How Nanoscience Translates into Technology: The Case of Self-Assembled Monolayers, Electron-Beam Writing, and Carbon Nanomembranes

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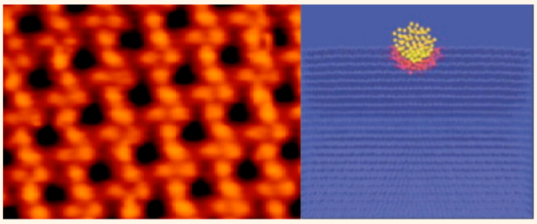
ABSTRACT One of the great quests in nanotechnology is to translate nanoprecision materials science into practical manufacturing processes. The paper by Angelova *et al.* in this issue of *ACS Nano*, which discusses the production of functional carbon-based membranes with a thickness of 0.5 to 3 nm, provides instructive insight into how researchers are pulling together complementary strands from a quarter century of nanoscience research to develop novel, hybrid processing schemes. In this Perspective, we reflect on the progress that is taking place in the two principal component technologies combined in this scheme, namely, (i) control of self-assembled monolayers, including their detailed atomic structures, and (ii) electron-induced manipulation and processing of molecular layers, as well as considering (iii) remaining challenges for thin membrane production in the future.



As described in this issue of *ACS Nano*, the scheme of Angelova *et al.*,[1] from Bielefeld, Ulm, Mainz, and Frankfurt, first assembles thiol-containing molecules on gold surfaces, then cross-links them by electron irradiation before release of the resulting membranes from the substrate and (optional) subsequent thermal treatment to yield thin carbon "graphene" sheets. The paper is the latest in a series dating back to the demonstration of cross-linking in self-assembled monolayers (SAMs) by electron irradiation in 1999[2] and their release to form free-standing membranes in 2005.[3] The key new point in this paper is the replication of the molecular arrangement in the SAMs—as controlled by the selection of the individual molecules themselves from a wide-ranging possible library—into the morphology of the resulting membranes and sheets, so that, for example, regular arrays of pores can be produced in the membranes. In this Perspective, we set in context the two research areas that are combined together in this membrane production scheme: (i) SAMs, including new insights into their detailed atomic structures, and (ii) electron-beam writing and atomic manipulation in adsorbed molecular (as opposed to polymer) layers. We also consider (iii) issues affecting further development of thin membrane production, such as nanopore production. An underlying theme is the richness of the pool of nanoscience research, which technologists can now dip into at will.

Self-Assembled Monolayers. The first step in making carbon nanomembranes (CNMs) involves the assembly of aromatic thiol molecules on gold substrates into densely packed, self-assembled monolayers. This is an important step because the number of carbon atoms per unit area can be controlled by selection of the appropriate molecular precursor. The natural tendency of the thiol molecules to form a dense molecular layer with a regular structure also ensures that the carbon atoms are uniformly distributed over the surface and, hence, leads to the uniform thickness of the final CNM. An interesting aspect of CNM formation from SAMs is that the structural and functional properties of the SAMs can be passed on to the CNMs. Since SAMs can exist in a range of structural phases on Au(111),[4] a high degree of control over the

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fabrication process is possible. The efficiency of electron-induced cross-linking of the molecules is expected to be highly dependent on the lateral positioning of the molecules as well as the nature of the S−Au bonding at the interface. Regarding the structure of SAMs on Au(111), it is perhaps surprising that nearly 30 years after the first description of alkanethiol SAMs on Au(111) by Nuzzo *et al.*,[5] the S−Au bonding mechanism is still a subject of debate.[6,7] For many years, it was assumed that the bonding between thiolate and the Au(111) surface involved a simple S−Au interaction where the S atom sat at one of the high symmetry sites on an otherwise perfect (111) substrate.[8] Recent studies, however, find evidence of Au adatoms being involved in the anchoring of the thiolate.[7,9−11] A more realistic structural model based on the Au-adatom-dithiolate motif has been proposed.[12] The Au-adatom-dithiolate entity, alternatively known as the staple motif, has also been identified on the surfaces of Au nanoparticles.[6]

> An interesting aspect of carbon nanomembrane (CNM) formation from self-assembled monolayers (SAMs) is that the structural and functional properties of the SAMs can be passed on to the CNMs.

