RAPID COMMUNICATION

# Scanning tunneling microscopy study of molecular growth structures of Gd@$C_{82}$ on Cu(111)*

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The coverage and temperature-dependent nucleation behaviors of the Gd@$C_{82}$ metallofullerenes on Cu(111) have been studied by low-temperature scanning tunneling microscopy (LT-STM) in detail. Upon molecular deposition at low temperature, Gd@$C_{82}$ molecules preferentially decorate the steps and nucleate into single layer islands with increasing coverage. Further annealing treatment leads some of the Gd@$C_{82}$ molecules to assemble into bright and dim patches, which are correlated to the adsorption induced substrate reconstruction. Upon sufficient thermal activation, Gd@$C_{82}$ molecules sink into the Cu(111) surface one-copper-layer-deep, forming hexagonal close-packed molecular islands with intra-molecular details observed as striped patterns. By considering the commensurability between the Gd@$C_{82}$ nearest-neighbor distance and the lattice of the underlying Cu(111), we clearly identified two kinds of in-plane molecular arrangements as $(\sqrt{19}\times\sqrt{19})$R23.4° and $(\sqrt{19}\times\sqrt{19})$R36.6° with respect to Cu(111). Within the assembled Gd@$C_{82}$ molecular, island molecules with dim–bright contrast are spatially distributed, which may be modulated by the preexisted species on Cu(111).

**Keywords:** metallofullerene, self-assembly, nucleation behaviors, scanning tunneling microscopy

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## 1. Introduction

Endohedral metallofullerenes have stimulated great interest because of their unique structures and electronic properties, which have been extensively studied both theoretically and experimentally with regard to being associated with the exchange of electrons between the entrapped metal complex and the fullerene cage.[1–7] Moreover, in fullerene-based electronic applications, the molecular orientation, adsorption geometry, and packing density of fullerene strongly influence the conductance, and the formation of well-ordered fullerene structures can greatly improve the performance of the device, which motivates a considerable amount of research on the adsorption, structures, and/or self-assembly of fullerene-based adlayers on metal surfaces.[8–11] For fullerenes absorbed on a metal substrate, the hybridization of molecular frontier orbitals with the wave functions of the underlying metal substrate results in an inhomogeneous charge distribution around the carbon cage, which further affects the orientations and nucleation behaviors as well as the electronic structures of the fullerenes.[10–16]

Here, we present a scanning tunneling microscopy (STM) study of the molecular growth and nucleation behaviors of Gd@$C_{82}$ molecules on Cu(111). Apart from the spatially averaged diffraction techniques, such as X-ray powder diffraction[1,17] and X-ray absorption near-edge structure,[18,19] STM can elucidate the structural and electronic properties of the fullerenes at molecular spatial resolution.[11,14,20] By well characterizing the annealing induced Gd@$C_{82}$ assemblies, we find that step-by-step annealing induces a one-copper-layer-deep hole forming under every Gd@$C_{82}$ molecule. Upon sufficiently high temperature annealing, Gd@$C_{82}$ molecules fully sink into the Cu(111) surface, one-copper-layer-deep, forming hexagonal close-packed molecular islands. By considering the commensurability between the Gd@$C_{82}$ nearest-neighbor distance and the lattice of the underlying Cu(111), we rationalize two kinds of in-plane molecular arrangements as $(\sqrt{19}\times\sqrt{19})$R23.4° and $(\sqrt{19}\times\sqrt{19})$R36.6° with respect to Cu(111).

## 2. Experimental details

The experiments were conducted in an ultra-high-vacuum (UHV) chamber (base pressure better than $1\times10^{-10}$ Torr) equipped with a commercial low-temperature scanning tunneling microscope (LT-STM, UNISOKU, Japan). A single-crystal Cu(111) (MaTecK, Germany) was cleaned by repeated cycles of $Ar^+$ sputtering (600 eV, 20 min) and UHV annealing (850 K for 15 min). The temperature was monitored by an infrared pyrometer and further calibrated by a thermal couple.

