. Q. Ding and S. H. Yang, *J. Am. Chem. Soc.* **118**, 11 254 (1996).

⁸J. Q. Ding, N. Lin, L. T. Weng, N. Cue, and S. H. Yang, *Chem. Phys. Lett.* **261**, 92 (1996).

⁹C. Park, B. O. Wells, J. DiCarlo, Z. X. Shen, J. R. Salem, D. S. Bethune, C. S. Yannoni, C. Booth, and F. Bridge, *Chem. Phys. Lett.* **213**, 196 (1993).

¹⁰H. Shirohara, M. Inakuma, M. Kishida, S. Yamazaki, T. Hashizume, and T. Sakurai, *J. Phys. Chem.* **99**, 13 690 (1995).

¹¹N. Lin, J. Q. Ding, S. H. Yang, and N. Cue, *Phys. Lett. A* **222**, 190 (1996).

¹²S. Hino, H. Takahashi, K. Iwasaki, and K. Matsumoto, *Phys. Rev. Lett.* **71**, 4261 (1993).

¹³L. Moro, R. S. Ruoff, C. H. Becker, D. C. Lorents, and R. Malhotra, *J. Phys. Chem.* **97**, 6801 (1993).

¹⁴S. Bandow, H. Kitagawa, T. Mitani, H. Inokuchi, Y. Saito, H. Yamaguchi, N. Hayashi, H. Sato, and H. Shinohara, *J. Phys. Chem.* **96**, 9609 (1993).

¹⁵C. S. Yannoni, M. Hoinkis, M. S. deVries, D. S. Bethune, J. Salem, M. S. Crowder, and R. D. Johnson, *Science* **256**, 1191 (1992).

¹⁶M. Takata, B. Umeda, E. Nishibori, M. Sakata, Y. Saito, M. Ohno, and H. Shinohara, *Nature (London)* **377**, 46 (1995).

¹⁷N. Tanaka, Y. Honda, M. Kawahara, M. Kishida, and H. Shinohara, *Thin Solid Films* **281-282**, 613 (1996).

¹⁸S. Nagase and K. Kobayashi, *Chem. Phys. Lett.* **201**, 475 (1993).

¹⁹S. Nagase and K. Kobayashi, *Chem. Phys. Lett.* **231**, 319 (1994).

²⁰K. Lassonen, W. Andreoni, and M. Parrinello, *Science* **258**, 1916 (1992).

²¹J. Schulte, M. C. Bohm, and K. Dinse, *Chem. Phys. Lett.* **259**, 48 (1996).

²²D. M. Poirier, M. Knupfer, J. H. Weaver, W. Andreoni, K. Laasonen, M. Parrinello, D. S. Bethune, K. Kikuchi, and Y. Achiba, *Phys. Rev. B* **49**, 17 403 (1994).