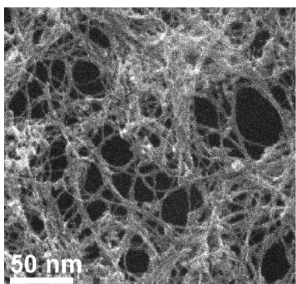


## Adding It Up: Why Multiple Catalysts Are Better for Single-Walled Nanotube Formation

■ Since the discovery of single-walled carbon nanotubes (SWNTs), several groups have shown that the use of binary catalysts significantly improves yield when using the chemical vapor deposition (CVD) method of synthesis.



However, the mechanisms behind how mixed catalysts improve SWNT yield are unknown. Most efforts to elucidate the roles of the catalyst have found that the catalyst goes beyond simply nucleating and promoting growth of the carbon nanotubes to active involvement in the

catalytic decomposition of the hydrocarbon feedstock.

To clarify the mechanism involved in mixed catalytic systems of SWNT synthesis, Tetali *et al.* (p 3839) performed studies on SWNT syn-

thesis using laser evaporation. This method involves evaporating a graphite target containing catalytic material in a reactor at elevated temperature within a buffer gas. With the ability to control parameters including temperature, pressure, and flow

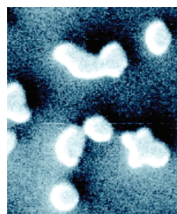
rate, the researchers explored different catalyst combinations using Ni, Co, and Mo in a range of ratios. They found that binary or ternary catalyst mixtures lead to higher yields compared to single metal catalysts, with the best yield produced using a combination of all three metals. Further observations suggest that the mixing of catalysts alters the catalyst cluster size distribution, maximizing the clusters' potential to form a hemispherical cap at nucleation and, hence, to form a SWNT. The authors suggest that better understanding of the roles of catalysts could further improve synthetic yields of SWNTs.

## Electron Beam Lithography Heats Up Raman Hot Spots

■ Researchers are continually seeking ways to improve the analytical capabilities of surface-enhanced Raman scattering (SERS) through the development of new and better substrates. A central focus of these improvements is increasing the number of "hot spots", or areas that enhance the Raman signal. Currently, the most popular type of SERS substrate is simple colloidal Au or Ag nanoparticles in the 10–150 nm size range. However, hot spots in these substrates occur randomly, making them extremely difficult to create or to predict consistently.

To improve upon current SERS substrates, Wells *et al.* (p 3845) developed

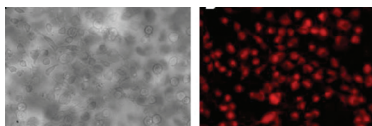
a new method for creating substrates using electron beam lithography (EBL) along with combinatorial spectral mapping. The researchers created EBL patterns from randomly arranged, computer-generated arrays of shapes. They used two types of nanometer-sized shape sets: pointed shapes, including stars, crescent moons, and so on, or rounded shapes including eight different circles or ellipses. They created Ag arrays using these patterns and grouped them into  $5 \times 5 \mu\text{m}$  cells, then surveyed the cells for enhanced SERS signals using benzenethiol.



The researchers found regions that remained consistently "hot" in the same pattern over two trials, with the difference between highest and lowest signals in the cells ranging by more than a factor of 44 in signal. Using the cells identified as the best performing, the team was able to clone large arrays that yielded electromagnetic enhancement of  $5 \times 10^8$  with good uniformity. The authors note that further enhancement of the Raman signal may be possible by manipulating the shapes and sizes of nanoparticles.

## NanoGUMBOS Add Spice to Biomedical Imaging

■ Near-infrared (NIR) fluorescent materials have long been applied as biomedical imaging contrast agents. Several materials in the nanometer regime have been exploited specifically for *in vivo* imaging since their fluorescence falls in the spectrally inactive region of 700–1100 nm, which enables deep-tissue imaging. Consequently, investigators are interested in developing nanomaterials that are biocompatible, nontoxic, and tunable, while exhibiting well-defined delivery behavior.



To meet this need, Bwambok *et al.* (p 3854) developed a new class of fluorescent nanomaterials they call GUMBOS (group of uniform materials based on organic salts). These GUMBOS are derived from ionic liquids that melt above physiological temperature. This low melting point stems from the asymmetry of component ions and the resultant poor crystal packing of the parent ionic liquids, which leaves these materials open to design. As proof of concept, the researchers crafted several new GUMBOS using a cyanine dye as the cation and various anions selected for their different hydrophobicities, geometries, and masses. The resulting materials dis-

played variable physical properties, including melting point and solubility, dependent upon the anion used. In each case, the GUMBOS were excellent absorbers of NIR irradiation, fluorescing strongly in the desired wavelengths. Experiments showed that these particles were well-absorbed in cells, suggesting the potential for using GUMBOS for cellular imaging. In addition, the authors suggest that exploiting the GUMBOS robustness could eventually lead to novel multifunctional hybrid materials.

