C_{70} ordering on nanostructured $SrTiO_3(001)$

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The nanostructured (7 × 4) surface of $SrTiO_3(001)$ is used as a template to order C_{70} into single-molecule-wide chains and linear islands.

Chemical self-assembly of atoms and molecules on surfaces plays a central role in prospective nanotechnologies.[1,2] For example, molecular electronic memory devices could be assembled from arrays of carbon nanotubes on surfaces,[3] and cellular automata computers could be made from regularly arranged grids of fullerene molecules.[4,5] Developing such systems requires the ability to controllably deposit, and efficiently order suitable molecules into useful configurations. Nanostructured surfaces, with appropriate chemical characteristics and structural patterns, can act as templates to assist the molecular assembly process. The molecules themselves must exhibit functional traits that can be exploited in potential technologies, and be compatible with the assembly process. Fullerenes[6] are among the most attractive molecules for surface-based assembly schemes because the cage-like characteristics of fullerenes enable them to host magnetic or optically active atoms within them.[7]

The $SrTiO_3(001)$ surface is a good candidate to investigate as a template for ordering molecules because slight changes in the surface stoichiometry gives rise to a wide range of surface structures[8–11] and ordered nanostructures.[12] Some of these surfaces have been shown to be effective templates for ordering molecules, including fullerenes.[13,14] Here we use atomic resolution scanning tunneling microscopy (STM) to demonstrate the ordering of C_{70} on a (7 × 4) nanostructured surface of $SrTiO_3(001)$. The results are compared to C_{70} island assembly on a flat c(4 × 2) reconstructed surface of $SrTiO_3(001)$.

The (7 × 4) nanostructured surface is one of a collection of nanostructured surface phases of $SrTiO_3(001)$.[12] These nanostructured phases are mostly made of Ti^{+4}-rich species. The nanostructures typically form in domains, covering the surface, and exhibit different surface crystallography including the (6 × 2), (9 × 2), (12 × 2), (6 × 8), and (7 × 4) periodicities. The (7 × 4) surface is made of protruding 'crossdot' nanostructures that align themselves into ordered 2D arrays.[12]

The substrates are 0.5%-weight Nb-doped $SrTiO_3(001)$ single crystal samples, supplied by PI-KEM Ltd UK. After introducing the samples into a JEOL UHV STM, model JSTM 4500s, they are degassed through resistive heating and annealed for several hours. The template-making process, described in detail elsewhere,[12,14] involves argon ion sputtering at 0.5 keV, and subsequent annealing in UHV between 700 °C and 900 °C. Temperature measurements are made with an optical pyrometer. c(4 × 2) surfaces are prepared by sputtering and subsequent annealing at 780 °C for 2 h. Nanostructured (7 × 4) surfaces, made from cross-dot arrays, are prepared by sputtering and subsequent annealing at 870 °C for 3 h.

C_{70} was supplied by M.E.R. Corporation (Tuscon, Arizona, USA), with a nominal purity of 99%. The C_{70} was further purified to >99.9% through high performance liquid chromatography (HPLC), and transferred into Createc Knudsen cells on the STM system. The Knudsen cells, degassed and then heated at 360 °C, were used to evaporate C_{70} molecules for 10–60 min. 0.05–0.50 monolayer coverage was achieved for each deposition. Samples were heated between 150 °C and 180 °C during the deposition process. The template patterns and molecular ordering were investigated through UHV STM. Etched W tips were used for imaging the sample surfaces at room temperature with a bias voltage applied to the sample.

Experiments of C_{70} ordering were first performed on the c(4 × 2) reconstruction of $SrTiO_3(001)$. The c(4 × 2) surface, which is well characterized,[10,11] is shown with high resolution STM in Fig. 1a. Features of the c(4 × 2) reconstruction can be resolved and a step-edge that zig-zags in the [100] and [010] directions can be seen. C_{70} is deposited on the c(4 × 2) surface heated at ~180 °C for 35 minutes. Fig. 1b shows a room temperature STM image of the c(4 × 2) surface covered in 0.3 monolayers of C_{70}. Clusters of C_{70} form islands that are just a few molecules across, are 0.8 nm in height, and contain molecules with a close-packed separation (van der Waals diameter) of 1.0 ± 0.1 nm. Some molecules in the islands are not close-packed, and the orientations of the islands appear random.

