Bio Focus

Complex microstructures emerge from chirality and competitive restrictions

Crystals are generally perceived as objects exhibiting long-range atomic symmetry with overall simple morphologies. As an example, rock salt has a cubic crystallographic structure. Grains of salt encountered in daily life have visibly smooth surfaces. With this perception, morphological complexity in crystals is difficult to imagine and explain. However, sea urchins and marine organisms called coccolithophores display morphological complexity while containing single-crystal components with intricate geometrical shapes. The emergence and existence of such complex geometry in these biological crystals has remained a biomineralization mystery. The surprise stems from the fact that these organisms do not grow from highly defined and size-disperse nanoscale components and, therefore, the wide size distribution is expected to result in disorganized structures. Entropic and enthalpic considerations would further favor random and compact aggregates lacking any morphological distinction.

A team of researchers led by Nicholas A. Kotov at the University of Michigan has now taken a major step toward addressing this question. Kotov says that the study was prompted by the need to better understand the origin of the complexity of inorganic and composite structures in living organisms. "They have to deal with quite 'messy' building blocks with wide size distributions, yet demonstrate amazing sophistication in shapes and functions while having very limited means and resources."

In the study reported in *Science* (doi:10.1126/science.aaz7949), the researchers looked at "chirality" as the potential key enabler of complexity in microparticles. An object is said to be chiral if it is distinct from its mirror image, such as the clockwise-counterclockwise "flavors" of a molecule. To enable complex structures, nanosheets of gold thiolate were synthesized with their surfaces capped with cysteine as ligand molecules. Cysteine is a chiral amino acid that comes in *L*- (clockwise) and *D*- (counterclockwise) flavors. Using either of *L*- or *D*-cysteine, chiral nanosheets were realized that aggregated to give surprisingly complex spiky spheres. On the other hand, using *L*- and *D*-cysteine ligands simultaneously resulted in flat nanosheets that lacked chirality and led to relatively less complex and flatter morphologies.

"The communities of nanoparticles have to develop complex structures in order to satisfy multiple competitive interactions and restrictions that are imposed on the assembly process. It turns out that in this process, the polydispersity matters less than the symmetry of individual building blocks, which determines the final organization of the building blocks," Kotov says.

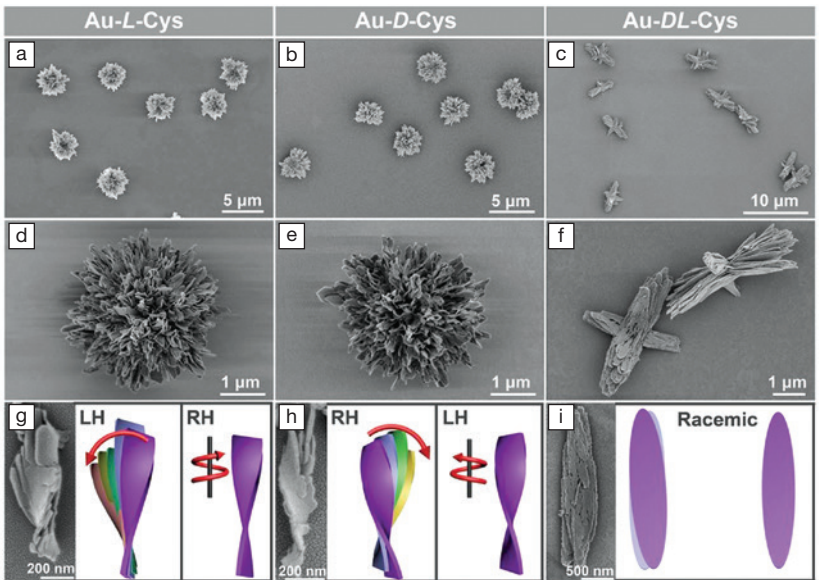
An outstanding aspect of this work is the completeness it provides by explaining the complex structures synthesized and quantifying the emerging complexity. This was enabled by developing computational models that suggested that the spiky spheres made by *L*- or *D*-cysteine are, in fact, among the most complex structures made artificially to date, outcompeting the complexity found in naturally occurring sea urchins and coccolithophores.

"The path to this discovery had to go through enumeration of complexity, which was utterly nontrivial. We developed a method to calculate the complexity of nanoscale assemblies based on graph theory. It allowed us to compare the complexity of different structures that we synthesized and those found in biology rigorously. It turned out that synthetic nano-assemblies can actually outcompete the biological structures in complexity," Kotov says.

The chirality of these particles provides them with exciting optical and chemical properties. Photons exiting the particles upon light absorption undergo polarization in a two-step process: *first*, due to chirality of the nanosheets, and *second*, due to overall chiral morphology of the microparticle. Furthermore, their spiky geometry and presence of charged ligands result in stable dispersions in both hydrophobic and hydrophilic media, an interesting demonstration of colloidal stability. Kotov says the discovery can have multiple technological consequences.

"It provides the universal energy-efficient path to create numerous complex particles, materials, and, perhaps, even device components. The chiral hedgehog particles that resemble skeletons of marine organisms called coccolithophores can be used in catalysis, optoelectronics, drug delivery, and energy technologies," Kotov says.

Ahmad R. Kirmani



Scanning electron micrographs (SEMs) of microparticles formed by aggregation of (a) *L*-cysteine capped (Au-*L*-Cys), (b) *D*-cysteine capped (Au-*D*-Cys), and (c) *L*,*D*-cysteine capped (Au-*DL*-Cys) gold thiolate nanosheets. (d–f) Enlarged SEMs of (a–c), respectively. (g–i) SEMs of segments of these microparticles with corresponding schematics illustrating their chirality. Credit: *Science*, AAAS, Wenfeng Jiang, The Kotov Lab, University of Michigan.

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