Hierarchical 3-D printing of nanoporous gold could 'revolutionize' electrochemical reactor design

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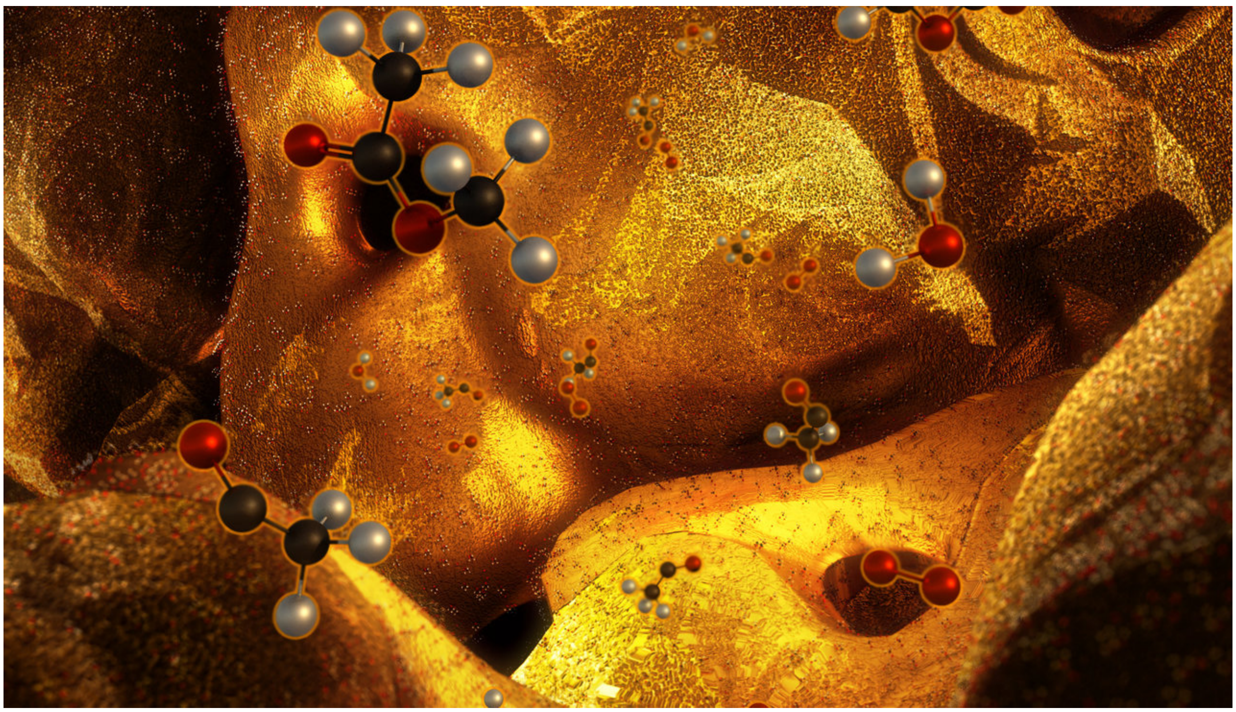

Lawrence Livermore National Laboratory researcher Cheng Zhu and former Lab postdoc Wen Chen created inks made of gold and silver microparticles. After printing, the 3D parts were heated to allow the particles to coalesce into a gold-silver alloy. The parts were put into a chemical bath that removed the silver (a process called “dealloying”) to form porous gold within each beam or filament. Credit: Ryan Chen/LLNL

Nanoporous metals are superior catalysts for chemical reactions due to their large surface area and high electrical conductivity, making them perfect candidates for applications such as electrochemical reactors, sensors and actuators.

In a study published today in the journal *Science Advances*, Lawrence Livermore National Laboratory (LLNL) researchers, along with their counterparts at Harvard University, report on the hierarchical 3-D printing of nanoporous gold, a proof of concept that researchers say could revolutionize the design of chemical reactors.

"If you consider traditional machining processes, it's time consuming and you waste a lot of materials—also, you don't have the capability to create complex structures," said LLNL postdoctoral researcher Zhen Qi, a co-author on the paper. "By using 3-D printing we can realize macroporous structures with application-specific flow patterns. By creating hierarchical structures, we provide pathways for fast mass transport to take full advantage of the large surface area of nanoporous materials. It's also a way to save materials, especially precious metals."

