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Adsorption and manipulation of endohedral and higher fullerenes on Si(100)-2×1

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The adsorption of the endohedral fullerene, La@C_{82}, and the higher fullerene, C_{84}, on Si(100)-2×1 is investigated using a scanning tunneling microscope (STM) operating in ultrahigh vacuum. Both molecules are found to adsorb directly above the dimer rows that are formed on the Si(100)-2×1 surface, as well as in trough sites midway between dimer rows. Adsorption above dimer rows, not observed for C_{60}, is attributed to the larger radius of curvature of these fullerene cages. The response of La@C_{82} to manipulation by the tip of the STM is also investigated. Molecules in either adsorption site may be manipulated with a threshold gap impedance ~1.0 GΩ. Owing to a near-commensurability between the molecular diameter of La@C_{82} and the lattice constant of the Si(100) surface, close-packed arrangements of molecules may be formed.

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The properties of fullerenes and related materials continue to attract widespread interest, particularly in relation to electronic materials and crystal growth.[1] Transistors based on carbon nanotubes[2] as well as C_{60} thin films have been fabricated.[3] A further notable aspect of fullerenes is the demonstration of precise placement of single molecules using the tip of a scanning tunneling microscope (STM). This has been achieved for C_{60} on both semiconductor[4,5] and metallic[6] surfaces using a STM operating at room temperature. More recently these experiments have been extended to placement of the substituted fullerene derivative $C_{59}N$, which was positioned on the Si(100)-2×1 surface, and it has been speculated that endohedral fullerenes would also be susceptible to manipulation.[7] A particularly interesting aspect of the manipulation of endohedral fullerenes is that the fullerene cage acts as a molecular scale package that can be used to transport and position an encapsulated atom with nanometer scale precision. It has recently been suggested that this technique might be used to assemble nanostructures for quantum-information processing in which the electron or nuclear spin associated with the encapsulated atom acts as a quantum bit (qbit) of information.[8–10]

In this paper we investigate the adsorption of endohedral fullerenes using a STM operating at room temperature and demonstrate that these molecules are indeed susceptible to STM manipulation. We choose to investigate the properties of a La endohedral, La@C_{82}, adsorbed on Si(100)-2×1 and find that molecules are adsorbed in two possible sites positioned either directly above or midway between the dimer rows formed on this surface. The same adsorption sites are observed for the higher (nonendohedral) fullerene, C_{84}, indicating that the differences between these molecules and C_{60} are due to the size of the fullerene cage rather than the presence of the endohedral atom. Molecules in either adsorption site may be manipulated and close-packed pairs of molecules may be formed using manipulation.

The experiments were carried out using 6×3-mm^2 pieces of an *n*-type Si(100) wafer. Samples are loaded into an ultrahigh-vacuum (UHV) system, outgassed at ~800 °C overnight, then flash annealed to ~1200 °C for 60 s. This is followed by further annealing at 800 °C for ~10 min, after which the sample is allowed to cool to room temperature. This procedure results in a (2×1) reconstruction with a low defect density. STM images of the surface are acquired at room temperature using electrochemically etched polycrystalline W tips. The tips were cleaned in UHV by electron beam heating.

The preparation of the La@C_{82} and C_{84} charges is described elsewhere. Both molecular species are prepared by arc burning of graphite rods followed by isolation and purification using high-performance liquid chromatography (HPLC).[11,12] The purity of La@C_{82} was higher than 95%, while C_{84} contained a 2:1 mixture of the two most common isomers, D_2 and D_{2d}.

