Communication

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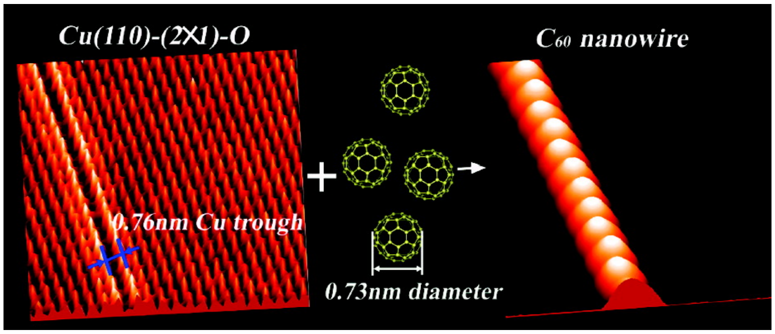

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Nanoscale Templating of Close-Packed C_{60} Nanowires

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The search for methods of fabrication of one-dimensional (1D) supramolecular nanostructures of organic semiconductors is being pursued vigorously because of their exotic electronic behavior and potential applications.[1] The linear chains of fullerene represent reduction of the supramolecular concept to its lowest dimension with potentially rich transport properties derived from fullerene solids.[2] C_{60} molecules have been assembled into 1D structures by various means such as incorporation into nanotubes, by using alkane side-chain interactions and structured molecular films, and with Au chain templates on the Ni(110) surface.[3] These studies show that preformed templates are beneficial for assembling ordered 1D nanostructures of C_{60} molecules.

We investigate the Cu(110)-(2 × 1)-O reconstructed surface as a possible template. Oxygen interacts strongly with the Cu(110) surface forming O−Cu−O rows oriented along the <001> direction with Cu atoms added in bridging positions between adjacent O atoms. As oxidation approaches a full monolayer coverage, the O−Cu−O rows form a periodic "supergrating" composed of nearly perfect (2 × 1)-O domains cut by occasional bare Cu(110) regions.[4] The dosing conditions define the width of the Cu regions. Pederson et al. have found a strong preference of C_{60} molecules to adsorb on the Cu regions of such supergratings.[5] With the width-adjustable Cu trough template and preferential adsorption in mind, we, therefore, asked if C_{60} molecules would self-assemble into nanowires on bare Cu regions of one atom width? Our experimental finding of the self-organization of linear, closed-packed, single molecule wide C_{60} wires in Cu troughs confirms the hypothesis.

The Cu(110)-(2 × 1)-O surface is formed by dosing 6.8 Langmuir of high purity O_2 on clean Cu(110) at 250 °C. Figure 1a1 shows the resulting surface composed of >100 nm wide oxide domains interrupted by 0.76 nm wide, atomically perfect, linear, one atom wide bare Cu gaps. According to the schematic representation in Figure 1a2, the gap between the oxide domains corresponds to $3a_0$, where a_0 is the 0.25 nm interatomic Cu−Cu distance along the $\langle 1\bar{1}0 \rangle$ direction.[4] The width of the gap is quite near the hard-sphere diameter of C_{60} molecules (0.73 nm).

On top of this surface we sublimate C_{60} molecules (99.9% purity, Aldrich) from a resistively heated evaporator. STM constant current topographic images are acquired using a typical current of 0.1 nA and bias voltage of 0.45 V. The d*I*/d*V* images are acquired by positioning the STM tip at each point at constant current. The d*I*/d*V* spectra are then measured using the standard lock-in method. All STM measurements are performed at 77.3 K.

Figure 1b1 shows an STM topographic image representative of adsorption of C_{60} molecules at the surface temperature of 80 °C. With this procedure, the majority of the C_{60} molecules assemble into 1D structures along the Cu troughs. This confirms the strong preference of C_{60} molecules to adsorb on the bare Cu domains.[5]

