JACS
EDITORIAL

Published on Web 12/22/2010

Surface Patterning: More than Just Scratching the Surface

The ability to pattern surfaces with monolayers and multilayers is a central focus of numerous chemical studies because of the implications in fields ranging from sensor design to microelectronics. Goals vary from patterning single molecules at the sub-nanometer scale to forming vast assemblies over macroscopic areas. Moreover, this chemistry can range from simple homogeneous systems to mixed monolayers with complex patterns. Advances have come on numerous fronts, as illustrated by the 21 publications discussed in this issue of *JACS* Select that have recently appeared in the *Journal of the American Chemical Society*.[1−21]

One technique, originally pioneered by Liu and co-workers,[22] involves directly scratching the surface at the nanoscale. This technique, known as nanografting, uses the tip of a scanning probe microscope to "nanoshave" a self-assembled monolayer (SAM) and then backfill the bare region with molecules introduced into the bulk solution. The technique has traditionally been shown to form patterns of 100 nm^2 or less. Recently, however, **Ye** and co-workers have brought this technique down to the single-molecule level with the precision assembly of DNA.[1]

Electrochemical patterning techniques have also been popular. **Yousaf** and co-workers were able to employ hydroquinone chemistry to pattern surface ligands that could be exploited for cell attachment and differentiation.[2] By contrast, **Fréchet** and co-workers were able to form two different surface chemistries via the oxidation or reduction of a benzoquinone-terminated SAM.[3] The use of photopatterning and click chemistry also continues to remain highly attractive. For example, **Popik**, **Locklin**, and co-workers attached a cyclopropenone to an activated ester on a polymer layer via photochemistry.[4] Also, **Velders** and co-workers demonstrated the functionalization of substrates using alkyne-β-cyclodextrin.[5] Click chemistry and electrochemistry have been elegantly combined in work by **Hapiot** and co-workers.[6] This group used electroreduction followed by click chemistry to pattern monolayers of azidomethylferrocene on carbon substrates.

In addition to patterning SAMs on glass, gold, carbon, or plastic, the patterning of additional substrates continues to become easier to do and better understood. Perhaps the most pursued system in the past year has been graphene sheets and particles. Graphene is a conductor, while

