

**STM study of one-dimensional cluster formation of fullerenes: Dimerization of  $Y@C_{82}$** 

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(Received 3 June 1997)

We have studied one-dimensional cluster formation of  $C_{60}$ ,  $Y@C_{82}$ , and  $Gd@C_{82}$  along the step of the Cu(111)  $1\times 1$  surface using a scanning tunneling microscope. It is found that the dimer is most abundant only for  $Y@C_{82}$  which has one unpaired electron delocalized over the carbon cage, while the monomer is dominant in the cases of  $Gd@C_{82}$  and  $C_{60}$ . It was concluded that the preferential dimer formation of  $Y@C_{82}$  is mainly due to the interaction between the unpaired electrons. The interaction energy among fullerene molecules was estimated based on Walton's cluster theory. [S0163-1829(97)05735-4]

Fullerene molecules<sup>1</sup> have attracted much attention together with nanotubes as a promising new material because of their unique structures and chemical properties. A scanning tunneling microscope (STM) has been used for characterization of the molecules, in particular, to investigate their processes of adsorption and mechanisms of thin film growth on various surfaces.<sup>2</sup> It has been well-documented, from those studies, that the balance between the molecule-molecule and substrate-molecule interactions is critical for determining the morphology and crystal orientation of thin films.<sup>2</sup> It is, thus, very important to understand the interaction among the molecules on surfaces.

Endohedral metallofullerenes<sup>3,4</sup> are presently most interesting among the various fullerenes. Because of the charge transfer from the encapsulated metal atom to the cage, the electronic properties of fullerenes are modified significantly. Charge transfer and the resulting electronic properties of metallofullerene molecules are best investigated with electron-spin resonance (ESR). It was concluded, based on the ESR hyperfine splitting, that the  $Y@C_{82}$  molecule,<sup>5,6</sup> as well as  $La@C_{82}$ ,<sup>7-9</sup> possesses one electronic spin or unpaired electron primarily located over the carbon cage while  $Gd@C_{82}$  and  $C_{60}$  do not.<sup>10,11</sup> Recently, Furusaka *et al.*<sup>12</sup> reported that  $Gd@C_{82}$  has a magnetic moment which indicates an existence of an unpaired electron similar to  $Y@C_{82}$ . We, however, used the carefully purified samples which are ESR silent. It was, thus, speculated that  $Y@C_{82}$  may exhibit unique molecular interactions due to the unpaired electron.<sup>9,13,14</sup>

In this study, we investigated, using an STM, the size distribution of one-dimensional clustering of  $Y@C_{82}$  and  $Gd@C_{82}$  and pristine  $C_{60}$  adsorbed on the Cu(111)  $1\times 1$  sur-

face and elucidated the interesting effect of the unpaired electron on cluster formation. On the Cu(111) $1\times 1$  surface the fullerene molecules are quite mobile as we have documented with various fullerenes.<sup>15,16</sup> When a small amount of fullerene was deposited on the surface, all deposited molecules segregated to the terrace edge, and the linear clusters formed along the terrace edge. Two-dimensional island growth did not take place until the edge was filled with the fullerene. Therefore, we can regard the cluster formation process of these molecules as one-dimensional at a small coverage.

Cleaning of the copper surface, sublimation/deposition of the fullerenes and the STM observations were carried out under the ultrahigh vacuum (UHV) conditions with a base pressure of  $5\times 10^{-11}$  Torr. Details of the STM used were published elsewhere.<sup>17</sup> A (111) oriented single-crystal copper sample was cleaned by repetitive Ar sputtering and annealing at approximately 500 °C. Upon obtaining clean flat surfaces determined by STM observations, the fullerene molecules are deposited by resistive heating of a Ta foil which contains the fullerenes. During the deposition, the Cu substrate was kept at room temperature. Based on our systematic investigation,<sup>2,16</sup> we know that all molecules are deposited on the surface in the form of a single molecule and that the clusters formed on the surface.<sup>18</sup> Purity of the fullerene samples was >99.8% for  $Gd@C_{82}$  and  $Y@C_{82}$ , and 99.99% for  $C_{60}$ , as revealed by high-performance liquid chromatography. The details of producing and purifying the fullerenes were reported elsewhere.<sup>18</sup>

