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Spotlights

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Spotlights on Recent *JACS* Publications

FROM NANO TO MACRO FOR DEALLOYED BIMETALLIC CATALYSTS

Chemical dealloying, a process that selectively leaches one metal out of an alloy—a two-metal mixture—has recently emerged as way to synthesize nanosized particles composed of a core rich in the less noble metal, like cobalt or copper, surrounded by a shell of the more noble one, like platinum. This type of core−shell nanoparticle with a platinum shell can act as a catalyst in fuel cell reactions, in which chemical energy from a fuel is turned into electricity. Dealloyed nanoparticles may have catalytic activity, resulting in more efficient fuel cells, but the atomic process during the dealloying is not fully understood.

Mehtap Oezaslan and co-workers determined the structure of dealloyed core−shell catalysts of various sizes using Pt−Co and Pt−Cu alloy nanoparticle precursors (DOI: 10.1021/ja2088162). The researchers leached Co or Cu from the particle surfaces, leaving behind a pure Pt shell, and they found that particle size had a significant impact on morphology and composition. The smallest particles, less than 5 nm in diameter, formed spheres of a platinum-poor alloy core surrounded by a platinum shell. However, as size increased to up to 10 nm, the nanoparticles contained multiple metal cores.

The authors suggest that these findings close the gap in our understanding between the morphology of highly active Pt nanoparticle catalysts for fuel cells and the corrosion of macroscale metal alloys in industrial settings. **Christen Brownlee**

URANIUM NITROSYL COMPLEX—UNUSUAL IN STRUCTURE, MAGNETISM, AND BONDING

The first-ever actinide nitrosyl complex has been synthesized, combining uranium, cyclopentadienyl ligands, and nitric oxide. Lanthanide and actinide complexes are known to bind small molecules that are electronically similar to $NO^{\bullet}$, but previous attempts to form nitrosyl complexes with lanthanides and actinides produced only bimetallic oxide compounds.

In a collaboration led by William J. Evans, Filipp Furche, and Jeffrey R. Long, researchers used a uranium compound with three bulky cyclopentadienyl ligands (Cp′) that they thought would sterically block formation of bimetallic species (DOI: 10.1021/ja2096128). Reacting the uranium compound with $NO^{\bullet}$, they succeeded in forming Cp'_3UNO. Using spectroscopy, magnetic susceptibility, X-ray crystallography, and density functional calculations to analyze the product, the scientists were surprised to find that, electronically, the complex contains U^{4+} bound to NO^- as $-U{-}N{=}O$ in a linear geometry. That combination of electronic structure and geometry is unusual, because other linear nitrosyl complexes are formally NO^+. The complex demonstrates that electropositive actinides can bind and activate small molecules in ways that are not observed for transition metals. **Jyllian Kemsley,** ***C&EN***

REDOX-SWITCHABLE NEAR-IR ORGANIC MATERIAL

Most organic materials used in optoelectronics such as LED or LCD displays function in the ultraviolet or visible region. The unique electrical and optical properties of near-infrared (NIR)-absorbing organic materials, however, may enable their application in fiber-optic telecommunication devices or for photodynamic therapy in medicine. Optoelectronics researchers are particularly interested in switchable molecules that can be used in devices operating in the NIR region.

Atsuya Muranaka, Masanobu Uchiyama, and co-workers have synthesized a hemiporphyrazine, a planar aromatic structure that has not been previously observed (DOI: 10.1021/ja210410c). The new compound was formed by oxidizing a nonaromatic precursor, and the resulting product exhibits an intense absorption at ~850 nm, in the NIR region. The researchers were surprised to find that the oxidation of the hemiporphyrazine was reversible and that the redox reaction could cycle several times between the two states.

NIR-absorbing organic molecules can be used for tissue bioimaging because NIR light can penetrate deep into tissues. For the same reason, NIR materials may be used for photodynamic therapy, in which a photosensitizing drug can be locally activated by a specific wavelength of light. **Sonja Krane, Ph.D.**

WEIGHING IN ON METABOLOMICS

While genomics is the study of the genes in an organism and proteomics offers a global view of the proteins, metabolomics analyzes the entire collection of metabolites, small molecules generated as part of the normal life cycle. Compounds called ascarosides are metabolites found in the commonly studied nematode model organism, *Caenorhabditis elegans*. Ascarosides serve as signaling molecules that are fundamental to the development and behavior of the nematode, but little is known about their various chemical structures or how they are made.

Now, Frank Schroeder and co-workers use a highly sensitive method called liquid chromatography−tandem mass spectrometry (LC-MS/MS) to characterize the *C. elegans* metabolome (DOI: 10.1021/ja210202y). In LC-MS/MS, a complex mixture of components is physically separated by liquid chromatography, and then the individual molecules are identified by determining their masses and characteristic fragmentation patterns. Using this method to compare the metabolomes of a series of *C. elegans* mutants, the researchers detected ascarosides of much greater structural diversity than anticipated and discovered that ascarosides are created in a modular fashion using building blocks from three basic metabolite pools: carbohydrates, fatty acids, and amino acids. In addition, they found that several of the enzymes involved in ascaroside formation are highly conserved in animals.

This study shows that comparative spectroscopic analyses of mutant metabolomes represent a powerful tool for deciphering

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the structures of small-molecule signals and their biosyntheses.
Eva J. Gordon, Ph.D.

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