Electronic structure and properties of highly ordered C_{60} nano arrays on Au (111): STM & DFT study

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Abstract. Template assisted assembly of molecular nano arrays is one of the key steps towards molecular electronics and fullerene is one of the potential structural building blocks in fabrication of identical molecular nano arrays for miniature devices such as photovoltaic devices and single-molecule transistors. In this report, the reconstructed Au (111) with defect areas (steps) has been used as a template to assemble the highly ordered C_{60} nano array at low coverage studied with scanning tunnelling microscopy (STM) in conjunction with density functional theory (DFT). The interaction between the substrate and C_{60} nano arrays is strong enough to change the geometrical shape of C_{60}. As a result of strong interaction, the C_{60} molecule appears to be deformed into ellipsoidal shape which causes the reduction of C_{60} nano arrays on step sites of Au (111).

1. Introduction

Fullerene is one of the potential structural building blocks in fabrication of identical nano scale structures for miniature devices, such as photovoltaic devices and single-molecule transistors.[1] In addition to be a flexible building-block material, fullerenes are also a kind of electron acceptors that can offer an ease of fabrication of donor-acceptor nanojunctions.

Until now, the investigation of self-assembled structures of C_{60} on flat metal surfaces has been focused on monolayer structures by many research groups. [2] To our knowledge, a few reports have been done on the investigation of adsorption behavior of C_{60} residing on the step of vicinal metal surfaces which have been used as novel templates to prepare controllable nanostructures.[3] One big advantage of this method is that it can avoid introducing of impurities. Since no more experimental procedures are required, using vicinal gold templates saves much time than other methods as well.

Vicinal gold surfaces are useful for controlling the nano scale structure in specific energetic sites. One of the templates is Au (111) which has been studied extensively for the formation of 2 D arrays of metal islands. Adsorption of molecules occurs preferentially at defects such as step edges and kinks at room temperature. [4] For the adsorption of C_{60} on Au (111) at room temperature, the molecules quickly move to the preferential adsorption sites (steps).

In this work, we found that there is an apparent shortening of C_{60} arrays residing on linear steps of Au (111) by analyzing the line profile of STM topography. Our calculations using Density functional Theory (DFT) suggest that the shortening is due to the molecular distortions in the middle of arrays caused by the elongation of the C-C bond length and pit formation on the gold layer.

2. Experimental details

All experiments were carried out in an UHV chamber (base pressure $< 10^{-10}$ mbar) equipped with an Omicron LT-STM operated at 77K. A tungsten tip was used, and all STM measurements were performed in a constant-current mode. The Au (111) single-crystal substrate was cleaned by several cycles of Ar+ sputtering (U=1.0kV) and subsequent annealing (T=300°C for 5 minutes, measured by a thermocouple directly attached to the crystal). C_{60} was purchased from Sigma Aldrich and used without further purification. The C_{60} was sublimed at 650 K from crucible to Au (111) surface that was held at room temperature for 1 minute. STM images of interested surface areas are obtained at~77 K.

3. Results and discussion

It is necessary to determine the crystallographic features of Au (111) substrate used as a template for C_{60} growth before the study of the adsorption behavior of it. The Au (111) surface we choose is of not only large area of terrace (50 %) but also linear steps (45 %) and kinks site (5 %). Even though, the substrate we choose is not a well prepared vicinal surface, some part of it is a good candidate as a natural template for growing of nano arrays. As a result of contraction in the [$\underline{1}$10] direction, the herringbone reconstruction forms. The reconstruction pattern can be seen in STM topography image of clean Au (111) surface in Fig. 1 (a). It occurs due to the two different surface atom packings, which are separated by two bright corrugation lines, alternatively. HCP (hexagonal closed packing) exists between two neighboring lines, whereas the wider-distance line area composed FCC (face centered cubic packing) lattices as shown in Fig. 1(b).
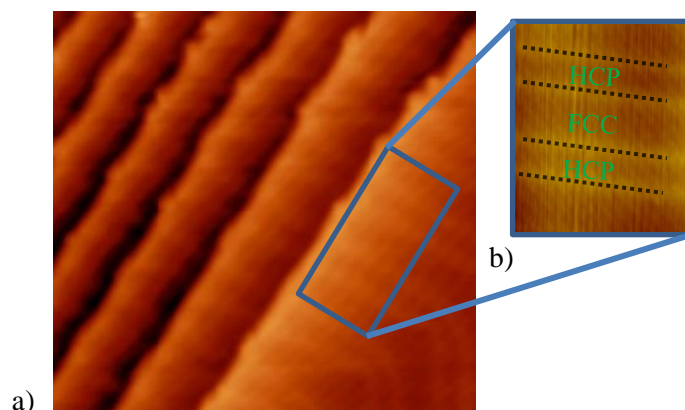