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A small amount of metallofullerene Gd@$C_{82}$ powder was obtained in a crucible by evaporating the methylbenzene solvent and recrystallizing. After degassing in UHV at 800 K for more than 20 h, the Gd@$C_{82}$ molecules were sublimated at 820 K onto the Cu(111) substrate, during which the vacuum was better than $8.0\times10^{-10}$ Torr and the temperature of the substrate was kept at about 200 K. STM measurements were performed at liquid nitrogen temperature with Pt–Ir tips. Before measurements, the tip was sputtered to get rid of the contamination and oxidation. All the STM images were recorded in the constant-current mode at a stabilizing current $I$ with bias voltage $V$ applied to the sample. Due to the energy-dependent variation of molecular electronic structures, the height profiles presented here were measured under the same tunneling conditions.

## 3. Results and discussion

A series of topographic STM images of Gd@$C_{82}$ molecules adsorbed on Cu(111) at molecular coverage ranging from 0.002 ML to 0.400 ML (ML: monolayer) are shown in Fig. 1. The spherical bright spots correspond to Gd@$C_{82}$ molecules. At the very initial adsorption stage (Fig. 1(a)), Gd@$C_{82}$ molecules selectively decorate the edges of the Cu(111) substrate with a preference of locating at the bottom of the edges. Most of the Gd@$C_{82}$ molecules exist as individual molecules, whereas some others aggregate into $(Gd@C_{82})_2$ clusters. Further deposition leads to the molecules aggregating into bigger clusters as shown in Fig. 1(b). The molecular clusters grow out from the step edges not only on the lower terraces but also on the upper ones. It is worth noting that before the step edges are saturated by the molecules, some Gd@$C_{82}$ clusters randomly distribute inside the terraces. The sites at which the molecules start to aggregate on the terrace are still unclear and this phenomenon cannot rule out the potential contribution of the defects. With increasing the molecular coverage to 0.400 ML, Gd@$C_{82}$ assemblies (10–20 nm) form as shown in Fig. 1(c). The shape of the fullerene assemblies is irregular, to some extent similar to a fractal, within which no close-packed molecular direction can be found. Obviously, the second-layer Gd@$C_{82}$ molecules start to gather on the top of the first layer. From the line profile (Fig. 1(d)), Gd@$C_{82}$ molecules of the first and the second layers both have the same apparent height of about 0.90 nm.

At the initial growth stage, due to their relatively high mobility, Gd@$C_{82}$ molecules diffuse on the Cu(111) surface and prefer to nucleate at the step edges or at the defects, which are energetically more favorable sites than the terrace. Moreover, as a consequence of the charge transfer from a charge-rich Cu(111) surface to Gd@$C_{82}$ molecules together with the Smoluchowski effect,[21,22] the molecules grow by expanding mostly on the lower terrace. The Gd@$C_{82}$ clusters grow out-

