

Catalyst development bridges bioinspiration and materials discovery.

## Search for water-splitting catalysts for global usage

By **Melissae Fellet**  
Feature Editor **David M. Tiede**

Two widely available compounds, carbon dioxide and water, could be a source of renewable fuel in the future. In this scheme, electrocatalysts split water, generating oxygen gas along with protons and electrons used to reduce carbon dioxide into hydrocarbons. Research investigating water splitting for sunlight-driven fuels production ranges from the deciphering of structures and mechanisms in photosynthesis to the discovery of new solid-state and molecular catalytic materials. Hybrid materials that combine molecular catalysts on a solid surface could be used to build integrated devices that harvest sunlight to produce fuel.

In photosynthesis, the protein complex photosystem II performs water splitting using a five metal atom  $Mn_4CaO_5$  cluster housed inside the enzyme. This metalloenzyme has long-served as a paradigm for developing efficient water-splitting catalysts based on abundant first row transition metals. Crystallographic studies using x-ray-free electron lasers in Japan and the United States have resolved the structure of the  $Mn_4CaO_5$  cluster photosystem II. This work also captured some of the intermediate oxidation states, leading to water splitting and O–O bond formation.

These structures, combined with spectroscopy and advanced computational techniques, are providing an understanding of photosynthetic water splitting at the atomic scale. Based on earlier structures, a team comprised of researchers from China, Japan, and Germany synthesized a molecular  $Mn_4CaO_5$  cluster that mimics many of the key structural features of the natural cofactor. The synthetic cluster lacks catalytic activity due, in part, to the absence of an open coordination spot for substrate water. It seems the secret to photosynthetic water splitting lies not only in the metal atom cluster, but also in the electronic communication between the cluster and the surrounding photosystem II protein, the organization of a ring of substrate water molecules, and built-in pathways for redox-coupled proton transfers. Metalloenzymes often distribute catalytic function across an individual metal center, as well as the thru-space interactions between the metal and the protein. Recreating both relationships in an artificial water-splitting catalyst is difficult because of the present lack of synthetic frameworks to create a comparably sophisticated coordination environment.

However, structurally simpler catalysts—thin-film materials—have long been known to split water when used as cathodes and anodes in electrochemical cells. Vigorous present research aims to develop catalyst films that are stable, efficient, and made from

cheap earth-abundant elements. But no material or combination of materials has been found that meets all of these requirements yet, especially for direct solar-driven water splitting, said Ian Sharp, Lawrence Berkeley National Laboratory. While catalyst development continues in the lab, companies continue to integrate current precious metal catalysts into commercial water-splitting electrolyzers for laboratory- and industrial-scale applications. And new research relationships advance the catalysts toward larger scale applications, such as transportation fuel. In October 2016, the US Department of Energy started HydroGEN, a consortium between national laboratories, academia, and industry to further the applications of water-splitting materials. “It’s still basic research from an industrial perspective, but it’s addressing challenges to create the foundation for a new technology,” said Sharp.

First discovered more than a century ago, thin films of iridium oxide remain the most active and stable water-splitting catalysts under acidic conditions. They are used today in commercial electrolyzers that split water to produce hydrogen, but iridium catalysts cannot be a solution for global-scale solar fuel production because iridium is one of the scarcest elements on the planet.

To find water-splitting catalytic materials that could be used on a global scale, aggressive research worldwide is being used to investigate a range of nano- to mesostructured thin-film metal oxide catalysts and amalgams made with earth-abundant metals, such as manganese, nickel, cobalt, and iron. However, difficulty in identifying, characterizing, and controlling sites where catalysis occurs poses barriers for rapid materials optimization.

Insights from the inner workings of photosynthetic metalloenzymes indicate a path toward controlled catalysis using artificial molecular catalysts. These catalysts contain a single or a small number of metal atoms coordinated by a specific set of ligands, and they provide a way to study relationships between structure and reactivity by observing the changes in reactivity in response to atomic variations in ligand structure. Further, molecular catalysts also represent a way to minimize the amount of metal used for a device that produces solar fuels.

