

“In photocatalysis, and plasmonic photocatalysis in particular, all [these factors] have strong implications for then design and synthesis of future catalysts,” she adds.

The ability to scrutinize photocatalytic reactions in such detail will help identify the nanoscale properties of catalytic particles that most affect performance. Controlling the structure and size of nanoparticles offers the possibility of maximizing their catalytic activity, for example, by determining the location of hot spots, utilizing heating, or the excitation of hot electrons.

Andrea Baldi, of the Dutch Institute for Fundamental Energy Research (DIFFER), believes that the results are impressive.

“These measurements are extremely challenging because of the needs to operate in an ETEM and couple light onto the sample,” he points out. “It is remarkable that the authors have been able to gather a statistically significant number of photocatalytic events and derive a mechanistic understanding of the underlying plasmon-activated process. To my knowledge, this is the first time that the catalytic activity of an antenna-reactor complex (i.e. a plasmonic nanoparticle antenna in the proximity of a reactive catalytic particle) has been characterized with this level of spatial resolution.”

The combination of ultrahigh resolution microscopy with the use of in situ environmental conditions provides a powerful tool to study the performance of functional nanomaterials, he adds.

“The technique presented here is a beautiful example of such synergy and has the potential to be developed further,” he told Nano Today. “For example, I could envision experiments in which light is not only used to excite plasmon resonance, but also to

detect photocatalytic reaction intermediates and products via surface enhanced-Raman spectroscopy. It would also be interesting to extend these studies to the liquid phase and look at plasmonic effects for both heterogeneous and homogeneous catalytic reactions.”

Paul Mulvaney of the University of Melbourne, Australia agrees, adding: “Vadai and colleagues have taken a remarkable and elegant approach to the problem of resolving catalytic reactions. I think the results are quite remarkable. . . [and] demonstrate that a wide range of catalytic systems can now be investigated with unparalleled spatial resolution.” He believes optical excitation is extremely promising to probe photochemical catalytic reactions and will open up new avenues of research.

“This includes the potential to study CO₂ and N₂ reduction as well as potentially CO oxidation. The potential to resolve the role of individual facets in the hydrogenation reactions is tantalizing,” he says. “The fact they can determine which facets hydrogen desorbs from or adsorbs to first and how fast these steps occur is critical for modeling heterogeneous catalysts.”

The approach is currently limited by the need for samples suitable for analysis in TEM, cautions Vadai, and does not allow control over the polarization of light. But the researchers hope to overcome these issues and expand the approach to encompass the study of general chemical reactions, rather than just phase transitions, including in the liquid phase.

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3D fabrication shrinks objects down to size

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What if microscale objects could be simply shrunk down to the nanoscale? Researchers from Massachusetts Institute of Technology (MIT), Harvard University, and Wyss Institute for Biologically Inspired Materials have devised just such a technique that could enable the fabrication of almost any complex three-dimensional nanostructure [Oran et al., *Science* **362** (2018) 1281, <https://doi.org/10.1126/science.aau5119>].

The ability to design and create complex, three-dimensional objects on the nanoscale will be essential to a new generation of miniscule electronic, photonic, plasmonic, and metamaterial devices. Current fabrication routes fall into two main categories, top-down processes such as photolithography and bottom-up approaches including direct laser writing. Each approach has its advantages and limitations, but Edward S. Boyden and his colleagues have come up with an entirely new tactic.

“We have developed a new way to fabricate nanoscale three-dimensional objects by physically shrinking patterns of material,” explain Boyden, first author Daniel Oran, and researcher Samuel G. Rodrigues. “This allows us to fabricate a wide variety of objects that it wasn’t possible to fabricate previously.”

Instead of building up three-dimensional objects by depositing layers of material, the researchers hypothesized that it should be possible to deposit material directly into a three-dimensional scaffold. The team created a scaffold made from the hydrogels polyacrylate and polyacrylamide, which are porous enough to allow reagents into the scaffold, but robust enough to allow precise positioning of deposited material. Crucially, these hydrogels have one additional and very useful characteristic: the ability to expand and contract by a factor of 10 (Fig. 1).

The process begins by patterning an expanded hydrogel scaffold with reactive chemical groups using a laser. Functional materials are then deposited onto the patterned scaffold via conjugation chemistries. This step can be repeated multiple times to deposit different species like gold, silver, or cadmium telluride nanoparticles in three dimensions (Fig. 2).

“You attach the anchors where you want with light and later you can attach whatever you want to the anchors,” explains Boyden. “It’s a bit like film photography – a latent image is formed by exposing the sensitive material in a gel (in this case fluorescein) to light.

