

The nuclei of  $^{12}\text{C}$  isotope, which is dominant in carbon materials, has spin zero. However, the  $^{13}\text{C}$  isotope, which accounts for  $\sim 1\%$  of carbon nuclei, has spin  $1/2$ . Good understanding of hyperfine interactions and the ability to control them are thus required to overcome spin relaxation and decoherence. Recently, O.V. Yazyev at the Swiss Federal Institute of Technology (EPFL) in Lausanne, Switzerland, used accurate first principles calculations to show that hyperfine interactions in graphene fragments can be accurately described in terms of only the local distribution of low-energy electron spins and the local atomic structure.

As reported in the April issue of *Nano Letters* (DOI: 10.1021/nl072667q; p. 1011), Yazyev applied all-electron density functional theory implemented in a commercially available quantum chemistry software package. This approach has previously been shown to predict hyperfine coupling constants in excellent agreement with experimental results. Yazyev calculated hyperfine coupling constants for  $^{13}\text{C}$  nuclear spins in a dozen electron- and hole-doped graphene fragments  $\sim 1$  nm in size, providing a database containing over 200 coupling values. Yazyev found that the isotropic (Fermi contact) and dipolar hyperfine couplings in the graphene structures are about equally important. Their magnitudes are significant but generally smaller than those in materials comprised of heavier elements, such as gallium arsenide. Both Fermi contact and dipolar hyperfine coupling constants (for  $^{13}\text{C}$  and other nuclear spins from substitution impurities and edges) were fitted to a simple expression composed of terms that account for onsite and nearest-neighbor conduction electron spin populations. Yazyev said that the parameters thereby obtained provide a tool for predicting the hyperfine interactions in arbitrary  $sp^2$  carbon nanostructures. This will allow the engineering of nanoscale devices with optimal spin relaxation and decoherence times. Yazyev further said that “the ‘contaminant’ nuclear spins, e.g. the spins of protons at the edges of graphene nanostructures, have to be considered seriously because their hyperfine couplings were found to be surprisingly high. A chemical way for decoupling these spins has to be devised in [the] future.”

STEVEN TROHALAKI

### Gradiantly Alloyed $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ Colloidal PL QDs Developed by One-Pot Synthesis

Colloidal photoluminescent (PL) semiconductor nanocrystals have attracted significant attention over the past decade from

the viewpoints of both fundamental science as well as potential applications. When the sizes of the spherical semiconductor nanocrystals become less than or comparable to that of a photogenerated exciton in bulk materials, quantum confinement effects become operative. Quantum dots (QDs) can absorb and then re-emit light in spectral regions that are not covered by their corresponding bulk materials. Now K. Yu and co-workers at the National Research Council of Canada have introduced an innovative synthesis method for three-component QDs that enhances control of blue emission by creating gradients in alloy composition.

Ternary alloy QDs have opened the way to bandgap engineering with stoichiometry as well as size. The research team proposed that two well-known binary QDs, CdS and ZnS with bulk bandgaps of 2.48 eV and 3.7 eV as well as with zincblende lattice constants at room temperature of  $5.835\text{\AA}$  and  $5.406\text{\AA}$ , should provide a useful blend with high blue emission efficiency owing to their low lattice mismatch. Ideally, a gradient ternary ZnCdS QD should have a Zn-rich outer layer for efficient blue emission as well as low toxicity.

As reported in the April 3 issue of the *Journal of Physical Chemistry C* (DOI: 10.1021/jp710852q; p. 4908), the researchers developed an efficient approach to the synthesis of high-quality ZnCdS QDs with Cd-rich inner cores and Zn-rich outer shells. The approach features synthetic reproducibility and easy scale-up. Emphasizing “green,” environmentally friendly synthesis by using air-stable chemicals, such as zinc stearate, cadmium acetate dihydrate, and elemental sulfur, the researchers monitored the temporal evolution of the optical properties of the resulting growing QDs, and systematically characterized the QD structure and composition by solid-state nuclear magnetic resonance (NMR), x-ray photo-electron spectroscopy, powder x-ray diffraction, and transmission electron microscopy. The solid-state NMR included cross polarization (CP) and dipolar dephased cross polarization.

