



Figure 1. The protein nanopatterning technique combines nanoimprint lithography (Steps I–IV) with molecular-assembly patterning by lift-off (Steps V–VIII). Reprinted in part with permission from *Nano Letters* 4 (10) (October 13, 2004) p. 1909. © 2004 American Chemical Society.

ibility. Recently, however, M. Textor from the Swiss Federal Institute of Technology and colleagues from the Paul Scherrer Institute, the University of Siena, and the Centre Suisse d'Electronique et de Microtechnique have demonstrated a parallel process that is both versatile and economical to pattern proteins onto surfaces with nanoscale resolution.

As reported in the October 13 issue of *Nano Letters* (p. 1909), Textor and co-workers created this method by combining a “top-down” approach—NIL—and a “bottom-up” approach—molecular assembly patterning by lift-off (MAPL). Textor, with other colleagues from his institution, previously published a description of MAPL in *Advanced Functional Materials* (August 2004, p. 749).

To begin the eight-step process of the combined method (see Figure 1), substrates were prepared by sputter-coating silicon wafers or Pyrex plates with 12 nm of transparent niobium oxide (Nb_2O_5). In the NIL component, substrates were then spin-coated with 125 nm of poly(methyl methacrylate) (PMMA) and baked for 1 min at 170°C (Step I). Silicon nanopatterned stamps, which were prepared by electron-beam writing and reactive ion etching, were replicated by imprinting into the substrate (Step II). The stamp was demolded from the substrate in Step III. A nanostructured surface with PMMA/

Nb_2O_5 contrast was then obtained by etching the residual PMMA of the nanoimprinted regions (Step IV).

In the MAPL component, which transforms the PMMA/ Nb_2O_5 -contrasted surface into a biologically functional nanopattern, the method begins by dipping the sample into a solution of biotin-functionalized copolymer—polycationic poly(L-lysine)-graft-poly(ethylene glycol)/poly(ethylene glycol)-biotin (PLL-g-PEG/PEG-biotin; about every fourth lysine had a grafted PEG chain and half of all PEG chains were biotinylated)—that adsorbs onto both the PMMA and Nb_2O_5 surfaces (Step V). The remaining PMMA was stripped with acetone (Step VI) and the newly exposed Nb_2O_5 surfaces were backfilled with nonfunctionalized copolymer, PLL-g-PEG, that resists adsorption of proteins (Step VII). The substrate was dipped into a buffered solution of fluorescently labeled streptavidin (a protein that has a high affinity for the biotin ligand), which bonds specifically to the biotinylated areas (Step VIII).

The researchers characterized the nanostructures at each fabrication step. For example, atomic force microscopy showed that 100 ± 10 nm PMMA/ Nb_2O_5 stripes (with a regular line pattern of 400 nm periodicity) resulting from Step IV had widths comparable to those initially imprinted in Step II. The fluorescently labeled strepta-

vidin that adsorbed onto the stripes were imaged with scanning near-field optical microscopy, verifying the selective adsorption onto the biotin-functionalized-polymer pattern. The researchers also used their technique to fabricate similar biopatterns on the micron scale.

The researchers said that the surface density of bioactive molecules can be quantitatively controlled by diluting the functionalized copolymer with nonfunctionalized copolymer in Step V. In addition, the researchers said that the “PEG polymer can be functionalized with a variety of bioactive groups and thus allows a great flexibility in terms of surface chemistry.”

STEVEN TROHALAKI

Optical Waveguiding Observed in CdS Nanowires

Among many other potential applications, nanotechnology is believed to have promise for developing new photonic materials. C.J. Barrelet, A.B. Greytak, and C.M. Lieber from Harvard University have recently characterized cadmium sulfide (CdS) nanowire structures that are employed as photonic circuit elements. As reported in the October 13 issue of *Nano Letters* (p. 1981), the CdS nanowires can be used as subwavelength optical waveguides with exciting properties. Smooth CdS nanowires were synthesized using gold nanoparticles as catalysts, and by employing either molecular precursors or laser ablation of a solid CdS target. Optical studies were performed by locally injecting photoluminescence light along the nanowire, using a diffraction-limited laser spot to excite the CdS bandgap. Spatial maps generated by scanning optical microscopy reveal the efficiency with which the nanowire waveguides light from input to output. For a relatively straight 50 μm nanowire, there is no measurable loss. This demonstrates that semiconductor nanowires can act as extremely efficient subwavelength waveguides.

Charles Lieber's team also demonstrated that nanowires can provide a waveguide medium able to guide light around sharp bends having a radius of curvature much smaller than the wavelength with little loss. “Quantitative analysis of intensity versus position shows a low loss of about 1 dB associated with guiding light through acute angle structures,” Lieber said.

Furthermore, the researchers made a nanowire-based electro-optic modulator whereby the intensity of the light being carried in an active waveguide can be varied by applying a voltage across the waveguide. Also, Lieber said that they achieved an electronically controllable

way of injecting light locally into a nanoscale photonic circuit.

The research team showed that the nanowires could even be successfully assembled into crossed and complex structures while still providing efficient waveguiding properties. These wires may thus become practical for usage in photonic elements with complex topology.

The research helps to resolve the fundamental problem of how to manipulate light in increasingly complex ways at very small scales, the researchers said. Their studies should have significant input on the development of novel computing technologies.

"However," Lieber said, "there are still remaining issues related to techniques to actually assemble such nanostructures efficiently and accurately."

If nanoscale assembling techniques are advanced further, CdS nanowire-based photonic elements may soon become reality in tomorrow's photonic circuits.