The La@C_{82} was dissolved in CS_2 and then loaded into a Ta crucible by allowing droplets of solution to dry. We estimate the total mass of the charge to be ~0.3 mg. This charge is thoroughly outgassed by annealing and then sublimed at 510 °C onto the clean Si(100)-2×1 surface, which was held at room temperature. The deposition rate was 0.1 monolayers (ML)/hour. The C_{84} (total mass of charge ~0.3 mg) was loaded in a similar manner and was sublimed at 455 °C at a rate of 0.005 ML/h. These fullerenes appear to have a lower stability against the heating, which is required for outgassing and deposition as compared with C_{60}. Consequently the number of samples that may be prepared using this material is limited to ~5 before the charge is exhausted. In previous experiments the presence of both La@C_{82} and C_{84} has been

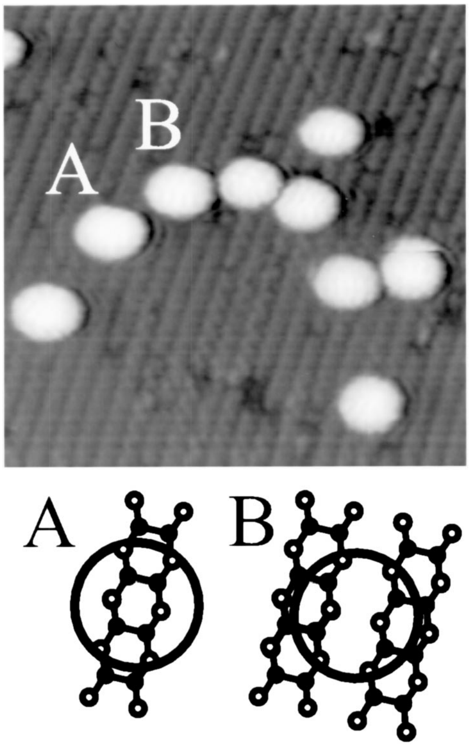

FIG. 1. STM image ($15 \times 15\ \mathrm{nm}^2$) of 0.03 ML of La@$C_{82}$ adsorbed on Si(100)-2×1. Si dimer rows run from top to bottom and molecules are adsorbed either directly (A) above or (B) midway between dimer rows. Scan parameters are −3.5 V and 0.1 nA.

verified from the ordering of various surface phases on the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface.[13]

Figure 1 shows an image of a Si(100)-2×1 surface on which 0.03 monolayers (ML) of La@C_{82} have been deposited. The dimer rows are resolved in the background.[14] The apparent diameter of the La@C_{82} molecules is $\sim 2.2 \pm 0.04$ nm and their height is 0.85 ± 0.02 nm. The apparent diameter of isolated molecules is greater than the intermolecular spacing in bulk La@C_{82}, 1.12 nm,[15] due to convolution with the STM tip. Approximately 35% of the molecules are adsorbed directly above dimer rows (see molecule *A* in Fig. 1), while the remaining molecules are centered in a trough, midway between dimer rows (molecule *B* in Fig. 1). For C_{60} the only adsorption site observed is configuration *B*.

This difference in adsorption site may be related to the higher radius of curvature of the endohedral species. In addition to its larger overall size, there are regions on the La@C_{82} cage where a hexagonal face is connected to five hexagonal faces and only one pentagonal face. This should be compared with C_{60}, for which all hexagonal faces are connected to three hexagonal and three pentagonal faces. These local regions of lower radius of curvature will lead to a higher degree of sp^2 hybridization and differences in reactivity. Note that simple molecules, such as benzene and pentacene, with sp^2 hybridized electrons are found to adsorb above dimer rows.[16,17]

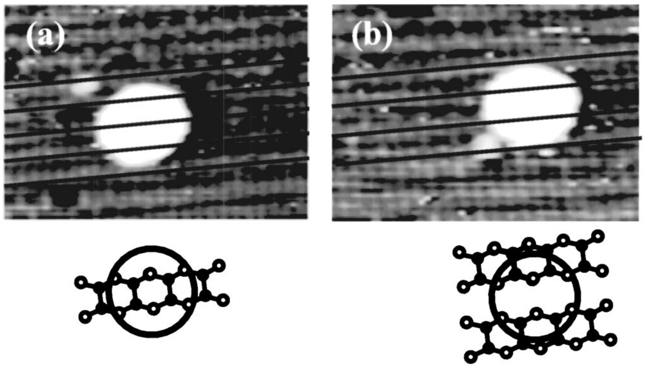

FIG. 2. STM images of C_{84} molecules adsorbed above a (a) row ($9 \times 6\ \mathrm{nm}^2$) and (b) trough ($8.6 \times 7\ \mathrm{nm}^2$) site. Scan parameters are −3.0 V and 0.1 nA.

