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CHARACTERIZATION AND MANIPULATION OF NANOSTRUCTURES BY A SCANNING TUNNELING MICROSCOPE

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Abstract. The recent rapid advances in nanotechnology are due in large part to our newly acquired tools in measuring and manipulating nanostructures, even individual atoms or molecules. As a class of useful tools, scanning probe microscopy, especially scanning tunneling microscopy, provides us the special method to describe the locally physical and chemical properties of nanostructures, and even help us to manipulate nanostructures for constructing new nano-scale apparatus. Here we report our studies on fullerene molecules and quantum dots by using a ultra-high vacuum low-temperature scanning tunneling microscope with emphases on the following aspects: identifying orientational configurations of individual fullerene molecules on different material surface; novel topological order in 2-D C_{60} domains; single molecule manipulation and negative differential resistance molecular device involving two C_{60} molecules; size-dependent single electron tunneling effects in 2-D Au clusters; tunable single electron tunneling behavior of ligand-stablized 3-D gold particles; and electrochemical capacitance of a width-variable nano-junction.

1. INTRODUCTION

Scanning probe microscopy (SPM) has fundamentally changed the way that we deal with the nanoworld by its abilities of "seeing" and "moving" atoms and individual molecules directly. Concomitant developments in experiment and theory have allowed an extended range of nanostructures to be studied, and have demonstrated exciting physical, chemical, mechanical and electronic phenomena. In the longer term, SPM will evolve into inexpensive, easy-to-use sensors and/or diagnostic devices with broad applications. Utilizing tunneling current intensity as a parameter of adjusting tip coordinate, scanning tunneling microscope (STM) achieves the highest spatial resolution and also can probe electronic phenomena. Since STM was invented, it has already displayed huge potential in characterization and manipulation of nanostructures, such as distinctly showing the electronic properties of single-walled carbon nanotubes [1]; forming and observing quantum mirage [2]; constructing single molecular amplifier [3]; inducing all steps of a chemical reaction [4].

In the following, we will present our studies on fullerene molecules and metal quantum dots by using an STM. Single molecules and metal quantum dots are two typical systems of nanostructures, and their physical, chemical, mechanical and electronic properties are markedly influenced by various phenomena on the nanometer scale, such as quantum effects. Single molecules are of interest as they exhibit discrete, abundant electronic states with relatively stable atomic configuration, and participate in physical and chemical procedures as comparatively independent units. Metal quantum dots are commonly considered as model systems and can be used to explore quantum effects on the nanometer scale, such as single electron tunneling. Therefore, we classified our paper into two sections:

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STM imaging and manipulation of single fullerene molecules, and single electron tunneling and Coulomb blockade effects in metal quantum dots.

2. PHYSICS AND CHEMISTRY WITH SINGLE FULLERENCE MOLECULES

An active research field in nano-science and technology is single molecular physics and chemistry. It is our aim that new types of materials and molecular functional apparatus can be devised and constructed by controlling and manipulating single molecules according to our will. As a unique species, fullerene molecules have shown tremendous potential in single molecular science research and application. The elegant cage structure of C_{60} molecule brings the C_{60} solid many interesting physical and chemical properties [5]. In addition to the translational orders in the traditional solids, there are also molecular orientational orders in a C_{60} solid, which is a basic issue for studying the fullerene-based materials. On the other hand, C_{60} molecules form an interesting new family of adsorbates on surfaces because of their three-dimensional character on the atomic scale. A unique fundamental property of this type of adsorbates is various possible molecular orientations with respect to the host substrate. Here we report our experimental studies of identifying orientational configurations of the C_{60} molecules on different surfaces and manipulation them for constructing single molecular device using low temperature STM.

Identifying orientational configurations of the C_{60} molecules. The STM images of individual C_{60} molecules on a Si(111)-(7×7) surface are site and bias voltage dependent. At all adsorption sites, our results of tunneling spectroscopy indicated that strong interaction between Si and C_{60} leads to the mixing of the C_{60} molecular orbitals with the Si surface states. We also found that the local density of states (LDOS) of the adsorbed C_{60} molecules was site dependent and the result was attributed to the different surface atom arrangements and dangling bonds configurations. Because of this strong interaction, the electronic structure of C_{60} molecule is modulated, and a stripe-like internal structure in the negative bias STM images was observed. On the contrary, we found that the positive bias STM image is almost the same as that of a free C_{60} molecule. Combined with the local density approximation (LDA) calculations we have shown that the molecular orientation of the adsorbed fullerenes with respect to the Si substrate can be determined unambiguously [6].