Reported in 1982, the first molecular catalyst for water splitting was built using ruthenium. Researchers have since expanded the library of molecular water oxidation catalysts to include compounds containing iridium, iron, cobalt, or manganese used by natural photosynthetic machinery to split water. The ability to tailor the structure of these catalysts provides opportunities to

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maximize their performance. In 2016, Shigeyuki Masaoka and his colleagues at the Institute for Molecular Science, Okazaki, Japan, synthesized a molecular catalyst containing five iron atoms that outperformed the photosynthetic complex with remarkable reactivity ( $>10^3 \text{ s}^{-1}$ ) and stability ( $>10^6$  turnovers).

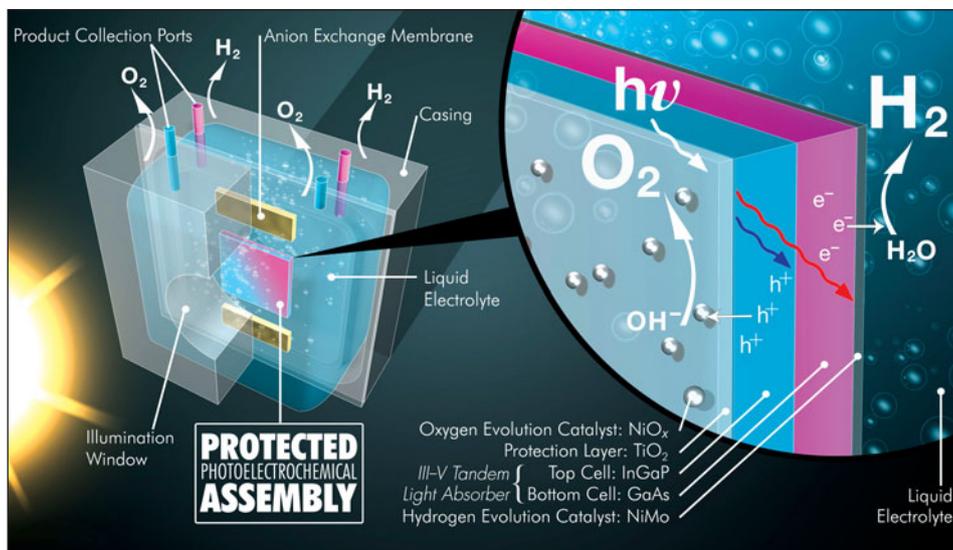
However, organic ligands typically used to synthesize a molecular catalyst tend to oxidize as a side reaction during water-splitting chemistry, causing the catalyst complexes to decompose during continuous reaction. One way to stabilize these catalysts is to attach them to a semiconducting surface, creating a hybrid material with the enhanced stability of a thin-film catalyst and the tailored activity of a molecular catalyst.

Gary Brudvig and colleagues, at Yale University, created a hybrid material for water splitting by bonding a molecular iridium oxide catalyst to the surface of an electrode made from nanoparticles of tin-doped indium oxide (ITO). The iridium complex modified ITO was more active than solid-state iridium oxide catalyst material, and it remained active after 12 hours of continued electrolysis. Although the structure of the iridium complex stabilized on the oxide surface is not known, analysis showed that the iridium pyridylalkoxide ligand coordination remained intact.

Because molecular catalysts lose activity faster than thin-film catalysts, they are generally thought to be more useful as research tools than potential materials in commercial water-splitting devices. But a Connecticut-based company is challenging that thinking. Catalytic Innovations is commercializing a molecular iridium catalyst attached to metal electrodes for industrial processes that already involve water splitting, including zinc refining and wastewater treatment.

Both surface-supported thin-film and molecular water-splitting catalysts are finding applications in research labs around the world, as scientists build devices that collect sunlight and use the solar energy to power a water-splitting catalyst for fuel production. In the United States, researchers at the Joint Center for Artificial Photosynthesis, a US Department of Energy research program involving scientists at the Lawrence Berkeley National Laboratory, the California Institute of Technology, and other universities, are developing integrated devices for solar fuel production using thin-film mixed metal oxide water-splitting catalysts.

Researchers at the Swedish Consortium for Artificial Photosynthesis use molecular catalysts for their integrated devices. Licheng Sun, at KTH Royal Institute of Technology, and his colleagues, attached two different ruthenium complexes to a nanostructured



Semiconducting materials (blue and pink) in the center of this device collect sunlight and transfer the charges to electrocatalysts that split water to produce hydrogen and oxygen gas. Adapted with permission from the Joint Center for Artificial Photosynthesis/Caltech. © 2015 Darius Siwek.

titanium dioxide surface. One complex, a photosensitizer, collects visible light and transfers electrons to the metallic anode. The same complex also collects electrons produced by neighboring ruthenium water-splitting catalysts. The device produced  $1.7 \text{ mA cm}^{-2}$ , the highest current density among integrated photoelectrochemical devices containing molecular catalysts.

