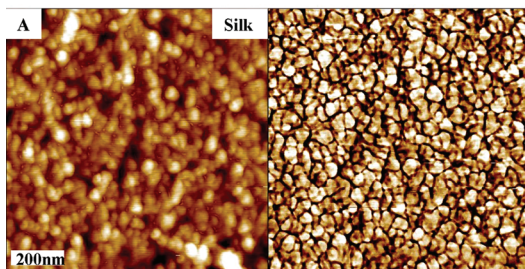


## Strong as Silk Nanocomposites

Materials inspired by nature, or directly derived from it, have served as the basis for advanced materials with unique and useful properties. These materials have several advantages over wholly synthetic ones, such as high biocompatibility, biodegradability, and nontoxic manufacture. One natural material of growing interest is silk, a substance historically sought for clothing and other fabrics, but now gaining increasing attention due to its excellent mechanical properties, including high elastic modulus and toughness. Because silk does not have enough mechanical robustness for some applications, researchers have created reinforced silk-based bulk materials, films, and fibers by adding inorganic nanofillers. However, these materials have often had inherent drawbacks, including compromised mechanical and optical properties.

In an effort to create better, more robust silk-based nanocomposite materials, Kharlampieva *et al.* (p 7053) developed a novel bottom-up method to create silk fibroin membranes embedded with silica particles with silsesquioxane cores or clay nanoplatelets. To fabricate these nano-



composites, the researchers used a one-step approach involving mixing silk and

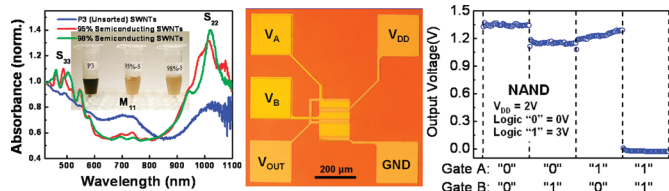
glutaraldehyde solution that acts as a cross-linker, followed by the nanofiller dispersions. These materials demonstrated linear growth, a sign of robust assembly. Indeed, mechanical tests showed up to a 6-fold increase in elasticity and an 8-fold increase in toughness compared to plain silk, an effect orders of magnitude improved from silk nanocomposites prepared with more traditional layer-by-layer methods. Both nanocomposites exhibited low optical absorption, which could be useful for applications that require transparency. The results suggest that this method is viable for creating silk nanocomposites, which could be further customized for particular applications based on incorporating different inorganic species.

## Keep 'Em Separated

Single-walled carbon nanotubes (SWNTs) exhibit an array of interesting and functional electrical properties, such as high carrier mobility and current-carrying capacity, making them a logical choice for use in thin film transistors (TFTs). However, SWNTs also have the notable drawback of being composed of two species, metallic and semiconducting. Previous research has solved some problems in creating viable electronic applications by using highly purified semiconducting preparations. Despite this progress, many questions remain, including what factors affect the performance of TFTs made of these purified preparations, whether trade-offs exist when using preparations of different purity, and whether these TFTs can be used to create integrated circuits.

To answer these questions, Wang *et al.* (p 7123) deposited thin films of either 95 or 98% semiconducting SWNTs on Si/SiO<sub>2</sub> substrates, fabricating TFTs that they used to test the electrical performance of each purified mixture. Results showed that the TFTs with 95% semiconducting nanotubes had on/off ratios of more than 10<sup>4</sup> at the highest channel lengths. The 98% mixture had improved on/off ratios compared to unsorted nanotubes but showed lower on-currents than the 95% mixture. Additionally, as channel length increased, mobility decreased for TFTs in the 95% mixture and

increased for those in the 98% mixture. These findings suggest that the 95% mixture might be useful for applications requiring high mobility, and the 98% mixture might be useful for applications requiring high on/off ratios. The researchers demonstrated the latter by creating integrated logic gates including inverters, NAND, and



NOR. They suggest that these purified nanotube TFTs could hold the key to state-of-the-art nanotube electronics.

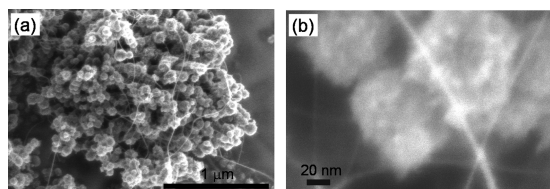
## Nanohorn of Plenty for Field Emission Lamps

Single-walled carbon nanotubes (SWNTs) are known for their unusual electrical properties, and investigators have been aware for more than a decade that electrically conductive carbon nanotubes with high aspect ratios can emit electrons in low electrical fields. Consequently, SWNTs could eventually form the basis for field emission displays and field emission lamps. To make these two applications scalable and cost-effective, the preferred method for depositing nanotubes on

cathode substrates is printing. However, SWNTs have poor dispersibility in solution, forming bundles that distribute unevenly in electrodes and lead to patchy light emission in the final product.

Seeking a way to improve dispersion, Yuge *et al.* (p 7337) looked to single-walled carbon nanohorns (SWNH), electrically conductive nanoparticles that disperse well in solvents. These particles, each an irregularly shaped tube about 2–5 nm in diameter, can group together into clusters of 2000, forming aggregates that resemble dahlia flowers 80 to 100 nm across. The researchers grew SWNTs on SWNH using chemical vapor deposition and Fe catalysts. Though the SWNT

did form bundles on the SWNH, they were distinctly thinner than those that typically form in solution, forming groups 10 nm thick or less. The resulting hybrid SWNT–SWNH product dispersed well in ethanol solution and printed uniformly on electrodes. The final product was a bright field emission lamp that glowed evenly, a testament to the homogeneous distribution made possible by the dual particles. The authors suggest that combination SWNT–SWNH nanoparticles could eventually make other applications that rely on SWNT's field emission properties possible.