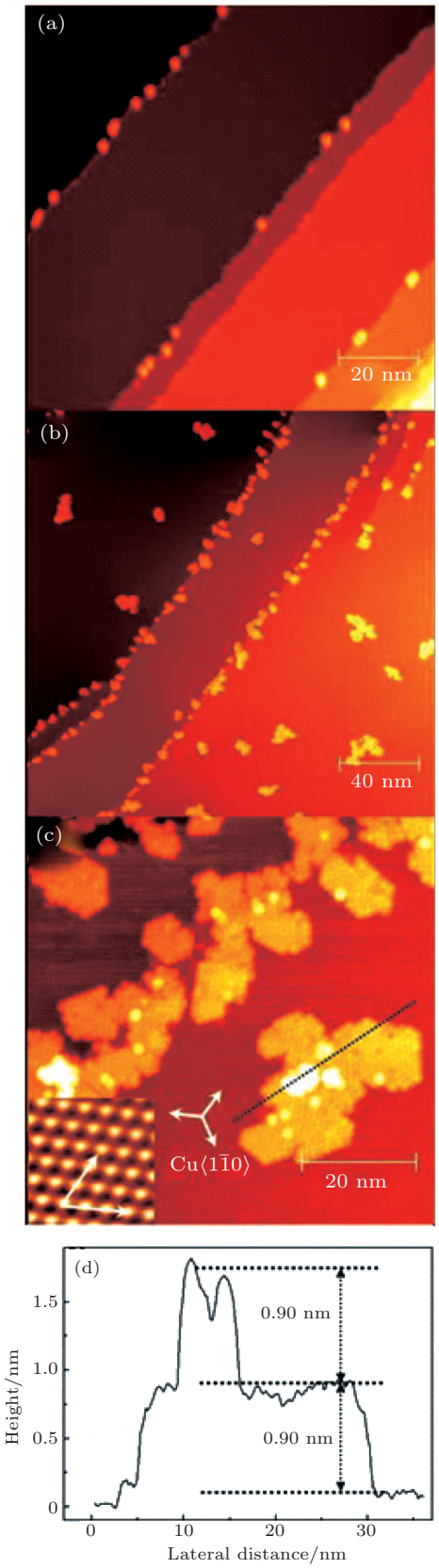



**Fig. 1.** (color online) STM images of Gd@$C_{82}$ molecules adsorbed on Cu(111) kept at 200 K with increasing molecular coverage: (a) 0.002 ML, (b) 0.070 ML, and (c) 0.400 ML, recorded at sample bias of 2.00 V and tunneling current of 10 pA. Inset: atomic resolution STM image of the pristine Cu(111) showing the $\langle 1\bar{1}0\rangle$ vectors. (d) Line profile (2.00 V, 10 pA) cossing Gd@$C_{82}$ molecular island indicating the apparent height of one and two layers of as-deposited Gd@$C_{82}$ molecules.

ward as mobile molecules attach to the existing molecules and expand into irregular islands. Upon further deposition, the second molecular layer forms before Gd@$C_{82}$ molecules completely cover the Cu(111) surface, indicative of a strong intermolecular interaction.

When annealing the sample covered with 0.400 ML Gd@$C_{82}$ molecules at 450 K, most of the top-layer fullerenes move down and rearrange with the sublayer ones as shown in Fig. 2(a). As evidenced in Fig. 2(b), the intra-molecular details are observed as three or four striped patterns, which reflect the distribution of the electronic localization of the $C_{82}$ cage with certain energy. The change in the direction of the striped structures corresponds to a change in the molecular orientation. The greater variety of molecular orientations is induced by the random orientation of the fullerenes on the Cu(111) surface. As we know, Gd@$C_{82}$ is a slightly elliptical $C_{2V}$ molecule with the encaged Gd bonding off-center.[23] Consequently, it is difficult to directly discern the molecular adsorption configurations within the assemblies by STM observations. As shown in Fig. 2(c), STM simulations reveal the observed stripe structure corresponding to the "lying-down" molecular adsorption configurations with encaged Gd located at one side of the carbon cage. The change in the direction of the striped structures corresponds to the random azimuthal orientation of the fullerenes. There is no preferred close-packed direction found inside the molecular islands. It is interesting that part of Gd@$C_{82}$ molecules assemble into bright patches, which are approximately 0.20 nm higher than the other regions. Previously, this apparent height difference was correlated to the underlying monolayer copper adatom aggregation induced by Gd@$C_{82}$ molecules.[24] From the height profile (the inset of Fig. 2(b)), the apparent height of the dim regions is ∼0.68 nm, approximately 0.20 nm lower than that before annealing (Fig. 1(d)), which suggests that these Gd@$C_{82}$ molecules sink into the Cu(111) surface by ∼0.20 nm, which is the apparent height of one monolayer of copper. It is in agreement with the previous STM observations that upon thermal activation, fullerenes induce the underlying substrate to form vacancy reconstructions, for example, $C_{60}$ on copper[25–27] and Pt(111).[11] It is expected that under every Gd@$C_{82}$ molecule in the dim regions a one-copper-layer-deep hole forms upon annealing. So the apparent height of the dim regions is lower than that of the bright patches, under which the outermost Cu layer remains unaffected.