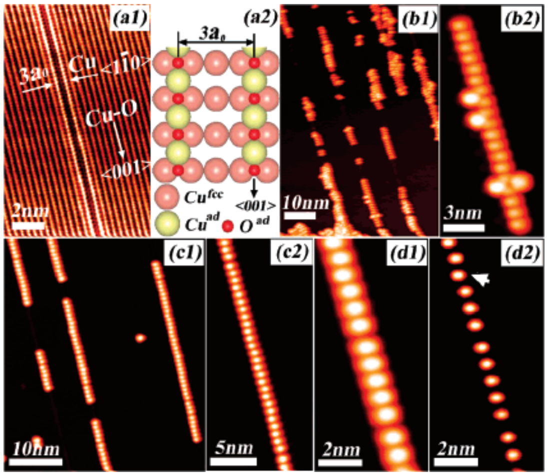

Figure 1. (a1) High-resolution STM topographic image showing a $3a_0$ wide (a_0 = 0.25 nm) Cu trough aligned in the $\langle 001 \rangle$ direction cutting two domains of the O−Cu−O added rows; (a2) schematic illustration of the atomic structure of the Cu troughs; (b1) the partial self-assembly of C_{60} molecules into 1D structures after deposition onto the "supergrating" at 80 °C; (b2) C_{60} molecules decorating the edge of the main 1D structure before annealing; (c1) STM topographic image showing perfectly organized, closed-packed C_{60} nanowires after annealing the sample at 250 °C; (c2) a representative C_{60} wire consisting of 26 molecules; (d1) STM image showing the arrangement of C_{60} molecules in an ordered pentamer and a "disordered" hexamer, which are separated by a one unit cell gap (0.36 nm); (d2) the white arrow highlights the ostensibly displaced C_{60} molecule in the "disordered" hexamer in a lower contrast image.

Such structures, however, have many defects with molecules adsorbing on the oxide layer next to the main 1D structure (Figure 1b2). The regularity of structures is greatly improved by high-temperature annealing. After annealing at 250 °C, long linear C_{60} wires are formed (Figure 1c1), indicating that C_{60} molecules flow into more favorable structures with optimal molecule−metal and intermolecular interactions, leading to the formation of close-packed 1D wires. Dosing C_{60} molecules directly at high temperature leads to similar results. C_{60} wires with lengths exceeding 100 nm are obtained in the experiments. Because on wider Cu troughs at a lower surface oxidation level, C_{60} molecules form a distorted hexagonal phase with the preferred aggregation direction along the $\langle 1\bar{1}3 \rangle$ azimuth,[5] the 0.76 nm Cu troughs are essential for self-assembling into wires. Lower evaporation speed is also important for long wire formation.

Figure 1d1 shows a high-resolution STM image of a linear C_{60} pentamer and hexamer. The average nearest-neighbor distance of 1.07 ± 0.02 nm is three times the Cu−Cu distance (0.36 nm) along the $\langle 001 \rangle$ direction. The pentamer and hexamer are separated by the same 0.36 nm interval. This intermolecular distance within a chain is ~7% larger than in C_{60} solid (1.005 nm),[6] indicating close packing of C_{60} molecules within nanowires.

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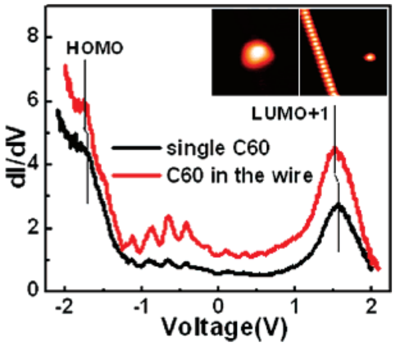

Figure 2. Typical dI/dV spectra acquired on a single C$_{60}$ molecule and a molecule in the middle of a wire. Spectra were recorded at the center position of the molecules. Tunneling parameters were $V = 1.0$ V, $I = 0.08$ nA before taking the spectra. The dominant peaks correspond to HOMO (−1.7 V) and LUMO+1 (1.55 V) states. Smaller peaks around −0.8 V are not identified and also appear in the spectra of the O/Cu(110) substrate. The LUMO state expected around E_f is not evident.[7] The STM topographic images in the insets show the single C$_{60}$ molecule and C$_{60}$ wire.