MARKUS J. BUEHLER

Silica-Based Nanocomposite Turns Cotton into Superhydrophobic Fabric

Surfaces with water contact angles larger than 90° are deemed superhydrophobic. A superhydrophobic cotton fabric would have a myriad of commercial and industrial applications; however, cotton fabric has a highly hydrophilic surface with a water contact angle of 0°. Widely studied sol-gel methods for coating fibers to provide hydrophobic properties are based on fluoroalkyl compounds. These are expensive processes that carry byproducts, which could potentially damage the environment if fluorine compounds were dispersed or endanger human health after skin contact. W.A. Daoud, J.H. Xin, and X. Tao from the Hong Kong Polytechnic University have now presented an alternative coating method based on a silica nanocomposite. Among other advantages of using this silica-based nanocomposite are its transparency and the capability to be processed at a low temperature compatible with cotton and other fabrics.

As reported in the September issue of the *Journal of the American Ceramic Society* (p. 1782), the researchers mixed tetraethoxyorthosilicate (TEOS), 3-glycidylpropyltrimethoxysilane (GPTMS), and HCl in the optimal ratio of 1:0.118:0.008, respectively. They added hexadecyltrimethoxysilane (HDTMS) in 10 wt% of TEOS, obtaining a modified silica sol. The cotton fabric samples were first cleaned with a non-ionic detergent at 80°C for 30 min, then dipped in the modified silica sol for a minute, padded, air-

dried for 2 h and cured at 120°C for 1 h.

Measurements of the water contact angle were taken 1 min after placing a drop on the fabric, reporting 141°. Absorbency in uncoated cotton fabric was reported as 170% by volume of water sprayed, and after coating the absorbency decreased to 3%. The researchers conducted a standardized accelerated laundry test to simulate the effect of five consecutive wash cycles. After each wash cycle, the low level of absorbency increased and the water contact angle decreased continuously. After 30 wash cycles, the absorbency was up 17% and the water contact angle was 105°, still representing a highly hydrophobic fabric. Most of the increase in absorbency occurred after the first few wash cycles, and the hydrophobic properties reached a plateau after 15 cycles. The researchers attribute this high level of adherence to the addition of GPTMS to the modified silica sol.

The research team also studied the effect of the nanocomposite coating on the integrity of cotton fabric. Tearing strength did not change significantly, and tensile strength decreased less than 5%. When the investigators measured the permeability of the fabric (i.e., the ability of air to penetrate with a constant airflow), they reported a small increase after coating. This increase in permeability is an effect of the coating structure, they said, which deposits as round drops adhering to the fabric fibers. Therefore, they said, the nanocomposite coating enables cotton fabric to achieve consistent levels of water impermeability without losing its original properties.

SIARI SOSA

Structurally Ordered Polymer Electrolytes Prepared by Casting under Magnetic Field

Despite efforts in the past 20 years to improve the conductivity of polymer electrolytes (PEs), the maximum conductivity of solid PEs remains around 10⁻⁵ S/cm at room temperature. The problem is that in such semicrystalline materials commonly derived from the archetypal helical poly(ethylene oxide) (PEO), most of the helices lie parallel to the film plane, leading to low conductivity in the perpendicular direction where it is most important for electrochemical cells. Based on the idea that ionic conduction could be created by the movement of cations inside the helix and anions outside the chain, a group of researchers had recently used a stretching procedure to make a new group of structural ordering PEs from the archetypal helical PEO. In more recent work, the

researchers pursued the use of magnetic field—a non-mechanical means—to achieve orientation of the PEO helices perpendicular to the plane of the film. D. Golodnitsky of Tel Aviv University in Israel, S.H. Chung of William Paterson University in New Jersey, S. Suarez of Hunter College of the City University of New York, and their colleagues have found that the ionic conduction of their PEs could be increased in one direction by a longitudinal alignment of the helices. The researchers published their studies in the November issue of *Electrochemical and Solid-State Letters* (p. A412).

As reported, while casting Li:P(EO)_n PEs (*n* = 3, 7, and 20), a strong magnetic field (0.8 T) produced from samarium-cobalt permanent magnets in the standard dipole arrangement was applied. Two different field configurations were used during the casting procedure: One was homogeneous and the other was highly inhomogeneous. After the solvent evaporation, a 100- μ m-thick film was formed. In order to promote reorientation of the PE chains, diamagnetic alumina and ferromagnetic iron oxide were used as the additives. The incorporation of these nanosized inorganic fillers made a significant contribution to the magnetic field in PEs, the researchers said.

The orthogonally oriented macro- and microstructural changes of polymer segments and chains were studied from scanning electron microscopy and ⁷Li-nuclear magnetic resonance spectroscopy. The PE's conductivity and PE/electrode interphase resistance were studied by a computer-interfaced frequency-response analyzer with a frequency range of 1 MHz to 0.1 Hz. Because the magnetic field was applied during the whole film casting process, both intra- and interchain ion mobilities were promoted by one order of magnitude. The researchers found that the lithium transference number increased from 0.2 to 0.6 in the magnetic-field-oriented PEs, which is important in battery applications; the resistance of the solid electrolyte interphase generated on the lithium electrode decreased by more than one order of magnitude. Due to the ability to make anisotropic, shape-persistent but flexible materials with preferred orientation, the researchers said this technique may enhance power in lithium batteries and possibly be applied in nanoscale technology.

LUCY YUE HU

Spin Separation Achieved in GaAs Heterostructure

L.P. Rokhinson of Purdue University, Y.B. Lyanda-Geller of the Naval Research