



tetrahedra were synthesized using a commonly used hot-injection method and a core-shell growth method. This is an interesting choice of quantum dot shape as most previous studies looked at spherical or near-spherical geometries. Having found earlier that their truncated tetrahedral quantum dots (TTQDs) self-assembled into exciting and complex superstructures when the colloid was left to dry on a rigid silicon substrate, the research team was interested in understanding how increased interparticle interaction would modify the self-assembly.

To this end, the researchers carefully dropped the TTQD colloidal solution (in cyclohexane) atop a non-interacting liquid subphase (ethylene glycol) of different polarity. This helped the two liquid phases to avoid mixing and gave the TTQDs increased time to interact. Once the top phase evaporated, the dried structures were isolated and studied using x-ray scattering and electron microscopy. A thorough characterization of the structures showed that the TTQDs had, in fact, self-assembled into tenfold QCSLs. This was surprising since the TTQDs are single-component nanoparticles.

The normal practice during nanocrystal synthesis is to cover the surfaces with surfactants, the role of which is to impart colloidal stability to the nanocrystals and to enhance their optical properties by securing their surfaces from unwanted oxygen and moisture attack. One set of the surfaces of the TTQDs was intentionally covered with a different surfactant than the others. This surface-specific surfactant coating had crucial implications when TTQDs were allowed to interact during self-assembly. Surface facets with similar surfactants had enhanced affinity to come closer, enhancing self-assembly and leading to decagonal units. Importantly, it was found that during self-assembly, the decagons could flexibly share edges and transform into polygons of five to nine edges wherever necessary to fill gaps.

“The present work is a fascinating discovery on quasicrystalline assemblies from anisotropic nanocrystals,” says Xingchen Ye, an assistant professor of chemistry at Indiana University Bloomington, and an expert in quasicrystalline self-assembly. “The observed tenfold rotational symmetry is distinct from the dodecagonal symmetry

predicted by computer simulations of assemblies of hard tetrahedra, motivating further investigations on how details of shape and interaction anisotropy encoded at the single-nanocrystal level lead to mesoscopic ordering.”

The demonstration of QCSLs from single-component building blocks enabled by the discovery of the “flexible polygon tiling rule” has opened a new realm in the field of quasicrystalline structures and will enrich the tool chest for chemical synthesis of superstructures. “We have demonstrated a fundamentally new type of quasicrystal. The decagons form quasicrystalline superlattices by making their edges flexible, utilizing our flexible polygon tiling rule,” Chen says. “Our findings have implications for research in materials science, chemistry, mathematics, and even art and design.”

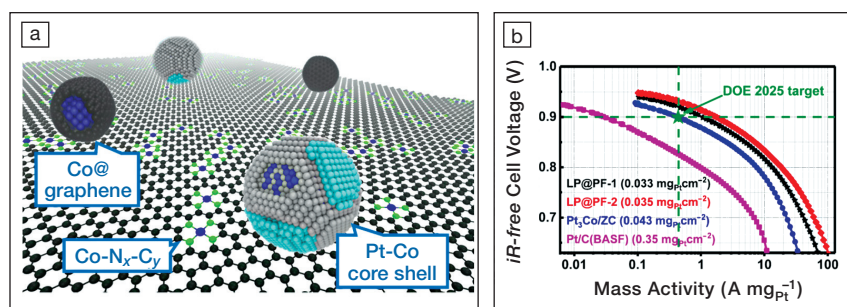
Quantum dot superlattices are increasingly being explored for electronic and optoelectronic applications with claims of enhanced charge transport and optical properties due to increased order. The present study is anticipated to soon bring into view the exciting subfield of quantum dot QCSL electronics.

Ahmad R. Kirmani

ENERGY FOCUS

Functionalized-carbon-supported Pt-Co alloy nanoparticle catalyst yields reduced-cost fuel cells

Fuel cells are electrochemical devices that convert chemical energy stored in fuels (e.g., hydrogen gas) into electricity. Their functionality relies on a rapid oxygen reduction reaction (ORR) for energy generation. Since ORR is a non-spontaneous process with a high reaction potential barrier, electrocatalysts containing noble metals (e.g., Pt) are typically used to reduce this barrier and improve the fuel cell energy efficiency. The scarcity and high cost of Pt is one of the reasons hindering broad adoption of fuel cells. A research team led by Di-Jia Liu, a senior chemist at Argonne National Laboratory, recently developed a novel ORR catalyst with record low Pt mass ($0.035 \text{ mg}_{\text{Pt}}/\text{cm}^2$) that outperformed



(a) An illustration of the microstructure of the developed catalyst: Pt-Co nanoparticles and graphene-wrapped Co nanoparticles anchored on a Co, N-containing carbon surface. (b) Tafel plots of output voltage versus mass activities of four oxygen reduction reaction catalysts. LP@PF-2 is the best catalyst the researchers synthesized. The green star marks the performance set by the 2025 target of the US Department of Energy (DOE), Fuel Cell Technologies Office. Credit: Di-Jia Liu.

its commercial counterparts. This breakthrough was reported in a recent issue of *Science* (doi:10.1126/science.aau0630).