The nanostructured template used to order C_{70} is illustrated in the STM image of Fig. 2a. The surface is made up of arrays of

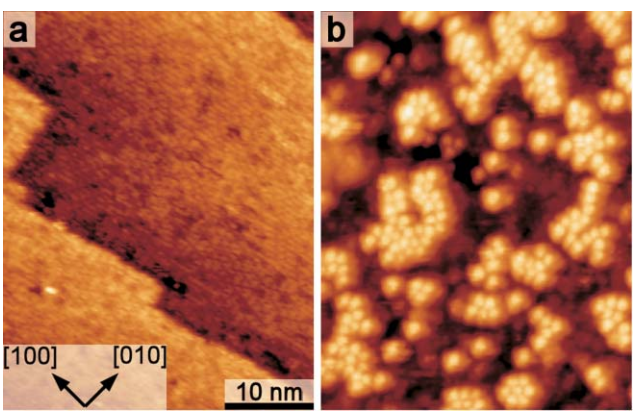

Fig. 1 Close-packed ordering of C_{70}. STM images of: (a) the c(4 × 2) reconstructed surface of $SrTiO_3(001)$, and (b) C_{70} islands deposited on the c(4 × 2) surface. Imaging conditions: (a) V_s = +0.9 V, I_t = 0.06 nA; (b) V_s = +2.6 V, I_t = 0.10 nA.

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'crossdots' that form the (7 × 4) overlayer.[12] Crossdots are protrusions on the $SrTiO_3$(001) surface, and exhibit crosslike features which are uniform in shape and orientation. Arrays of crossdots order in two-dimensions, creating the (7 × 4) surface pattern (which are structurally different from the 'waffle' structures used in a previous study[13]). Upon an initial deposition, where C_{70} coverage is around 0.05 monolayers, linear one-molecule-wide chains of C_{70} form on top of a line of crossdots, as shown in Fig. 2b. The direction of the molecular chain corresponds to the direction in which the underlying crossdots exhibit a ×4 periodicity, *i.e.* the [100] direction in all the images of Fig. 2. Here, the C_{70} molecules are situated centrally in between two crossdots in the ×4 direction. The periodicity along the chain is 1.56 ± 0.03 nm, or 4 times the lattice parameter of $SrTiO_3$. These chains typically reach 8 to 10 molecules in length. Two-molecule-wide clusters of C_{70} can also be observed, as demonstrated in the STM image of Fig. 2c. For these clusters, chains of C_{70} also assemble on top of a line of crossdots, typically reaching lengths of three molecules. The second adjacent row of C_{70} in the clusters are situated in the valleys between two lines of crossdots, as shown by the arrows in Fig. 2c.

