Engineers look inside nanoparticles to explore how their shape improves energy storage

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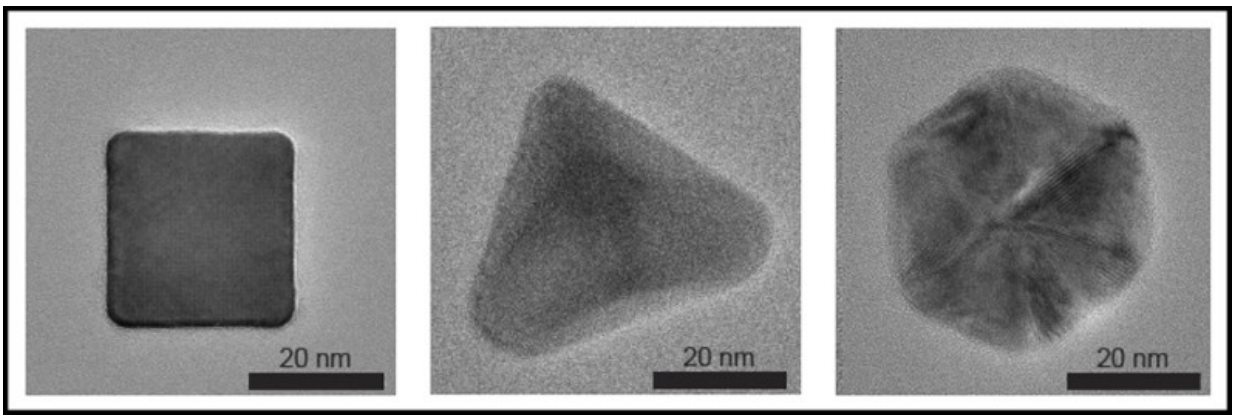

Stanford engineers studying the structures of phase-changing nanoparticles have found that shape matters. Materials composed of cubes and pyramids, for instance, may yield more efficient batteries than those made of icosahedra. Credit: Dionne Group

Many recent big technological advances in computing, communications, energy and biology have relied on very small materials, nanoparticles, with dimensions less than 1/1,000th the thickness of a sheet of paper. However, it can be hard to determine the best nanomaterials for these applications because observing nanoparticles in action requires high spatial resolution in "messy," dynamic environments.

In a recent step in this direction, a team of Stanford engineers has obtained a first look inside phase-changing nanoparticles, elucidating how their shape and crystallinity – the arrangement of atoms within the crystal – can have dramatic effects on their performance.

The work, which is described in *Nature Materials*, has immediate applications in the design of energy storage materials, but could eventually find its way into data storage, electronic switches and any device in which the phase transformation of a material regulates its performance.

For instance, in a lithium ion battery, the ability of the battery to store and release energy repeatedly relies on the electrode's ability to sustain large deformations over several charge and discharge cycles without degrading. Recently, scientists have improved the efficiency of this process by nanosizing the electrodes. The nanoparticles allow for faster charging, increased energy storage and an extended lifetime, but it is unknown which nanoparticle shapes, sizes and crystallinities produce the best performance. Addressing this question served as inspiration for the present study, "Reconstructing solute-induced phase transformations within individual nanocrystals."

Generally, it is difficult to determine whether the behavior of a collection of nanoparticles is the result of each individual component performing similarly or if it is the average output of high and low performers. Jennifer Dionne, an assistant professor of materials science and engineering, and her group have been studying the behavior of individual particles to establish a stronger link between structure and function that can direct the design of next-generation energy storage materials.

In this experiment, Dionne's group examined how varying the shapes and crystallinity of palladium nanoparticles affected their ability to absorb

and release hydrogen atoms – an analog to a lithium-ion battery discharging and charging. They prepared cubic, pyramidal and icosahedral nanoparticles and developed novel imaging techniques to look inside nanoparticles at various hydrogen pressures, determining where the hydrogen was located.

The technique relied on an environmental transmission electron microscope, allowing the engineers to discern exactly how the hydrogen was distributed within the nanoparticles and to do so with incredibly high – sub-2-nanometer – resolution.

"This instrument is one of only a handful of its kind and allows us to study materials in their working environment," said Tarun Narayan, lead co-author of the study and a recent PhD graduate from Dionne's group.

The microscope enables analysis of particles using several different techniques, such as direct imaging, diffraction and spectroscopy.

"Each technique offers different information that can be combined to gain a complete, multi-dimensional understanding of the system," said Andrea Baldi, a postdoctoral co-author and now a faculty member at the Dutch Institute for Fundamental Energy Research (DIFFER) in the Netherlands.

The researchers found that nanoparticle structure significantly influences performance. The icosahedral structures, for instance, show reduced energy storage capacity and more gradual hydrogen absorption than the single crystalline cubes and pyramids. High-resolution maps of the particles demonstrate that hydrogen is excluded from the center of the particle, thus lowering the overall capacity to incorporate hydrogen. Structural characterization shows that the gradual absorption of hydrogen occurs because different regions of the particle absorb hydrogen at different pressures, unlike what is observed in single

crystals.

"We could not have envisaged making in situ observations like this at the atomic level even a few years ago, and so what the team has demonstrated and achieved is remarkable in the materials imaging field," said co-author Robert Sinclair, a professor of materials science and engineering.

Ai Leen Koh, a staff scientist at Stanford's Nano Shared Facilities who was also an author on the work, said that "these results show how in situ environmental electron microscopy can be used to look inside individual nanoparticles exposed to hydrogen gas at real time."

"With this ability to peer inside nanoparticles during their operation, we can help design champion materials for next-generation energy storage devices," said Dionne, who is also a member of Stanford Bio-X and of the Stanford Neurosciences Institute, and an affiliate of the Stanford Precourt Institute for Energy.

More information: Tarun C. Narayan et al. Reconstructing solute-induced phase transformations within individual nanocrystals, *Nature Materials* (2016). DOI: 10.1038/nmat4620

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