More than hundred STM images were taken after deposition of each fullerene on the surface and the cluster size distribution was compiled. In this paper, term "coverage" is

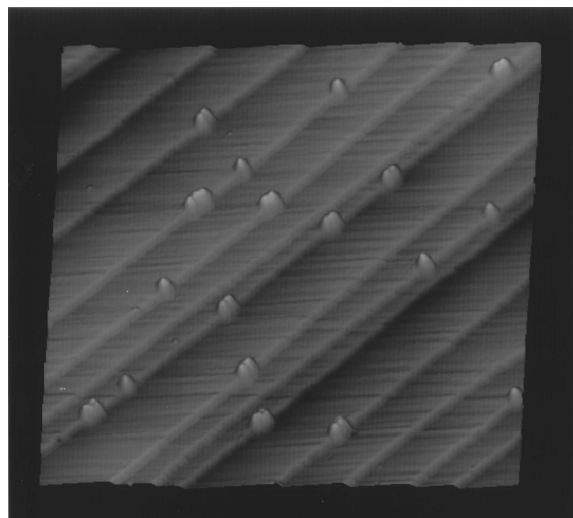


FIG. 1. STM image of  $Y@C_{82}$  adsorbed on the  $Cu(111) 1 \times 1$  surface ( $V_{\text{sample}} = -1.2$  V). The observed area is  $730 \text{ \AA} \times 730 \text{ \AA}$ . All molecules are adsorbed at monoatomic step edges.

defined as a ratio of the step occupied by fullerene to the total step length. Since the intermolecular (van der Waals) distance of  $Y@C_{82}$  and  $Gd@C_{82}$  is  $11.8 \text{ \AA}$  and that of  $C_{60}$  molecules is  $10.0 \text{ \AA}$ , the coverage of  $Y@C_{82}$  and  $Gd@C_{82}$  ( $C_{60}$ ) is defined as (the number of molecules)  $\times 11.8 \text{ \AA}$  ( $10.0 \text{ \AA}$ ) / (total step length). The terms ‘‘dimer’’ and ‘‘trimer’’ are used to describe clusters of size 2 and 3, respectively, and do not imply that the clusters are formed with covalent bonds or other chemically strong bonding between carbon atoms.

Figure 1 is a typical STM image of the  $Y@C_{82}$  molecules adsorbed on the  $Cu(111) 1 \times 1$  surface. All three types of fullerenes studied exhibited the same adsorption behavior, forming one-dimensional clusters along terrace edges of monoatomic height. From these STM images, we can determine the size of individual clusters and obtain the cluster size distribution. The cluster size distributions obtained for  $Y@C_{82}$ ,  $Gd@C_{82}$ , and  $C_{60}$  are shown in Fig. 2. The coverages are small; 2.8%, 3.7%, and 4.1% for  $Y@C_{82}$ ,  $Gd@C_{82}$ , and  $C_{60}$ , respectively. In the case of  $C_{60}$ , the monomer is most abundant, and then the abundance decreases with the cluster size. This is also true for the cluster size distribution of  $Gd@C_{82}$ . In a histogram of  $Y@C_{82}$ , however, the dimer is most abundant. In general, at larger cov-

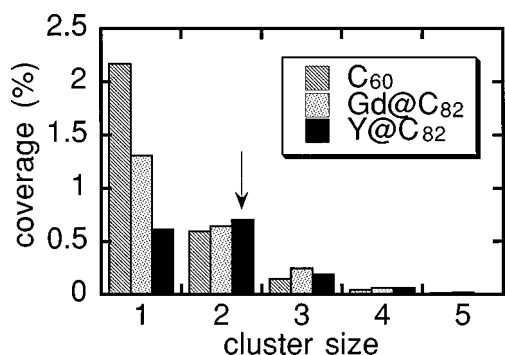


FIG. 2. Cluster size distributions of  $C_{60}$ ,  $Gd@C_{82}$ , and  $Y@C_{82}$ . Coverages are small; 4.1%, 3.7%, and 2.8% for  $C_{60}$ ,  $Gd@C_{82}$ , and  $Y@C_{82}$ , respectively.

