Nano Focus

"Hidden" mid-gap electronic states control charge transport and photoconduction in semiconducting nanocrystal films

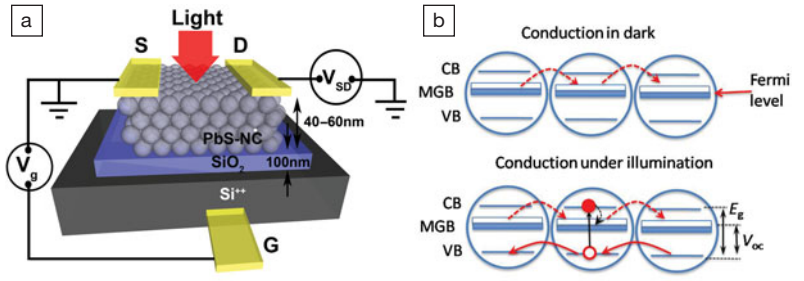
Semiconductor nanocrystals (NCs) are promising materials for applications in light-emitting diodes, field-effect transistors, photodetectors, and solar cells, including generation-III devices that exploit effects such as carrier multiplication. Semiconductor nanocrystals have a variety of novel properties that can be controlled by the dimensions, shapes, and internal structures of the NCs, but poor understanding of charge transport in films generated from these particles hinders progress in realizing NC-based devices. Recently, researchers at Los Alamos National Laboratory, New Mexico, have fabricated optical field-effect transistors (OFETs) based on lead sulfide (PbS) NCs and have used them to elucidate the charge-transport mechanism in the dark and under illumination. Through spectrally resolved studies of gate-voltage–dependent photoconduction, they demonstrated the existence of a mid-gap band (MGB) which plays an important role in charge conductance both in dark and under illumination.

As reported in the September 27 online edition of *Nature Communications* (DOI: 10.1038/ncomms1492), P. Nagpal and V.I. Klimov fabricated OFET devices, with a channel comprising PbS NCs treated with ethanedithiol, and gold gate and source electrodes (see Figure). While hole injection was much more efficient than electron injection in the dark, illumination of these devices with monochromatic light resulted in a dramatic increase in the source–drain current even at low light intensities, demonstrating a higher mobility of charges responsible for photoconduction compared to carriers responsible for charge transport in dark. In the case of white light illumination, application of a negative gate voltage resulted in an overall increase in photocurrent across the entire spectrum. Simultaneously, two new spectral features at ~0.9 eV and ~1.5 eV were detected in the photocurrent spectrum. These features were explained by the involvement of the "hidden" MGB states.

The researchers concluded that in dark, charges were transported by a weakly conducting network of MGB states. This transport could be explained in terms of either electron or hole conductivity depending on whether the Fermi level was near the bottom or the top of the MGB, respectively. Under illumination, charge transport was dominated by quantum-confined NC states that formed a more conductive network as a result of greater overlap of electronic wave functions. In this case, MGB still played an important role as its occupancy, that could be varied by gate bias, controlled recombination dynamics of the band-edge charges.

Klimov said, "This study has broad implications for electronic and optoelectronic applications of semiconductor NCs, and specifically suggests that design guidelines should be different for devices operating in the dark (diodes and transistors) and under illumination (photodetectors and solar cells)." He further added, "These findings also help to rationalize many previously unexplained observations such as [the] dramatic effect of surface treatments on 'dark' conductivity of NC films, relatively weak sensitivity of conductance to size polydispersity of the NCs, and a significant deviation of the photovoltage of NC-based solar cells from the nominal bandgap energy."

Mousumi Mani Biswas



(a) A schematic of the optical field-effect transistor made from PbS nanocrystals (NCs) treated with ethanedithiol. (b) "Dark" conductance in NC films is mediated by mid-gap band states whereas photoconductance is dominated by photogenerated holes transported by quantum-confined NC states. MGB is mid-gap band, CB is conduction band, and VB is valence band. Reproduced with permission from *Nat. Commun*. (DOI: 10.1038/ncomms1492). © 2011 Macmillan Publishers Ltd.

Aluminum transformed to noble-metal-like catalyst for activating molecular hydrogen

Activation of molecular hydrogen plays an essential role in many industrial processes such as the synthesis of ammonia, the hydrogenation of organic compounds in petroleum refining. As current processes typically rely on the use of expensive noble metal catalysts or aluminum which is susceptible to oxidation, there is significant interest in identifying cheaper and more efficient ways to activate molecular hydrogen under relatively mild conditions.

As reported in the November issue of *Nature Materials* (DOI: 10.1038/nmat3123; p. 884), Y.J. Chabal of the University of Texas–Dallas, S. Chaudhuri of Washington State University, and their colleagues have achieved this goal and have demonstrated that very small amounts of titanium incorporated in aluminum surfaces can activate molecular hydrogen at temperatures as low as 90 K. The team combined infrared reflection–absorption spectroscopy and first-principle calculations to identify

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the atomistic arrangement of the Ti-containing catalytically active sites present on Ti-doped single-crystal Al(111) surfaces. They found that hydrogen can spill over from the catalytic sites onto bare aluminum. It then combines with CO molecules adsorbed on the catalytically active sites to form a complex with activated hydrogen, which can be removed at remarkably low temperatures (115 K; possibly as hydrogenated CO molecules).

