

Spotlights on Recent JACS Publications

■ A CUT ABOVE OTHER GRAPHENE ANALOGUES

Graphene is an incredible electron conductor. It is stable, nontoxic, not too expensive, and can be produced in atomically thin sheets. Graphene would be the ideal material for electronic components, if only it had a band gap—an energy range with no allowable electron states. Without a band gap, an electronic switch can only turn on—there are no digital 0's, only 1's. While graphene can be modified to produce a band gap, these changes tend to degrade its other useful properties. For these reasons, researchers have been searching for a graphene analogue—a material with ultrahigh conduction, but also a band gap. There have been some advances, but so far, few materials can rival the electronic properties of graphene.

Mircea Dincă and colleagues create a metal–organic graphene analogue with a non-zero band gap and electrical conductivity that exceeds that of others in its class, as well as most organic conductors (DOI: 10.1021/ja502765n). The new material can exist as a conductive black powder or a dark blue-violet film. Though the researchers need to perform more studies to fully understand what drives the material's unusual properties, they note that this work may help to generate other similar compounds with exotic electronic attributes.

Jenny Morber, Ph.D.

■ BETTER CONTROL OVER PLATINUM HYBRID PARTICLES

Platinum nanoparticles facilitate chemical reactions to create new materials, clean pollutants, and power fuel cells. They also are prized for drug delivery, medical imaging, and medical therapies. Combining platinum with other compounds in the creation of nanoparticles can enhance their performance and reduce the costs.

But making hybrid particles from platinum can be challenging, because a single approach may produce vastly different particles. Jill Millstone and her team investigate the details behind mixed platinum nanoparticle formation (DOI: 10.1021/ja504294p).

The researchers study how platinum deposits onto gold particles in solution, and find that the physical and chemical form of platinum used in the reaction is critical. The seed particle surface chemistry also affects platinum deposition. Likely due to compounds clinging to the gold surface, in many cases platinum is deposited onto the gold seeds in well-spaced lines.

With this information, the team creates a suite of gold and platinum hybrid nanoparticles. This result should provide guidance to those working to develop platinum-containing nanoparticles tailored to specific uses. Careful control over synthesis should allow researchers to improve performance in current applications, and spur the development of new ones.

Jenny Morber, Ph.D.

■ FROM NO RINGS TO TWO: A LEAP IN ANNULATION CHEMISTRY

Functionalized carbocycles such as bicyclo[4.3.0]nonanes—trans-fused hydroindanes with angular substituents—have long presented a challenge to synthetic chemists. Existing approaches to fused carbon ring systems typically require challenging precursor preparation or tedious post-annulation modification, and these obstacles hamper the synthesis of hydroindane targets.

Following recent success in making dihydroindanes, Glenn Micalizio and co-workers have now developed a convergent and stereoselective strategy to construct angularly substituted trans-fused hydroindanes (DOI: 10.1021/ja504374j). Starting from trimethylsilylalkynes and 4-hydroxy-1,6-enynes, two types of acyclic substrates, the transformation yields bicyclic hydroindanes with well-defined stereochemistry through titanium(IV) metallacycle-mediated reductive coupling.

This highly concise approach creates three carbon–carbon bonds and two stereocenters with simultaneous ring fusion in a single operation. This reaction is likely to significantly simplify the total synthesis of natural products having this ubiquitous carbocyclic framework; more broadly, the new reaction complements current strategies for general carbocycle construction.

Xin Su, Ph.D.

■ OXYGEN TOLERANCE OUT IN THE OPEN

Researchers looking for catalysts for hydrogen–oxygen fuel cells need materials that will endure the reactive presence of oxygen, or at least continue to work after exposure to oxygen. Certain bacteria have hydrogen-converting enzymes—called hydrogenases—with promising properties for tolerating oxygen. A research team led by Lars J. C. Jeuken has investigated such an enzyme by trapping it in a lipid membrane similar to the environment in the membrane of the ubiquitous soil bacterium *Ralstonia eutropha* (DOI: 10.1021/ja503138p).

The team makes the enzyme more at home by including ubiquinone, a natural substrate for this enzyme. They place the membrane and enzyme on an electrode and measure the enzyme's catalytic activity with voltammetry and chronoamperometry. The experiments reveal that the nickel- and iron-bearing heterotrimeric membrane-bound hydrogenase (MBH) continues its activity under oxidative redox conditions and rapidly recovers after being inactivated by oxygen. MBHs in the membrane might be able to exchange electrons with each other via a “distal” iron–sulfur cluster, a property the team speculates may help explain how MBH reductively detoxifies oxygen.

Lucas Laursen

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■ AXIAL LIGAND TUNING IN HEME PROTEIN CATALYSIS

Different classes of heme enzymes are thought to rely heavily on the influence of their axial ligands for catalytic tuning. By varying the ligand, Nature can utilize the same heme cofactor to carry out a variety of functions. Recently, Michael Green and co-workers have quantified these axial influences, suggesting that the basicity of the ferryl (or compound II) intermediate governs reactivity in these systems.

C–H bond-activating cysteine-ligated heme enzymes have been shown to possess a high Fe(IV)–OH pK_a (~ 12), but there has been much controversy over the basicity of ferryl intermediates in histidine-ligated peroxidases and globins. Now, Green and co-workers use a variety of spectroscopic methods to probe the structure, and specifically the acidity of the iron-bound hydroxide group, in myoglobin compound II (DOI: 10.1021/ja503588n).

Their findings enable them to determine the upper limit of the hydroxide pK_a . Knowledge of this thermodynamic parameter provides insight into Nature's ability to tune catalytic function via metal ligation. This study adds to our growing appreciation for how enzyme structure influences catalytic activity.

Eva J. Gordon, Ph.D.