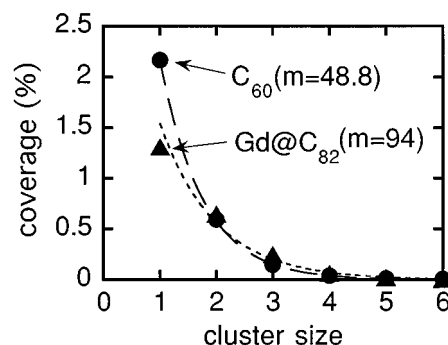


FIG. 3. Cluster size distribution curves of  $C_{60}$  and  $Gd@C_{82}$ . This plot demonstrates that the curves can be fitted well with exponential curves.

erages, the formation of larger clusters is expected. We note that the coverage of  $Y@C_{82}$  is smaller than that of  $C_{60}$  or  $Gd@C_{82}$ . The fact that only  $Y@C_{82}$  which is at the smallest coverage among them shows a dimer-rich size distribution must mean that a unique interaction occurs between the  $Y@C_{82}$  molecules at the terrace edge.

According to the ESR studies, a pair of hyperfine-splitting (HFS) peaks was observed only for the  $Y@C_{82}$  spectrum among those three fullerenes being studied here. It was interpreted due to the interaction between unpaired electrons and  $I = 1/2$  yttrium nuclei.<sup>5,6</sup> The HFS structure is explained with a model that three electrons are transferred from a Y atom to the carbon cage, resulting in a lone electron spin on the cage. It is natural to speculate under the present situation that *the preferential dimer formation of  $Y@C_{82}$  is due to the unpaired electron which  $Y@C_{82}$  alone possesses*. Since three electrons are transferred from the encapsulated Y atom to the carbon cage, the overall picture is similar to that of Li atoms, which have an unpaired electron and make a  $Li_2$  molecule. Similar to the covalent bond in the  $Li_2$  molecule, the unpaired electron exerts an attractive interaction only to form a dimer, not a trimer or tetramer. However, the interaction energy between  $Y@C_{82}$  molecules is much smaller than that of Li atoms due to the large intermolecular distance.

In order to qualitatively interpret the cluster size distributions we observed, we use a model of cluster formation originally proposed by Walton<sup>19</sup> which is obtained by minimization of a free energy and thus can be applied to the cases of equilibrium. According to his theory, the density of cluster of size  $s$ ,  $N_s$ , can be described by  $N_s = N_1 \exp(E(s)/kT) (\frac{1}{4} N_1)^{s-1}$ , where  $N_1$  is the density of monomer and  $E(s)$  is a formation energy of a cluster of size  $s$  from  $s$  monomers. Term  $\frac{1}{4}$  which is not in its original formula enters because the fullerene molecules being studied presently occupy four Cu atoms when they form clusters at terrace edges. If one assumes that the cluster formation is solely by the nearest-neighbor pairwise interaction, the formation energy  $E(s)$  is  $(s-1) \times E_p$ , where  $E_p$  is the pairwise interaction energy, because the number of pairs in a one-dimensional size  $s$  cluster is  $s-1$ . The cluster size density can be written as  $N_s = N_1 [\frac{1}{4} N_1 \exp(E_p/kT)]^{s-1}$ . The cluster size density changes exponentially with the cluster size  $s$ . This is the case of the cluster formation of  $C_{60}$  and  $Gd@C_{82}$ ; their size distributions can be fitted nicely with

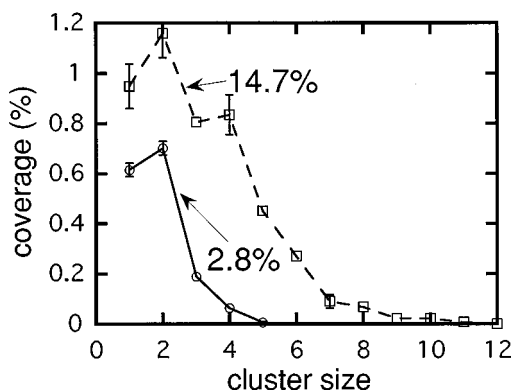


FIG. 4. Cluster size distribution curves of  $Y@C_{82}$  at coverages of 2.8% (same as that of Fig. 2) and 14.7%. At both coverages, the dimer is dominant among the clusters.

exponential curves as is shown in Fig. 3. From the fitting, the value of  $\exp(E_p/kT)$  ( $=m$ ) is estimated to be 48.8 and 97 for  $C_{60}$  and  $Gd@C_{82}$ , respectively. The exponential fitting of the cluster size distribution of  $C_{60}$  and  $Gd@C_{82}$  means that their cluster formation can be explained by considering only the pairwise interaction between the nearest-neighbor molecules.