Along with improving device performance, putting a molecular water-splitting catalyst onto a semiconducting surface in an integrated device can also change its behavior in unexpected ways, said Leif Hammarström of Uppsala University, who is also one of the coordinators of the consortium. Active molecular catalysts can potentially generate products rapidly, so they quickly use the high-energy charges generated from visible light. Otherwise, these charges may perform side reactions that destroy ligands or corrode materials. The result is a kinetic stabilization of the material and catalyst: With fewer side reactions, the catalyst produces more fuel. Kinetic stabilization, and other effects, can make supported molecular water-splitting catalysts more stable in functional devices than in isolated test systems, said Hammarström.

Researchers working in both molecular and thin-film water-splitting catalysts, as well as those commercializing these catalysts agree: collaboration between scientific fields, cooperation between academic and industrial researchers, and insights from related technology such as fuel cells help advance the growth of water-splitting catalysts. The same sophisticated techniques that provide insights into natural water-splitting photosynthetic catalysts also advance the development of novel functional materials for solar water splitting. “We do not know what the ultimate solar fuel device looks like,” said Hammarström. “As a field, we’re working on the best way to put it together, from device engineering to materials discovery and design.” □



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# BARIUM FERRITE SITE OCCUPANCY USING RIETVELD ANALYSIS

Barium ferrite has attracted considerable interest in the fields of permanent magnets and perpendicular magnetic recording due to its strong uniaxial anisotropy and high Curie temperature. The magnetic properties, especially magnetic anisotropy, can be controlled by an appropriate doping element, such as Al. The Rietveld method is one of the few techniques including single crystal X-ray or neutron diffraction, EXAFS and solid state NMR that can analyze the occupancies of specific sites when the same element can be in multiple different sites in one crystal structure. Below is an example of Al and Fe site occupancy analysis done using the Rietveld method.

The sample was Al doped ferrite ( $BaAl_xFe_{(1-x)}O_{19}$ ) with a small amount of  $Ba_{0.79}Al_{10.9}O_{17.14}$ ,  $BaAl_2O_4$  and  $Al_2O_3$ . Figure 1 shows the Rietveld refinement result. The data was collected on the SmartLab diffractometer and PDXL software was used for the data analysis.

The ferrite has five Fe sites that can be replaced by Al as shown in Figure 2. Their site occupancies were refined during the Rietveld analysis. The results are shown in Table 1.

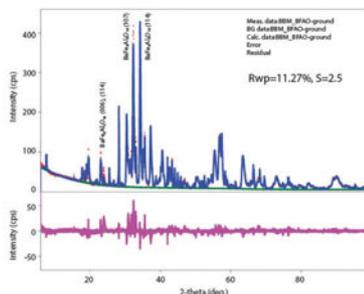


Figure 1: Rietveld refinement result

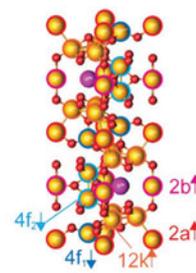


Figure 2: Al doped ferrite ( $BaAl_xFe_{(1-x)}O_{19}$ ) structure and five Fe sites (The arrows indicate the spin direction.)

The refined Al and Fe site occupancies shown in Table 1 indicate that Al does not replace Fe in five different sites randomly but replaces the spin up sites preferably. This explains the nonlinear relationship between this material's magnetic property and Al doping rate, and helps one understand the doping mechanism and ultimately control the material's magnetic properties.

Spin	Wyckoff	AET	Fe [%]	Al [%]
Up	2a	6a	0.41(2)	0.59(2)
Up	2b	5c	0.89(3)	0.11(3)
Down	4f <sub>1</sub>	4a	1.00(17)	0.00(17)
Down	4f <sub>2</sub>	6a	0.96(19)	0.04(19)
Up	12k	6a	0.871(17)	0.129(17)

Overall  $x = 0.128$

Table 1: Refined Al and Fe site occupancies



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