In order to confirm that geometrical differences in cage size are responsible for adsorption above dimers, rather than electronic differences arising from interactions between the cage and the endohedral atom, we have also investigated the empty higher fullerene, C_{84}. Monolayer and higher coverages of this molecule have previously been studied by Wang *et al.*[18] Figure 2 shows STM images of a submonolayer (0.0025 ML) coverage of C_{84} adsorbed on the Si(100)-2×1 surface. We find that, as for La@C_{82}, adsorption occurs both directly above the dimer rows and also in trough sites.

The deposition of further La@C_{82} results, as for C_{60}, in a disordered monolayer termination followed by, for room-temperature deposition, the formation of disordered islands. This is illustrated in Figs. 3(a) and 3(b), which show STM images of the surface for a coverage of, respectively, 1 and 1.5 ML of La@C_{82}. The sample shown in Fig. 3(b) was annealed at 150 °C, after which multilayer islands with a high degree of order are observed—see Fig. 3(c). Note the regular hexagonal arrangement of molecules in this island,

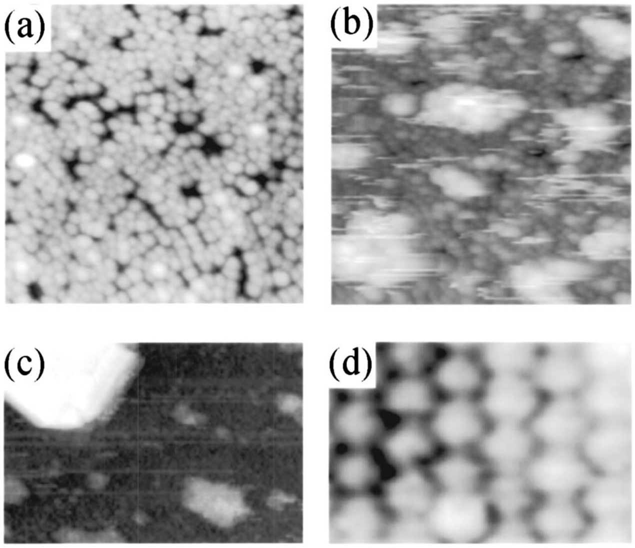

FIG. 3. (a) Near-monolayer coverage of La@C_{82} adsorbed on Si(100)-2×1 ($23 \times 23\ \mathrm{nm}^2$; 3 V, 0.3 nA); (b) 1.5 ML coverage ($30 \times 30\ \mathrm{nm}^2$; −3.5 V, 0.05 nA); (c) 1.5 ML coverage following annealing at 150 °C for three minutes, $100 \times 70\ \mathrm{nm}^2$; −4 V, 0.05 nA); (d) enlargement of the faceted island in (c) showing molecular ordering ($12 \times 5\ \mathrm{nm}^2$).

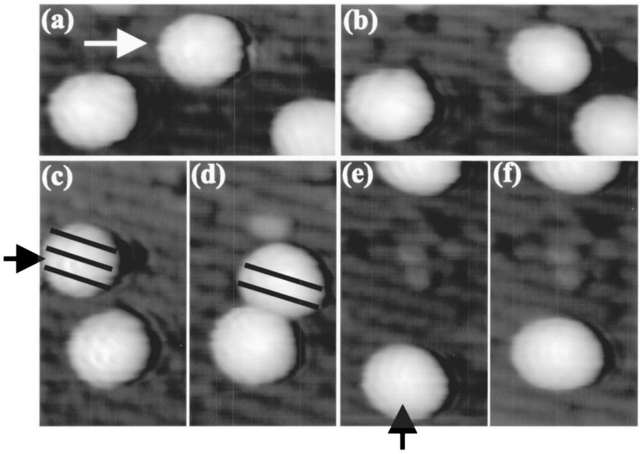

FIG. 4. Manipulation of La@C_{82} endohedrals, manipulation parameters -0.8 V, -1.2 nA. (a) and (b) show manipulation along a trough between two dimer rows ($6\times12\ \mathrm{nm}^2$); (c) and (d) show manipulation from a dimer to a trough adsorption site; (e) and (f) show manipulation across a dimer row ($4\times9\ \mathrm{nm}^2$).