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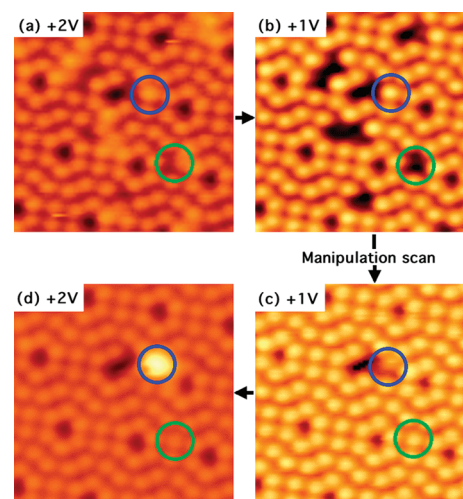
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## Physisorbed Molecules Take the Heat

■ Researchers have searched for at least three decades for a way to overcome the nonspecific nature of thermal chemistry. For example, thermalization can spread energy from the selective beam of a laser throughout a molecule, causing both wanted and unwanted effects. However, Sakulsermsuk *et al.* (p 7344) suggest that thermal energy could be put to good use in an entirely new way: driving atomic manipulation through bond-selective chemistry.

Demonstrating this possibility, the researchers used scanning tunneling microscopy (STM) to dissociate the C–Cl bond in chlorobenzene molecules chemisorbed on a Si(111)-7 × 7 surface. Though such atomic manipulation experiments typically take place at cryogenic temperatures, the scientists show that this dissociation can take place at room temperature and above. Their calculations show that

a one-electron dissociation for the C–Cl bond is exponentially dependent on temperature, with an Arrhenius energy barrier of  $0.8 \pm 0.2$  eV. This energy value correlates to the barrier between the molecule's chemisorbed and physisorbed precursor states. Since the physisorbed state is the more weakly bound of the two, STM can be used to promote efficient one-electron dissociation triggered by thermal excitation, similar to the gas-phase negative-ion resonance process. The authors note that further experiments are necessary to establish whether the results are generalizable to other molecules, as well as electron, photon, or plasma-driven processes. However, since the concept of weakly bound physisorbed precursor states is well-established, they suggest



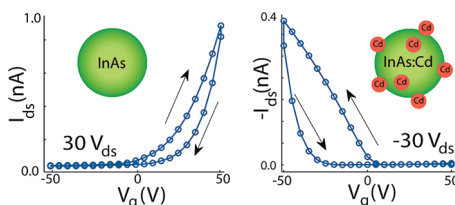
that this mechanism may eventually be used for selective chemistry in other systems.

## Doing the Switch

■ In electronic applications such as solar cells or photodetectors, nanocrystal (NC) films may eventually replace bulk semiconductors. Currently, intrinsic carrier density controls the function of most semiconductor NC-based devices. However, for NC films to become a viable alternative, researchers must be able to control the carrier type and concentration. While previous research has identified several ways to change the carrier type by doping NC films with charge carriers, none have reported a way to do this stably and before films are deposited on their substrates.

Searching for such a method, Geyer *et al.* (p 7373) tested the addition of Cd,

a stable transition metal that can be added predeposition, to InAs NC films. Like bulk InAs, InAs NC films have n-type conduction. However, the researchers' tests show that incorporating Cd reliably switches these films to p-type conduction. Additionally, InAs films with the added Cd showed fundamentally differ-



ent dark current and photocurrent properties compared to those without Cd,

suggesting that this incorporated metal significantly changes the density of states within the band gap. A third NC film, composed of InAs particles coated with a shell of CdZnSe, showed ambipolar switching behavior. The researchers have two potential mechanisms to explain these phenomena. First, Cd may act as a substitutional impurity by occupying an In lattice position. Second, Cd bound to the surface may create an acceptor state by passivating the InAs donor state. Regardless, the authors note that adding Cd provides a simple and stable way to control carrier type in InAs NC films.

## Polarizing Findings

■ Understanding the physical, chemical, and electronic coupling between molecules and surfaces is pivotal to the development of molecular devices and controlled interfaces. However, measuring these interactions can be tricky because the interface is buried. A new approach exploits the coupling between the electrons of the molecules and those of the substrate by measuring the polarizability of the attached molecule. The polarizability can be influenced by the molecules' orientation and the topography of the substrate.

Moore *et al.* (p 7630) developed a means of measuring the polarizabilities of single attached molecules using scanning tunneling microscopy in conjunction with microwave frequency generators. This technique deforms the molecules' electron clouds, with feedback enabling

simultaneous measurements of both polarizability and molecular topography with molecular resolution. The researchers used this method to measure the polarizability of four different families of molecules adsorbed to Au{111} surfaces, with structures ranging from fully saturated to fully conjugated, as well as single-molecule switches in two different conductance states. They found that each adsorbed molecule's polarizability was consistent with the results of density functional theory calculations, increasing both with length and the number of multiple bonds.

For the single-switch molecules, the measured polarizability was directly related to differences in the interactions between the substrates'

and molecules' electron clouds in ON and OFF conductance states. In the switch molecules, nitro-functionalized oligo-(phenylene ethynylene), calculations suggest that the conductance state change is also related to an oxidation state change in the functional group. The authors suggest that this method can be useful for evaluating the behavior of other conductive or switchable molecules, which could prove useful in developing novel molecular devices.

