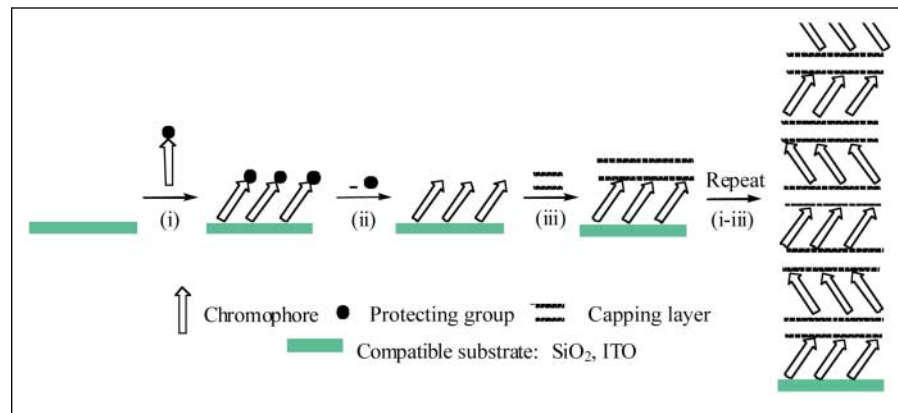


Self-Assembly of Organic/ Inorganic Superlattice Structures May Enable Novel Photonic Devices

Novel organic-based electro-optic (EO) components have the potential to greatly increase the rates of information transmission. The preparation of an organic EO superlattice consisting of layers of chromophore molecules separated by polysiloxane films was recently reported by M.E. van der Boom and T.J. Marks of Northwestern University and their colleagues both at Northwestern and the University of Arizona. The intrinsically acentric superlattice was prepared by a simple and efficient "one-pot" wet chemical self-assembly procedure and exhibited high structural regularity and excellent EO response properties. The researchers said that the material, synthetic method, and nanoscale control of the fabrication may contribute to a simplified method of macroscopic device fabrication.

As communicated in the January issue of *Chemistry of Materials*, the superlattice was prepared by allowing a layer of chromophore molecules to chemisorb onto a hydrophilic substrate, chemically de-protecting the chromophore film, and growing a thin polysiloxane layer ($-\text{SiO}_2-$) which is capable of covalently binding another layer of chromophore molecules. The researchers used the known chromophore 4-[[4-[N,N-(*tert*-butyldimethylsiloxy)ethyl]amino]phenyl]azo]pyridine, which was modified with an *n*-propyl-3-trimethoxysilane functionality to allow strong covalent binding to silicon, glass, or indium tin oxide (ITO)-coated glass substrates. The chromophore layer was then treated with *n*- Bu_4NF to remove the *t*-butyldimethylsilyl protecting groups, resulting in a large density of reactive surface hydroxyl sites. The de-protected chromophores were treated with a hep-



Schematic representation of iterative self-assembly of acentric organic/inorganic superlattice structures. Reproduced with permission from *Chem. Mater.* **13** (2001) p. 16. Copyright 2001 American Chemical Society.

tane solution of octachlorotrisiloxane, which cross-linked and capped the chromophores with a robust polysiloxane film. The formation of this film enhances the stability and planarity of the structure. The hydrophilic polysiloxane layer was then exposed again to a chromophore solution, and the process was repeated until the desired number of layers had been deposited. The researchers reported the synthesis of superlattices having up to six bilayers. Each bilayer was determined to be ~ 20 Å thick. (See Figure.)

Characterization of the superlattice by synchrotron x-ray reflectivity and optical (UV-visible) spectroscopy showed that equal densities of chromophores are deposited in each layer and that the chromophore orientations are uniform. Second harmonic generation measurements revealed that the chromophores have a uniform polar alignment and structural regularity. The high structural regularity was further confirmed by atomic force microscopy on a six-bilayer assembly that indicated that the surface is smooth and featureless, with less than 8% roughness. The lattices were found to be thermally and photochemically robust and exhibited a very large EO response.

According to the researchers, this self-assembly approach is applicable to other chromophores and is more efficient than existing synthetic routes to EO materials. The fact that the entire preparation can be carried out in one reaction vessel makes this approach easily adaptable to automation. Furthermore, the layer-by-layer modularity of self-assembled superlattice building-block incorporation raises the intriguing question of whether other functional constituents (e.g., optical, elec-

tronic, magnetic, and mechanical) could be intercalated as part of the self-assembly process. The strong binding of the modified chromophores to silicon, glass, and ITO allows ready integration of these structurally tailored photonically/electronically functional materials into novel electro-optic devices.