A challenge for the new Au-adatom-dithiolate motif is how to account for the established $(\sqrt{3} \times \sqrt{3})\text{-}R30^\circ$ structure, which together with its $c(4 \times 2)$ variations has been widely regarded as the signature of alkanethiol monolayers on Au(111). While earlier studies suggest that these structures may have their origin in the S−Au bonding,[8] recent investigations[13] show that the $(\sqrt{3} \times \sqrt{3})\text{-}R30^\circ$ structure is most likely due to the van der Waals interactions between the hydrocarbon tails. If the van der Waals interaction is weak, for instance, between short-chain alkanethiols, the corresponding SAM forms a (3 × 4) phase at a coverage of 1/3 of a monolayer (ML) instead of the $(\sqrt{3} \times \sqrt{3})\text{-}R30^\circ$ structure. Figure 1a−c shows scanning tunneling microscopy (STM) images from methylthiolate (MT), ethylthiolate (ET), and propylthiolate (PT) monolayers. All three images are from Au(111) surfaces with saturation coverages of 1/3 monolayer. The common feature of these images is the (3 × 4) lattice of the adsorbate. The (3 × 4) phase is dictated by the S−Au bonding. The distance between neighboring alkyl chains within the (3 × 4) phase is rather nonuniform. As the chain length increases, the van der Waals interactions become stronger. Hence, for butanethiol and above, the van der Waals interactions are strong enough to force the Au-adatom-dithiolate units to shift positions, leading to the $c(4 \times 2)$ structure and ultimately a $(\sqrt{3} \times \sqrt{3})\text{-}R30^\circ$ type structure. For SAMs of aromatic thiols, the structure at saturation coverage is not quite the same as that of the nonbranched alkanethiols. The packing density is unlikely to reach 1/3 ML if the tail group of the thiol molecule is too bulky.

A thorough understanding of the bonding mechanism between Au and thiolate is not only desirable for improving the quality of the CNMs but also valuable for other applications in science and technology as diverse as electron transport across a single-molecule junction,[14] effective passivation of Au nanoparticles,[15] protein adsorption,[16,17] and the patterned growth of microcrystals.[18]

Electron-Induced Manipulation and Processing of Molecules. The cross-linking between the molecules in the SAM in the scheme of Angelova *et al.*[1] derives from the selective breaking of molecular bonds under low-energy electron-beam irradiation. The demonstration of electron-induced, bond-selective dissociation in SAMs dates from the mid-1990s (see, for example, ref 19) and manifests the negative ion resonance states that play such a ubiquitous role in electron−molecule dynamics at surfaces,[20] including the bond-selective manipulation of individual molecules with the scanning tunneling microscope (STM) at the very lowest energies.[21−23] Electron-induced modification of SAMs remains an active area of research and application today, enabling, for example, "oxygen fixation"[24] or spatially selective nanoparticle attachment after electron-beam lithography.[25,26]

More generally, electrons are now widely used to achieve high-resolution lithographic patterning of resist films for nanofabrication. Several mechanisms can be exploited to create cross-linked thin films (negative-tone resists), either directly through radiation chemistry (conventional resists) or *via* intermediate catalytic sensitizers (chemically amplified resists). Traditionally, the resist film has been polymeric. Polymers confer a number of advantages, such as the ability to spin coat low-defect density amorphous films and the ability to incorporate multiple chemical moieties to tailor the performance of the material to the requirements of the application. As low-molecular-weight materials tend to crystallize upon spin coating, they were not considered to be good candidates for resists. However, as the lithographic resolution feature size has shrunk, there has been increasing interest in the use of low-molecular-weight materials.