We have found that, in the case of the cluster formation of  $Y@C_{82}$ , the size distribution cannot be fitted with exponential curves. Figure 4 shows size distribution curves of the  $Y@C_{82}$  clusters for two different coverages, 2.8% and 14.7%. Both curves have the peak at the dimer, and neither of them can be fitted with an exponential curve. These results show that the cluster formation energy  $E(s)$  is not a linear function of cluster size, and thus, its cluster formation cannot be explained with the nearest-neighbor pairwise interaction alone. *In order to explain the size distribution of  $Y@C_{82}$ , the interaction energy which depends on the cluster size should be considered.*

Values of an energy gain  $\Delta E(s) [=E(s) - E(s-1)]$  to form a  $Y@C_{82}$  cluster of size  $s$  from a cluster of size  $s-1$  and a monomer, are shown in Fig. 5, calculated from the cluster size distribution of Fig. 2. Energy gains for  $C_{60}$  and  $Gd@C_{82}$  are also plotted in Fig. 5, 101 meV for  $C_{60}$  and 117 meV for  $Gd@C_{82}$ , independent of the cluster size and equal to the pairwise interaction energy. The larger energy for  $Gd@C_{82}$  means that  $Gd@C_{82}$  has the stronger attractive interaction, resulting in larger cluster formation. In the case of  $Y@C_{82}$ , however, the energy gain of the dimer is 172 meV, much larger than those of  $Gd@C_{82}$  and  $C_{60}$ , while the values for trimer and tetramer are  $\sim 140$  meV and the energy for a pentamer is identical to the value of  $Gd@C_{82}$ .  *$Y@C_{82}$  molecules have the strong interaction in forming the dimer. A straightforward interpretation is that the dimer formation is due to the interaction originated at the unpaired electron localized in the cage of the  $Y@C_{82}$  molecule. Although it is similar to the covalent bond in the  $Li_2$  molecule, the interaction energy gain unique to the dimer formation of  $Y@C_{82}$  is only 55 meV compared with those of  $Gd@C_{82}$ , much smaller than that of the normal covalent bond, due to the fact that the molecules forming the dimer are separated further apart by the large nearest-neighbor distance (11.8 Å).*

As for the origin of interactions in the cases of  $Gd@C_{82}$  and  $C_{60}$ , it is safe to assume that they are attributed to the

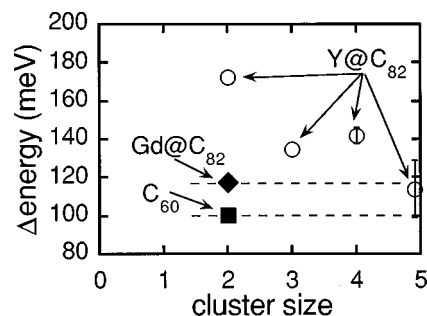


FIG. 5. Energy gain to form a cluster of size  $s$  from a size  $(s-1)$  cluster plotted as a function of cluster size  $s$ . For the cases of  $C_{60}$  and  $Gd@C_{82}$ , the energy is independent of the cluster size, while a large energy gain for the dimer formation is evident for the case of  $Y@C_{82}$ .

van der Waals interaction, which is the main interaction in bulk  $C_{60}$ .<sup>20</sup> The dipole-dipole interaction, screened by the Cu substrate, also has a significant contribution to the interactions of  $Gd@C_{82}$  and  $Y@C_{82}$  molecules because these molecules have large dipole moments as a result of a charge transfer from the encapsulated metal to the cage.<sup>5,6,18,21</sup> The important point, however, is that the dipole-dipole interaction is size independent and does not play any special role in dimer formation. It contributes to certain energy gain in cluster formation (the energy difference of 16 meV between  $Gd@C_{82}$  and  $C_{60}$ ), but works equally for all sizes of the clusters. It can, in principle, be included in the nearest-neighbor pairwise interaction. That is the reason why cluster formation of  $Gd@C_{82}$ , which may have a dipole moment, can still be sufficiently explained with the model which considers only the nearest-neighbor pairwise interaction.