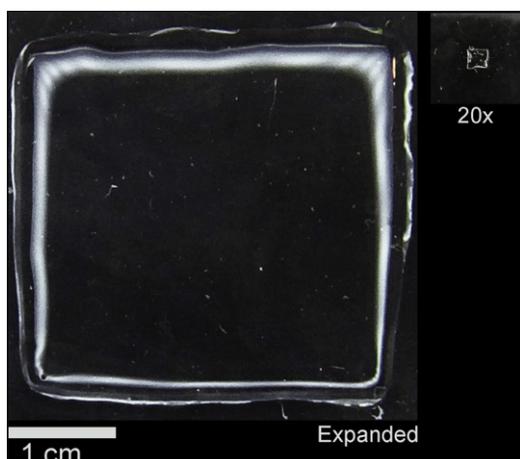


Fig. 1. Photos of the hydrogel scaffold before (left) and after (right) shrinking. The gel in the image shrinks by a factor of 20 in each dimension. All the water is expelled from the gel in the process, leaving behind a hard plastic scaffold. [Credit: Daniel Oran.]

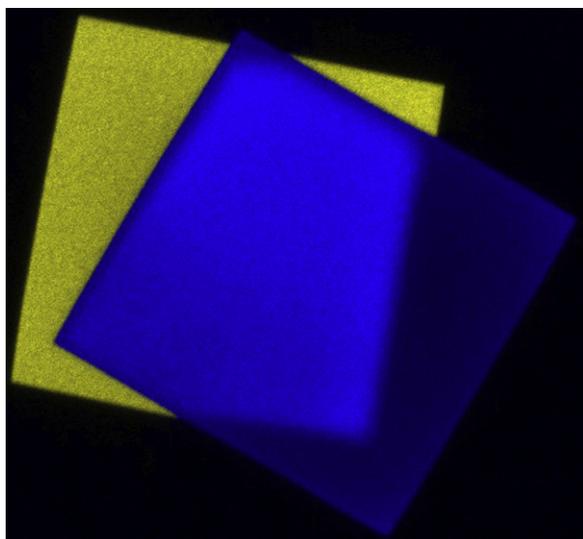


Fig. 2. Image of gold nanoparticles (yellow) and semiconductor nanocrystals (blue) patterned in different patterns within a single sample, demonstrating the ability of Implosion Fabrication to pattern multiple different materials together. [Credit: Daniel Oran.]

Then you can develop the latent image into a real one by attaching another material, such as silver, afterwards.”

Finally, the entire scaffold is shrunk using acid or a solution containing divalent cations such as magnesium chloride and then dehydrated. The shrinking process contracts the object by a factor of 10 in each dimension, resulting in a 1000-fold overall volume reduction.

“Most lithography techniques in use today are limited to two dimensions,” point out Boyden, Oran, and Rodriques. “By contrast, we have no limitations on the geometries that we can

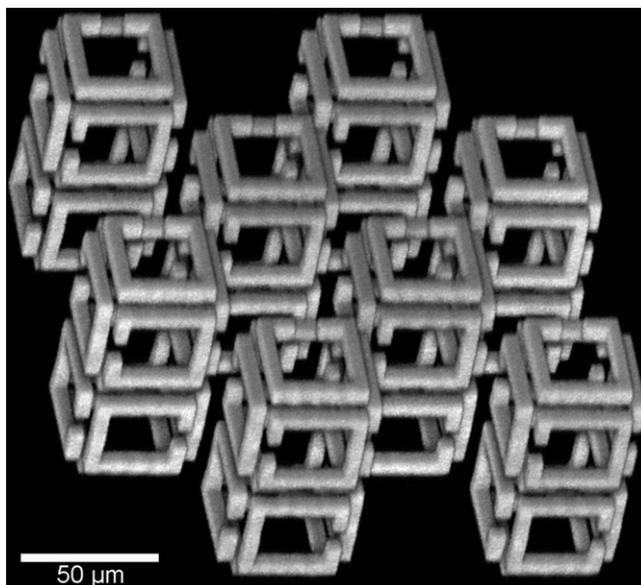


Fig. 3. Image of a 3D pattern of antennas created with Implosion Fabrication. Silver was subsequently deposited on this pattern, (although this image was taken prior to metallization). Scale bar is 50 μm . [Credit: Daniel Oran.]

fabricate – structures don’t need to be self-supporting or connected – and we [can] directly pattern more functionally useful materials like metals or semiconductor nanocrystals.”

The team dubs the process ‘implosion fabrication’ or ‘ImpFab’, demonstrating that it can produce structures with complex architectures ranging in scale from hundreds of nanometers to several microns (Fig. 3).

“Currently, we are only limited by the size of the substrate you can use and the working distance of the objective lens,” point out the researchers. “But potentially new lenses could be developed that overcome this limitation.”

The researchers hope to expand the technique to other kinds of materials and believe that the simple and easy process could open up new avenues of research, particularly in optics.

“Implosion fabrication is very fast and almost all of the processing is in aqueous phase, so it can be easily automated using a fluidics setup,” say Boyden, Oran, and Rodriques.

In a *Perspective* [*Science* **362** (2018) 1244, <https://doi.org/10.1126/science.aav5712>], Timothy E. Long and Christopher B. Williams of Virginia Tech comment:

“The ability to process free-form, multi-material nanostructures with discontinuous nanowires will enable next generation designs of photonic, electronic, and mechanical metamaterials, as well as microelectronics, actuators, and sensors.”

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