For negative-tone cross-linking resists, where the size of the molecules in the resist film effectively limits the minimum achievable feature size, molecular-resist materials offer the potential for higher resolution than polymers. In addition, as feature sizes shrink, it has been necessary to use ever thinner resist films to avoid aspect-ratio-related pattern collapse due to the capillary forces on resist patterns as the developer dries. For film thicknesses below 50 nm, where interface effects dominate over the bulk polymer properties (for instance, suppressing the glass transition temperature), it is

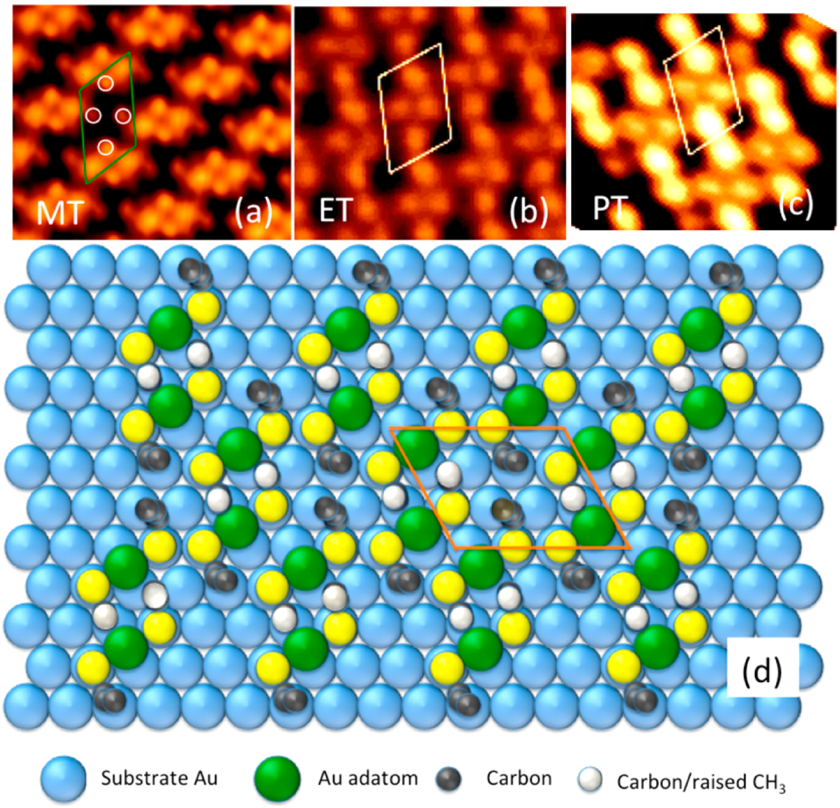

Figure 1. Self-assembled monolayers of methylthiolate (MT), ethylthiolate (ET), and propylthiolate (PT) form the 3 × 4 phase at saturation coverage as shown by the scanning tunneling microscopy images in (a−c). For MT, the protrusions are from the methyl groups and also the Au adatom. For ET and PT, the Au adatom is not visible in the images. The 3 × 4 unit cell is illustrated in each image. The 3 × 4 phase is constructed from zigzag rows of Au-adatom-dithiolate shown in (d). The filled yellow colored circles are S atoms. Adapted with permission from ref 13. Copyright 2012 Elsevier.

found that the critical aspect ratio of collapse decreases, and the film thickness reduction with feature size is no longer linear but accelerated. Molecular films are typically carbon-rich, allowing successful pattern transfer with far thinner films,[27] while the high degree of cross-linking, as seen in the CNMs in Angelova *et al.*,[1] gives enhanced mechanical stability.

Fujita first demonstrated that a molecular glass, based on the calixarene oligomer, could be used as a high-resolution negative-tone electron-beam resist.[28] It has subsequently been shown that a wide array of low-molecular-weight materials, such as polyphenols[29] (similar in form to the hexaphenylbenzene used to create CNMs as shown in Figure 1d, 3a of the paper by Angelova *et al.*[1]), inorganic silsesquioxanes,[30] fullerenes,[31] and triphenylenes[32] cross-link under electron-beam irradiation. Indeed cross-linking between phenol rings in individual SAM molecules has been demonstrated under electron-beam lithography,[33] although these SAMs are typically then used as a template for the growth of a relief structure rather than as a resist themselves.[26]

