

edition of *Nature Nanotechnology* (DOI: 10.1038/NNANO.2011.213).

The researchers first deposited a 2 nm BaTiO₃/30 nm La_{0.67}Sr_{0.33}MnO₃ bilayer onto a (001)-oriented NdGaO₃ substrate using pulsed laser deposition. They then patterned an array of 10 nm Au/10 nm Co top contacts onto the bilayer. These contacts were then probed using a conductive atomic force microscope tip to measure the piezoresponse and electroresistance of each junction. A hysteretic behavior in the junction resistance was observed, which is consistent with ferroelectric polarization switch-

ing of the BaTiO₃ layer, and the tunnel resistance of the junction was shown to strongly depend on the write voltage, as shown in the figure. The magnitude of the OFF/ON ratio was also observed to change by over two orders of magnitude, which corresponds to a nearly 10,000% increase in junction resistance. This is a significant improvement over conventional tunneling magnetoresistive memories, which typically show only a fourfold OFF/ON ratio.

The researchers next measured the switching stability of over 50 junctions, and recorded an average switching ratio

of 64 with little variation in *I-V* behavior over 900 read/write cycles. The power consumption of these devices (~10 fJ/bit) is also lower than that of other non-volatile memory technologies, making these junctions appealing for a wide range of memory applications.

The research team believes that these devices can be optimized using strain engineering, electrical boundary conditions, and even magnetic electrodes to achieve further improvements in performance and could potentially compete with other non-volatile memory technologies.

