

graphene layers, which eventually form the nanofibers, were assisted by dynamic formation of monoatomic step ledges on the graphene–Ni interface.

The researchers performed density functional theory calculations to understand the origins of the interfacial process and the transport of C and Ni atoms along the graphene–Ni interface. The surface transport of the C atoms was shown to be the rate-limiting step for the nanofiber growth. The experimental results and theoretical calculations indicate that the step edges on the Ni surface act as growth centers for graphene growth because C binds more strongly to such sites. This mechanism is likely to be of broad significance for any metal-catalyzed nanofiber growth, according to the researchers. They said that this study reveals the first direct glimpses of the initial stages of nanofiber growth using nanoscale real-time growth observations. Metallic step-edges acting as spatio-temporal dynamic growth sites may be important for understanding other types of catalytic reactions and nanomaterial syntheses.

GOPAL RAO

Variation of Electron Level Enables Semiconducting-to-Metallic Transition in Single Phenalenyl-Based Molecules

Quantum transport properties of single-molecule electronic devices are affected not only by the choice of molecules but also by the interface structures used. K. Tagami and M. Tsukada from the University of Tokyo and L. Wang from Southern Yangtze University in China studied theoretically the conductive properties of single boron- and nitrogen-substituted phenalenyl molecules ($C_{13}H_9$) and found that they can tune the properties of the molecules from semiconducting to metallic depending on the type of central atom used. The researchers reported in the February issue of *Nano Letters* that by changing the type of central atom from carbon to nitrogen or boron, they can dramatically alter the transport properties of the system.

The researchers calculated the atomic coordinates (i.e., the size) of each molecule, and connected it to electrodes by bonding a mercapto-vinyl group to the α or β site, which is the second- and third-nearest to the central atom site, respectively. Molecules connected through β sites demonstrate a conduction channel that is energetically very close to the Fermi energy of the gold electrodes. In contrast, with the connection through the β site, nitrogen- and carbon-containing phenalenyl molecules become semicon-

ducting, while the boron-type displays metallic properties. The researchers also found that when the electrodes are connected to the β sites, the conductance through the carbon-containing phenalenyl molecule is spin-dependent. The researchers said that the change in the transport features originates from the spatial distribution of the nonbonding molecular orbital, which has amplitude only on the α sites. These features do not change when the researchers substitute the central atom of phenalenyl with the nitrogen; however, if they substitute it with the boron atom, then the quantum transport occurs through the orbitals that have amplitude both on α and β atomic sites.

EKATERINA A. LITVINOVA

Stationary Light Pulses Created

Achieving direct control over the propagation of light is a goal that is interesting both from a fundamental scientific standpoint and for practical applications. If developed, the ability to control light pulses may lead the way to new advances in nonlinear optics and quantum computing. Recently, a team of physicists from Harvard University and Lebedev Institute of Physics, Moscow, temporarily stored light pulses as electromagnetic energy. Previous research efforts have stored localized light pulses as holographic imprints, but this work improves on those studies by actually trapping photons in an atomic medium.

As reported in the December 11, 2003, issue of *Nature*, M. Bajcsy, A.S. Zibrov, and M.D. Lukin designed a technique for the creation, storage, and controlled release of stationary light pulses. The main concept is based on the principle of electromagnetically induced transparency (EIT), which uses one or more "control" laser beams to modify the optical properties of a medium. The methods described in this work employ a weak "signal" laser beam containing the photons that will be stopped, and two control lasers: a forward-directed (FD) beam and a backward-directed (BD) beam.

The experimental realization of this idea is carried out using an optically dense medium of Rb vapor contained in a small cell and open to the appropriate laser beams. The group first maps a signal pulse onto the Rb by firing a signal pulse at the Rb gas as it is illuminated by the FD control beam, similar to previous EIT experiments. Turning off the FD beam stores the signal on the Rb atoms, and subsequently turning on either of the control beams converts the stored excitation back into light, propagating in the direction of the applied beam. The

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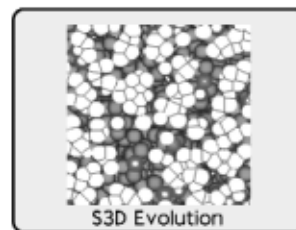
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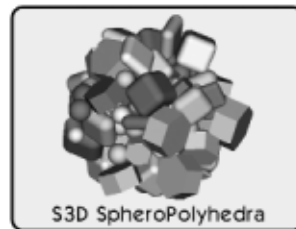
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notable innovation of the work is then achieved by simultaneous application of the FD and BD control beams. This produces an interference pattern that causes the Rb atoms to act like tiny mirrors, effectively trapping the light pulse inside the medium. The pulse is then released in the forward direction by turning off the BD beam. In this fashion, the researchers brought light to a halt.

