

Spotlights on Recent JACS Publications

■ WATER SPLITTING GETS A BOOST FROM MINERAL-BASED CATALYST

Tewodros Asefa, Wei Chen, Xiaoxin Zou, and colleagues have created a stable non-noble-metal material that reduces the energetic cost of splitting water (DOI: [10.1021/jacs.5b08186](https://doi.org/10.1021/jacs.5b08186)). The production of hydrogen from water is viewed by some as a “holy grail” for green energy, but researchers have struggled to create catalysts that sufficiently reduce the reaction’s energy requirements. Currently, the most efficient catalysts are made from rare and costly noble metals. Researchers have tried boosting the performance of alternative catalysts containing Earth-abundant metals by manipulating their geometry to increase the density of the most catalytically active facets, but these unstable structures often deteriorate.

Here, the authors report that highly faceted Ni₃S₂ nanosheet arrays grown on nickel foam are stable, made from Earth-abundant materials, and catalyze both the hydrogen evolution and oxygen evolution half-reactions necessary for water splitting. Ni₃S₂ occurs in nature as the mineral heazlewoodite and has intrinsic metal-like behavior from its network of Ni bonds. Experiments and theoretical calculations confirm the importance of this material’s high-index facets for its excellent catalytic performance.

An efficient, low-cost method to make hydrogen from water would mean clean renewable energy. The integration of dual functionality, excellent activity, and durability into a single material system makes this water-splitting catalyst an impressive addition to the toolbox.

Jenny Morber, Ph.D.

■ STABLE SUPERATOMS ON GRAPHENE SURFACES

Since the discovery of the soccer-ball-like carbon fullerene, researchers have rushed to study and develop the unique properties of superatoms—nanostructures of a few to 100 atoms. Superatoms that surround a captive metal atom are of particular interest because their properties can be tweaked by changing only the metal core. But to explore and fully exploit the properties of metal-encapsulating superatoms, they need to be immobilized onto a solid substrate, which can be a difficult task.

Atsushi Nakajima and colleagues deposit a 16-atom silicon cage, surrounding a tantalum metal atom, onto an inert graphite substrate (DOI: [10.1021/jacs.5b08035](https://doi.org/10.1021/jacs.5b08035)). The researchers use X-ray photoelectron spectroscopy to evaluate the structure’s physical and chemical properties, finding that the deposited Ta@Si₁₆ is extremely stable, even at temperatures up to 700 K and with exposure to oxygen.

The discovery and manipulation of superatoms hint at the ability to engineer basic matter into building blocks customized for specific purposes, with unique attributes. The robustness of Ta@Si₁₆ superatoms suggests the feasibility of combining them into new cluster-based materials or incorporating them into novel devices that take advantage of their unique properties.

Jenny Morber, Ph.D.

■ ALUMINUM COMPLEXES FOR EASY ENANTIOMER DISCRIMINATION BY ¹H NMR

Hyunwoo Kim and Min-Seob Seo report new chiral octahedral aluminum complexes that can be used for direct chiral analysis of charged molecules by NMR spectroscopy (DOI: [10.1021/jacs.5b09555](https://doi.org/10.1021/jacs.5b09555)).

Chiral analysis, as a tool to characterize stereoisomers, is important in synthetic chemistry as well as in the pharmaceutical and biopharmaceutical industry. While NMR spectroscopy is widely accepted as one of the most convenient techniques for the determination of chemical structures, it is seldom used for direct chiral analysis due to the lack of good chiral solvating agents that would produce a chemical shift response when mixed with chiral analytes.

To tackle this issue, Kim and Seo prepare anionic chiral aluminum complexes with newly designed hexa-dentate N₂O₄ ligands. These complexes demonstrate ion-pair interactions with charged chiral molecules and can be used as highly efficient chiral solvating agents that work with a wide range of chiral substrates, including some commercial racemic drugs. Unlike earlier methods that rely on lanthanide shift reagents, which can cause significant line broadening, this new protocol gives sufficient peak resolution for racemic analytes in polar or nonpolar solvents and shows great potential for simple, fast, and convenient chiral analysis of bioactive molecules.

Lingling Chen, Ph.D.

■ SEQUENCING RNA FROM BOTH SIDES

Though current enzyme-based sequencing methods excel at reading DNA directly, RNA must first be reverse-transcribed, effectively deleting important post-transcriptional chemical modifications. Mass spectrometry can detect those modifications, but a broadly generalizable MS-based approach has not yet been developed.

Here, Jack Szostak and colleagues describe a generic, label-free, bidirectional strategy for sequencing modified RNA oligonucleotides (DOI: [10.1021/jacs.5b09438](https://doi.org/10.1021/jacs.5b09438)). The RNA strands are briefly digested in formic acid, size-separated via HPLC, and mass-analyzed to yield both 5’ and 3’ fragment ladders, from which the final sequence is determined. The authors test their approach on oligonucleotides modified with methylcytosine, 2-thiouridine, biotin, or a fluorescent dye, generating complete sequence ladders in most cases. Sequence gaps—as they find with a 2’-hydroxymethyl modification—are closed using tandem MS.

Though the method is currently limited to RNA molecules about 30 bases long, technical improvements should extend its reach, the authors write, adding that it should be applicable to both naturally occurring short RNAs and novel synthetic structures. “In principle, any linear informational polymer with known monomer composition could be sequenced bidirectionally by a generalization of the presented method and algorithm,” they conclude.

Jeffrey M. Perkel

Published: November 3, 2015