



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 de-

rived 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 tempera-

tures. 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 H₂. 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.

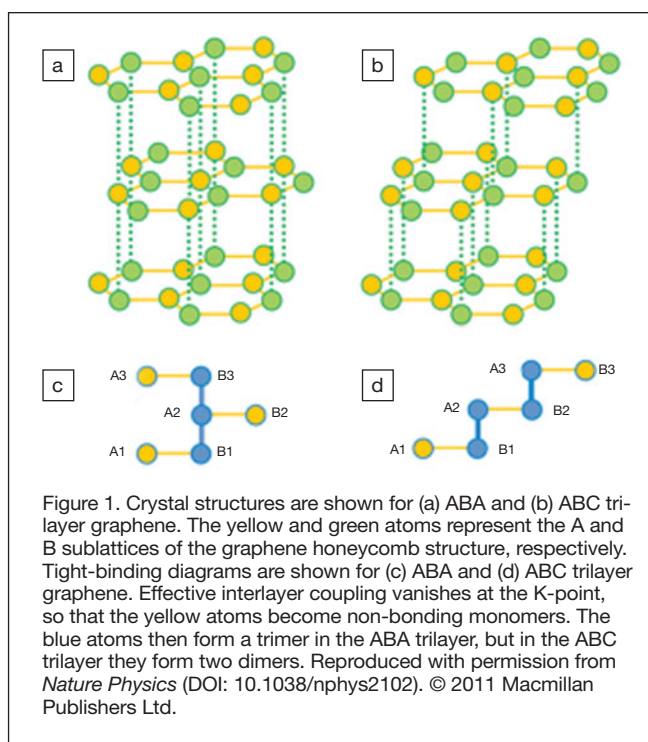
As reported in the September 25 online edition of *Nature Physics* (DOI: 10.1038/nphys2102), the researchers investigated graphene trilayer samples from exfoliated kish graphite (a nearly ideal crystal precipitated from molten iron) on SiO₂/Si substrates. Infrared and Raman spectroscopy was used to sample 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.

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 cal-

culations 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-



gies and two monomers with zero energy (see Figure 1d), so that application of a perpendicular electric field results in different potentials at the bottom and top layers. This lifts the degeneracy of

the two monomers and induces a bandgap.

The researchers said, “Our work suggests that a tunable bandgap can be induced in thicker graphene samples

with ABC (rhombohedral) stacking order, thus providing a still broader class of materials with a tunable bandgap.”

Steven Trohalaki

Octapodal nanocrystals self-assemble into micrometer superstructures

Researchers have created octapodal nanoparticles that self-assemble on a number of levels to ultimately generate micrometer-sized superstructures. Their work opens the door to fast and reversible cation exchange systems, the possibility of building three-dimensional (3D) ion sensors and porous electrodes, and other applications arising from the ability to establish complex geometries of dielectric and conductive materials.

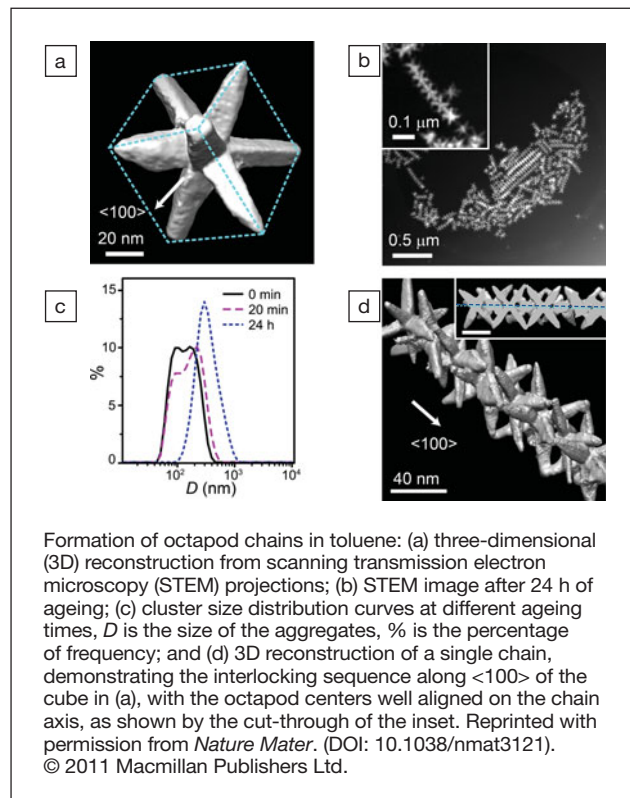
K. Miszta from the Instituto Italiano di Tecnologia in Genova, Italy, J. de Graaf and R. van Roij from Utrecht University, the Netherlands, and their colleagues reported their discovery of this phenomenon in the November issue of *Nature Materials* (DOI: 10.1038/nmat3121; p. 872). By growing eight CdS pods out of a CdSe core, the researchers were able to fabricate monodisperse, colloiddally predictable octapods that approached 100 nm in diameter. These octapods self-assembled into linear chains of interlocked octapods up to 400 nm in length in a tolu-

ene solvent. After aging the toluene solution for 24 hours, the addition of acetonitrile to the toluene caused the chains to precipitate out into 3D ordered superstructures 2 μm in length, composed entirely of self-assembled chains.

To create these structures, the researchers modified a previous procedure which allowed for unprecedented homogeneity and monodispersity of particles. The team coated the particles with hydrophobic surfactant molecules to improve interactions before immersing them in toluene. The toluene octapod solution (250 μL) was aged for 12–24 hours, and then mixed with 1 mL of acetonitrile. Two to five hours later the researchers transferred the resulting precipitate to a conductive substrate for scanning and transmission electron microscopy analysis. Aggregation in solution was

monitored by dynamic light-scattering microscopy. The concentration of octapods in the final solution was on the order of 10^{-8} molar.

Benjamin Scheiner



Graphene allows ultrashort pulse generation in solid-state laser

Graphene is a point-bandgap semiconductor with a linear dispersion of electrons with low energy that can be described by the Dirac equation involving relativistic effects. It also possesses large polarizability when illuminated by light, that is, large optical nonlinearity. These unique characteristics, in combi-

nation with the ultrafast relaxations of charge carriers (electrons and holes) in this material, in the femtosecond and picosecond time scale, suggest that graphene can be useful as an ultrafast saturable absorber (SA), that is, a material in which absorption of light decreases when the light intensity increases, and in a very short period of time. This property is fundamental for the generation of ultrashort light pulses in laser technology. Furthermore, graphene can be

used for this application in a very broad spectral range without requiring modification of the electronic bandgap. F. Rotermund from Ajou University, South Korea, B.H. Hong from Sungkyunkwan University, South Korea, and their colleagues have reported in the October 15 issue of *Optics Letters* (DOI: 10.1364/OL.36.004089; p. 4089) the fabrication of high-quality, large-area graphene SAs and their application for efficient mode-locking of a solid-state laser operating