

Just as for humans, allowing perovskites to soak up sun helps them to relax and makes them more efficient. Constantly illuminating a triple-cation hybrid perovskite thin film expands its crystal lattice, which relaxes strain, researchers report in *Science* (doi: 10.1126/science.aap8671). This, in turn, aligns the material's crystal planes and repairs defects, as well as lowers the

energy barrier at the perovskite-contact interface, improving the material's power-conversion efficiency.

Recent studies have shown that light-induced structural changes play an important role in the optoelectronic properties and stability of devices. But such studies on mixed-cation halide perovskites are lacking. Wanyi Nie, Aditya Mohite, and their colleagues at Los Alamos National

Laboratory illuminated formamidinium-methylammonium cesium lead iodide perovskite thin films using a standard 1-sun source for 180 minutes.

The efficiency of solar cells made with the films went up from 18.5% to 20.5%. Light soaking did not compromise the cells' stability: they worked with minimal degradation for 1500 hours under standard full-spectrum solar illumination.

While halide perovskites are making strides toward commercial devices, their inorganic perovskite oxide counterparts have also attracted attention for solar cells. Devices made from these ferroelectric perovskites are highly stable and have high open-circuit voltages, but they have shown limited efficiencies.

In a *Nature Photonics* (doi:10.1038/s41566-018-0137-0) paper, Canadian researchers demonstrate an alternative route to making high-performance solar cells from perovskite oxides. They made a device from a composite bismuth-manganese-oxide thin film with two different crystal phases—BiMnO₃ and BiMn₂O₅—which had a power-con-

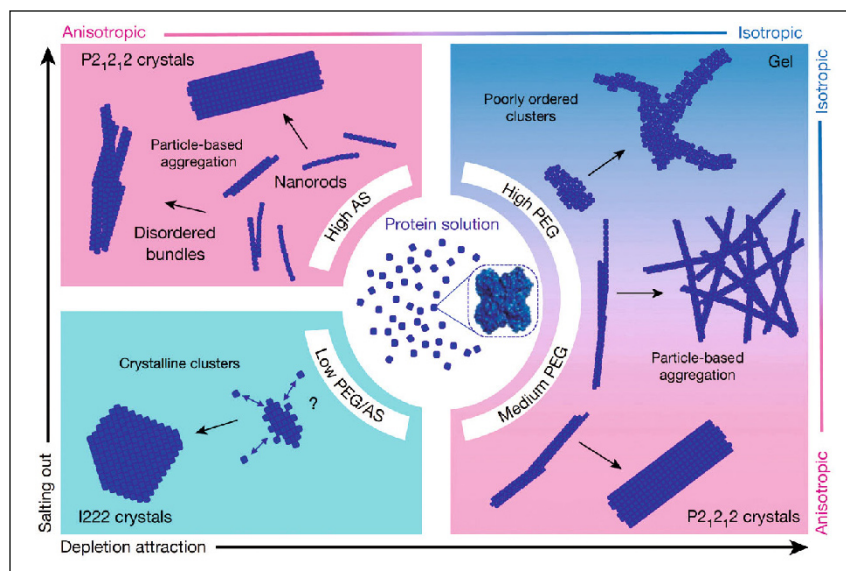
version efficiency of around 4.2%. Inorganic perovskite oxides are ferroelectric. They do not conduct charge carriers well, leading to low photocurrent density and hence low efficiency. But in the mixed material, ferroelectric BiMnO₃ grains are incorporated into semiconducting BiMn₂O₅, which boosts photocurrent density.

Bio Focus

Cryo-transmission electron microscopy reveals protein nucleation pathways

Nucleation is the initial stage of crystallization, a process in which individual building blocks (e.g., atoms and molecules) assemble into various crystalline structures, or "polymorphs." Polymorphs usually exhibit different physicochemical properties due to their diverse structures, and hence are suitable platforms to demonstrate "structure-function" relationships. Therefore, understanding the nucleation and crystallization mechanisms leading to distinct polymorphs is critical. Now, by using cryo-transmission electron microscopy (cryo-TEM), a group of researchers—from the Centre National de la Recherche Scientifique-Université Grenoble Alpes, France; Technische Universiteit Eindhoven, The Netherlands; and the Vrije Universiteit Brussel, Belgium—has directly observed how the protein glucose isomerase nucleates as different polymorphs. Their findings were recently published in *Nature* (doi:10.1038/nature25971).

"One of the most elusive moments to observe the crystallization process is



Schematic illustration depicting the pathways that glucose isomerases take to nucleate into different polymorphs depending on the type and concentration of the nucleation initiators. AS: ammonium sulfate; PEG: poly(ethylene glycol). Both AS and PEG are nucleation initiators. Credit: *Nature*.

the nucleation stage, when a nucleus, or crystalline embryo, is formed," say the authors. To study the nucleation processes of glucose isomerase, they rapidly froze the solutions containing the protein molecules and nucleation initiators at different time intervals during the nucleation. This process stopped the nucleation and allowed

direct imaging of the morphologies of the resultant crystalline structures using state-of-the-art cryo-TEM.