The fundamental understanding derived in this work provides a guide to identifying the active sites needed for the formation of complex metal hydrides for hydrogen storage applications. In addition, these studies show that, in place of expensive and less available noble metals, an inexpensive and abundant metal such as aluminum can be turned into an active catalyst by selectively placing Ti atoms on the surface, thus enabling activation of molecular hydrogen and facilitating CO and hydrogen removal at low temperatures. Furthermore, even though high concentrations of CO can block the Ti sites, thereby inhibiting catalytic activity toward hydrogen activation, the active sites show a promising tolerance to low contamination levels of CO in H_2. Lower desorption temperatures occur under these conditions, which frees up the active sites. This work provides the first direct evidence that Al doped with Ti can carry out the essential first step of molecular hydrogen activation.

Jean Njoroge

Electrically tunable bandgap observed in ABC-trilayer graphene

Graphene's hexagonal honeycomb lattice leads to a band structure that can be represented by two cones that touch at and are symmetric about the Dirac energy. Single-layer graphene therefore has a zero bandgap and the electrons and electron holes have the same properties. With no bandgap, however, it is difficult to control the electrical conductivity of graphene and opening of a tunable bandgap would represent a significant step forward in exploiting graphene in electronic and photonic applications.

One approach to achieving a bandgap is through the use of materials consisting of crystallographically stacked layers of graphene. While a bandgap has been induced in AB-stacked bilayer graphene through application of a perpendicular electric field, this does not occur in typical trilayer graphene, which exhibits ABA, or Bernal stacking, due to its mirror symmetry (see Figure 1a). The recently discovered rhombohedral trilayer graphene, which has ABC stacking (see Figure 1b), has, however, been predicted to exhibit an induced bandgap.

Now, T.F. Heinz and co-researchers from Columbia University along with E. Capelluti from the Institute for Complex Systems, Italy, and Instituto de Ciencia de Materiales de Madrid, Spain, have used theory and experiment to demonstrate bandgaps as large as 120 meV in ABC-trilayer graphene.

As reported in the September 25 online edition of *Nature Physics* (DOI: 10.1038/nphys2102), the researchers investigated graphene trilayer samples from exfoliated kish graphite (a nearly ideal crystal precipitated from molten iron) on SiO_2/Si substrates. Infrared and Raman spectroscopy was used to sample thickness and stacking order. For both ABA and ABC trilayer graphene samples, the researchers induced high doping densities and electric fields in the samples with an electrolyte top gate, and monitored the band structures with infrared conductivity measurements.

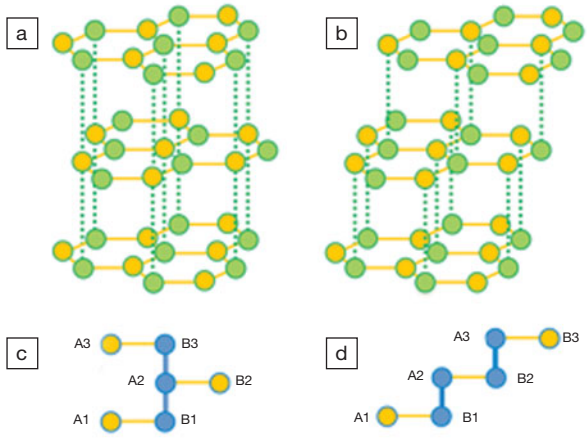

Figure 1. Crystal structures are shown for (a) ABA and (b) ABC trilayer graphene. The yellow and green atoms represent the A and B sublattices of the graphene honeycomb structure, respectively. Tight-binding diagrams are shown for (c) ABA and (d) ABC trilayer graphene. Effective interlayer coupling vanishes at the K-point, so that the yellow atoms become non-bonding monomers. The blue atoms then form a trimer in the ABA trilayer, but in the ABC trilayer they form two dimers. Reproduced with permission from *Nature Physics* (DOI: 10.1038/nphys2102). © 2011 Macmillan Publishers Ltd.

The researchers observed no signature of bandgap opening for ABA trilayer graphene, while, for similar electric fields, a sizable bandgap of 120 meV was observed for the ABC trilayer. The implications of the different crystal structures of the two trilayers were demonstrated with tight binding calculations that accounted for interlayer coupling and the capacitance of the electrolyte top gate.

Representing the ABA trilayer by one trimer and three monomers (see Figure 1c), the researchers showed that although a vertical electric field lifts the degeneracy of the two monomer states on the bottom and top layers, it influences neither the middle-layer monomer state nor the non-bonding trimer state. This remaining degeneracy precludes bandgap induction.

In contrast, the ABC trilayer is represented by two dimers with finite ener-

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