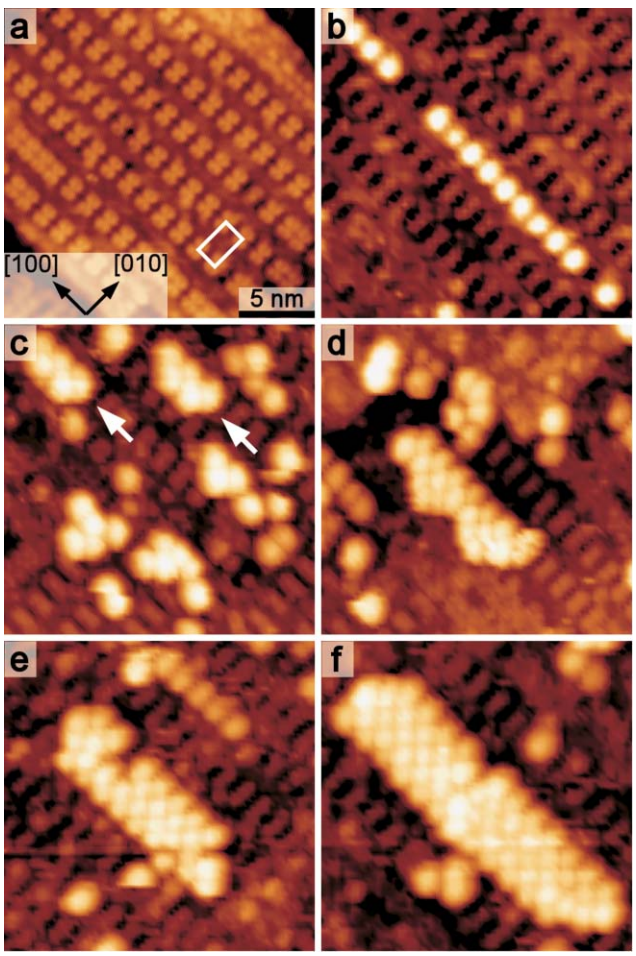

Fig. 2 Growth of epitaxial C_{70} islands on the nanostructured template. STM images of: (a) the naked surface of $SrTiO_3$(001) made up of crossdot arrays with the (7 × 4) periodicity (white rectangle), (b) a one-molecule-wide chain of C_{70} molecules assembled on top of a row of crossdots, (c) several clusters of C_{70} including two-molecules-wide clusters (pointed out with arrows), (d) three-molecule-wide island of C_{70}, (e) four-molecule-wide island of C70, (f) five-molecule-wide island of C_{70}. Imaging conditions: (a) V_s = +1.0 V, I_t = 0.10 nA; (b) V_s = +2.6 V, I_t = 0.10 nA; (c–f) V_s = +2.3 V, I_t = 0.10 nA.

Upon further C_{70} deposition, where coverage reaches up to 0.10 monolayers, the chains and clusters of C_{70} lengthen and widen to form islands. The island shown in the STM image of Fig. 2d is 7 molecules long and reaches three molecules in width. One of the rows of molecules is aligned centrally on a line of crossdots, in the same way that the one-molecule-wide chains are situated in Fig. 2b. Fig. 2e shows a C_{70} island which is 4 molecules wide. The widest islands observed reach a width of 5 molecules, as shown in Fig. 2f. The centre-to-centre separation between adjacent rows is 0.93 ± 0.07 nm, for islands that are 4 and 5 molecules wide. The length of the islands are only restricted by the coverage of molecules deposited and the size of the underlying crossdot domain in the ×4 direction.

To analyze the results, it is instructive to first look at the close-packed geometry of C_{70} on a $SrTiO_3$(001) surface, which is achieved on the c(4 × 2) surface (Fig. 1). The structural features of the c(4 × 2) reconstructions are small compared to the size of C_{70} molecules. This enables the molecules to naturally assemble through molecule–molecule interactions and exhibit close-packing. The close-packed separation, measured at 1.0 ± 0.1 nm, is in agreement with other STM studies of C_{70} on semiconducting surfaces.[15–17] C_{70} islands, as with other fullerenes,[14] appear to have no epitaxial relationship with the c(4 × 2) substrate. Further, only small close-packed islands have formed among the almost random assembly of C_{70} molecules. The results thus show that a c(4 × 2) substrate has negligible influence on the ordering configurations of C_{70}.

A nanostructured (7 × 4) surface of $SrTiO_3$(001), on the other hand, strongly influences the way in which C_{70} molecules assemble (Fig. 2). The epitaxial relationship between the C_{70} arrangements and the crossdot arrays is apparent in the series of STM images from Fig. 2. At low coverage, C_{70} molecules assemble into one-molecule-wide chains, and two-molecule-wide clusters. The one-molecule-wide chains on crossdots create preferential bonding sites for a second row to form, hence enabling the creation of clusters. At greater surface coverage, the C_{70} orders into wider and longer islands. Islands of C_{70} are between three and five molecules wide. The maximum width observed is five molecules, or 4.6 ± 0.2 nm. A key question that arises from these results is; why do the C_{70} islands not grow beyond 5 molecules in width? In order to answer this question, it is useful to investigate the bonding sites on the substrate.