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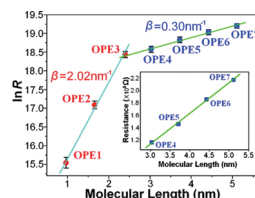
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## Making Connections: Investigating Charge Transport Mechanisms at Molecular Junctions

Over the past several decades, molecular electronics has developed into an interdisciplinary topic with the goal of constructing and implementing nanometer-scale circuits based on single-molecule devices. To maximize device efficiency, researchers must achieve a fundamental and comprehensive understanding of charge transport mechanisms in molecular junctions. So far, experiments in donor–bridge–acceptor (D–B–A) systems have shown that nonresonant tunneling is the predominant mechanism in short molecular wires, where molecular resistance varies exponentially with length. Hopping conduction predominates in longer wires, where resistance has a weak length dependence. However, there remains uncertainty in the behavior of molecular junctions, such as molecules wired directly between metal

electrodes. Thus, further insight is needed on the effects of donors and acceptors on the intrinsic conduction of a conjugated bridge.

Toward this, Lu *et al.* (p 3861) investigated charge transport mechanisms in oligo(*p*-phenylene ethynylene) (OPEs). The researchers synthesized wires composed of OPE molecules strung end-to-end of various lengths, ranging from 1 to 7 OPE moieties, terminated by amines. They then self-assembled these wires into dense monolayers on a Au electrode, with the molecules adsorbed on the substrate in an upright position. Using modified scanning tunneling microscopy (STM) break junction measurements and



conducting probe atomic force microscopy, Lu *et al.* were able to determine electronic decay constants, single-molecule resistance, and current–voltage characteristics. The researchers found that the charge transport mechanism varied with the length of the OPE wires, observing a clear transition from tunneling to hopping near 2.75 nm. Quantum chemistry calculations confirmed that OPE wires with more than three repeating units appear to be channels for hopping conduction. This systematic study sheds new light on the length dependence of the transport mechanism for OPE-based devices. The authors note that they are currently performing similar analysis with much longer OPE wires and ferrocene-based OPE molecules.

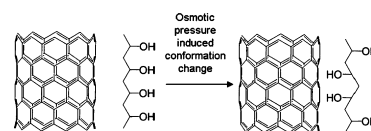
## Photoluminescent Nanotubes in Hydrogels: A Bright Idea for Biosensing

Since individual single-walled carbon nanotubes (SWNTs) and their metallic-free bundles exhibit near-infrared (NIR) photoluminescence, a region of the electromagnetic spectrum in which blood and tissue are transparent, they have been proposed as a potential component of biomedical optical sensors. Carbon nanotubes have been previously embedded in hydrogels, cross-linked polymer matrices that can swell in the presence of water, and are highly biocompatible; however, little is known about the properties of this aggregate material and its utility as a sensor.

To characterize this material, Barone *et al.* (p 3869) synthesized polyvinyl

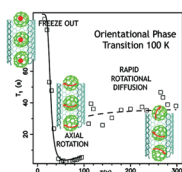
alcohol hydrogels embedded with SWNTs, adding varying amounts of glutaraldehyde as a cross-linking agent. They measured Raman scattering frequencies from these embedded SWNTs. The researchers found that, as the cross-linking density and hydration state of the hydrogel increased, Raman scattering frequencies from the SWNT upshifted. Increases in cross-linking density also led to a clear red shift in the photoluminescent emission maxima. Examining these results, the researchers concluded that strain alone cannot explain the observed shifts, proposing instead a new mechanism in which the hydrogel cross-linking density and internal

pressure induce changes in the local dielectric around each nanotube. Testing a possible application, the researchers fashioned a model glucose sensor using apo-glucose oxidase chemically attached to the hydrogel matrix. Exposure to glucose causes the photoluminescence signal to change reversibly and in real-time. The authors suggest that this aggregate material could yield novel platforms for *in vivo* detection.



## Consider the Peapods: Investigating Fullerenes Encapsulated in Nanotubes

The structure of single-walled carbon nanotubes (SWNTs) provides a unique quasi-one-dimensional space that has the potential to encapsulate molecules. Several groups have suggested that such entrapped molecules may behave differently than those in bulk because of the confinement and reduction in the number of nearest-neighbor molecular structures, providing the possibility for interesting potential applications in nanometer-scale electronics, chemistry, and biomedicine. Though SWNTs and their entrapped molecules have been studied as a hybrid material, little is known at



the experimental level about the actual packing and dynamics of the encapsulated species.

To learn more about these entrapped molecules, Abou-Hamad *et al.* (p 3878) undertook a study of  $C_{60}$  molecules inside SWNTs (structures called “peapods”) through temperatures ranging from 300 K down to 5 K using carbon-13 nuclear magnetic resonance. Using high-resolution magic angle spinning techniques, the researchers found that

~32% of the encapsulated molecules, a minority termed  $C_{60}^r$ , are rotationally blocked at room temperature. About

68% of the molecules, called  $C_{60}^b$ , appear to undergo molecular reorientational dynamics. The researchers’ results show that this majority of fullerenes undergoes a phase transition at 100 K from continuous rotational diffusion to uniaxial rotations. At 25 K, the molecules freeze out. Their observations suggest that the significant changes in the dynamic properties of these molecules result from the reduction of the number of nearest neighbors and the smooth interaction of the fullerenes with the SWNTs’ side walls. The authors suggest that these findings add to the limited body of knowledge of these encapsulated species.