Engineering earth-abundant catalysts that mimic platinum in renewable energy technologies

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Graduate student Sean Hunt, lead author on the paper. Credit: Melanie Kaufman

When one considers nonrenewable resources, the first to come to mind are fossil fuels: petroleum, coal, and natural gas. The rapid depletion of these unsustainable resources has sparked global research on renewable-energy technologies, such as fuel cells, electrolyzers, and lithium-air batteries.

Unfortunately there is a common unsustainable thread that links these burgeoning technologies: a dependence on platinum-group metals (PGMs). These elements—platinum, palladium, rhodium, iridium, ruthenium, and osmium—are the six least-abundant in the Earth's lithosphere, yet are the most stable and active catalysts. Even with efficient recycling, numerous studies have indicated that the Earth simply does not contain enough PGMs to support a global renewable-energy economy. Thus, PGMs can be considered unsustainable resources that are currently needed to enable renewable energy technologies.

MIT graduate student Sean Hunt, postdoc Tarit Nimmandwudipong, and Yuriy Román, an assistant professor of chemical engineering, have an idea for how to replace PGMs with metals that are more plentiful. In a paper published recently in the journal *Angewandte Chemie*, the team explained its process of synthesizing these alternative catalysts.

"Because the PGMs tend to be the most active and stable catalysts in virtually all relevant thermal and electrocatalytic processes, our research sought to answer an exciting question," Hunt explains. "Rather than finding new materials to replace PGMs in specific reactions, is it possible to modify the electron density of earth-abundant early transition metals [groups IV to VI on the periodic table] to catalytically mimic the PGMs?"

In the simplest sense, one can imagine that tungsten, with six valence electrons, can be electronically modified to mimic platinum, which has 10 valence electrons, by reacting it with carbon (four valence electrons) to give the ceramic material tungsten carbide (WC). Numerous studies have shown that WC is indeed platinumlike, and able to catalyze important thermo- and electrocatalytic reactions that tungsten metal cannot—such as biomass conversion, hydrogen evolution, oxygen reduction, and alcohol electrooxidation. Importantly, tungsten is more than three orders of magnitude more abundant than platinum in the

Earth's crust, making it a viable material for a global renewable-energy economy.

However, both WC and platinum are heterogeneous catalysts, meaning that they require nanoparticle formulations to create high surface areas and invoke quantum confinement effects to maximize the rates of chemical reactions. While platinum nanoparticles are relatively easy to synthesize, until now, there have been no known methods to synthesize WC nanoparticles less than 5 nanometers and devoid of surface impurities. As Hunt explains, "Tungsten carbide forms at very high temperatures, typically over 800 degrees Celsius [1500 degrees Fahrenheit]. These high temperatures cause nanoparticles to sinter into large microparticles with low surface areas. Methods to date that alleviate this agglomeration instead result in nanoparticles that are covered with excess surface carbon. These surface impurities greatly reduce, or completely eliminate, the catalytic activity of WC."

To solve this problem, the MIT team developed a "removable ceramic coating method" by coating colloidally dispersed transition-metal oxide nanoparticles with microporous silica shells. At high temperatures, they show that reactant gases, such as hydrogen and methane, are able to diffuse through these silica shells and intercalate into the encapsulated metal oxide nanoparticles. This transforms the oxide nanoparticles into transition metal carbide (TMC) nanoparticles, while the silica shells prevent both sintering and excess carbon deposition. The silica shells can then be easily removed at room temperature, allowing the dispersal of nonsintered, metal-terminated TMC nanoparticles onto any high-surface-area catalyst support. This is the first method capable of this result.

The team has also been successful in synthesizing the first nonsintered, metal-terminated bimetallic TMC nanoparticles. Electrocatalytic studies have shown that these materials are able to perform hydrogen evolution and methanol electrooxidation at rates similar to commercial PGM-

based catalysts, while maintaining activity over thousands of cycles. The catalytic activities obtained were more than two orders of magnitude better than commercial WC powders and WC nanoparticles made by current state-of-the-art synthesis methods that do not prevent sintering or surface carbon deposition.

Next steps include the synthesis of other bimetallic TMCs, as well as transition metal nitride (TMN) nanoparticles. The team is investigating these materials for other electrocatalytic reactions as well as thermal catalytic reactions, such as hydrodeoxygenation for biomass reforming.

"This new method unlocks a broad range of monometallic and heterometallic transition metal carbide and nitride nanoparticles that researchers previously have been unable to synthesize or study," Román says. "While our research focuses mainly on the sustainable replacement of PGMs in thermal and electrocatalytic applications, we also anticipate broader impacts of our new TMC and TMN technologies outside catalysis. Because of their unique chemical, mechanical, and electronic properites, carbides and nitrides have garnered much attention for use in applications as diverse as supercapacitors, medical implants, optoelectronics, coatings, and high-temperature materials for the aerospace and nuclear sectors."

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