SELF-ASSEMBLY

A controlled attraction

“the ionic colloidal crystals we can build have the potential to evolve well beyond the structural complexity of the atomic solids”

Of all multicomponent crystals, the assembly of ionic solids to satisfy Coulombic interactions is perhaps the most intuitive. And, in the same way that they drive the formation of common salts, Coulombic interactions can also drive the assembly of colloidal particles. Now, Stefano Sacanna and co-workers from New York University and the University of California San Diego have shown how the attachment of uncharged polymers on the surface of charged colloidal particles can help to control their assembly in water into proper gemstones, through a process called polymer-attenuated Coulombic self-assembly.

The organization of colloidal particles into ordered structures necessitates a careful balance between attractive and repulsive interactions, so that the particles can approach one another close enough that attractive interactions dominate but not so close that the aggregation becomes chaotic. “Colloidal stability is classically explained using Derjaguin–Landau–Verwey–Overbeek theory, which considers the balance between the attractive van der Waals interactions

and repulsive electrostatics,” explains Sacanna. “We can build target architectures by encoding specific attractive forces in the components of our colloidal mixtures. These might be simple entropic forces or highly tailored supramolecular interactions. But simply mixing oppositely charged components doesn’t often lead to controlled colloidal assembly, because the particles will come into contact with one another, binding chaotically and irreversibly.”

DNA molecules are commonly used to decorate the surface of the colloidal particles to control their assembly into precise lattices by exploiting the specific base-pairing interactions. Sacanna and colleagues wanted to explore a different approach that does not require the use of any biomolecule and instead relies on the pure balance of the electrostatic interactions of the charged particles in water.

Their system consists of oppositely charged particles decorated with a non-ionic surfactant, dispersed in a solution of sodium chloride. When in solution, a double layer of opposite charges is formed around each particle, the thickness

of which — the Debye length — depends on the salt concentration in the solution. Therefore, the attraction and repulsion of the charged particles can be controlled by tuning both the polymer and Debye length. If the polymer is much shorter than the Debye length, the particles will aggregate chaotically. If the polymer is much longer, the particles remain dispersed in the solution. When the polymer length is similar to the Debye length, the balance of repulsive and attractive interactions is just right and the charged particles will aggregate in organized fashion structures.

“In other words, once you find a way to fix the distance between colloidal particles — here we use polymers as spacers — virtually any charged particle can act as a model ion, assembling with oppositely charged partners into crystal structures similar to ionic solids,” says Sacanna. By changing the size ratio of the charged particles, the team was able to obtain cubic, lamellar or needle-like crystal structures.

“Our study offers a straightforward approach to colloidal crystal engineering in which particles of different size and composition can be easily mixed to form a new class of colloidal crystals,” says Sacanna. “The library of colloidal building blocks available to us is constantly growing, so the ionic colloidal crystals we can build have the potential to evolve well beyond the structural complexity of the atomic solids that inspired them. Our assembly approach is an important step towards a predictable and modular microfabrication technology in which bulk functional materials nucleate and grow spontaneously from soups of common colloids,” he concludes.

Gabriella Graziano

ORIGINAL ARTICLE Hueckel, T. et al. Ionic solids from common colloids. *Nature* **580**, 487–490 (2020)
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