



1.5 M ammonium sulfate, the former assembled into nanorods of  $\sim 1.7$  nm width and  $\sim 12$  nm length. Within the next 15 min to 30 min, these nanorods combined into dimers, trimers, and eventually into bundled long fibers ( $\sim 800$  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

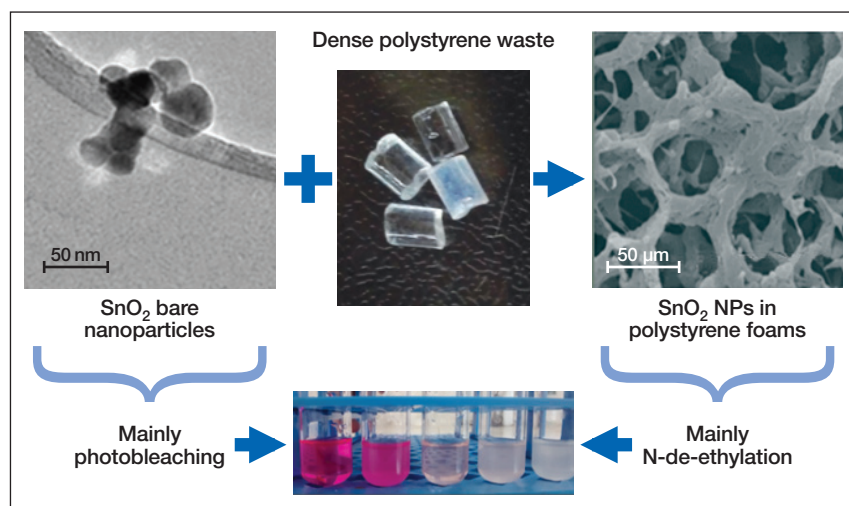
### Nano Focus

#### 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/acsaami.7b19834).

Nanofoams of PS and tin oxide ( $\text{SnO}_2$ ) 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  $\text{SnO}_2$  takes an ordered form. The highest surface area was observed for the foam synthesized at  $700^\circ\text{C}$ , and the highest particle size was observed at  $900^\circ\text{C}$ . Transmission electron microscopy confirmed the formation of the nanofoam.



Schematic describing preparation of  $\text{SnO}_2$ -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  $\text{SnO}_2$  alone), and N-de-ethylation (using  $\text{SnO}_2$ -PS nanofoams). Credit: Rodrigo J. de Oliveira.

UV-vis absorption helped to track the degradation of the RhB dye. During the photocatalytic process, the characteristic absorption band of the dye decreases with a shift in the absorption maximum from 554 nm to 534 nm, demonstrating degradation. Two mechanisms take place during this process. Cleavage of the chromophore results in a decrease in the maximum absorption, while the peak displacement is related to the N-de-ethylation mechanism. Complete degradation is characterized by a shift in the absorption maximum from 554

nm to 498 nm. The photocatalytic activity in the presence of PS/SnO<sub>2</sub> foam results in 98.2% degradation of RhB.

The porous structures of the nanofoams offer more active catalytic sites due to the favorable reaction of OH radicals on the foam surface, and the dye molecules enable efficient degradation. Furthermore, the foam from the waste material can be reused up to four times without compromising the photocatalytic activity. However, loss of efficiency is observed with the fifth cycle. “As this work has established the proof of principle, we are now looking for more

stable systems such as polymer/gold, from the catalytic point of view,” Oliveira says.

Hicham Idriss, a research fellow at the Saudi Basic Industries Corporation (SABIC), appreciates the study. “The article deals with using styrene foam (commonly called Styrofoam) as support for a wide-bandgap semiconductor for dye degradation. The work is sound and convincing. However, the wide-bandgap semiconductor used, SnO<sub>2</sub>, is only active under UV, making its potential for application very limited,” he says.

**Rahim Munir**

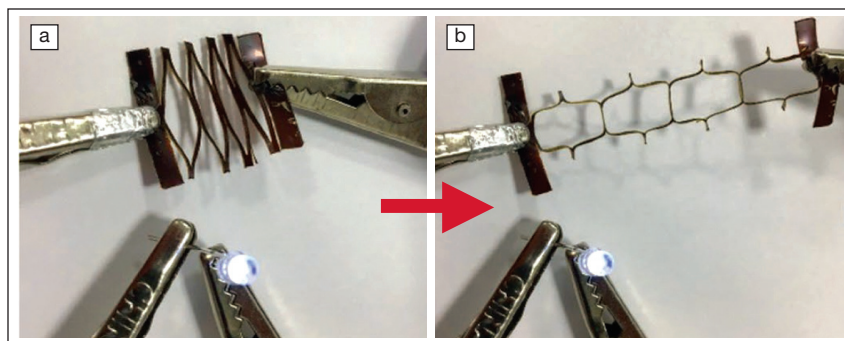
### Origami-shaped conducting polymer stretches like an accordion

A group of researchers from University at Buffalo, The State University of New York and Temple University has developed a material that is both electrically conductive and can stretch like an accordion, as published in a recent issue of *Advanced Materials* (doi:10.1002/adma.201706390).

The material introduced by Ying-Shi Guan and co-workers is a combination of a stretchy polymer, termed TFB (poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl)diphenylamine))]), and a conductive polymer, termed P3BT (poly(3-butylthiophene-2,5-diyl)), together known as PthTFB. This hybrid material by itself is not sufficient for wearable electronics, but the implementation of three advances allows this material to gain the desired properties.

The first is a technique that allows the polymer molecules to self-assemble into a very flat and very uniform film, with a minimum thickness of  $\approx 12$  nm. This was achieved by dropping the solution of polymer molecules onto the surface of water, where the Marangoni effect (also responsible for causing wine to flow up the sides of glasses) stretches the droplet into a film. This thin film can be deposited on a surface and is moderately stretchable and weakly conductive. However, it becomes less conductive the more it is stretched.

The second advance exploited the geometry of a type of origami called



A kirigami polymer film (a) before and (b) after being stretched, as part of a circuit that lights an LED. Credit: *Advanced Materials*.

*kirigami* (Japanese for *cut paper*), which produces structures that can fold compactly and stretch immensely. The film by itself can stretch by an extra 15% of its length before breaking, and it becomes less conductive in the process. After the PthTBF is deposited on kirigami-cut paper, the film can be stretched by 2000% (20 times its length) without breaking, and it still conducts electricity just as well.

The conductive polymer in the film, P3BT, does not conduct well, and is thus not ideal for electronics. However, if iodine is included in the water when the film forms, iodine atoms can be incorporated within the film, boosting the transfer of charge between the polymers and significantly enhancing the electrical conductivity. The iodine-doped films conducted electricity at 4 S/cm, which is 8000 times better than the initial recipe, giving it an electrical conductivity 100 $\times$  higher than that of seawater.

With these three developments, the material is foldable, stretchable, and electrically conductive. When asked about its implementation in consumer devices, researcher Shenqiang Ren says, “The development of stretchable materials and devices shown here can open up the development of new mechanically designed smart electronics, such as artificial skin, wearable electronics, and stretchable energy devices.” His research group has more in store besides wearable devices, with “ongoing efforts ... to integrate energy transduction schemes into our systems, such as organic piezoelectrics, and photovoltaics, and thermoelectrics,” Ren says.

“This is a very interesting study with some promising results,” says Aaron Mascaro, a nanoelectronics researcher at McGill University. “This could definitely be implemented in wearable smart fabrics and stretchable sensor materials.”

**Alex Klotz**