Electrospray Deposition of C$_{60}$ on a Hydrogen-Bonded Supramolecular Network

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An electrospray technique has been successfully used to deposit C$_{60}$ onto a hydrogen-bonded supramolecular template held in an ultrahigh vacuum environment. Characterization of the surface by in situ scanning tunneling microscopy shows the size-selective trapping of C$_{60}$ dimers and heptamers within a 3,4,9,10-perylene tetracarboxylic diimide (PTCDI)/melamine network. We demonstrate that ultrahigh vacuum electrospray deposition (UHV-ESD), where energetic molecules impact onto a substrate, is compatible with surfaces which have been functionalized through the incorporation of hydrogen-bonded templates.

Introduction

Within the rapidly developing area of nanoscience, there is great interest in systems which combine ordered nanoscale structures with novel optical, electronic, and magnetic properties. The ability to produce nanoscale structured materials with predetermined geometries is of paramount importance to the future production of nanodevices. Unfortunately, many of the molecules with potential for the manufacture of nanomaterials (e.g., functionalized/endohedral fullerenes, porphyrins, single molecule magnets) are thermally labile and as such may not be deposited in vacuum by conventional methods such as sublimation. Electrospray (ES) ionization provides a highly promising route for the deposition of nonvolatile molecules onto surfaces in ultrahigh vacuum (UHV). The technique is widely used in mass spectroscopy to introduce large and fragile molecules into the gas phase and it has shown promise as a method of depositing polymers and biomolecules into vacuum. We have previously demonstrated that carbon nanotubes can be deposited from a liquid suspension onto a surface held in high vacuum using an in vacuo implementation of ES ionization with ex situ characterization using atomic force microscopy. More recently, we have shown that differential pumping of an ES molecular beam from air to UHV can be used to deposit fullerene molecules from solution onto a Au(111) surface at pressures as low as 1 × 10$^{-8}$ mbar for in situ scanning tunneling microscopy (STM) and synchrotron-based electron spectroscopy studies.

Although the UHV-ESD of molecules (C$_{60}$) onto metal substrates has been demonstrated, little is known about how the ES deposition (ESD) process could affect surfaces that have been functionalized by supramolecular networks. The formation of two-dimensional supramolecular structures has been extensively studied, and it has been shown that such structures may be used to facilitate the production of well-ordered templates with network cavities with dimensions on the order of nanometers. Such nanoscale templates are ideally suited to the capture of additional moieties which may be used to further functionalize the surface. A number of studies on the host–guest architecture of molecular species, deposited by conventional thermal methods, trapped within the pores of supramolecular structures have been carried out, but until now the compatibility between the use of ES deposition and self-assembled templates has not been explored.

We address the question of the potentially destructive nature of UHV-ESD by studying a previously investigated bimolecular network, formed from 1,3,5-triazine-2,4,6-triamine (melamine) and 3,4,9,10-perylene tetracarboxylic diimide (PTCDI) (molecular structures shown in Figure 1a and b), as a test system for the UHV-ESD of C$_{60}$. These molecular “building blocks” are known to self-assemble into open-pored hexagonal and parallelogram networks. Earlier work has shown that the open pores of these networks may trap either heptamers or dimers of C$_{60}$, depending upon the dimensions of the network cavities. The diagrams here show possible orientations for the trapped molecules.
in the hexagonal and parallelogram network pores, respectively. These previous studies provide the ideal experimental background to analyze the effects of substituting a thermal deposition technique for UHV-ESD. Here, we report a methodology for the UHV-ESD of molecular species onto hydrogen-bonded networks and provide evidence that the test system of ES C$_{60}$ deposited upon a bimolecular melamine/PTCDI network produces structures that are comparable to those produced by thermal deposition.

**Experimental Methods**

A 4 mm × 8 mm gold on mica substrate (thickness of 1500 Å; supplied commercially by Agilent) was loaded into a UHV system with a base pressure of 5 × 10$^{-11}$ Torr. The sample was cleaned by Ar ion sputtering (6 × 10$^{-6}$ Torr, 1 keV, ∼3 µA) and subsequent annealing (∼500 °C). Images of the surface were acquired using a scanning tunnelling microscope, housed within the UHV system, using electrochemically etched tungsten tips, and operating in constant current mode at room temperature. Images of the surface taken after the sputter–anneal cycle show the characteristic (22 × √3) herringbone reconstruction of the Au(111) surface. The supramolecular network was prepared by the sequential deposition of PTCDI and melamine, using Knudsen cells, followed by a short anneal at ∼100 °C as described previously. This process facilitates the formation of two coexisting bimolecular networks: one with hexagonal pores and the other with parallelogram shaped pores (the structures of these networks are shown in Figure 1d and e, respectively).