The trick exploited by the research team was to vary reactivity during the QD synthesis to form the composition gradients. A Cd-rich core is initially formed, as evinced by the redshifting of the bandgap absorption and emission in the early growth stage. With proper choice of reactants and concentrations, there is a gradual formation of Zn-rich outer layers because of the depletion of Cd in the reaction medium. The outermost layer can be made to consist of ZnS with little cadmi-

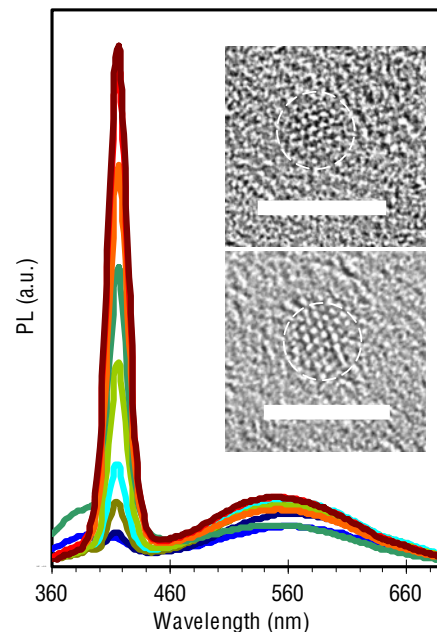


Figure 1. Emission spectra (excitation wavelength 350 nm) of the growing ZnCdS nanocrystals from the synthetic batch with a feed molar ratio of 3Zn-to-1Cd-to-4S. The colors represent different growth periods at  $240^\circ\text{C}$  in minutes (1–180 min.); “fixation” of both the bandgap absorption (at  $402\text{ nm} \pm 1\text{ nm}$ ) and emission (at  $415\text{ nm} \pm 1\text{ nm}$ ) is pronounced. The inset transmission electron micrographs represent the nanocrystals with 8-min. (top) and 180-min. (bottom) growth periods, with a scale bar of 5 nm. Reprinted with permission from the *Journal of Physical Chemistry C* **112** (13) (April 4, 2008) p. 4908. ©2008 American Chemical Society.

um. Such an accumulation of ZnS in the outer layers directly leads to an effective core-shell structure, which coats and protects the CdS-rich core, giving rise to the observed “fixation” of bandgap absorption and emission, as shown in Figure 1.

The researchers tuned the feed Zn-to-Cd-to-S stoichiometry to form high-quality  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  QDs exhibiting sharp exciton absorptions, narrow PL emissions, and high PL quantum yield up to 23%. With relatively high Zn and S feed amounts, the resulting gradiently structured ZnCdS QDs exhibited superior photostability against UV irradiation and relatively long shelf time in common organic solvents as compared to that of the binary counterparts. The enhanced UV resistance and storage stability of the nanocrystals can be explained by the “coating” effect of the Zn-rich region. In the later growth stage, Zn diffuses into the inner CdS-rich core, leading to a blueshifting of the bandgap.

Solid-state magic angle spinning (MAS)

NMR spectroscopy played a crucial role in verifying the growth of the Zn-rich outer shell. First,  $^{13}\text{C}$  MAS spectra with proton cross polarization with and without dipolar dephasing showed that the organic capping ligand, stearate, is firmly attached by the carboxyl group to the surface, with only the extremities of the alkyl chain showing any signs of motion. (This contrasts with earlier observations of tri-octylphosphine oxide capping molecules hopping around on the surface of CdSe and CdTe QDs). With attached organic groups it was then possible to obtain  $^{113}\text{Cd}$  MAS spectra with and without  $^1\text{H}$  cross polarization and thus distinguish surface versus core Cd atoms. The signal of surface Cds with coordinated carboxyl groups was observed to decrease as the Zn content of the QD increased, and eventually disappeared when there was more Zn than Cd. The disappearance of this signal attests to the depletion of Cd in the surface layers, since Cd should still be visible if it were present in the surface layers in the same ratio as the overall Zn:Cd composition. An increasing chemical shift of the signal of the core Cd also demonstrated a ZnCdS alloy with increasing Zn content.

According to the researchers, the study describes the synthesis–structure–property relationships of ternary ZnCdS alloys. Ternary ZnCdS QDs, with intense PL emission and narrow full width at half maximum, are excellent candidates as blue luminescent materials for various applications, and this study presents a new and easy method for their synthesis, said the researchers.

GOPAL RAO

### CNT Turfs Demonstrate Coordinated Buckling

Carbon nanotubes (CNTs) have had an impact on multidisciplinary scientific fields, and their properties have led to widespread use in structural, electrical, and thermal applications. Dense fields of intertwined, vertically-oriented carbon nanotubes are known as CNT turfs. Realizing the importance of studying the mechanical behavior of turfs bonded to a semiconductor-based substrate, A.A. Zbib, S.Dj. Mesarovic, and D.F. Bahr of Washington State University; E.T. Lilleodden of the GKSS Research Center, Germany; and D. McClain and J. Jiao of Portland State University have recently prepared patterns of vertically aligned CNTs on photolithographically prepared silicon wafers.