(1) Josephs, E. A.; Ye, T. *J. Am. Chem. Soc.* **2010**, *132*, 10236–10238.
(2) Luo, W.; Chan, E. W. L.; Yousaf, M. N. *J. Am. Chem. Soc.* **2010**, *132*, 2614–2621.
(3) Unruh, D. A.; Maudlin, C.; Pastine, S. J.; Rolandi, M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2010**, *132*, 6890–6891.
(4) Orski, S. V.; Poloukhtine, A. A.; Arumugam, S.; Mao, L.; Popik, V. V.; Locklin, J. *J. Am. Chem. Soc.* **2010**, *132*, 11024–11026.
(5) González-Campo, A.; Hsu, S.-H.; Puig, L.; Huskens, J.; Reinhoudt, D. N.; Velders, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 11434–11436.
(6) Leroux, Y. R.; Fei, H.; Noël, J.-M.; Roux, C.; Hapiot, P. *J. Am. Chem. Soc.* **2010**, *132*, 14039–14041.
(7) Mativetsky, J. M.; Treossi, E.; Orgiu, E.; Melucci, M.; Veronese, G. P.; Samorì, P.; Palermo, V. *J. Am. Chem. Soc.* **2010**, *132*, 14130–14136.
(8) Sinitskii, A.; Tour, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 14730–14732.
(9) Sutter, P.; Sadowski, J. T.; Sutter, E. A. *J. Am. Chem. Soc.* **2010**, *132*, 8175–8179.
(10) Zhou, W.; Ding, L.; Yang, S.; Liu, J. *J. Am. Chem. Soc.* **2010**, *132*, 336–341.
(11) Chen, J.; Chan, Y.-H.; Yang, T.; Wark, S. E.; Son, D. H.; Batteas, J. D. *J. Am. Chem. Soc.* **2009**, *131*, 18204–18205.
(12) Smith, A. M.; Vinchurkar, M.; Gronbech-Jensen, N.; Parikh, A. N. *J. Am. Chem. Soc.* **2010**, *132*, 9320–9327.
(13) An, Z.; Lee, S.; Oppenheimer, H.; Wesson, J. A.; Ward, M. D. *J. Am. Chem. Soc.* **2010**, *132*, 13188–13190.
(14) Ke, Y.; Douglas, S. M.; Liu, M.; Sharma, J.; Cheng, A.; Leung, A.; Liu, Y.; Shih, W. M.; Yan, H. *J. Am. Chem. Soc.* **2009**, *131*, 15903–15908.
(15) Cui, Y.; Pattabiraman, A.; Lisko, B.; Collins, S. C.; McAlpine, M. C. *J. Am. Chem. Soc.* **2010**, *132*, 1204–1205.
(16) Cini, N.; Tulun, T.; Decher, G.; Ball, V. *J. Am. Chem. Soc.* **2010**, *132*, 8264–8265.
(17) Andres, C. M.; Kotov, N. A. *J. Am. Chem. Soc.* **2010**, *132*, 14496–14502.
(18) Hozumi, A.; Bien, P.; McCarthy, T. J. *J. Am. Chem. Soc.* **2010**, *132*, 5602–5603.
(19) Yoon, S.-J.; Chung, J. W.; Gierschner, J.; Kim, K. S.; Choi, M.-G.; Kim, D.; Park, S. Y. *J. Am. Chem. Soc.* **2010**, *132*, 13675–13683.
(20) Seo, W.; Phillips, S. T. *J. Am. Chem. Soc.* **2010**, *132*, 9234–9235.
(21) Bernecker, A.; Wieneke, R.; Riedel, R.; Seibt, M.; Geyer, A.; Steinem, C. *J. Am. Chem. Soc.* **2010**, *132*, 1023–1031.
(22) Liu, G.-Y.; Xu, S.; Qian, Y. *Acc. Chem. Res.* **2000**, *33*, 457–466.

graphene oxide is an insulator. In a clever experiment, **Samorì**, **Palermo**, and co-workers employed conductive atomic force microscopy to image large areas of graphene and graphene oxide in films only a few layers thick.[7] Electrical defects could be mapped and created. The latter was done via an electrochemical tip-induced reduction process, whereby an initial graphene oxide area was rendered conducting. Also, **Tour** and co-workers demonstrated the ability to pattern graphene nanostructures into two-dimensional arrays of patches with varying periodicity and distances between the graphene neck widths.[8] The assemblies were patterned with colloidal microspheres and may have electronic applications. One especially important issue with single-layer-sheet graphene films is the type of surface on which they are supported. The underlying substrate can bend the graphene films and otherwise change their electronic and chemical properties. **Sutter** and co-workers worked with graphene supported on Ru(0001).[9] They were able to intercalate oxygen between the metal and the graphene sheet, which lifts the film away from the metal and restores the characteristics of isolated graphene monolayers. In addition to graphene and graphene oxide, a variety of closely related nanomaterials have received increasing attention. One such material is carbon nanotubes, which have been catalytically grown from a variety of surfaces. Recently, **Liu** and co-workers showed it was possible to control the growth of carbon nanotubes from a single substrate with both vertical and horizontal orientation.[10] This discovery allowed for the fabrication of complex three-dimensional patterns from the substrate and should aid in the exploitation of these films in nanoelectronics.

Beyond graphene films, the self-assembly of inorganic quantum dots has been widely explored. **Batteas** and co-workers showed it was possible to create a film of CdSe on glass substrates and pattern the fluorescence emission using light.[11] The radiation oxidized the semiconductor nanoparticles and thereby tuned the emission with sub-micrometer spatial resolution in a process the authors dubbed "lithosynthesis".