Using UHV-ESD, C$_{60}$ was transferred onto the network from a solution of toluene/acetonitrile (1 mg/mL of C$_{60}$ dissolved in a 4:1 solution, by volume). The ES experimental apparatus, built in-house, has already been described in detail elsewhere. In summary, a solution containing the molecules to be deposited is passed through a stainless steel emitter held at constant temperature. Images of the surface taken after the sputter–anneal cycle show the characteristic (22 × √3) herringbone reconstruction of the Au(111) surface. The supramolecular network was prepared by the sequential deposition of PTCDI and melamine, using Knudsen cells, followed by a short anneal at ∼100 °C as described previously. This process facilitates the formation of two coexisting bimolecular networks: one with hexagonal pores and the other with parallelogram shaped pores (the structures of these networks are shown in Figure 1d and e, respectively).

**Results and Discussion**

Supramolecular hydrogen-bonded structures were formed on a Au(111) substrate, as described above, giving rise to coexisting bimolecular networks with hexagonal and parallelogram shaped pores. Figure 2 shows STM images of the network produced prior to the ES deposition of C$_{60}$. Figure 2a is an STM topograph showing several small domains of the parallelogram network (labeled A). Regions of the parallelogram network with dimensions of 20 nm × 20 nm were typically observed. Islands of close-packed PTCDI (labeled B) which have not been converted into the network arrangement are seen to coexist with the hydrogen-bonded networks as well as with regions of the gold substrate (labeled C). Although the majority of the ordered structures are composed of the parallelogram network, under these annealing conditions, small regions of the hexagonal network are also observed (shown in Figure 2c).

The series of STM images shown in Figure 3 provide insight into the effect of energetic C$_{60}$ and solvent molecules colliding with the network structure during ES deposition. Figure 3a shows an image of the surface morphology after a 2 min ES deposition of C$_{60}$. From the image, it is possible to identify several areas of interest. The dashed box labeled A shows a region of a parallelogram network with rows of C$_{60}$ dimers trapped within the pores. Area B is a region of a hexagonal network with C$_{60}$ heptamers filling the pores, while area C shows an area of a network which appears to have been reordered during ES deposition. The area to the right of the image is a large island of close-packed PTCDI and is free of adsorbed C$_{60}$. Figure 3b shows an area with a similar structure as that of region B, where a regular array of trapped C$_{60}$ clusters, with each cluster being formed from seven molecules in a hexagonal arrangement, are identified as heptamers trapped in the hexagonal shaped pores of the underlying network structure. Second layer growth of C$_{60}$ is also observed, with the extra layer of molecules filling the spaces in between the trapped heptamers, leading to the “bright” open pore structure seen in the center of the image. The images shown here compare well with results obtained following sublimation of C$_{60}$ onto a hexagonal network, producing structures analogous to those seen in Figure 3b. The “streaky” scan lines observed in the top section of the image are indicative of the presence of diffusive molecules, suggesting that some molecules are not completely immobilized by the presence of the network. Trapped C$_{60}$ dimers mixed in among the heptameric structure demonstrate that defects, of the type reported in previous work, are also present on the surface.

Due to their size and shape, the parallelogram network pores provide trap sites for dimers of C$_{60}$. The bright rectangular features present in the central region of the images shown in Figure 3a (region A) and C have a periodicity, and an apparent height, which agrees with that previously measured for the thermally deposited C$_{60}$ trapped within the parallelogram network pores (dimensions of 30.7 ± 0.4 Å by 19.4 ± 0.3 Å (ref 19) and an apparent height of ∼6 Å), allowing us to attribute these features to trapped C$_{60}$ dimers. The observed size-selective trapping of the C$_{60}$ dimers within the pores of the parallelogram network is in excellent agreement with previous thermal
deposition experiments.\textsuperscript{19} In addition to the trapped molecules, there are several islands of close-packed C\textsubscript{60} visible in the image. These islands have the same apparent height as the dimers, indicating that the close-packed domains are formed on the clean Au(111) surface and not on top of the PTCDI regions. Areas of close-packed PTCDI (e.g., the region to the right of the image in Figure 3a) are free from C\textsubscript{60}, providing further evidence that the adsorption of C\textsubscript{60} onto PTCDI is unfavorable, as observed in the previous sublimation experiments. The similarities between the arrangements of the trapped dimers, and the preferential formation of C\textsubscript{60} islands upon areas of clean gold, produced by the two different deposition techniques leads us to postulate that the surface mobility of C\textsubscript{60} is not changed significantly by altering the method of deposition.