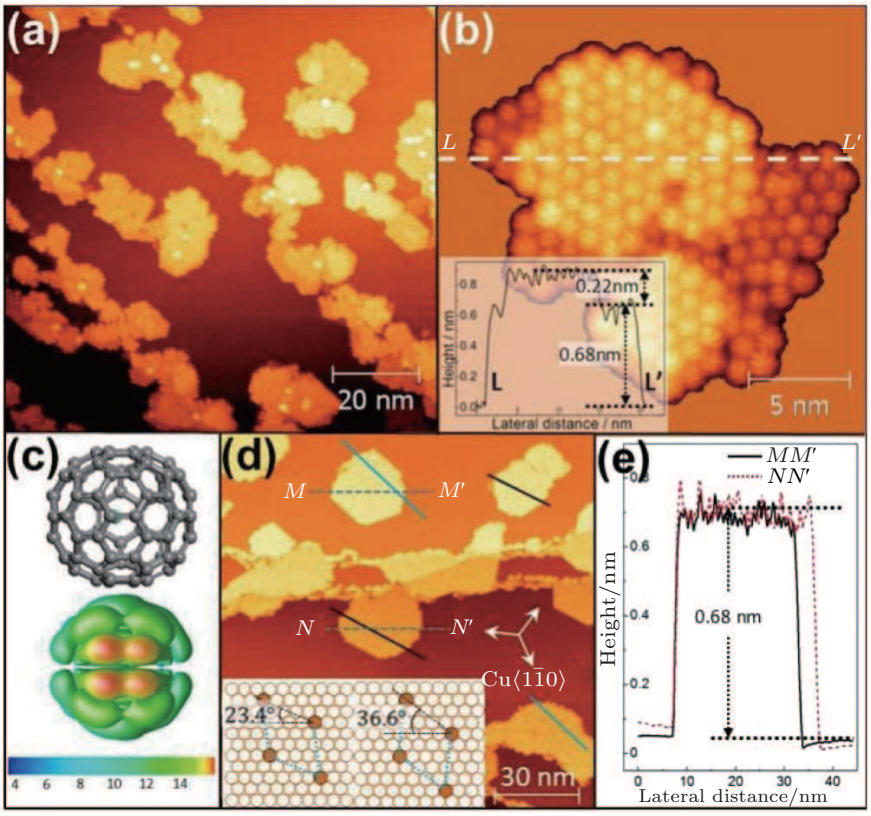



**Fig. 2.** (color online) (a) STM image (2.00 V, 40 pA) of 0.400 ML Gd@$C_{82}$ molecules on Cu(111) surface after annealing at 450 K for 15 min. (b) High resolution STM image (−1.20 V, 50 pA) of an isolated island obviously showing the bright molecular patch. Inset: the line profile (2.00 V, 10 pA) along $L$–$L'$ indicates an apparent height difference of approximately 0.20 nm. (c) Molecular adsorption configuration and corresponding STM simulation. (d) STM image (2.00 V, 10 pA) of the sample after annealing at 850 K for 15 min. Two kinds of molecular orientations are marked by blue and black solid lines. The inset shows the the height profiles (2.00 V, 10 pA) crossing the molecular islands, revealing the apparent height of ∼ 0.68 nm.

Further annealing at 850 K encourages the second-layer Gd@$C_{82}$ molecules to rearrange with the first-layer ones, forming molecular islands with bigger size and more regular periphery as shown in Fig. 2(d). The bright assembled Gd@$C_{82}$ patches (as shown in Fig. 2(b)) disappear, and the height profiles (inset of Fig. 2(d)) crossing the molecular islands reveal an apparent height of approximately 0.68 nm on average. It can be understood as a direct consequence of sufficiently high temperature inducing a one-copper-layer-deep hole to form under every Gd@$C_{82}$ molecule. The in-plane molecular arrangement becomes ordered, forming a hexagonal close-packed structure. A close inspection of the assembled molecular islands reveals two kinds of molecular lattice orderings. Gd@$C_{82}$ molecules assemble into compact molecular islands with a nearest-neighbor (N–N) distance of 1.17±0.02 nm on average. As shown in the inset of Fig. 1(c), the N–N distance of Cu atoms is measured to be 0.27±0.01 nm. In terms of the unit vectors $\boldsymbol{i}$ and $\boldsymbol{j}$ on the Cu(111) surface, the molecular lattices described as $\boldsymbol{r}_1 = 2\boldsymbol{i}+3\boldsymbol{j}$ and $\boldsymbol{r}_2 = 3\boldsymbol{i}+2\boldsymbol{j}$ are rotated 36.6° and 23.4° with respect to the Cu $\langle 1\bar{1}0 \rangle$ direction, respectively, perfectly fitting the measured molecular lattice with a mismatch less than 1%. Thus, as shown in the inset of Fig. 2(d), the lattice ordering structures are determined as $(\sqrt{19}\times\sqrt{19})$R23.4° and $(\sqrt{19}\times\sqrt{19})$R36.6° relative to Cu(111), respectively.