Polysubstituted triphenylene derivatives demonstrate high-resolution, negative-tone behavior in both chemically amplified[32] and conventional resist formulations.[34] These derivatives are polycyclic aromatic hydrocarbons, similar to the hexa-*peri*-benzocoronene derivatives used to form CNMs (see ref 1 Figure 1d (3b−3d)). The sharp peak in the small-angle X-ray scattering (SAXS) spectrum of a spin-coated triphenylene film, shown in Figure 2a,[34] shows that the molecules are well ordered on the surface (a hydrogen-terminated degenerately n-doped Si(100) wafer), with the molecule perpendicular to the surface, as shown in the inset to Figure 2a. A film exposed to varying doses of electrons at 30 keV becomes insoluble in organic solvents, such as monochlorobenzene, for doses in excess of 2−3 × 10^{-3} C/cm^2. It can be seen from the Fourier transform infrared spectroscopy (FTIR) data shown in Figure 2b[34] that the aromatic peaks apparent in the unexposed film (i) disappear after exposure to such doses (ii−iv), indicative of cross-linking of the triphenylene cores.

Fullerene derivatives have also been shown to work as both conventional[35] and amplified[31] negative-tone resists. After exposure to a sufficient dose of electrons, the intensity of the fullerene pentagonal pinch mode, as measured using Raman spectroscopy, is significantly reduced and spectra characteristic of glassy carbon are observed. Electrical measurements of the exposed fullerene films[36] show that the film, which is highly insulating when unexposed, has a conductivity comparable with glassy carbon or graphite after electron-beam irradiation.

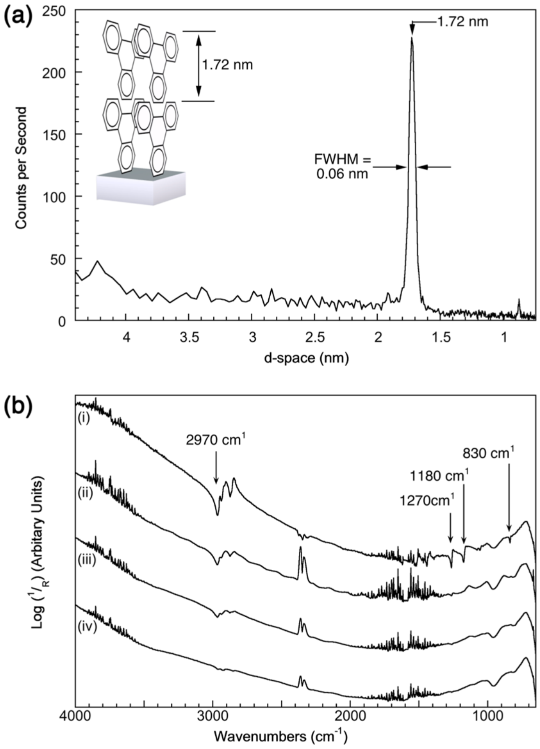

Figure 2. (a) Small-angle X-ray scattering data showing a high level of molecular ordering in a 100 nm thick film of a triphenylene derivative spin coated on silicon, and (b) Fourier transform infrared spectroscopy spectra of a triphenylene film (i) prior to electron-beam irradiation and after doses of (ii) 2.8 × 10^{-3} C/cm^2, (iii) 6.8 × 10^{-3} C/cm^2, and (iv) 1.2 × 10^{-1} C/cm^2. Adapted with permission from ref 34. Copyright 2000 AVS Publications.

It can be seen, therefore, that a variety of chemical pathways can be utilized to create cross-linked thin resist films from a wide range of molecules including SAMs, molecular glasses, triphenylenes, and fullerenes. The paper by Angelova *et al.*[1] in this issue of *ACS Nano* has demonstrated that, starting from a library of broadly similar SAM molecules, it is possible to tailor the properties of CNMs, for example, to produce ultrathin films with or without nanopores. As the processes of radiation chemistry become increasingly well understood, it should be possible to extend this approach. Materials developed for electron-beam lithography, and for related techniques such as lamella-directed self-assembly,[37] provide attractive candidates to engineer novel, mechanically stable composite films, with topographic and chemical structuring from nano- to macroscale in both lateral and vertical dimensions. Such materials will have applications in diverse areas of technology from metamaterials and electronics to biomimetics.

