

Spotlights on Recent JACS Publications

■ CATALYSIS BY DESIGN: SINGLE-ATOM ALLOY CATALYSTS

Platinum is a valuable and widely used heterogeneous catalyst for hydrogenation, oxidation, and fuel cell reactions. Unfortunately, strong Pt–CO binding makes these catalysts highly susceptible to poisoning by even the minute amounts of carbon monoxide present in many hydrogen gas streams. Researchers led by Charles Sykes and Maria Flytzani-Stephanopoulos have now tailored platinum's properties by alloying individual atoms of the element copper in a new type of system termed a single-atom alloy (SAA) that, in this case, optimizes catalytic activity in the presence of carbon monoxide (DOI: [10.1021/jacs.6b03339](https://doi.org/10.1021/jacs.6b03339)).

Using scanning tunneling microscopy and infrared spectroscopy, the researchers investigate the binding strength of carbon monoxide to a variety of platinum structures within the platinum–copper alloys. They find that carbon monoxide binds more weakly to single platinum atoms than to platinum clusters, so the SAA design leaves more CO-free active platinum sites available for catalysis. These surfaces exhibit minimal poisoning in both model and realistic catalysts for reactions such as acetylene hydrogenation. The SAA approach could be used with many other metal combinations in order to improve catalysts for industrially important processes that are prone to carbon monoxide poisoning.

Dalia Yablon, Ph.D.

■ STRUCTURALLY CHARACTERIZING A NESTED METAL NANOPARTICLE

Structure determination of metal nanoclusters and their stabilizing surface ligands helps provide a fundamental understanding of these materials, including how some species come together to form larger nanoparticles. Unfortunately, the structural characterization of large nanoclusters presents a more formidable challenge than characterizing smaller metal nanoclusters. Now, Quan-Ming Wang, Yu-Mei Lin, and co-workers report the characterization of a large 110-atom bimetallic nanocluster decorated with both alkynyl and chloride ligands (DOI: [10.1021/jacs.6b04471](https://doi.org/10.1021/jacs.6b04471)).

Using single-crystal X-ray crystallography, the researchers find that this gold and silver nanocrystal, Au₈₀Ag₃₀, is composed of four layers in a Matryoshka, or Russian nesting doll, pattern. The innermost layer is a distorted Au₆ octahedron that is wrapped up by the second layer, containing 35 gold atoms. A bimetallic third layer consisting of 18 gold atoms and 30 silver atoms is topped by a fourth layer of 21 gold atoms. Further investigation identifies 42 alkynyl surface ligands as well as 9 chloride ligands.

The team finds that excluding chloride from the synthesis reaction inhibits nanocrystal formation, indicating that this critical ion plays an important stabilizing role beyond simply serving as a counterion. The authors suggest that the crucial role of halides should be considered in future design and synthesis of new metal nanoclusters.

Christen Brownlee

■ TOWARD ARTIFICIAL NITROGENASES: IRON-BASED ACTIVE SITE MIMICS

Nitrogenases are a unique type of bacterial enzymes that can reduce nitrogen to ammonia, a process critical to all life forms and thus fascinating to chemists. Unlike most artificial nitrogen fixation methods, which require high temperatures or pressures, nitrogenases rely on metal cluster-based cofactors to activate nitrogen under mild conditions, the most notable one being the iron–molybdenum cofactor (FeMoco).

In a new Perspective, Patrick Holland and Ilija Čorić summarize the latest advances in the design of FeMoco-mimicking iron complexes with bonding similar to the iron site in the enzyme, and discuss their mechanistic insights into biological nitrogen reduction (DOI: [10.1021/jacs.6b00747](https://doi.org/10.1021/jacs.6b00747)). These results reaffirm the central role of iron in nitrogen binding instead of molybdenum as previously believed. Moreover, the study of iron–nitrogen interactions in the presence of various ligands has extended the understanding of small-molecule activation in general.

To continue the quest for artificial nitrogenases, as the authors envision, model systems that can elucidate elementary steps involving partially reduced nitrogen are especially desirable. On the other hand, coupling reversible hydrogen loss with nitrogen binding will enable milder conditions for the entire catalytic process.

Xin Su, Ph.D.

■ NEW APPROACH TO CATALYTIC PRECISION POLYMERIZATION

Precise control over the macromolecular structure of polymers is essential to the development of functional polymer-based materials for applications ranging from biomedical devices to self-healing materials. But the vast majority of radical polymerization reactions performed today employ techniques that were invented more than a century ago and are unable to offer precise control over macromolecular parameters without compromising reaction rates.

Now, researchers led by Bernhard Rieger describe a new approach to catalytic precision polymerization (DOI: [10.1021/jacs.6b04129](https://doi.org/10.1021/jacs.6b04129)). The team carries out the precise polymerization of a class of Michael-type monomers with highly interacting Lewis pairs. In contrast to traditional rapid radical polymerization techniques, the new approach does not rely on water-soluble metal salt catalysts, which makes it an attractive alternative for both poorly soluble, nonpolar monomers and polar monomers that cannot undergo radical polymerization as a result of chain-transfer side reactions.

The technique also offers the possibility of controlling key parameters of the polymer products—such as molecular weight, microstructure, and tacticity—by the choice of the Lewis pair, which could ultimately lead to new approaches to tailor-made catalyst design.

Christine Herman, Ph.D.

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