ANDY FRANCIS

Multiple Bridging Groups Aid Absorption Properties of Ordered Porous Organic-Inorganic Hybrids

Organic-inorganic hybrid polymers in the form of periodic mesoporous organosilicas (PMOs) have highly ordered pore networks and large internal surface areas. Although similar in morphology, they are more mechanically and hydrothermally stable than ordered mesoporous silicas. One way to tailor the pore size in PMOs for specific applications (e.g., sorbents, sensors, and catalysts) is to vary the organic groups that bridge the inorganic moieties. Toward this end, a team of researchers at the Center for Bio/Molecular Science and Engineering within the Naval Research Laboratory, Washington, D.C., has synthesized and characterized a class of ordered PMOs with more than one type of organic group.

In an article published in the December 17, 2003, issue of *Chemistry of Materials*, investigator M.A. Markowitz and co-workers used a versatile surfactant templating technique to synthesize PMOs in which the organic bridging group was an ethylene homopolymer, a phenylene homopolymer, or an ethylene phenylene copolymer. In the current study, PMOs with organic copolymers were prepared with ratios of phenylene and ethylene precursor ratios of 3:1, 1:1, and 1:3. Analyses by the researchers of solid-state ^{13}C and ^{29}Si cross-polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra confirmed that the C-Si and Si-O bonds were stable during synthesis for all PMO polymers. In addition, the NMR spectra showed that extraction of the surfactant was complete. The researchers showed that powder x-ray diffraction patterns are consistent with

hexagonally packed arrays of round cylindrical voids (i.e., the pores), surrounded by the polymer matrix.

The researchers found that the pore size distribution was very narrow and centered at 4 nm. Although the researchers note a trend in pore size based on precursor ratio, the differences in pore size are small. Nitrogen sorption measurements obtained classic Type IV isotherms with large nitrogen capacities (0.9–1.1 cm^3/g at STP). The absorption capacity of the PMO prepared from a 1:1 ethylene phenylene precursor ratio is about 75% greater than the phenylene-bridged PMO and about twice that of the ethylene-bridged PMO. The researchers said this demonstrates that the phenylene-ethylene combination results in improved performance. A diphenylene-bridged organosilica was also previously reported to have high absorption capacity, but that material has an amorphous pore structure, which is disadvantageous for some applications. The researchers attribute this lack of pore order to the flexible nature of the diphenylene-bridging group. The ordered microstructure and mesoporosity obtained using the surfactant templating synthesis approach to prepare the PMOs allow for fast diffusion of molecules and lead to quick access to the large internal surface areas of these materials, making them more suitable for applications requiring rapid adsorption/desorption kinetics. The researchers also said that their synthetic protocol is versatile because they have synthesized and characterized more than 10 novel PMO copolymers using different combinations of a variety of organic bridging groups. Furthermore, the researchers said that their method has the “potential for the use in the synthesis of bimetallic oxides and sol-gel materials where the discrepancies in hydrolysis and condensation rates of the precursors has led to phase separation and inhomogeneous products.”

STEVEN TROHALAKI

Chiral Nanotubes Fabricated from Hierarchical Self-Assembly of π -Conjugated Building Blocks

Hydrogen-bond interactions between molecules are often used to design cyclic supramolecular structures. However, the

further assembly of these structures into more complex architectures has rarely been achieved. As reported in the December 22, 2003, issue of *Angewandte Chemie*, P. Jonkheijm from Eindhoven University of Technology, The Netherlands; A. Miura from Katholieke Universiteit Leuven, Belgium; and their colleagues report the self-assembly of π -conjugated oligo (*p*-phenylene vinylene) (OPV) precursors into helical nanotubular aggregates.

Initial observations by the researchers in scanning tunneling microscopy studies showed that the diamino-triazine-bearing OPV precursors can hydrogen-bond to form rosette structures with cavities. This inspired the researchers to study the behavior of these molecules in solution, to see if the rosettes would stack to form well-defined nanotubes. The researchers found that the rosette structures formed tubular aggregates in nonpolar solvents, with aspect ratios (i.e., ratio of length to diameter) that were as high as 1500. Small-angle neutron-scattering measurements confirmed the formation of cylindrical aggregates in solution.

The researchers also carried out detailed temperature-dependent optical absorption, fluorescence, and circular dichroism studies to research the melting of the aggregates to the monomeric molecular species. They found a two-step aggregation process: first, a transition from molecular-dissolved species into achiral stacked structures, and then their further evolution into helical stacks.

The researchers think that the building block molecules first form hexameric rosettes through hydrogen bonding at the diamino triazine ends, and these rosettes are then further held together in stacks by π - π interactions between the phenylene vinylene groups. Once the building blocks have been assembled into stacks, the chiral side chains introduce a handedness to this supramolecular structure.

A. Schenning (Eindhoven) said that this work demonstrates guidelines for programming π -conjugated molecules into self-assembled tubes for application in nano-sized electronics. Such designed structures may find use as sensors or for transport through the nanometer-sized cavities.

SARBAJIT BANERJEE

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