Another nanomaterial that can be patterned on planar substrates is phospholipid monolayers and bilayers. Supported lipid films are especially attractive in nanomaterial patterning because they are only in van der Waals contact with the substrate and retain the same two-dimensional fluidity at the liquid/solid interface that lipid membranes possess *in vivo*.[23] Physical characterization and understanding of these films has continued to grow. **Parikh** and co-workers demonstrated that the edges of bilayer films have different structures and physical properties than the middle of the films.[12] Specifically, the lipids near the edges possess greater order and higher phase transition temperatures. In a different study, **Ward** and co-workers attached calcium oxide monohydrate crystals to patterned bilayers containing the negatively charged lipid, phosphatidylserine.[13] The bilayer patches were patterned between areas containing the protein, osteopontin. These authors showed that the inorganic crystals attached to both the protein molecules and the lipids. The crystals showed preference to the protein portions in a reversible process that eventually led to larger crystal growth in the protein regions. In addition to proteins and lipids, the patterning of DNA on substrates has become more and more sophisticated with the advent of DNA orgami.[24] **Shih**, **Yan**, and co-workers demonstrated that they could use this strategy to create square lattices of packed DNA helices that have a flatter surface morphology than the honeycomb lattice.[14] Bionanomaterials can be explored beyond the molecular level by exploiting larger entities. For example, **McAlpine** and co-workers combined microcontact printing with phage display to recognize patterns created with molecular ink.[15]

Many technologies require multilayer surface patterning. Although this had been traditionally performed by Langmuir−Blodgett strategies, Decher showed well over a decade ago that thin films of opposite charge could be laid down on a surface in a layer-by-layer fashion simply by dipping the substrate into alternate solutions containing dissolved polymers, proteins, and related charged materials.[25] In a recent article, however, **Tulun**, **Decher**, and co-workers showed that they could develop layer-by-layer growth strategies that violate the simple rules for organizing such structures, even to the point where materials could be deposited onto a surface of like charge without an alternating ξ potential.[16] In a separate study, **Kotov** and co-workers used an inkjet printing strategy to bypass the multiple dipping steps normally required for layer-by-layer growth.[17] This work showed that it is possible to make rather complex surface patterns by this technique with relative ease.

In addition to patterning surfaces, scientists have been busy coming up with novel techniques for characterizing them. In a clever development, **Hozumi**, **McCarthy**, and co-workers exploited an ionic liquid to image surface patterns on the sub-micrometer scale.[18] The strategy works because of the differential wetting of the surface by the ionic liquid and is advantageous because the fluid is nonvolatile and appears to be nondestructive toward the surface pattern.

(23) Castellana, E. T.; Cremer, P. S. *Surf. Sci. Rep.* **2006**, *61*, 429–444.
(24) Rothemund, P. W. K. *Nature* **2006**, *440*, 297–302.
(25) Decher, G. *Science* **1997**, *277*, 1232–1237.

The creation of sensor materials opens up potentially novel avenues that could be exploited in conjunction with interfacial chemistry. For example, **Gierschner**, **Kim**, **Park**, and co-workers created stimuli response molecular sheets based upon cyanostilbene chemistry that exhibit luminescence switching in response to pressure, temperature, and various chemical vapors.[19] Also, the development of shape-changing materials by **Phillips** and co-workers, based upon the depolymerization of poly(phthalaldehyde), can be chemically triggered by using appropriate end-capping groups.[20]

Finally, the formation of high-surface-area and three-dimensional silica structures was accomplished via precipitation under mild conditions with variously tailored polyamines by **Geyer**, **Steinem**, and co-workers.[21]

The work cited above is only a small sampling of surface patterning and related research. It should, however, provide a taste for the state-of-the-art in a field that is rapidly moving and highly interdisciplinary. Remarkably, surface functionalization, patterning, and characterization borrows from virtually every field of chemistry and ties directly into engineering, materials science, biology, physics, and medicine. There is, however, still much room for further growth and development. As such, we really have only just "scratched the surface" in terms of the possibilities of the science and engineering of surface patterning.

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JA110962H