> The paper by Angelova *et al.* in this issue of *ACS Nano* has demonstrated that, starting from a library of broadly similar self-assembled monolayer molecules, it is possible to tailor the properties of carbon nanomembranes, for example, to produce ultrathin films with or without nanopores.

The Future of Membrane Production. A key feature of the paper by Angelova *et al.*[1] is the demonstration of the generation of different lateral structures (*e.g.*, pores) in the SAMs through the packing (self-organization) of larger molecules containing suitable functional groups, prior to cross-linking and release. Alternatively, one can envisage the release to form membranes of SAMs that have been prepatterned by any number of lithographic techniques—whether electron-beam, extreme ultraviolet, X-ray, ion beam, nanoimprint, or some other approach. The membranes could also be patterned after release (or indeed after graphitization), as the Bielefeld group and their collaborators have shown in a number of papers; one interesting example is the creation of nanopores, as relevant to applications in filtration, by irradiation of the membranes by slow, highly charged ions.[38] In this work, 10–20 nm diameter pores were produced. One direction for future exploration might be the creation of smaller holes with possible atomic-level precision by irradiation of the membranes with size-selected atomic cluster ions. Molecular dynamics simulations of the implantation of size-selected metal clusters into bulk graphite suggest that pores with diameter controlled by the cluster size might be generated,[39] as Figure 3 illustrates.[40]

An obvious question to ask, in relation to applications, is "how large can one make these nanometer-thick membranes?" Angelova *et al.*[1] suggest that their method is, in principle, scalable up to square meters if a defocused electron source is used (one wonders whether a plasma might do the job too?). No doubt there might be practical issues with the handling of such large thin structures, but we imagine they would not be insurmountable. As usual, the balance between, on the one hand, the uniqueness and industrial importance of the functionality achieved and, on the other hand, the economic cost of production (and of competing approaches) is likely to determine how widespread the industrial applications will be that will

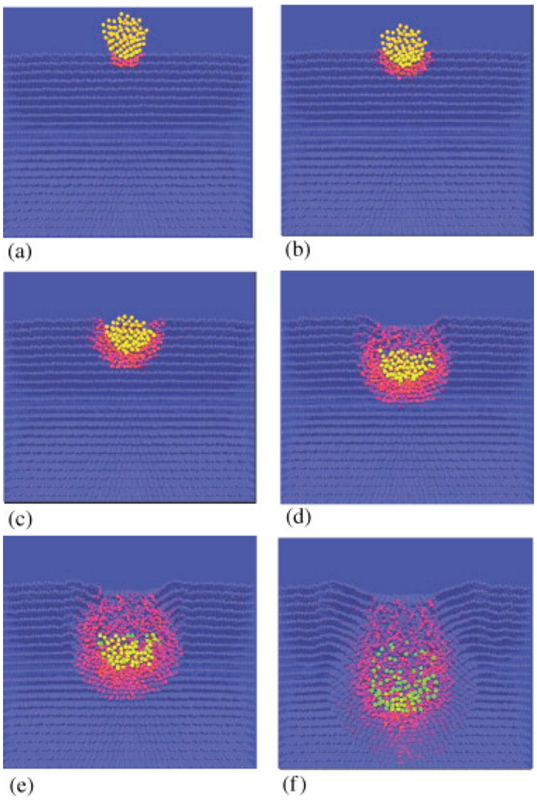

Figure 3. Snapshots from the molecular dynamics simulation of the implantation of a Ag_{200} cluster into graphite at 5 keV over the first 0.5 ps of its trajectory. Reprinted with permission from ref 40. Copyright 2007 Elsevier.

emerge. For the time being, the Bielefeld group has set up a small company[41] offering novel transmission electron microscopy grids for sale, and *ACS Nano* readers will no doubt wish them well.

More generally, the "carbon nanomembrane story" is an instructive one for the application—and funding—of nanoscience research. The application of the science often lies some way downstream and at bends in the river that one could not anticipate beforehand. Our technology may reach to the microscopic length scale, but it still needs a macroscopic time scale to mature.

Conflict of Interest: The authors declare no competing financial interest.

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