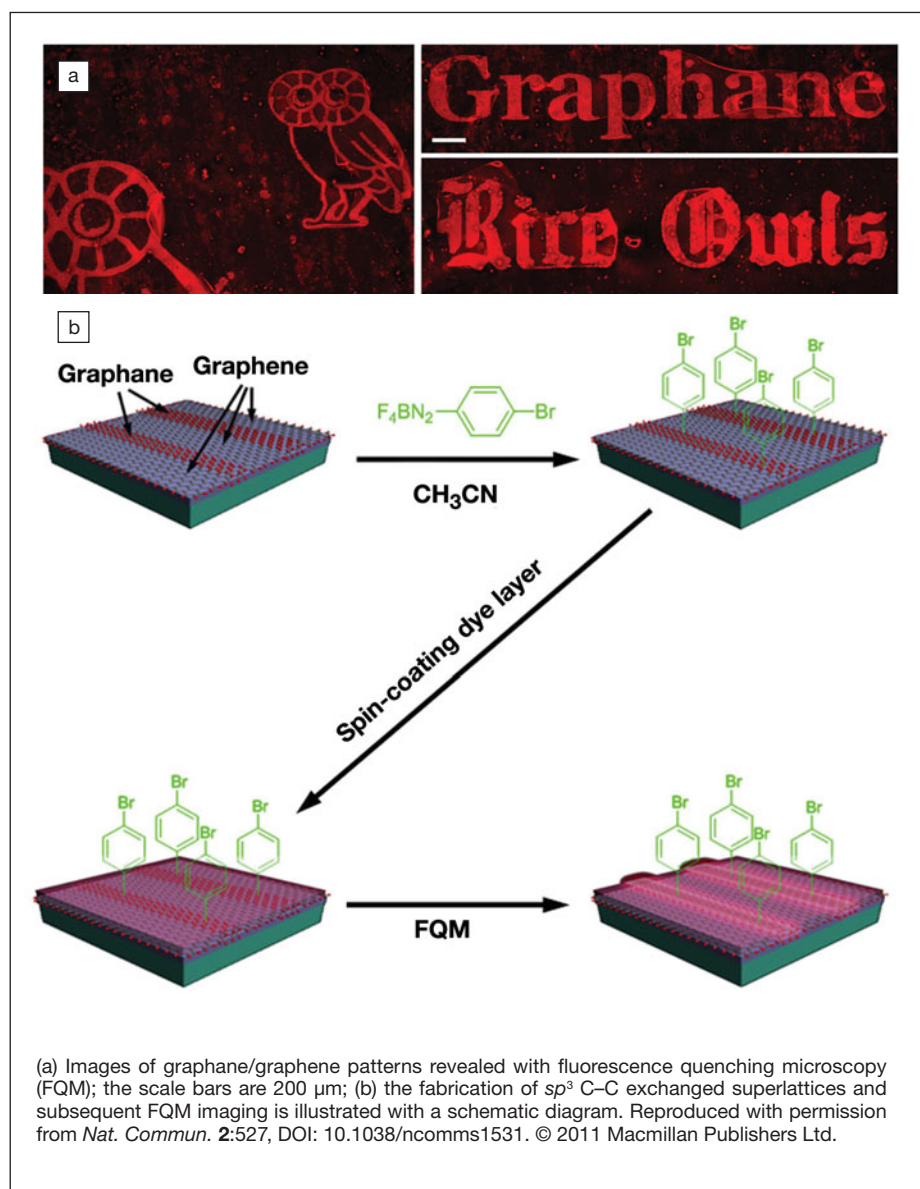
Steven Spurgeon

Nano Focus

Electronic properties of graphene modulated with chemical functionalization

Graphene, with its two-dimensional, hexagonal honeycomb lattice structure and semimetallic characteristics, has great potential for use in a diverse array of optoelectronic applications, especially now that synthetic routes for its large-scale synthesis have been demonstrated. One route to achieving this goal is through chemical functionalization, which can convert graphene, with its bandgap of zero, to a wide-bandgap semiconductor. In addition, patterned multifunctional regions could be used to form the superlattices required for devices such as chemical sensors and thermoelectrics. Toward these ends, J.M. Tour and colleagues at Rice University and Tianjin University have demonstrated a two-step process to first hydrogenate a pattern on the basal plane of graphene and then convert the hydrogens to a different functionality.

As reported in the November 29, 2011 issue of *Nature Communications* (DOI: 10.1038/ncomms1577), the researchers transferred graphene originally grown on Cu substrates to an insulating substrate (either quartz or SiO₂/Si) and then used conventional lithography to expose defined regions of the graphene to atomic hydrogen. Fluorescence quenching microscopy (FQM) was used to image





the regions of hydrogenated graphene, which are termed graphane; see (a) in the figure. Partial hydrogenation of the graphene was confirmed using Raman spectroscopy. Measurement of the electronic properties of this material using four-probe analysis demonstrated a gradual transformation from semimetallic graphene to a near insulating graphane-like material with increasing hydrogenation.

The researchers also further functionalized the graphene/graphane superlattice with 4-bromophenyldiazonium tetrafluoroborate. They proposed that

spontaneous electron transfer occurs from the graphane to the diazonium salt, generating an aryl radical that attacks the sp^3 C–H bonds to form new, covalent sp^3 C–C bonds; see (b) in the figure. Transmission electron microscopy and electron diffraction patterns of the diazonium functionalized films confirmed that the graphene structure survives the functionalization reactions. The extent of diazonium functionality was investigated using x-ray photoelectron spectroscopy, which showed that functionalized films containing as much as one new sp^3 C–C

bond for every 21.5 C atoms in the graphene domains could be achieved using this methodology.

The researchers said that their “two-step controlled covalent functionalization process permits modulation of the electronic properties of graphene’s basal planes and could hold promise for specifically patterned optoelectronic and sensor devices based on this exciting new material.”

Steven Trohalaki

Bio Focus

Self-assembled curved 3D structures with integrated microfluidic network achieved by differential cross-linking of polymer thin films

