Global scientific team 'visualizes' a new crystallization process (w/ video)

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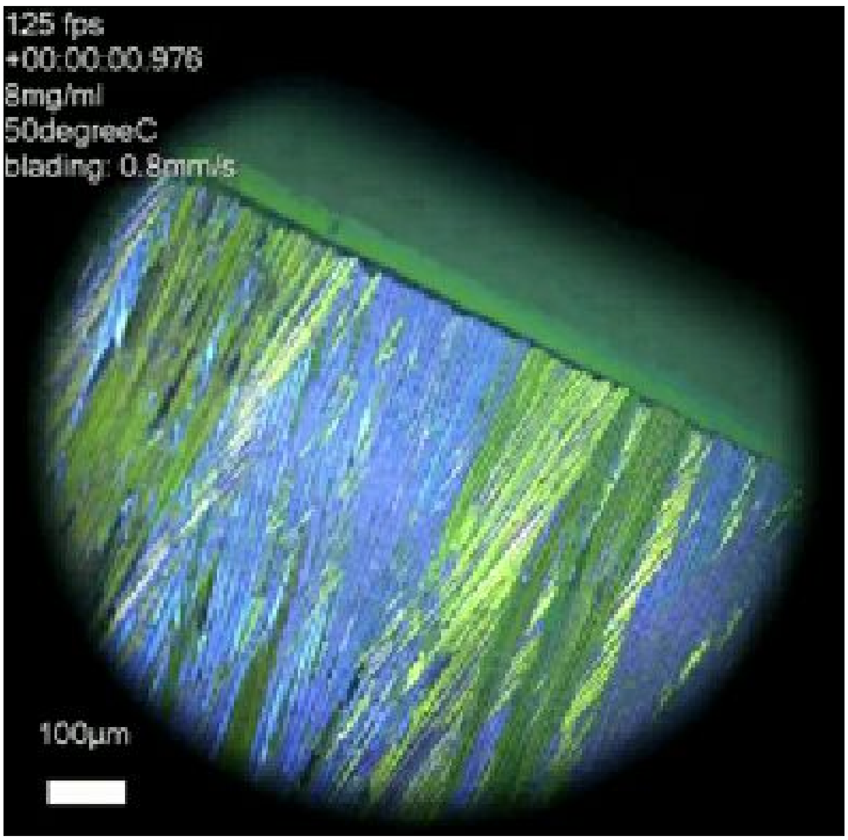

Sometimes engineers invent something before they fully comprehend why it works. To understand the "why," they must often create new tools and techniques in a virtuous cycle that improves the original invention while also advancing basic scientific knowledge.

Such was the case about two years ago, when Stanford engineers discovered how to make a more efficient type of thin, crystalline organic semiconductors. Their so-called "strained organic semiconductors" carried current faster than comparable systems, a big step toward producing flexible electronic devices that couldn't be built using rigid silicon chips.

Stanford Chemical Engineering Professor Zhenan Bao and her team dissolved organic molecules into a solution and deposited this liquid onto a flat surface. Their innovation was how they controlled the process through which those organic molecules assembled and crystallized as the liquid evaporated.

But Bao and her team wanted to understand why their process created such an electronically useful crystal lattice. The functionalities of any material are determined by how the building blocks are assembled and ordered. So they launched a new experiment with help from organic thin film characterization expert Dr. Aram Amassian, an Assistant Professor at King Abdullah University of Science and Technology (KAUST) in Saudi Arabia.

The process of crystallization normally occurs in the blink of an eye and the researchers needed to understand it at the nanoscale. To do this they had to create a way to record and visualize molecules as they formed crystals in slow motion.

In a paper published in *Nature Communications*, Professors Bao and Amassian reveal how they accomplished this feat: they combined a tiny, bright X-ray beam produced by the Cornell High Energy Synchrotron Source (CHESS) in Ithaca, New York, with high speed X-ray cameras to shoot a high speed movie showing how organic molecules form different types of ordered structures or crystals.

The paper explains why the Stanford process can produce such an ideal lattice – quick-evaporation of the solution coupled with the thinness of the liquid were part of the trick, but more surprises were in store. The researchers showed that once the liquid film becomes thin enough, also known as the confinement regime, the type of crystal can be selected with unprecedented control.

