sunlight and produce a drug intermediate for the antimalarial agent artemisinin [Liu et al., *Nano Lett.* **15** (2015) 3634].

"I am glad to see another example of a photosensitized semiconductor biohybrid for light-driven chemical production of the drug precursor shikimic acid," he told *Nano Today*.

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Nanoparticles focus new light on catalysis

Cordelia Sealy

Researchers at Stanford University have observed light-driven chemical reactions taking place on a single metallic nanoparticle catalyst [Vadai et al., *Nature Communications* **9** (2018) 4658, https://doi.org/10.1038/s41467-018-07108-x].

Metallic nanoparticles are emerging as a new class of plasmonic photocatalysts because they have a particularly strong response to illumination. Led by Jennifer A. Dionne, the researchers focused their attention on a combination of gold nanodiscs (100 nm in diameter) and palladium nanocubes (with side lengths of 30 nm). The gold discs act as antennas to focus and intensify incident light onto the palladium nanoparticles, which catalyze the reaction. In this case, a simple a hydrogenation reaction during which hydrogen atoms diffuse out of the palladium nanoparticles, transforming the material from a hydrogen-rich β-phase to a hydrogen-poor α-phase (Fig. 1).

"We were able to observe this chemical change upon illumination on a single nanoparticle, which is an important achievement," says first author of the study Michal Vadai. "Only single particle measurements allow one to understand whether specific site on a nanoparticle is more favorable for the reaction.",

The researchers used an environmental transmission electron microscope (ETEM) with an external light source to follow the catalytic reactions directly. Image contrast between the α- and β-phases enables the appearance of the phase transition to be clearly observed. This direct imaging is backed up by the detection of changes to the diffraction pattern and electron energy loss (EEL) signal as hydrogen is desorbed from the palladium nanocubes. The setup enabled the first experimental observations in real time of a light-activated reaction on a nanoparticle catalyst at nanoscale resolution.

"Real time observation of chemical reactions on a single particle allows one to understand the effect of light on different reactions steps," points out Vadai.

Optical excitation enhances the overall reaction kinetics by a factor of ∼10, but the researchers' findings indicate that plasmons affect individual reaction steps differently. In this reaction, when there is no illumination, nucleation initiates randomly at any corner of the palladium nanocubes. But under illumination when plasmons are generated, reactions are more likely to take place at corners closest to 'hot-spots' where light is most concentrated. Plasmons can also potentially open up new reaction paths as well, such as along the edges of the catalyst nanocubes.

"From a technological and experimental point of view, [our work] presents a new concept for studying plasmonic photocatalysts," says Vadai. "No other approach currently has these capabilities at such high spatial resolution."

Differences in nanoparticle type, size, or shape can affect catalytic activity, so the ability to observe what happens on an individual particle is very helpful to understanding the process, explains Vadai.

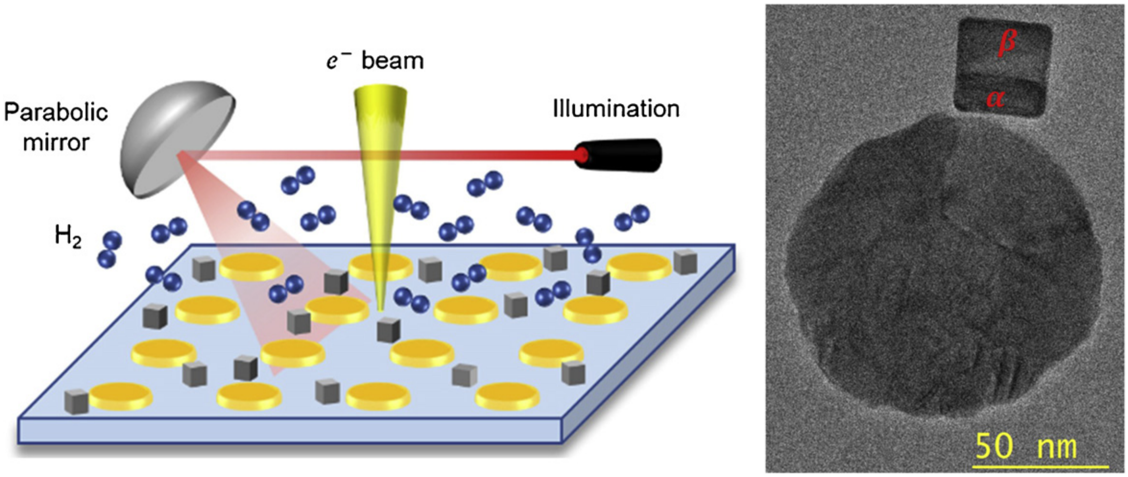

Fig. 1. (a) Schematic of light-coupled TEM. (b) TEM image of Au-Pd antenna reactor system showing the beta to alpha phase transition. [Credit: Jennifer Dionne's group.

"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. Rodriques. "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.