

Spotlights on Recent JACS Publications

■ GOLD ADATOMS GET CAUGHT UP IN PORPHYRIN'S TRAP

Recent studies have shown that atoms that diffuse on close-packed metal surfaces can influence the adsorption and assembly of molecules on those surfaces. At elevated temperatures, these so-called adatoms—short for “adsorbed atoms”—are known to continuously detach from the step edges on a crystal's surface and can in some cases even be trapped beneath molecules.

A new study led by Leonhard Grill reveals how single adatoms on a gold surface interact with and modify the electronic structure of porphyrin molecules in a very characteristic way, resulting in a “fingerprint” of molecules with adatoms underneath (DOI: 10.1021/ja510528x). Porphyrin derivatives are important in numerous biological processes and in solar energy conversion, and thus their adsorption configuration and surface dynamics have been studied widely. Using a combination of scanning tunneling microscopy (STM), density functional theory, and single molecule manipulation, the team shows the gold adatoms appear to be trapped by porphyrin molecules, and they propose a likely binding geometry.

Thiol molecules have long been known to be able to bind to gold adatoms, but trapping by porphyrin molecules was unexpected. The results illustrate the importance of considering native adatoms when interpreting STM studies of molecules on gold surfaces.

Christine Herman, Ph.D.

■ ORGANIC INITIATORS REPLACE METAL POLYMERIZATION CATALYSTS

Andrew Boydston and colleagues have developed a protocol for ring-opening metathesis polymerization (ROMP) that uses organic initiators rather than transition-metal catalysts (DOI: 10.1021/ja512073m). The new polymerization method could be a boon to makers of polymers with electronic or biological applications.

Currently, the applications of polymers produced using ROMP have been limited because traces of the transition metals used to initiate polymerization can be left behind in the product. That is a problem in electronic applications, where the residual metals affect the polymer's conductivity and capacitance. It is also troublesome for polymers with biological applications, because the metals used for ROMP are toxic.

The researchers use radical cations made from one-electron oxidation of electron-rich vinyl ethers. They suggest that the radical cation reacts with a double bond to produce a cyclobutane radical cation. If the double bond is part of a small ring system, such as in commonly used norbornene, then the ring's strain will prompt the cyclobutane radical cation to open up, initiating the polymerization process without the need for transition metal catalysts.

Bethany Halford, adapted from *Chemical & Engineering News* with permission.

■ SYNTHESIS OF A REACTIVE SUBPORPHYRIN WITH REDUCING POWER

Dongho Kim, Atsuhiko Osuka, and colleagues report the first synthesis of a subporphyrin borohydride, a strong reducing agent (DOI: 10.1021/ja5126269).

Subporphyrins, a class of ring-contracted porphyrins, have significant light-absorbing and fluorescent properties. Their reactivity and electronics are also highly tunable via an exchangeable axial substituent. So far, researchers have designed a variety of subporphyrin pigments by tuning these properties, but the compounds have further potential for a variety of applications.

Here, the researchers synthesize the first hydride of a boron subporphyrin, using DIBAL-H to reduce the methoxide precursor into subporphyrinato boron(III) hydride. They demonstrate its potential utility as a reagent in organic syntheses by effecting the reduction of an arylaldehyde and an imine in the presence of a catalyst.

The authors show that this electron-rich hydride reacts with water or hydrochloric acid to produce hydrogen gas and suggest that further study of the compound could reveal additional reactivities.

Deirdre Lockwood, Ph.D.

■ SO BETTER TOGETHER: IRON–NICKEL CATALYSTS FOR ELECTROCATALYTIC WATER SPLITTING

A team of researchers at the Joint Center for Artificial Photosynthesis (JCAP), SUNCAT, and the Stanford Synchrotron Radiation Lightsource (SSRL) led by Daniel Friebe and Alexis T. Bell has discovered the origin of catalytic enhancement in an iron–nickel catalyst that is commonly used for electrochemical splitting of water into oxygen and hydrogen (DOI: 10.1021/ja511559d).

This reaction is a key step in the efficient solar-powered generation of hydrogen from water. Hydrogen produced in this way has applications as an alternative, clean-burning fuel. Iron–nickel catalysts have been shown to have excellent activity in the oxidative step of this process—the oxygen evolution reaction; however, the mechanism and the nature of the active site are not fully understood.

Using a combination of in situ X-ray absorption spectroscopy and density functional theory calculations, the authors probe the short-range structure and electronic environment of the iron and nickel sites. Their studies reveal that the catalyst activity results from iron ions doped into the inactive nickel-based lattice. These insights may suggest new designs for water oxidation catalysts with increased catalytic efficiency.

Dalia Yablon, Ph.D.

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