Besides some fullerene vacancies, a dim–bright molecular contrast is observed from the STM image of one molecular island (Fig. 3). The bright–dim contrast among Gd@$C_{82}$ molecules would not originate from the molecular impurities or different fullerene isomers because the fullerene molecule has been purified by sublimation at 800 K in the crucible, which is thoroughly cleaned before filling with Gd@$C_{82}$. The thermal decomposition of the fullerenes during sublimation is also unlikely as the Gd@$C_{82}$ cages are stable at temperatures up to at least 1000 K.[5,6] The tip effect can also be ruled out because the bright–dim contrast is still observed after persistently cleaning the tip, iteratively scanning, or scanning with a different STM tip. Note that besides the assembled molecular island, some species are randomly distributed on the surface. Statistically, these species have a coverage of about 0.06/nm$^2$, which is comparable with the density of the dim fullerenes indicated by circles. As Gd@$C_{82}$ molecules adsorb on the Cu(111) surface, the charge transfer between the Gd@$C_{82}$ cage and the underlying Cu is unavoidable, which is possibly perturbed by these pre-existing species, and then the intrinsic electronic properties of the fullerenes would like to be modulated. Further theoretical calculation is needed to elucidate the exact association between the preexisted species and the dim fullerenes; this is already in progress.

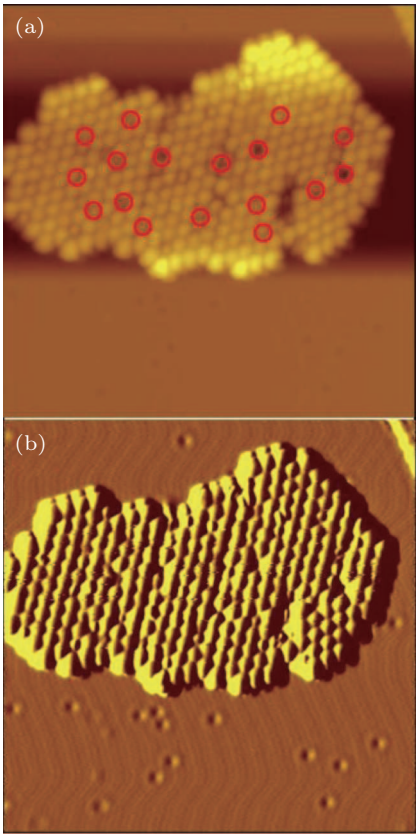



**Fig. 3.** (color online) (a) STM images (1.20 V, 50 pA) of a Gd@$C_{82}$ molecular island formed upon sufficient annealing treatment. The dim Gd@$C_{82}$ molecules are indicated by circles. For the sake of clarity, the corresponding current image is shown in panel (b).

## 4. Conclusion

We have studied the coverage and temperature-dependent adsorption structures of metallofullerene Gd@$C_{82}$ on Cu(111) by LT-STM/STS combined with STM simulations. It is found that upon low temperature deposition, Gd@$C_{82}$ molecules preferentially decorate the steps and nucleate into fractal-like single layer islands with increasing coverage. Step-by-step annealing treatment leads some Gd@$C_{82}$ molecules to assemble into bright patches, which are rationalized to be associated with the adsorption induced substrate reconstruction. Further annealing induces a one-copper-layer-deep hole to form under every Gd@$C_{82}$ molecule. By considering the commensurability between the Gd@$C_{82}$ nearest-neighbor distance and the lattice of the underlying Cu(111), we determine the structures as $(\sqrt{19}\times\sqrt{19})$R23.4° and $(\sqrt{19}\times\sqrt{19})$R36.6° within the hexagonal close-packed molecular island that forms upon sufficient annealing. Inside the assembled Gd@$C_{82}$ molecular island, a dim–bright molecular contrast is observed, which would like to be modulated by some species preexisting on Cu(111).

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