For C_{60} molecules on the surface of a multilayer C_{60} island with a (111) terminating plane, a (2×2) superlattice, which resulted from orientational order of the molecules, was observed by STM at low temperature. In each unit cell of the superlattice, one three-lobe and three dumb-bell like intramolecular patterns of the C_{60} molecules were clearly resolved. In combination with the theoretical analysis and simulation, the orientational configurations of the C_{60} molecules in (2×2) superlattice are determined [7].

Novel topological order in 2-D C_{60} domains. In contrast to the relative strong interaction of C_{60} molecules with Si and C_{60} surfaces, we found that a C_{60} array on a self-assembled monolayer (SAM) of alkylthiol is an ideal 2D model system. When the sample is cooled down to 5K, all C_{60} molecules in STM image with negative sample tunneling voltage (Fig. 1a) reveal an identical internal fine structure that closely matches the well-known cage structure. We observed difference of brightness between the stripes corresponding to C-C single and double bond in STM image. This is the first time that the C_{60} native cage structure has been seen in the STM, and even chemical bonds can be resolved. Moreover, this C_{60} 2D array exhibits a novel topological order originating from the molecular orientations. STM images show the 2D C_{60} forms a domain structure where the correlation function of the molecular orientation within a domain is constant anywhere (i.e. every C_{60} has the same orientation), but changes abruptly at domain boundaries. It is remarkable, however, that both the positional order and bond-orientational order are fully preserved across domain boundaries (Fig. 1b). We believe that the novel to-

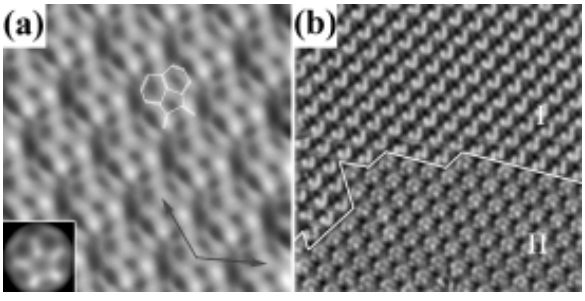

Fig. 1. a) STM image (35Å · 35Å) of a C_{60} lattice taken at 5K with -2.0 V sample bias (inset: theoretical simulation image); b) STM image (100Å · 100Å) of two molecular orientational domains and the domain boundaries.