Figure 1. (a) STM topography image of Au (111) at I_t = 20 nA, V_{bias}= 1 V; and (b) Magnified STM image of HCP domains and FCC domains of Au (111)).

After deposition of ~0.05 Mono Layer (ML) (1 ML corresponds to a closed pack full coverage of molecules on the surface) molecules on the Au (111) surface. All the molecules organized to form nano arrays at kink or linear step edge as shown in Fig. 2 (a). This is because the C_{60} molecules are mobile on the terrace until they reach the preferred adsorption site (steps or kinks). It is found that these C_{60} molecules decorate the FCC stacking region at a low coverage. This shows that the C_{60} molecules resides the kinks or steps selectively.

Our analysis reveals that 90% of C_{60} nano arrays consist of four or five molecules which are decorating at the step area of Au (111). The intermolecular distance or the nearest neighbor distance (NND) of two C_{60} is ~1 nm (in crystal).[5] Line profile analysis of C_{60} nano arrays (from center to center) were carried for several hundreds of STM topography images in order to reveal the actual length of C_{60} molecular nano arrays. Clear reductions of C_{60} array lengths were observed. The result clearly state that the spacing of two C_{60} molecules in three, four and five molecular arrays is less than 1 nm as shown in Table 1. These results uncover the fact that, as the amount of molecules increase in an array, the intermolecular nearest neighbor distance is reduced compared with the reported value of

NND. We believe that some C_{60} in the middle of an array may elongate which results in shortening of the array length.

We further increased the coverage of C_{60} in order to achieve the monolayer deposition of C_{60} for comparing with the result of nano arrays with short lengths. However, we obtained C_{60} islands instead of nano arrays. The nearest neighbor distance between two C_{60} in the newly deposited island is ~1nm. The three lobe structure of C_{60} island can be seen in Figure 2(a) for comparison of line profile analysis. The average results of line profile analysis from our experiment has a ~ 13% reduction of the nearest neighbor distance comparing with the C_{60} monolayer island on the flat terrace.
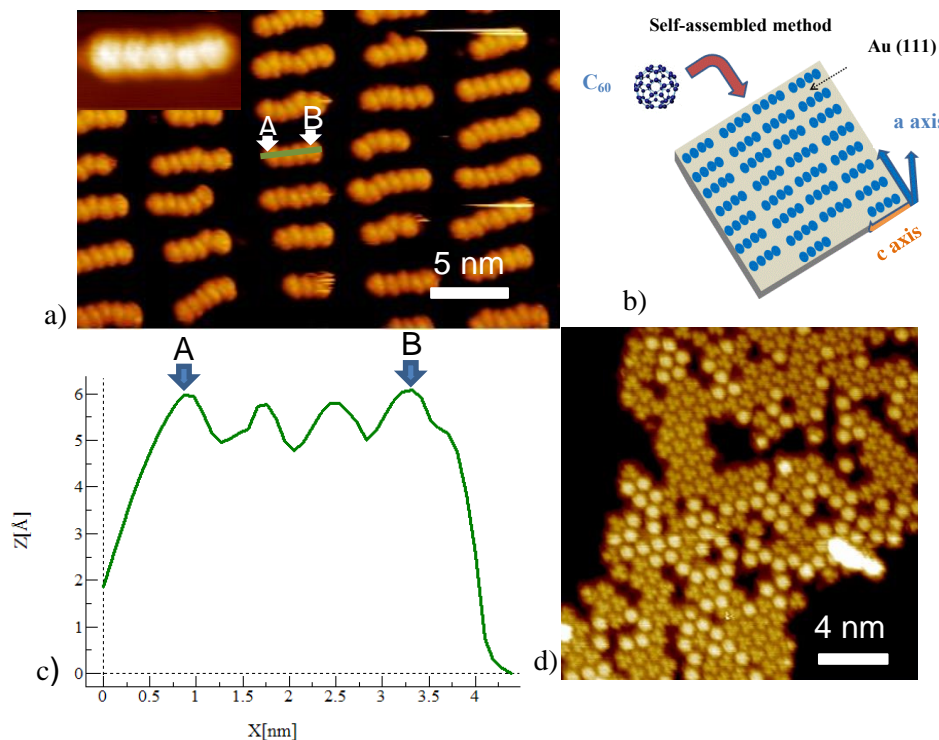