In a more far-reaching sense, the experiments reveal new ways to study and control crystallization, both of which will benefit other fields, such as pharmaceutical manufacturing, where the potency of pills can depend upon precisely controlling the crystal structure of active ingredients.

"This is an exciting paper because it represents an advance in instrumentation and methods with broad applicability in other fields, in addition to making an important finding for flexible electronics," said Gaurav Giri, first author of the paper.

Subtitle: The Squeegee Effect

Giri was a doctoral student in Bao's lab when the team first reported its new process for making fast organic semiconductors to Nature in December 2011.

In their initial paper, the Stanford engineers described how they applied a thin layer of solution to a heated surface. The solution contained organic semiconductor molecules that evaporated out of the solution and allowed the semiconductor to crystalize into a layer of crystals that could be used to make electronic circuits. They used a technique known as solution shearing to drag the thin layer of liquid across the surface, similar to how a window-cleaner uses a squeegee to clean glass.

In that first paper, Bao's team worked with Stefan Mannsfeld, a staff scientist at the Stanford Synchrotron Radiation Lightsource. He used X-ray scattering to reveal how the molecules in the crystalline layer lined up in a lattice that expedited electron flow.

But the Stanford engineers could not explain precisely why solution shearing packed the crystals into this beneficial structure, or polymorph. "We thought that understanding the mystery could lead to new developments and applications of our method," adds Bao.

Subtitle: A molecular dance

To accomplish their goal, the researchers had to understand how the molecules formed into a crystal as the solution evaporated.

They had some of the instrumentation required for the task. X-rays can reveal how molecules pack in a crystal much as dental X-rays can disclose the outlines of our teeth.

But teeth stay still during X-rays. Crystals grow and change rapidly. These crystals formed in milliseconds.

One key challenge was to record X-ray images of the molecular crystallization during the squeegee like process. Amassian and his team had to build a miniature squeegee that could be remotely operated in the safety of the X-ray hutch. Giri worked closely with Ruipeng Li, a postdoctoral fellow in Amassian's group, to integrate the solution-shearing set-up into the system. Amassian and Li had previously demonstrated X-ray movies of crystallization working with Dr. Detlef Smilgies, a scientist at CHESS.

To capture the growth process, the researchers used very bright X-rays produced by the synchrotron. They focused the synchrotron beam on a very small spot at the edge of the squeegee blade and fired it at intervals a few milliseconds apart as the squeegee dragged the thinning liquid until crystallization started.

Using a high speed X-ray camera they took snapshots of the molecular outlines revealed by the beam. Then they reassembled these snapshots to create an animated movie about the process of crystallization.

This had never been done before.

Subtitle: Movie with a plot twist

Watching the movies, the scientists found crystals forming in a highly unusual sequence. Crystals can take different forms. These are called polymorphs. The common form of any crystal is usually the most stable and should form last in a sequence of polymorph crystallization. But that was not the case with the crystals that were formed by the squeegee effect.

"We were stumped at first when the stable form appeared first at the air-liquid boundary, followed by other polymorphs," Amassian said. "This pointed to an unusual confinement effect possibly due to the thin liquid film trailing the squeegee."

The scientists confirmed their hypothesis by tuning the confinement conditions – thinning or thickening the liquid – to produce different polymorphisms. Giri discovered that solvents with different molecular sizes affected the formation of polymorphs. A Cornell team led by Professor Paulette Clancy helped with the computational analysis of the data.

Subtitle: Applications beyond semiconductors

Detailed knowledge of how to pack crystals with precise characteristics will help to make strained organic semiconductors more practical for use in new types if flexible electronic devices.

But the experiment will yield benefits beyond electronics and in other fields that require precise control over crystal polymorphism. Many drugs, for instance, are made from small molecules that must crystallize in just the right way to have the proper effect.

"We were of course pleased to demonstrate our initial hypothesis of confinement, but things got even more exciting when we showed the ease with which we could change the crystal formation within the confinement window," Amassian said.

Provided by Stanford University