The mechanical properties of individual single-walled and multi-walled CNTs have been studied both experimentally and theoretically using simulations like molecular dynamics and finite element

methods in tension, compression, or bending. However, the collective behavior of complex CNT geometries like CNT turfs has not received considerable attention. CNT turfs are complex structures of intertwined and nominally vertical tubes. The behavior of freestanding CNT turfs has been reported, but their potential use in contact switches necessitates further study. In the April 30 issue of *Nanotechnology* (DOI: 10.1088/0957), the researchers described the coordinated buckling behavior of collective CNT segments using experimental and theoretical approaches.

In the experiments, CNT turfs were grown using chemical vapor deposition from a catalyst containing glass. This led to turfs that were bonded to the growth substrate. The researchers measured the mechanical properties of turfs using localized compression by nanoindentation and uniform compression. They measured the tangent elastic modulus of CNT turfs with a blunt Berkovich tip of a 1000 nm radius using a triboscope in conjunction with a scanning probe microscope. Although the elastic modulus of a single CNT can be on the order of 1 TPa, researchers reported an average tangent modulus of  $\sim 15$  MPa. This can be expected from a collective response of CNTs in a turf, which is dominated by buckling/ bending of CNT segments. Uniform compression experiments were done to place an entire column width in compression, and coordinated reorientation and collective buckling in the layer were observed. Various turfs with 300  $\mu\text{m}$  diameters and heights varying from 25  $\mu\text{m}$  to 204  $\mu\text{m}$  were tested using a displacement-controlled compression tool. Other turf samples with 30  $\mu\text{m}$  turf radii and  $\sim 60$   $\mu\text{m}$  heights were compression-tested using load-controlled nanoindentation, employing a flat diamond punch.

The researchers developed a mechanical model that describes the buckling of these complex turfs, and the researchers were able to validate their findings from scanning electron microscope images. Researchers concluded that CNT turfs exhibit coordinated buckling in the bottom layer under uniform compression at nominal stresses of between 4.3 MPa and 0.2 MPa.

“The buckling stress depends mainly on the effective tangent modulus of the turf, its height, and its nanogeometry,” the researchers said. They said that their findings should help in materials selection and design of CNT-based materials that rely on the collective mechanical behavior of CNT turfs such as switches or future CNT integration into microelectronic packaging to take advantage of the thermal and electric conductivity of nanotubes.

ROHIT KHANNA

### Nanosized Optical Emitter Coupled to Gold Nanowires Enhances the Coupling Constant and the Surface Plasmon Density of States

Coupling of quantum systems with photon fields is crucial to develop quantum information processing tasks. There has recently been significant interest in using surface plasmons (SP) to propagate information through systems of nanowires. SP emission scales with decreasing nanowire radius, but so do SP propagation losses. Consequently, very small wires have not proven suitable for long-distance transmission of information via SP. S.D. Liu, M.T. Cheng, Z.J. Yang, and Q.Q. Wang from the Wuhan University, China, have demonstrated theoretically that a pair of nanowires of relatively large radii show a stronger coupling with an emitter and present smaller losses for SP propagation than when using only a single nanowire.

As reported in the April 15 issue of *Optics Letters* (p. 851), the researchers used the finite difference time domain (FDTD) simulation method to study the SP coupling, SP propagation, and far field emission for an oscillating dipole emitter coupled to a single and a pair of gold nanowires, with the emitter located at a distance  $\Delta$  from the surface of the nanowires, and forming an angle  $\theta$  with their axes.

The researchers showed that when using a pair of nanowires, the coupling with the emitter is stronger and the losses of SP propagation can be reduced. They also showed that the field could not be enhanced when the polarization of the emitter was vertical to the connection line between the central point of the two nanowires ( $\theta = 0^\circ$ ), while it was significantly excited when  $\theta = 90^\circ$ . At the same time, the spontaneous emission rate became faster, and while the SP wavelength ( $\lambda_{\text{SP}}$ ) was found to be constant for a single wire, the simulation results revealed that  $\lambda_{\text{SP}}$  could be tuned from 650 nm to 380 nm when the distance between the two nanowires was reduced from 60 nm to 5 nm. The generated plasmon field, which was proportional to the total spontaneous emission rate when coupling with one nanowire, increased for a pair of nanowires. The researchers then showed that the converted SP energy and the far field emission intensity of a pair of gold nanowires increased by about 4 times compared to those of a single nanowire.

These calculations demonstrated that the tight confinement between the two gold nanowires enhanced the coupling constant and the SP density of states, resulting in a stronger coupling without reducing their radii, and allowing SP to be transmitted over long distances.

JOAN J. CARVAJAL