Figure 2. (a) STM image of periodic arrays of C_{60} selectively residing on the step edge of Au (111), It = 20 nA, Vbias= 3.5 V. The inset (I_t = 20 nA, Vbias= 3 V) shows the intermolecular resolution image of one C_{60} nano array (b) Schematic representation C_{60} deposited by self-assembly method on Au(111); (c) Line profile along the green line in (a); and (d) STM topography image of C_{60} island obtained at 77 K using I_t = 20 nA , V_{bias}= 2 V.

Table 1. Summary of lengths, nearest neighbour distance (NND) or intermolecular distance of C_{60} molecular nano arrays.

	Array 1 (Two C_{60}) (nm)	Array 2 (Three C_{60}) (nm)	Array 3 (Four C_{60}) (nm)	Array 4 (Five C_{60}) (nm)
Length[a]	0.8620	1.7049	2.5601	3.38136
Intermolecular distance[b]	0.8620	0.8520	0.8503	0.8454

[a] The length from one end to the other end of the nano array.
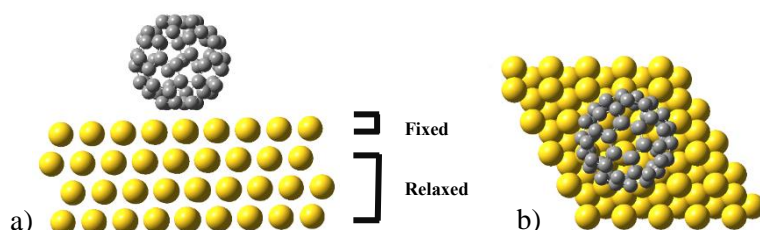[b] The center to center distance between two C_{60} molecules.

Figure 3. (a) Side view of adopted model for C_{60} sitting on the four atomic layers of gold. The bottom three layers are fixed and only the top layer is allowed to relax; and (b) top view of C_{60} on Au (111).
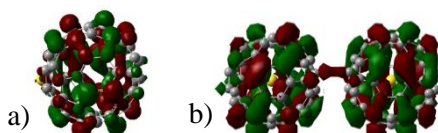

Figure 4. Computed lowest unoccupied molecular orbital of C_{60} on Au (111) with their respective relaxed structures: (a) one C_{60}; and (b) two C_{60}.

The DFT calculations were carried out using SIESTA [6] in order to provide better understanding of the STM results. The relaxed structure of system shows that some C-C bonds are elongated to certain extents. More theoretical calculations are necessary for the deformation trend in C_{60}. Moreover, the charge transfer from substrate to molecule could lead to the Jahn-Teller distortion due to covalent bond formation between the molecule and substrate.[7] To examine the electronic structure of C_{60} effectively at reasonable computational cost, we performed series of geometry optimizations with a certain number of gold atoms. The orbital distributions of the lowest unoccupied molecular orbital (LUMO) of C_{60} on Au (111) are plotted in Fig 4. These results indicate that the LUMO state of single C_{60} is not the same with other case like molecular array consists of two C_{60} as computed in Fig 4. The main reason is that the distribution of π orbital of two C_{60} is higher than the single C_{60}. It is obvious that the charge distribution increase with the number of C_{60} due to the π electron migrating between two C_{60} and the substrate, which might lead to the deformation of the orbitals.

4. Conclusion

To conclude, we investigated for the first time the reduction of nearest neighbor distance (NND) of C_{60} molecular arrays residing on the step sites of Au (111) which is less than 1 nm combining UHV STM experiments and DFT calculations. We proved that the shortening of nearest neighbor distance of nano molecular arrays is somehow related to the deformation of orbital as revealed by our DFT calculation based detail analysis. Our finding can be used to improve the identical nano scale structures for miniature devices such as photovoltaic devices and single-molecular transistors.

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