A difference in molecular size or lattice mismatch with the Cu terrace edges may affect their cluster formation processes. We, however, did not observe any difference in cluster formation between  $C_{60}$  and  $Gd@C_{82}$  molecules except their interaction energy while they have the different molecular size. On the other hand,  $Gd@C_{82}$  and  $Y@C_{82}$  showed a quite different size distribution in spite of their similar molecular size. We measured the intermolecular distances for the  $Gd@C_{82}$  and  $Y@C_{82}$  clusters adsorbed at terrace edges from STM images, but did not observe a significant difference. Thus, we believe that the effect of the size difference of the molecules or lattice mismatch does not play a significant role on the smooth Cu(111)  $1 \times 1$  surface.

In the analysis of our experimental results, we assumed that the clustering formation occurred in the equilibrium condition and estimated the values of interaction energy between fullerene molecules, based on the Walton theory applicable to the case of equilibrium and low coverages. In order to test whether it is really in equilibrium and whether the Walton theory is applicable to our experiments, we investigated the cluster formation processes of  $C_{60}$  in more detail, as a function of  $C_{60}$  coverage and flux rate. The cluster size distribution was measured in the  $C_{60}$  coverage range between 5.4% and 21.9% and in the flux rate between 0.18%/sec. to 3.4%/sec.

Our important findings are as follows: (1) The cluster size distribution or average cluster size did not depend on the flux rate. This indicates that the kinetics of the molecules was not

important in the present study. (2) At coverages smaller than 10%, the size distribution fits well with a single exponential curve, which is explained and consistent with the Walton equilibrium theory. At a coverage over 10%, however, the size distribution began to deviate from the theory, and the number of  $C_{60}$  monomer became smaller than that expected from the exponential curve. Therefore, we safely conclude that the cluster formation process in our experimental conditions is in equilibrium and that the Walton theory is valid as long as the fullerene coverage is less than 10%. Based on these results, we found that the exponential factor,  $\frac{1}{4}N_1 \exp(E_p/kT)$ , in the Walton's formula should be smaller than 1 in order to apply the theory.

The value of  $\frac{1}{4}N_1 \exp(E_p/kT)$  in our experiment shown in Fig. 2 is 0.27, <0.3, and 0.36 for  $C_{60}$ ,  $Y@C_{82}$ , and  $Gd@C_{82}$ , respectively. If one carefully looks at the size distribution of  $Gd@C_{82}$  clusters plotted in Fig. 3, one notices that the number of the monomer is slightly smaller than that expected from its fitting curve. Since the value of  $\frac{1}{4}N_1 \exp(E_p/kT)$  of  $Gd@C_{82}$  is 0.36, relatively large, this may be the reflection of slight deviation from equilibrium as mentioned above. But, in the cases of  $C_{60}$  and  $Y@C_{82}$ , where the coverage is small compared with that of  $Gd@C_{82}$ , the Walton theory

should be applicable, and its interaction energies obtained with the theory is meaningful.

In conclusion, we studied the cluster formation process of fullerene ( $C_{60}$ ,  $Gd@C_{82}$ , and  $Y@C_{82}$ ) molecules on the flat Cu(111)  $1 \times 1$  surface and found the preferential dimer formation only for  $Y@C_{82}$  which possesses an unpaired electron. This observation was interpreted based on the attractive interaction exerted between the unpaired electrons of two neighboring  $Y@C_{82}$  molecules. Although its interaction energy is small (<100 meV), the  $Y@C_{82}$  molecule on the terrace edge essentially behaves just like a Li atom, which also possesses an unpaired electron and forms  $Li_2$  molecules. The  $Y@C_{82}$  molecule is one of the first experimentally documented cases of the so-called "superatom" which was originally proposed for semiconductor heterostructure.<sup>22</sup> A concept regarding the molecule as a superatom<sup>13,14</sup> would provide us with a new scheme in understanding clustering and growth, and in designing new materials.

We acknowledge support by the New Frontier Program Grand-in-Aide for Scientific Research (No. 07NP0301) funded by Department of Education, Japan, and the National Science Foundation Grant No. DMR-9300704.

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