which is shown in an enlargement [Fig. 3(d)]. The intermolecular separation is found to be 1.14 ± 0.05 nm, consistent with the intermolecular spacing in bulk La@C_{82}, 1.12 nm.[15]

We have investigated the susceptibility of endohedral fullerenes to room-temperature manipulation using the tip of the STM. To induce manipulation we apply a technique used previously for C_{60} and $C_{59}N$ manipulation on Si.[4,5,7] Controlled manipulation is achieved by first moving the tip towards the surface (by increasing the tunnel current and decreasing the bias voltage) close to a target molecule. The tip is then moved in discrete steps of 0.6 nm along a trajectory that passes over the center of the target molecule. After each step the tunnel current is updated through feedback control. At the end of the tip trajectory (typical total length ~2.5 nm) the tip is retracted away from the surface by resetting the target tunnel current and sample voltage to values employed for scanning. A variation of this procedure in which the tip is left in the lowered position and returned to its starting position is used to distinguish attractive and repulsive modes of manipulation.[4,5]

Figure 4 shows examples of successful applications of this manipulation procedure. In each case the arrow indicates the direction of the tip trajectory during the manipulation procedure. Figures 4(a) and 4(b) show positions of a molecule before and after an application of the manipulation procedure. For this example, the tip is displaced at a small angle to the dimer rows. The resulting displacement of the molecule follows the dimer rows, with both the initial and final positions of the molecule in adsorption configuration *B* within the same trough. A similar guiding effect of the dimer rows was observed for both $C_{59}N$ and C_{60}.[5,7] Figures 4(c) and 4(d) show the manipulation of a molecule from a site above a dimer row to a trough site. Manipulation of a molecule resulting in a final position above a trough site was not observed, implying that the trough site has lower binding energy. Finally, Figs. 4(e) and 4(f) show the displacement of a molecule across dimer rows between two trough sites. In each example molecules are translated through 1–2 nm.

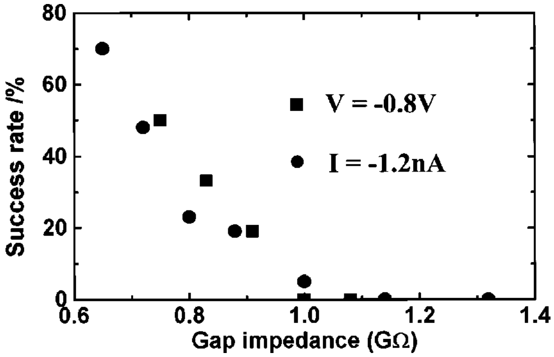

FIG. 5. Success rate for manipulation vs gap impedance obtained for a range of voltages but fixed current $I=-1.2$ nA (solid circles) and for a range of currents but fixed voltage $V=-0.8$ V (solid squares).

The dependence of molecular response on tunnel current and sample voltage is summarized in Fig. 5 for manipulation parallel to the dimer rows, for which the initial and final molecular position is in a trough site. The fraction of successful manipulation attempts (i.e., those that lead to a displacement of the target molecule) is plotted versus tunnel gap impedance. Two sets of data are presented in which ei-