Some areas of the supramolecular network have undergone a reordering process during the ES deposition procedure. Figure 4a and b shows STM images of surface domains that have different morphologies from those observed prior to ES deposition. Figure 4a shows a “mixed” phase of PTCDI and melamine where rows of PTCDI are stacked side by side and are separated by rows of close-packed melamine. This structure has been observed previously, and it is produced after the codeposition of melamine and PTCDI, prior to the further annealing stage which is required to form the network. It is similar to, but more ordered than, one of the mixed phases identified in ref 18. Figure 4c is a high resolution image (taken from a different set of experiments) showing rows of PTCDI separated by regions of melamine; the experimentally determined dimensions are shown (image is taken from a different set of experiments). (d) Model of the “mixed” phase of PTCDI and melamine with dimensions calculated using hydrogen bond distances obtained from DFT calculations.

The melamine/PTCDI ratio for this “mixed” structure is approximately 2:1 and is greater than the equivalent ratio for the hexagonal and parallelogram networks, with both being 2:3. Therefore, if a reordering process were to occur during the ES process, areas with an excess of PTCDI would be expected on the surface. The result of this reordering is shown in Figure 4b where, by analyzing the apparent height of the PTCDI islands, it can be seen that three distinct layers of close-packed PTCDI
have been formed. All PTCDI islands before UHV-ESD were only one molecule high; therefore, the resulting multilayered structure of islands following deposition provides evidence for the removal of PTCDI molecules from the bimolecular network during the creation of the "mixed" phase.

Image analysis of the STM data allows a quantitative picture to be obtained of the differences between the surface coverage of the supramolecular structures before and after the UHV-ESD of C₆₀. The overall melamine to PTCDI ratio, 1:2, is unaffected by exposure to electrospray deposition, but the relative abundance of the various phases does change. The coverage of the parallelogram network is reduced from 48 ± 9% before UHV-ESD to 15 ± 8% afterward. Conversely, the coverages of both the "close-packed" (PTCDI only) and "mixed" (melamine rich) molecular arrangements increase from ~10% to ~20% and from 0% to ~20%, respectively, suggesting the conversion of the parallelogram network into other phases.

It is possible that network reordering is mediated by solvent droplets arriving at the surface. Subsequent evaporation of the solvent may lead to a phase separation of the melamine and PTCDI molecules, producing the "mixed" phase observed. It may be possible to characterize and reduce this effect and also to investigate whether it is due to nanoscale solvation in droplets, by increasing the desolvation of the ES beam; this is a design feature which will be included in future models of the ES apparatus. We estimate an upper limit for the kinetic energy of the impinging C₆₀ molecules to be 360 meV, which is lower than the DFT calculated value for the PTCDI/melamine synthon landing measures. The structures observed in the STM images may be responsible for the change in network structure. All PTCDI islands before UHV-ESD were trapped within the network pores in a similar fashion to C₆₀. The overall melamine to PTCDI ratio, 1:2, is unaffected by exposure to electrospray deposition, but the relative abundance of the differences between the surface coverage of the supramolecular structures before and after the UHV-ESD.

The results discussed above show that it is possible to deposit molecules onto a hydrogen-bonded supramolecular network, in UHV, using ES deposition without the need for additional "soft landing" measures. The structures observed in the STM images provide clear evidence that C₆₀ dimers and heptamers may be trapped within the network pores in a similar fashion to molecules which have been thermally sublimed. The similarities in the structures produced by the two deposition techniques show that the organization of the guest C₆₀ molecules, that is, the size-selective trapping of molecules, is driven by similar microscopic processes, confirming UHV-ESD as a highly promising method for introducing guest moieties onto a preprepared (potentially fragile) nanostructured surface.

**Conclusion**

The viability of UHV-ESD for the deposition of molecules on a hydrogen-bonded network has been demonstrated. The nondestructive nature of the ES process, with respect to both deposited molecules and, partially, the hydrogen-bonded network, facilitates the investigation of the host–guest architecture for thermally labile, and/or nonvolatile, molecules which is not possible using conventional thermal techniques. Fragile molecules such as functionalized fullerenes, endohedral fullerenes, biomolecules, porphyrins, and single molecule magnets are all ideal candidates for future ES deposition experiments where optical, electronic, and structural information may be obtained for the adsorbed species.

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**References and Notes**

(28) Images were processed using the WSxM Develop 10.0 free software from Nanotec Electronica S.L. (http://www.nanotec.es).
(31) Calculations were performed using the DMol3 package.

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