“This discovery happened to us serendipitously,” Liu says. The researchers initially focused on the development of a

heterogeneous catalyst for gas-phase biofuel production. They synthesized several materials consisting of Pt-Co core-shell nanoparticles sprinkled on N-doped porous carbon substrates by thermal annealing Co/Zn zeolitic imidazolate

frameworks and Pt precursors. Afterward, “we could not help but to test their ORR catalytic activities in fuel cells since we are an electrocatalysis-fuel cell group, and the experimental setup was already there,” Liu says; “we were glad we did it.”

The developed ORR catalysts were fabricated into fuel cell membrane electrodes for performance evaluation. The electrodes contained ultralow Pt loadings, approximately one tenth of those used in commercial electrodes, while still exhibiting excellent ORR catalytic activity. At an output voltage of 0.9 V, the highest mass activity (current generated per milligram of Pt) was 1.77 A/mg_{Pt}, which exceeds a 2025 target (0.44 A/mg_{Pt}) set by the US

Department of Energy. The improved ORR catalytic activity was attributed to the synergistic catalysis between the Pt-Co nanoparticles and the Co, N-containing carbon support. Specifically, in addition to directly reducing O₂ to water over the Pt-Co nanoparticles, the N-coordinated cobalt (Co-N_x-C_y) sites on the substrate can also reduce O₂ to water and H₂O₂. The generated H₂O₂ then diffuses to the surface of nearby Pt-Co nanoparticles where it is eventually reduced to water.

Bao Yu Xia of Huazhong University of Science & Technology, China, says that the key deliverables of this work, “developing cost-effective and scalable approaches for some of the most

promising ORR catalysts with ultralow Pt contents,” as well as understanding their catalytic activities in fuel cells are vital to large-scale implementation of fuel cells. Xia was not involved in this study.

“This work brings out a new research direction and is far from complete,” Liu says. The research group is investigating various issues to further enhance the performance of their catalysts, including the optimal distance between the Pt-Co nanoparticles and the Co-N_x-C_y coordination sites, the influence of humidity on the synergistic catalysis, and the minimal Pt loading possible without sacrificing catalytic activity.

Tianyu Liu

NANO FOCUS

Shrinkage leads to nanoscale resolution in 3D geometries and with a variety of materials

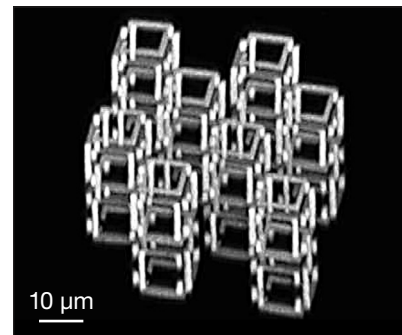
Optical metamaterials are structures that interact with light to challenge the laws of physics. They can exhibit a negative refractive index to be used in electromagnetic cloaks, for super-high resolution imaging, and for unusual color effects. To interact with electromagnetic waves, however, these materials have to possess dimensions comparable to the wavelengths, namely 100 nm and smaller. Such precision is enabled in state-of-the-art two-dimensional (2D) nanofabrication but remains challenging in three-dimensional (3D) geometries.

The research team of Edward S. Boyden at the Massachusetts Institute of Technology has developed a unique approach to fabricate 3D patterns with nanoresolution. The process, called ImpFab for “implosion fabrication,” was reported in a recent issue of *Science* (doi:10.1126/science.aau5119) and relies on the following principle. A porous hydrogel, typically a polyacrylate or a polyacrylamide, is swollen in an aqueous solution containing ions or organic molecules that readily diffuse through the pores and deposit at the surface of polymeric chains. Chemical reactions can occur, such as the growth of metallic nanoparticles from

ionic suspension, directly within the hydrogel. After this internal coating, the composite is shrunk down, and then further solidified by sintering to create metallic structures.

Since hydrogels can be 3D-printed at the microscale, this principle can be easily coupled with 3D printing. Using hydrogels with controllable cross-linking density, the homogeneous shrinkage occurring after dehydration results in retention of the shape, but a decrease in dimensions. As a result, 3D patterns with complex shapes and resolutions of 50 nm could be fabricated in silver. These were found to exhibit an electrical conductivity only about 10 times less than that of bulk silver despite the high porosity (see Figure).

Shweta Agarwala, a researcher at the Singapore Centre for 3D Printing and leading innovator in additive manufacturing for electronics and biotechnology, says that “currently, direct-writing of nanostructures is possible using non-contact methods like inkjet and aerosol jet, but the resolution is limited to 10 μm. Moreover, these techniques are able to print in 2D plane only. This research of using sacrificial scaffolds to pattern desired structures and shrinking them to achieve 3D nanoscale objects is fascinating.” Furthermore, Boyden emphasizes that “the contribution of the work is not just that we can achieve similar or better resolution, but rather that we have found



Fluorescence imaging of a silver nanostructure created with ImpFab. Credit: *Science*.

a way to do the patterning of many different materials in a modular fashion to achieve any geometry.” Indeed, the research team provides examples of patterning with fluorescent molecules, proteins and DNA, and several metals.

Daniel Oran and Samuel G. Rodrigues, the lead authors of the article, are excited by the possibilities that the method offers to create and study optical metamaterials. “There is a huge need for a robust and efficient way of generating 3D nanoscale features out of a variety of materials. We are eager to find collaborators in any domain where the benefit of arbitrary 3D geometry is paramount to asking new scientific questions or creating devices that would otherwise be impossible or impractical to fabricate,” Oran says.

Hortense Le Ferrand