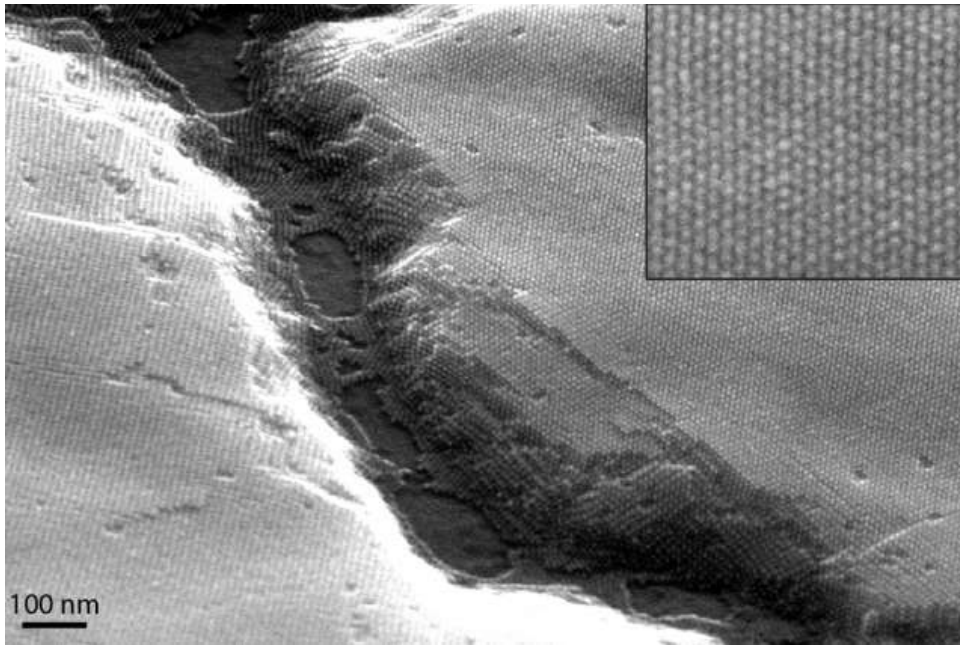


# MIT News

ON CAMPUS AND AROUND THE WORLD



A scanning electron micrograph of a nanocrystal superlattice shows long-range ordering over large domains.

Image courtesy of the Tisdale Lab.

## Nanocrystal self-assembly sheds its secrets

A new approach gives a real-time look at how the complex structures form.

**Michael Patrick Rutter | School of Engineering**  
**March 21, 2016**

The secret to a long-hidden magic trick behind the self-assembly of nanocrystal structures is starting to be revealed.

The transformation of simple colloidal particles — bits of matter suspended in solution — into tightly packed, beautiful lace-like meshes, or superlattices, has puzzled researchers for decades. Pretty pictures in themselves, these tiny superlattices, also called quantum dots, are being used to create more vivid display screens as well as arrays of optical sensory devices. The ultimate potential of quantum dots to make any surface into a smart screen or energy source hinges, in part, on understanding how they form.

Through a combination of techniques including controlled solvent evaporation and synchrotron X-ray scattering, the real time self-assembly of nanocrystal structures has now become observable in-situ. The findings were reported in the journal *Nature Materials* in a paper by Assistant Professor William A. Tisdale and grad student Mark C. Weidman, both at MIT's Department of Chemical Engineering, and Dettlef-M. Smilgies at the Cornell High Energy Synchrotron Source (CHESS).

The researchers anticipate their new findings will have implications for the direct manipulation of resulting superlattices, with the possibility of on-demand fabrication and the potential to generate principles for the formation of related soft materials such as proteins and polymers.