Combining 3-D printing through extrusion-based direct ink writing and an alloying and dealloying process, researchers were able to engineer the nanoporous gold into three distinct scales, from the microscale down to the nanoscale, reporting the hierarchical structure "dramatically improves mass transport and reaction rates for both liquid and gases." With the ability to manipulate the catalyst's surface area to generate electrochemical reactions through 3-D printing, researchers said the development could have a major impact on electrochemical plants, which today rely primarily on thermal energy.

"By controlling the multiscale morphology and surface area of 3-D porous materials, you can start to manipulate the mass transport properties of these materials," said LLNL researcher Eric Duoss. "With hierarchal structures you have channels that can handle transfer of reactants and products for different reactions. It's like transportation systems, where you go from seven-lane expressways down to multiple lane highways to thoroughfares and side streets, but instead of transporting vehicles we're transporting molecules."

Achieving the finished product required several steps. LLNL researcher Cheng Zhu and former postdoc Wen Chen created inks made of gold and silver microparticles. After printing, the 3-D parts were put into a furnace to allow the particles to coalesce into a gold-silver alloy. Then they put the parts into a chemical bath that removed the silver (a process called "dealloying") to form porous gold within each beam or filament.

"The final part is a 3-D hierarchical gold architecture comprising the macroscale printed pores and the nanoscale pores that result from dealloying," said Chen, who is currently a professor at the University of Massachusetts-Amherst. "Such hierarchical 3-D architectures allow us to digitally control the morphology of the macropores, which allowed us to realize the desired rapid mass transport behavior."

Zhu and Chen said the team's method is a model that could easily extend to other alloy materials such as magnesium, nickel and copper, offering a powerful toolbox to fabricate complex 3-D metal architectures with unprecedented functionalities in fields such as catalysis, batteries, supercapacitors and even carbon dioxide reduction.

Combining 3D printing with an alloying and dealloying process, researchers at

Lawrence Livermore National Laboratory and Harvard University were able to engineer nanoporous gold into microarchitectured hierarchical structures, a development that revolutionize the design of chemical reactors. Credit: Ryan Chen/LLNL

Chen, who focused on printing and post-processing parts, said the key to the process was developing inks with well-suited flow behavior, allowing them to form continuous filaments under pressure and to solidify upon exiting the printer's micro-nozzle to retain their filamentary shape.

The challenge in catalysis is in combining high surface area with rapid mass transport, according to LLNL researcher Juergen Biener, who develops new catalysts materials for IMASC, an Energy Frontier Research Center funded by the U.S. Department of Energy.

"While additive manufacturing is an ideal tool to create complex macroscale structures, it remains extremely difficult to directly introduce the nanostructures that provide the required high surface area," Biener said. "We overcame this challenge by developing a metallic ink-based approach that allowed us to introduce nanoporosity through a selective corrosion process called dealloying."

Biener said LLNL's extrusion-based approach is universal and scalable, provides tooling-free control over the macroscopic sample shape, and—most importantly—enables integration of nanoporosity in an application-specific engineered macroporous network structure. The combined advantages open a new design space for chemical reactor and energy storage/conversion devices, he said, adding that the resulting materials can potentially revolutionize the design of chemical plants by changing the scaling relations between volume and surface area.

The project is a Laboratory Directed Research & Development feasibility study feeding into a proposed strategic initiative led by Duoss and LLNL researcher Sarah Baker to create 3-D electrochemical reactors in which scientists could exert greater control over catalysts and reduce transport limitations. Researchers said instead of large electrochemical plants, typically located close to oil refineries or in remote areas, modular reactor networks could be created in a series that could be easily replaceable and transportable for relocation near sources of abundant renewable energy or carbon dioxide.

"There are a whole lot of scientific and engineering challenges left, but it could have significant impact," said Chris Spadaccini, director of LLNL's Center for Engineered Materials and Manufacturing. "Scaling up should be easier with small-scale reactors because you can parallelize. You could have an array of small 3-D reactors together instead of one large vessel enabling you to control the chemical reaction process more effectively."

Researchers said they are already starting to explore other materials that might be catalysts for other reactions. The LLNL team collaborated with Cynthia Friend, a professor of Chemistry and Chemical Biology at Harvard, through the Department of Energy's Frontiers Research Center. Harvard scientists performed tests on samples of the parts, showing that their hierarchical structures facilitate mass transportation.

LLNL co-authors included Marcus Worsley, Victor Beck, Jianchao Ye, along with Mathilde Luneau and Judith Lattimer at Harvard.

More information: Cheng Zhu et al. Toward digitally controlled catalyst architectures: Hierarchical nanoporous gold via 3D printing, *Science Advances* (2018). DOI: 10.1126/sciadv.aas9459

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