The preferential bonding site for the molecules are the spaces directly in between crossdots, centrally located along the centre-axis of a crossdot line (as in Fig. 2b), in the direction of the ×4 periodicity of the crossdot arrays (the [100] direction in the case of Fig. 2). This preferential bonding site is indicated as position K in Fig. 3. All the molecular islands include one row of molecules that sit directly along this preferred line of bonding sites. The two molecule-wide clusters, as well as the three- and four-molecule-wide islands illustrate that rows of molecules can also lie in valleys between lines of crossdots, adjacent to rows of molecules situated along the centre-axis lines of crossdots, *i.e.* in position L of Fig. 3. These adjacent rows of molecules exhibit a center-to-center separation of 0.93 ± 0.07 nm.

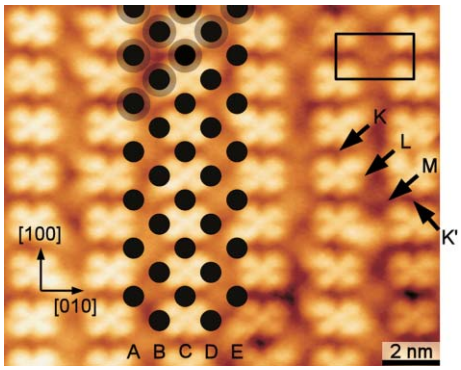

Fig. 3 Proposed geometry of the five-molecule-wide C_{70} islands. An STM image (V_s = +1.1 V, I_t = 0.10 nA) of the crossdot array surface fills the background. The rectangle illustrates the (7 × 4), or 2.73 × 1.56 nm^2 sized, unit cell of the surface. The dots depict the *x,y*-planar location of the C_{70} molecules. The opaque rings around the dots in the top area of the image indicate the 1 nm van der Waals diameter of C_{70}. The separation of the rows is 0.93 nm. Locations K, L, and M show the favoured bonding sites. Distances K–L and L–M are both 1.2 nm. Adjacent K and M sites are 0.87 nm apart, as indicated by the distance M–K′.

It is proposed that the five-molecule-wide C_{70} islands assemble as shown in Fig. 3. The locations of C_{70} molecules in the island are marked by the spots, collectively forming rows A through E. Row C represents the central row of molecules that align along the center axis of a crossdot line. Point K represents the generic bonding sites assumed by the molecules in row C. The other rows are situated in the valleys between crossdot lines. Rows B and D are equivalent, with molecules positioned at crossdot 'cusps', on the either side of the central crossdot line (pointed out by the generic location L). Rows A and E are equivalent, and are aligned with row C. However, the molecules in rows A and E are located in between corners, and not at the cusps, of two adjacent crossdots (point M in Fig. 3). Locations K, L, and M are sites that have a high bonding area between the molecule and the substrate. The sites thus exhibit binding strengths that overcome molecule–molecule interactions,[18] *i.e.* the π–π stacking forces that would otherwise cause C_{70} to assemble into close-packed islands instead of linear chains. If these three locations are the only surface bonding sites for C_{70}, then it is not feasible to add another row onto a five-molecule-wide island, as there is not enough room for the molecules to fit into nearby K- or M-type sites beside rows A or E. Hence, an island with more than five molecular rows cannot form.

In summary, it has been shown that a (7 × 4) nanostructured surface of $SrTiO_3$(001) can be used as a template to order C_{70} molecules into a number of linear configurations, including one-molecule-wide linear chains, two-molecule-wide clusters, as well as three-, four-, and five-molecule wide islands. Each configuration assumes a packing order that is commensurate with the substrate. The maximum width of a C_{70} assembly is observed to be around 4.7 nm, or 5 rows of C_{70}. An explanation for why these C_{70} islands do not expand beyond this width is given through analyzing the bonding sites of C_{70} on the (7 × 4) surface. The locations of the bonding sites are correlated to the size and geometry of the molecules in relation with the size and geometry of the substrate.

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