The researchers discovered that the type and the concentration of the nucleation initiators determined the pathways by which the protein molecules nucleated. Twenty seconds after mixing the isomerases with



1.5 M ammonium sulfate, the former assembled into nanorods of ~ 1.7 nm width and ~ 12 nm length. Within the next 15 min to 30 min, these nanorods combined into dimers, trimers, and eventually into bundled long fibers (~ 800 nm in length) or loosely attached fiber aggregates. In the meantime, prismatic-shaped and rhombic-shaped nanocrystals were also detected. Additionally, the researchers witnessed a similar nucleation pattern when 4.5% (w/v) poly(ethylene glycol) (PEG) was used as the nucleation initiator, but no nanorods were seen at early stages. When the PEG concentration was further increased to 7% (w/v), only protein gels composed of disorderly arranged protein clusters were obtained. These contrasting behaviors were

attributed to the inter-molecular interactions (isotropic repulsion and anisotropic attraction) among the individual protein molecules, which can be altered by nucleation initiators of different compositions and concentrations.

The pathways revealed in this study do not involve a metastable dense liquid intermediate state as reported in previous studies, and thus deviates from the current understanding of protein nucleation. Yuki Kimura of Hokkaido University, Japan, says, “Their achievements not only present a deeper understanding of nucleation of a protein material, but also open up opportunities for controlling polymorphs. I believe we have advanced into a new stage of the nucleation study

[since this work is published].” Kimura was not involved in this study.

“In a nutshell, our results are advancing the fundamental understanding of nucleation and polymorph selection. These insights are not only relevant for macromolecules but can also be translated to other crystal-forming substances including pharmaceutical compounds,” the authors say. “Now we are very interested to apply the same workflow to other protein molecules, because we are convinced, considering the complex nature of macromolecules, that many more unexpected findings will pop up along the (nucleation path) way.” The research team is also searching for alternative strategies to control polymorph selection.

Tianyu Liu

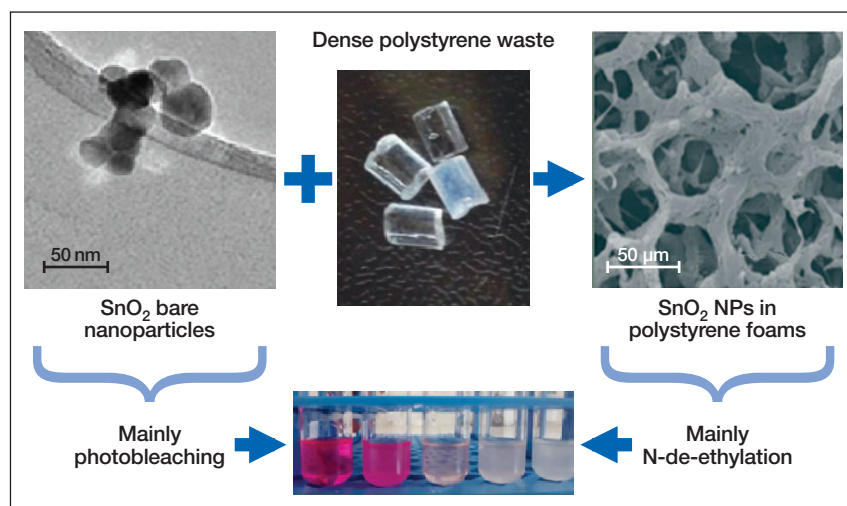
Nano Focus

Detoxifying the oceans by using reused polystyrene

Researchers have found a way to remove toxic chemicals from the sea using polystyrene (PS)—which is an abundant, undesirable waste product in the environment, arising from packaging, cutlery, and other disposable objects that are used on a daily basis. This

leads to many problems, and recycling of PS is still limited. A collaborative effort between researchers in Brazil and the UK has now found a valuable application for this waste polystyrene—to degrade toxic and carcinogenic dyes such as Rhodamine B (RhB) through photocatalysis. This work was reported in a recent issue of *ACS Applied Materials & Interfaces* (doi:10.1021/acsmi.7b19834).

Nanofoams of PS and tin oxide (SnO_2) were developed through a thermally induced phase-separation process combined with lyophilization, where the solvent is frozen and converted into vapor without going through the liquid phase. The concentration of PS in solution affects the strength of the resulting nanofoam. A 1% PS concentration in a cyclohexane solvent did not result in a stable nanofoam. Therefore, 2.5% and 5% solutions were employed to generate the stable nanofoams that are essential for the photocatalytic activity required to break down the dyes. This fabrication method has previously only been demonstrated to form oxide-based nanofoams. “Our article describes the fabrication and applications of new and exciting second-generation systems, which are now functional nanocomposite (polymer and oxide) foams,” says Rodrigo J. de Oliveira from Universidade Estadual da Paraíba, who is a lead researcher of the study. X-ray diffraction results revealed that polystyrene maintains its amorphous nature and the SnO_2 takes an ordered form. The highest surface area was observed for the foam synthesized at 700°C , and the highest particle size was observed at 900°C . Transmission electron microscopy confirmed the formation of the nanofoam.



Schematic describing preparation of SnO_2 -polystyrene (PS) nanofoams from waste PS leading to a porous material, and the two main photochemical mechanisms observed for photocatalytic degradation of RhB, photobleaching (using SnO_2 alone), and N-de-ethylation (using SnO_2 -PS nanofoams). Credit: Rodrigo J. de Oliveira.