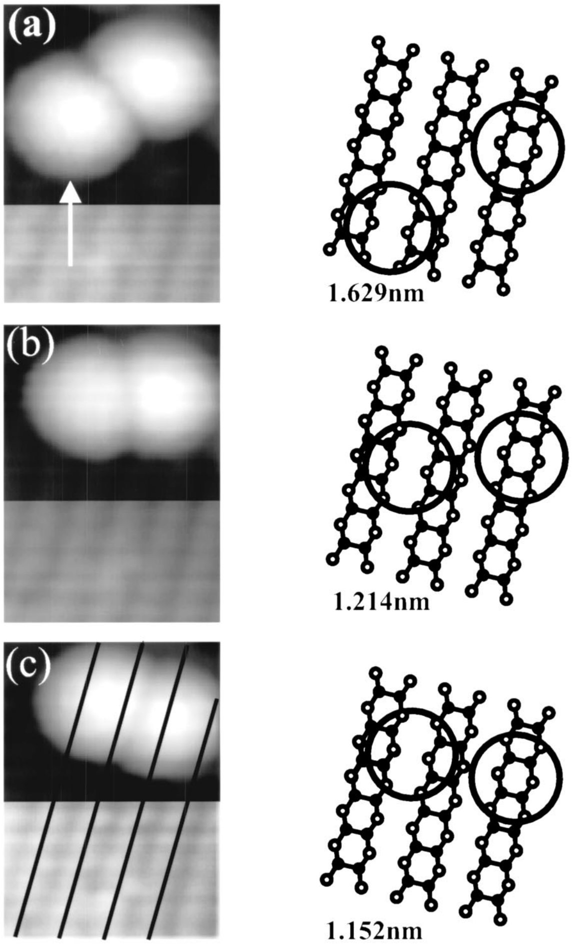

FIG. 6. Manipulation of a molecule along a trough to form a close-packed pair.

ther the sample voltage or tunnel current is held constant (at -0.8 V and -1.2 nA, respectively). In both cases the threshold for manipulation is found to be $\sim$1.0 GΩ, with the probability for manipulation rising to $\sim$70% for gap impedances less than 0.6 GΩ. For even lower gap impedances the tip was not sufficiently stable for manipulation experiments.

The controlled formation of a close-packed molecular pair using manipulation is shown in Fig. 6. One molecule is manipulated along a trough in two steps of, respectively, two and one lattice constants. After manipulation [Fig. 6(c)] there is a separation between the molecules of three-lattice constants, 1.152 nm. As discussed previously this is close to the intermolecular separation of La@C_{82}, 1.12 nm, and as such represents a close-packed pair. Furthermore, pairs are observed with the line connecting their centers oriented either parallel or perpendicular to the dimer rows, indicating that it is possible, in principle, to form extended noncollinear assemblies of close-packed molecules. Note that the minimum spacing for C_{60} molecules adsorbed in the same trough also corresponds to three-lattice constants, $\sim$0.15 nm larger than the intermolecular separation for bulk C_{60}. It may therefore be expected that intermolecular interactions arising from overlap of molecular orbitals would be much greater for adsorbed La@C_{82} molecules as compared with C_{60}.

The number of molecules that have been shown to be susceptible to manipulation at room temperature is extremely small and is restricted to $C_{59}N$, C_{60}, and a porphryn derivative.[5,7,19] The extension to La@C_{82} is therefore highly significant. The impedance threshold for manipulation of La@C_{82} is slightly lower than that for $C_{59}N$ and C_{60} (2 GΩ). However, a comparison of these three fullerenes, which have different sizes and exhibit widely varying chemical properties, reveals very few differences in their manipulation response. This confirms that the susceptibility to manipulation is a general property of the fullerene cage. Furthermore, the fact that for each of these fullerenes manipulation may be induced by varying either the tunnel current or the sample voltage (see Fig. 5) indicates that the interactions that lead to manipulation are not independently determined by either of these parameters. This suggests that manipulation is induced by direct, repulsive (Lennard-Jones) tip-sample forces rather than mediated by mechanisms related to electron-induced bond breaking or electrostatic effects.

One significant difference between La@C_{82} and the fullerenes previously studied is the observation of room-temperature adsorption directly above dimer rows. The demonstration that manipulation may be initiated for molecules in these sites [see Figs. 4(c) and 4(d)] provides further evidence that the susceptibility to manipulation is a general property of the fullerene cage and is not specific to a particular bonding configuration of the molecule.

In summary we have undertaken a study of the adsorption and manipulation of endohedral fullerenes on Si(100)-2×1. Molecules are adsorbed directly above dimer rows in sites not observed for C_{60}. A comparison with the adsorption of C_{84} indicates that this difference is due to the geometry of the cage rather than the presence of the endohedral atom. Molecular manipulation has been demonstrated for La@C_{82} and constitutes the use of a fullerene cage as a molecular package that may be used to transport and position an endohedral atom with subnanometer scale precision on a semiconductor surface.

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