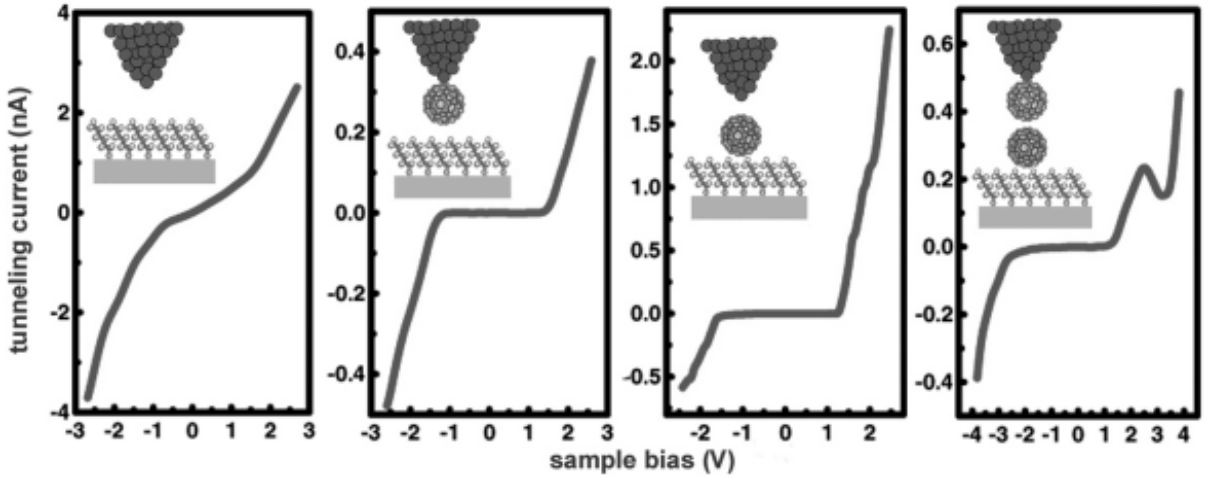

Fig. 2. The I-V curves obtained from four kinds of tunneling structures, as shown from left to right correspond to bare Pt–Ir tip over thiols, bare Pt–Ir tip over C_{60}, C_{60} tip over thiols, and C_{60} tip over C_{60}, respectively.

pological order observed here must be an intrinsic property of a 2D system [8].

Negative differential-resistance device involving two C_{60} molecules. The negative differential resistance (NDR) effect, which is characterized by the phenomenon of decreasing current with increasing voltage in the I-V curves, is the essential property of electronic devices such as Esaki tunneling diode. It has been shown experimentally and theoretically that atomic-scale NDR could arise in the tunneling structures with the tip of a STM and a localized surface site when the LDOS of them have adequately narrow features. The high symmetry of a free C_{60} molecule leads to the high-degenerate and narrow-featured LDOS. Using this property, we realized the NDR molecular device involving two C_{60} molecules by attaching one C_{60} molecule onto STM Pt-Ir tip and positioning this tip on another molecule physically adsorbed on the SAM. Such controllable tunneling structure and the associated known electronic states ensure the stability and reproducibility of the NDR device (Fig. 2) [9]. The simulated result of positive bias range agrees well with the experimental result, but NDR is found to be absent in the negative bias range. It is probably because that the unoccupied states are more extended than the occupied states of the tip-C_{60}. This assumption is reasonable considering the facts that C_{60} orbitals mix mainly with the localized d orbitals of Pt atom of tip in the occupied states and mix mainly with the extended s orbitals in the unoccupied states. This assumption is confirmed by further calculations.

3. SINGLE ELECTRON TUNNELING AND COULOMB BLOCKADE EFFECT IN METAL QUANTUM DOTS

Single-electron tunneling (SET) has been proposed as the basis of digital nano-electronics, including the key components for logic and memory devices [10]. Many efforts have been made both to reveal the physics of SET and to fabricate new types of SET devices. Of the many previous studies of the Coulomb blockade (CB) effect, only a few experiments used particles with well-characterized sizes. It is still a challenge to correlate the SET behavior with the particle size experimentally, even though it is well-known that both the single-electron charging energy and the discrete quantum energy levels are size-dependent. STM/scanning tunneling spectroscopy (STS) is a powerful tool for studying the SET behavior of particles with different sizes at nanometer scales in the double barrier tunneling junction (DBTJ) geometry. Moreover, the environmental parameters such as tip-particle distance can be easily adjusted.

Size dependent SET effect of two-dimensional gold clusters. By using STM/STS, we have systematically studied the current-voltage characteristics of 2-D Au clusters prepared by thermally deposited on alkanethiol SAM. The size of these 2-D clusters ranges from ~1 to ~10 nm in diameter, with a typical separation between the clusters of ~10 nm. The I-V curves display CB and Coulomb stair-