### Quantum dot disco

Tisdale and his colleagues are among the many groups who study hard semiconductor nanocrystals with surfaces coated with organic molecules. These solution-processable electronic materials are on store shelves now under a variety of names, incorporated into

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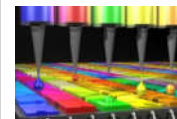
William Tisdale

Tisdale Lab

Department of Chemical Engineering

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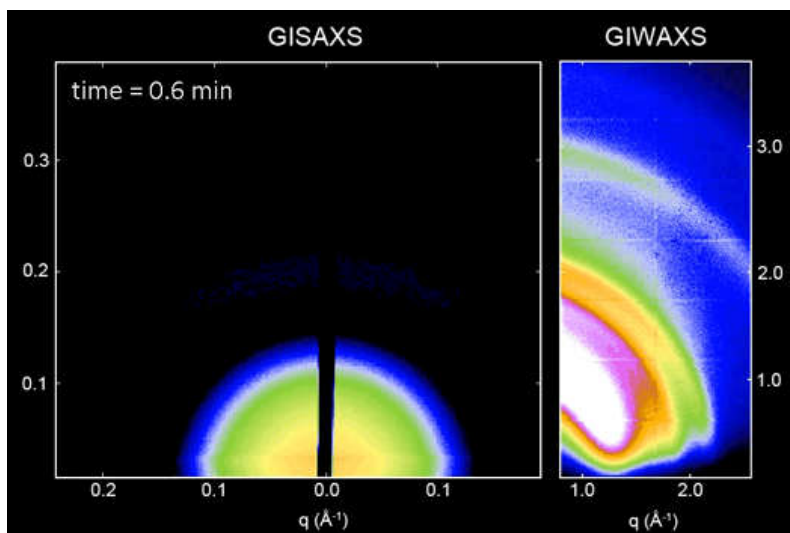
everything from lighting displays to TVs. They also are being eyed for making efficient solar cells and other energy conversion devices due to their ease of fabrication and low-cost manufacturing processes.

The broader adoption of these nanocrystals into other energy conversion technologies has been limited, in part, by the lack of knowledge about how they self-assemble, going from colloidal particles (like tiny Styrofoam balls suspended in a liquid) to superlattices (picture those same balls now dry, packed, and aligned).

Techniques including electron microscopy and dynamic light scattering have uncovered some aspects of the starting colloidal state and the final superlattice structure, but they have not illuminated the transition between these two states. In fact, such foundational work dates back to the mid-1990s with Mounji Bawendi's group at MIT.

"In the past 10 to 15 years, a lot of progress has been made in making very beautiful nanocrystal structures," Tisdale says. "However, there's still a lot of debate about why they assemble into each configuration. Is it ligand entropy or the faceting of the nanocrystals? The depth of information provided by watching the entire self-organization process unfold in real time can help answer these questions."

### Chamber of secrets



To make the nanoscale movie above, Tisdale's graduate student and co-author Mark Weidman took advantage of a Cornell-developed experimental chamber and a recently developed dual detector setup with two fast area detectors, while environmental conditions were changed during the formation of superlattices. Using lead sulfide nanocrystals, Weidman was able to conduct simultaneous small-angle X-ray scattering (capturing the structure of the superlattice) and wide-angle X-ray scattering (capturing atomic scale orientation and alignment of single particles) observations during the evaporation of a solvent.

"We believe this was the first experiment that has allowed us to watch in real time and in a native environment how self-assembly occurs," Tisdale says. "These experiments would not have been possible without the experimental capabilities developed by Detlef and the CHES team."

The use of nanocrystals with a heavy element (lead) and the brightness of the synchrotron X-ray source enabled sufficiently fast data collection that self-assembly could be observed in real time, resulting in compelling images and movies of the process.



Faculty highlight:  
William Tisdale



Running the color  
gamut

## A fine mesh

The discovery may lead to refined models for self-assembly of a wide range of organic soft materials. Moreover, the ability to watch the structure as it is evolving in real time also holds promise for intervening or directing the system into desired configurations, presaging a future how-to guide for creating superlattices.

Tisdale says that much more work needs to be done to gain insights about why nanocrystals self-assemble the way they do. He and his team plan to use their new technique to manipulate parameters such as solvent conditions as well as the size and shape of nanocrystals, and to more closely study the ligands on the surface as they seem to be the key driver for self-assembly.

“We hope that this study and technique will help to increase our understanding of colloidal self-assembly and, in the long term, enable us to direct nanoscale self-assembly toward a desired structure,” Weidman adds.

The work was supported as part of the Center for Excitonics, an Energy Frontier Research Center funded by the U.S. Department of Energy Office of Basic Energy Sciences. The Cornell High Energy Synchrotron Source (CHESS) is supported by the National Science Foundation and the National Institutes of Health/National Institute of General Medical Sciences.

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