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Template Ordered Open-Grid Arrays of Paired Endohedral Fullerenes

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Developing useful molecular systems, such as planar networks of molecules for novel molecular-electronic architectures,[1−4] requires the ability to control the way molecules assemble at surfaces. Many techniques exploit non-covalent directional bonding interactions between molecules, such as hydrogen bonding, to facilitate the molecular assembly process.[5−9] However, if the molecules lack such directional bonding attributes then it becomes difficult to develop novel molecular architectures using this approach. Fullerenes[10] are molecules that do lack these directional bonds but are otherwise very attractive candidates for molecular based nanotechnologies. Endohedral fullerenes[11] are of particular interest in this area, because the atomic species bounded within the fullerenes could be manipulated for storing and processing bits of information. For example, the magneto-optical activity[12] of the $Er_3N@C_{80}$ molecule[13] (Figure 1a) may prove useful in solid-state quantum information processing systems.[2−4,14]

Overcoming the challenge of coercing endohedral fullerenes to order into useful spatial configurations can be achieved through template-assisted assembly. A successful template requires the surface to be made up of patterned arrays of bonding sites for the fullerenes to adsorb onto. Impressive demonstrations of this have been achieved using pre-assembled molecular templates on metal or metal-terminated substrates.[15−18] Here we report how oxide crystal surfaces can be used as a template to controllably order endohedral fullerenes into two-dimensional (2D) open-grid arrays. This is compared to the ordinary close-packed ordering of endohedral fullerenes. The template is a nanostructured surface phase of (001) strontium titanate,[19] and the endohedral fullerenes are $Er_3N@C_{80}$ molecules[13] (Figure 1a).

The surfaces are prepared through an Ar^+ sputtering and annealing procedure, described in earlier work,[19] on 0.5%-weight Nb-doped $SrTiO_3$(001) single crystals in ultrahigh vacuum (UHV) conditions. $Er_3N@C_{80}$ molecules, or fullerenes, were deposited onto the surfaces from the vapor phase. Createc Knudsen cells, heated at 480 °C, were used to evaporate $Er_3N@C_{80}$ molecules for 20−30 min, allowing 0.15−0.20 monolayer coverage for each deposition. $Er_3N@C_{80}$ has advantages over other endohedral fullerenes[3,4] (e.g. $N@C_{60}$) in that $M_3N@C_{80}$ species (M = metal forming a planar M_3N species) are thermally stable[20,21] and can be readily evaporated onto heated substrates in UHV. The template patterns and molecular ordering are investigated through UHV scanning tunneling microscopy (STM) at room temperature. Etched W tips are used for imaging the sample surfaces at room temperature with a bias voltage applied to the sample.

Close-packed surface ordering of fullerenes is achieved on a c(4 × 2) surface reconstruction,[22,23] as shown in the STM images of Figure 1b,c. The c(4 × 2) surface was formed by annealing at 1090 °C for 30 min after sputtering. $Er_3N@C_{80}$ is deposited on the c(4 × 2) reconstructed surface with the surface heated at 250 °C to allow diffusion of the molecules. The height of the fullerene islands are typically on the order of 1 nm, while the close-packed periodicity of the fullerenes averages 1.19 ± 0.03 nm. There appears to be no epitaxial relationship between the $Er_3N@C_{80}$ islands and the underlying c(4 × 2) reconstruction.

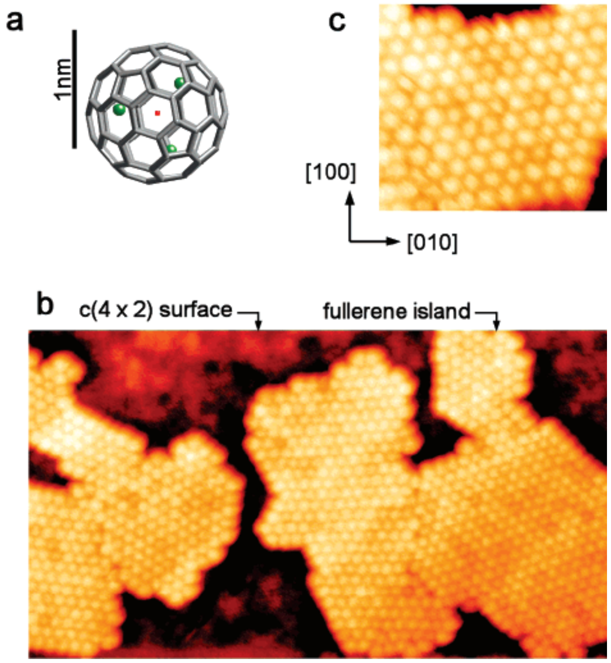

Figure 1. Close-packed ordering of endohedral fullerenes. (a) The $Er_3N@C_{80}$ molecule (Er = green, N = red); STM images of (b) $Er_3N@C_{80}$ molecule islands on a $SrTiO_3(001)$-c(4 × 2) terrace (55.4 × 31.3 nm^2; V_s = +1.6 V; I_t = 0.10 nA) and (c) a close-up of close-packed ordering in a $Er_3N@C_{80}$ molecule island (13.2 × 12.0 nm^2; V_s = +2.0 V; I_t = 0.30 nA).