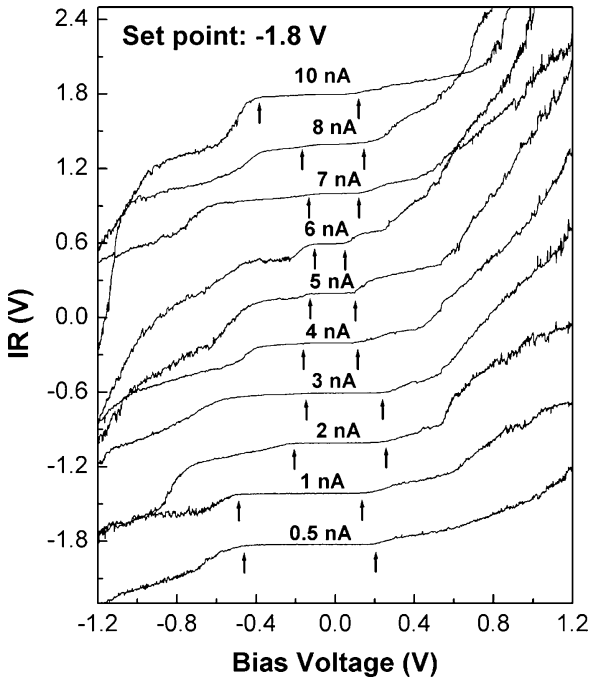

Fig. 3. A series of I-V curves taken at 5K for a 4 nm Au cluster at different set point tunneling current, where the vertical axis is rescaled by the set point tunneling resistance *R* for different set point tunneling current shown in figure. The CB width is indicated by arrows for each I-V curve. The curves are shifted vertically for clarity.

case with asymmetric behavior. The zero conductance gap width as a function of cluster size was measured, and it was found to be not consistent with parallel plate model calculation. We have developed a new approach, in which the 2D Au island is treated as metallic in the planar direction but non-metallic in the normal direction. The calculation result based on this model is in excellent agreement with experimental data. Moreover the calculation result based on the isotropic dielectric constant model is noted to be larger than the experimental data. Our approach can be shown to be equivalent to the orthodox theory in determining the gap width, but with the advantage to include the cluster anisotropy [11].

Tunable single-electron tunneling behavior of ligand-stablized gold particles. Ligand-stabilized 3-D gold particles from ~1.8 to ~15 nm were synthesized by the well-established two-phase method and heptanethiol was used as the stabilizing ligand. For ligand-stabilized 3-D gold particles, the SET behavior correlates well with their size, and can be fully accounted for by the theoretically calculated capacitances. Only the CB effect, e.g., equidistant spaced staircases, was observed in the I-V curves for gold particles with nominal sizes > 4.6 nm, for which the fitting capacitance values complied very well with the calculated results. For gold particles with a small core size (nominal 1.8 nm), a series of irregularly spaced current steps are observed, which is interpreted as originating from the discrete energy levels due to quantum size effect. By varying the distance between the STM tip and the particle through adjusting the set point current, the voltage spacing of Coulomb staircases can also be tuned within a certain range. Our experiment clearly shows that the SET behavior can be tuned through changing the particle size or adjusting the environmental parameters of the particles [12].

Electrochemical capacitance of a width-variable nano-junction. Being different from macro- and micro-structures, the capacitance of a nano-junction also can be affected by quantum effects in addition to the geometry and dielectric constant as theoretical studies have shown. But no experiment has been made to demonstrate these quantum effects.

We constructed a nanometer-sized DBTJ formed by positioned a STM tip above a 2-D Au cluster which resides on top of an alkanethiol SAM on Au(111), and did the first experimental attempt to investigate the capacitance behavior of this DBTJ [13]. By decreasing the STM tip-cluster separation *d*, it was observed that the capacitance first increases and then decreases at short separation (via the CB effect) (Fig. 3). The latter phenomenon is clearly non-classical behavior. The quantum effect was considered to be a possible mechanism for it: the capacitance is approximately satisfied by the formula: $1/C \propto 1/C_0+1/D_I+1/D_{II}$, where C_0 is the classical contribution based on geometry, D_I and D_{II} are the scattering local partial DOS (LPDOS) in the electrodes. When *d* is deceased to be so small that $1/C_0<1/D_I+1/D_{II}$ ($1/C_0 \propto d$), the quantum tunneling effect begins to dominate. LPDOS not only depend on the electrodes themselves but also on the geometry and the width of the barrier, and qualitatively are proportional to the dwell time of the electron in the nano-junction. When *d* is small enough, the dwell time is expected to be short since the electron can go through the barrier easily, which results in the increase of $1/D_I+1/D_{II}$ when *d* decease. This argument leads to a complicated *d*-dependent capacitance *C*.

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