GREGORY KHITROV

Potential Utility of Multiwalled Carbon Nanotube Field-Effect Transistors as Environmental Sensors Demonstrated

In the study of carbon nanotubes (NTs) as field-effect transistors (FETs), the silicon substrate usually also serves as the gate. However, with this method only weak field effects were observed in multiwalled nanotubes (MWNTs). Recently, collaborators at Universität Basel and École Polytechnique Fédérale de Lausanne in Switzerland have experimented with a new gating method, *electrochemical gating*, on a single MWNT. This method yields a much higher transconductance (gate-induced change on the electrical resistance) than the usual substrate back gating (BG) on MWNTs and demonstrates the extreme sensitivity of the MWNT FET to its surrounding environment—in this case, different electrolytes.

The researchers used single MWNTs with lithographically defined Au contacts evaporated over the NTs, fabricated on degenerately doped Si with a 400-nm-thick SiO_2 spacer layer. They positioned a micropipet over the device to deliver a LiClO_4 electrolyte droplet of a diameter ≤ 100 μm , thereby immersing the NT into the electrolyte. They used a Pt wire within the glass pipet as the gate contact, and

SBIR Update

MATECH Advanced Materials (Westlake Village, California) has been awarded a Phase I SBIR grant from the U.S. National Science Foundation to develop a new class of photocurable preceramic polymers to silicon nitride, an advanced ceramic material.

Powdermet, Inc. (Sun Valley, California) has been granted a six-month Phase I SBIR contract from the Department of Energy to further develop nanoengineered, oxide-dispersion-strengthened iron aluminate powders.

measured resistance of the NT devices at room temperature. An applied positive gate voltage U_g would polarize the NT-electrolyte interface by the attraction of cations. The gate capacitance C_g , formed by the double-layer capacitance, can be very large.

The researchers observed that while the initial gate-induced resistances $R(U_g)$ at $U_g = 0$ are comparable between liquid-ion gating and its BG counterpart, $R(U_g)$ has a maximum at $U_g = U_0$ in the electrolyte in the former, which is not observed in BG. This suggests that the NT has a *p*-type behavior for $U_g < U_0$ and *n*-type otherwise. The liquid-ion gating was also more effective than BG by a factor of more than 200. Time-independent measurements were carried out cyclically by sweeping U_g slowly (10 min/sweep); R change of about 20% with a small hysteresis was observed. Time-dependent measurements showed a much larger R change. In either case, U_0 was about 1 V in equilibrium.

According to the researchers, the MWNTs in air are hole-doped with a doping concentration of $\sim 10^{15} \text{ cm}^{-2}$ due to the adsorption of oxygen, leading to Fermi energy E_F of about 0.3–0.5 eV. The electrolyte induces further doping, most likely due to adsorption of the (weakly) oxidizing species (in this case, the perchlorate ion ClO_4^-), leading to a charge transfer which partially oxidizes the NTs. The oxidation is weak in the sense that the NT carbon network is still preserved. The use of a stronger oxidizing electrolyte would shift the curve $R(U_g)$ farther to the right, while a reducing solvent would shift it to the left. The doping magnitude also depends on the electrolyte concentration. Polarizing the NT by an electrolyte allows E_F to move over a wide range, resulting in a large resistance change. NTs are possibly the most sensitive FETs for environmental application because the mobile NT carriers are in intimate contact with the environment—in this case, the electrolyte. In their report

published in the February 19 issue of *Applied Physics Letters*, the researchers also present a model to explain the physics of this experiment.

WIRAWAN PURWANTO

Naturally Occurring Vacancies Shuffle Low-Index Metal Surfaces

R. van Gastel, E. Somfai, S.B. van Albada, W. van Saarloos, and J.W.M. Frenken of Universiteit Leiden have reported in the February 19 issue of *Physical Review Letters* that atoms on the surface of low-index metal surfaces are in motion due to an ultralow density of surface vacancies that rapidly diffuse throughout the surface. Since no experimental techniques are available with both the spatial and the temporal resolution necessary to follow the diffusion of naturally occurring vacancies in a low-index metal surface, the researchers employed embedded indium “tracer” atoms on a copper surface to visualize the diffusive motion of surface atoms. They concluded

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