The open-grid ordering of fullerenes is achieved on a template made of 2D arrays of trenches with highly ordered crosslike structures along them (Figure 2a). These trench arrays, termed waffles,[19] have an associated (6 × 8) surface periodicity. They can be formed after sputtering and repeated annealing (>1 h) near 945 °C and cover about one-sixth of the surface. Waffle structures decorated with $Er_3N@C_{80}$ are shown in Figure 2b. Fullerenes preferentially fill up the waffles in pairs. The pairs are aligned in the same [010] direction and spatially arranged in a repeated rectangular fashion, with a 3.10 × 2.35 ± 0.05 nm^2 unit cell. This corresponds to the (6 × 8) periodicity of the underlying waffles and is illustrated in the profiles of Figure 2c. The 2D ordering extends over distances limited only by the size of the waffle domains. Fullerenes “fit” into the waffles in a similar way to eggs fitting into an egg carton, though two fullerenes, and not one, fit into each void. Occasionally, larger separations between cross-links in the waffle structure are observed, and in these circumstances more than two fullerenes may fit in the trench. This can be seen in Figure 2b where most of the fullerenes appear as pairs, but four fullerene triplets can also be seen.

These results illustrate how topographic features of a substrate induce fullerenes to assemble into unique configurations. Molecule−

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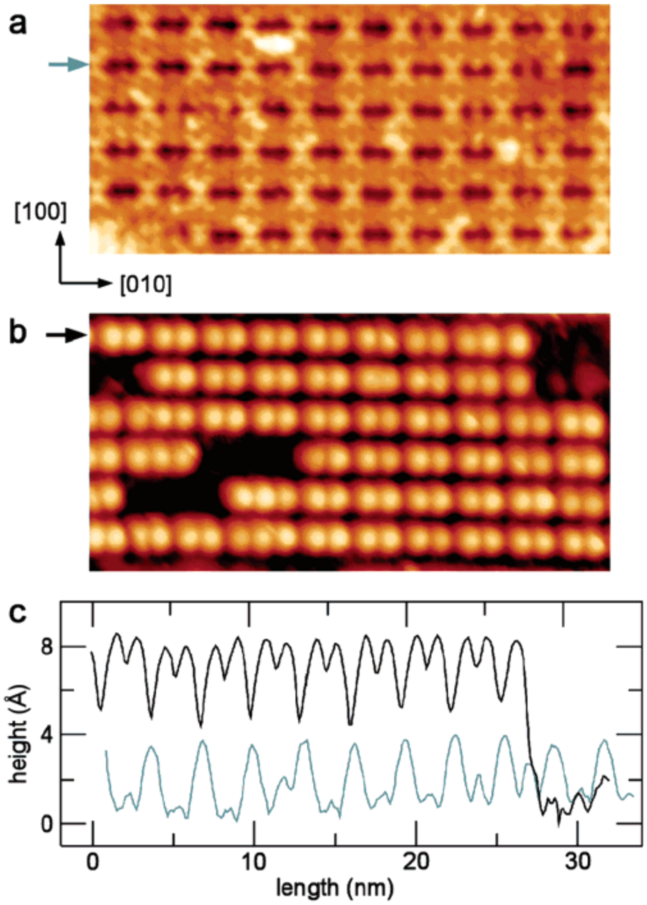

Figure 2. Open-grid arrays of paired endohedral fullerenes. STM images of (a) a template based on a $SrTiO_3$(001)-(6 × 8) "waffle" surface and (b) a self-organized 2D fullerene array that coincides with the topology of the waffle template. The profiles in panel c are drawn from where the corresponding arrows point to the STM images in panels a and b. Imaging parameters: (a) 31 × 16 nm^2; $V_s = +0.8$ V; $I_t = 0.3$ nA; (b) 31 × 16 nm^2; $V_s = +3.0$ V; $I_t = 0.1$ nA.

molecule interactions normally cause fullerenes to form close-packed structures on flat surfaces (Figure 1). However, for substrates that exhibit pronounced topographic features of similar dimensions to the fullerenes, other assembly configurations become possible. Such is the case for the (6 × 8) waffle surface of Figure 2, where substrate−molecule interactions drive fullerenes to assemble into 2D open-grid arrays. This assembly technique leads to systems that are coincident with the periodicity of the substrate and are stable at room temperature. Other fullerene molecules, such as C_{60}, can be substituted for, or mixed with, the $Er_3N@C_{80}$, enabling a variety of different fullerene assemblies to be engineered. Given the high dielectric, normally insulating, and optically transparent properties of $SrTiO_3$, there is potential for using this architecture as a foundation for developing novel molecular devices, such as cellular automata systems and solid-state quantum information processors.[2−4]

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