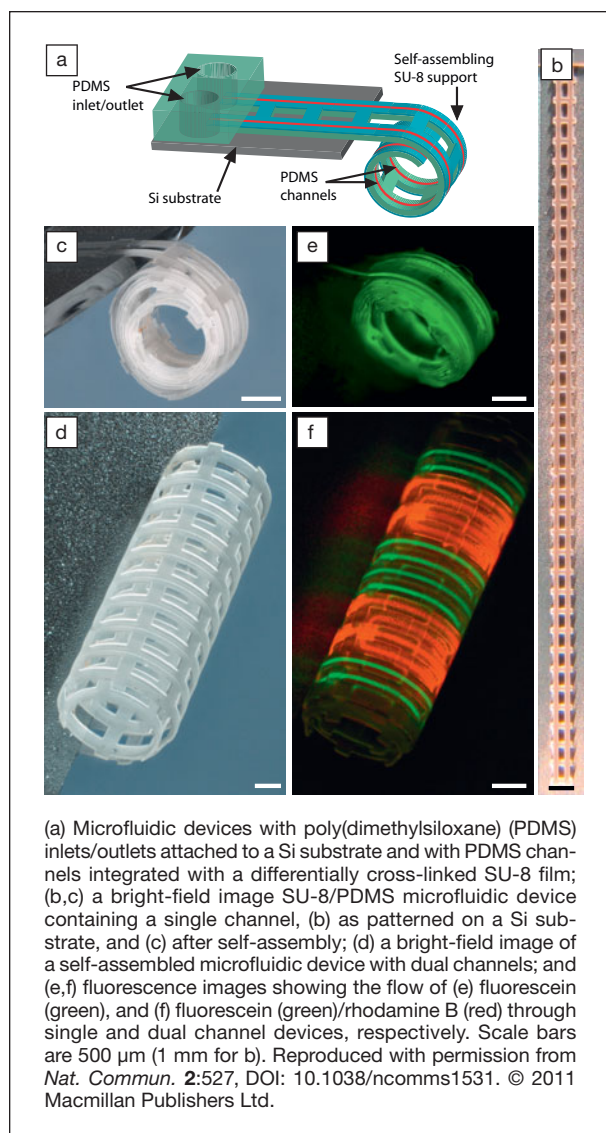
Materials with three-dimensional (3D) curved structures that contain embedded microfluidic channels are of great interest, providing mimics of natural structures such as leaves and tissues. These are permeated with vasculature systems to enable the efficient local transport of nutrients and waste products. Although self-assembly to 3D geometries can be obtained by introducing structural and mechanical heterogeneity in a material, integrating this with a microfluidic network to enable precise delivery of fluid in curved locations, or to create 3D vasculature, creates significant challenges. Recently, D.H. Gracias and colleagues from John Hopkins University have created such a self-assembled microfluidic network by integrating poly(dimethylsiloxane) (PDMS) channels in differentially photo-cross-linked SU-8 (a negative photoresist) thin films which spontaneously and reversibly curve on desolvation and resolvation.

As reported in the November 8, 2011 issue of *Nature Communications* (DOI: 10.1038/ncomms1531), the researchers first created heterogeneous SU-8 films with crosslink gradients (CLGs) along their thickness by exposing the films to

ultraviolet (UV) light. The films were then soaked in acetone to condition them and to generate stress gradients for self-assembly. The SU-8 films then spontaneously curved on desolvation by drying or the addition of water and then re-flattened when resolvated by organic solvents like acetone.

The radii of curvature strongly depend on UV exposure energy and the film thickness and a wide range of geometries could be obtained by simply varying the CLG using conventional photolithography.

The ability of these SU-8 templates to show reversible curvature could also be exploited to curve thicker polymeric films deposited on the surface of a prepared SU-8 film. Integration of microfluidic channels into the polymer film surface layer then enabled the construction of a curved microfluidic device. Fluid flow through the networks with single and dual channel devices established the functionality of the devices as a pathway for fluid transport to curved locations (see Figure).



(a) Microfluidic devices with poly(dimethylsiloxane) (PDMS) inlets/outlets attached to a Si substrate and with PDMS channels integrated with a differentially cross-linked SU-8 film; (b,c) a bright-field image SU-8/PDMS microfluidic device containing a single channel, (b) as patterned on a Si substrate, and (c) after self-assembly; (d) a bright-field image of a self-assembled microfluidic device with dual channels; and (e,f) fluorescence images showing the flow of (e) fluorescein (green), and (f) fluorescein (green)/rhodamine B (red) through single and dual channel devices, respectively. Scale bars are 500 μm (1 mm for b). Reproduced with permission from *Nat. Commun.* 2:527, DOI: 10.1038/ncomms1531. © 2011 Macmillan Publishers Ltd.

The SU-8/PDMS devices are bio-inert and remain curved in culture media.