It is of particular interest to learn how the electronic properties evolve from single C$_{60}$ molecules to 1D molecular wires. Typical dI/dV versus V spectra for an isolated C$_{60}$ molecule and within a molecular wire are shown in Figure 2. Two dominant molecular states, HOMO and LUMO+1 appear strongly in the spectra.[7] An energy downshift of 30∼40 meV is observed when C$_{60}$ molecules assemble into wires. The small shift, implying weak intermolecular interaction is not surprising since the HOMO and LUMO+1 are localized molecular states. The delocalization is strongly state dependent, with certain higher states exhibiting free-electron like delocalization along the wire.[8]

When presented with decreased contrast, the pentamer in Figure 1d looks perfectly regular, while the hexamer has one C$_{60}$ molecule displaced from the line defined by the remaining molecules. Such “disorder” is present in most C$_{60}$ wires, and cannot be healed by further annealing. Imaging the spatial distribution of the LUMO+1 state, in Figure 3, reveals that the displacement is a manifestation of the orientation of the C$_{60}$ molecule in two equivalent adsorption configurations. Figures 3a1 and 3a2 show the topographic and the dI/dV images at the LUMO+1 energy of a single C$_{60}$ molecule located in the Cu(110) trough. The dI/dV image shows a “distorted bright-ring” structure with a “dark ear” to its left. The bright ring and dark ear are associated, respectively, with the LUMO+1 local density of states of adjacent pentagonal and hexagonal carbon rings on the C$_{60}$ shell.[7] The presence of one prominent dark ear is consistent with 5−6 bonding where the pentagonal ring is tilted slightly to the right from the surface normal, bringing the hexagonal ring up into view.[9] A model for such a tilted C$_{60}$ molecule is shown in the inset to Figure 3a2. Here the carbon pentagon tilts off normal to the $\langle 1\bar{1}0\rangle$ azimuth. Figure 3 panels b1 and b2 show that in the ordered wire, the dark ear feature is present on the same (left) side of the wire. Figure 3 panels c1 and c2 by contrast reveal a left-right alternation of the dark-ear feature, characteristic of a disordered wire. The asymmetric dI/dV spatial distribution is postulated to arise if the C$_{60}$ molecule is bound into the Cu trough through the 5−6 C−C bonds oriented along the $\langle 001\rangle$ azimuth.[9] Because the C$_{60}$ molecule bonding to the surface is independent of orientation, the inline and displaced molecules have the same dI/dV spectra. The fact that we find ordered wires indicates some preference for C$_{60}$ molecules to assume orientational order, but the energy gained by ordering must be much less than the barrier to reorientation.

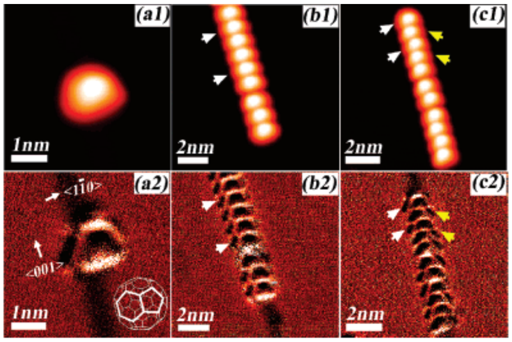

Figure 3. Panels a1, b1, and c1 show STM topographic images, respectively, of single C$_{60}$ molecule, ordered, and disordered C$_{60}$ wires. (a2, b2, and c2) The corresponding dI/dV images of the LUMO+1 peak (1.55 V). The dI/dV map of a single C$_{60}$ molecule reveals the top pentagon (distorted bright ring) and, to its left, the adjacent hexagon (dominant “dark ear”) representative of the asymmetric 5−6 bond adsorption of C$_{60}$ molecules on Cu(110). The asymmetric bonding allows two adsorption orientations. C$_{60}$ molecules form an ordered wire when the adsorption orientation is the same for every molecule (identified by arrows in panel b2). Random orientational (identified by arrows in Figure 3c) creates the apparent disorder in topographic images. The dI/dV maps reveal that its origin is in the orientation rather than displacement of C$_{60}$ molecules. In the perspective view of a 5−6 bond adsorbed C$_{60}$ molecule in the inset to panel a2, the upper pentagon−hexagon rings are shown as solid lines.

In summary, we present a simple approach to produce close-packed C$_{60}$ wires on a Cu(110)-(2 × 1)-O supergrating template. C$_{60}$ molecules self-organize into long 1D structures over large distances. This method may also be applicable for other fullerenes and large organic molecules, with a strong preference to bond on exposed Cu-metal troughs. The self-assembled structures offer a means to study 1D electronic properties of organic conductors.

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