HIERARCHICAL NANOSTRUCTURES

Nanoshells show their metal

Spherical nano- and mesoscale assemblies are pervasive in biology, where anisotropic lipid chains organize themselves into elaborate vesicles and proteins assemble into large viral capsids. These hollow organic spheres — nanoshells in materials science parlance — are key to compartmentalization and transport in nature. Inspired by this, we have long sought to make nanoshell motifs from inorganic materials with desirable electronic and catalytic properties. The drawbacks are that inorganic compounds have high surface energies and crystallize in polyhedral rather than spherical shapes. Nevertheless, it appears that careful tuning of interactions between polyhedra allows their assembly into the desired nanoshells, as a team led by Peijun Zhang, Petr Král and Nicholas Kotov describe in *Nature Chemistry*.

Inorganic nanoshells are typically prepared by deposition of the desired material on a spherical template. Subsequent template removal can be cumbersome and wasteful, with the methodology being at any rate unsuitable for the preparation of small shells. To develop a better approach, Kotov recalls that they "looked for conditions under which nanoparticles are attracted to each other strongly enough to aggregate into supraparticles". For the products to be hollow, he notes that the van der Waals forces must be largely balanced by electrostatic repulsions, whereby "thermodynamic equilibrium would be established and the inner particles are pushed to the surface".

Such behaviour was coaxed out of cadmium sulfide (CdS) nanoparticles, which take the form of polydisperse truncated tetrahedra with pH-dependant surface charges. Hydrolysis of thioacetamide in the presence of Cd^{2+} ions affords CdS particles, which then assemble into nanoshells. The latter only form at certain pH values: when CdS precipitates from solutions with a pH less than 5, the resulting particles experience insufficient electrostatic repulsion and simply aggregate into non-hollow supraparticles. However, the same experiment conducted at pH 9.5 affords nanoshells that average 22 nm in diameter, with thicknesses (3–5 nm) — determined using transmission electron microscopy (TEM) tomography — that coincide well with the individual nanoparticle size. The shells can be engineered to feature 2-nm pores, and the overall structure does not collapse because it has a small but non-trivial charge equivalent to 55 electrons. TEM images reveal that the shells comprise ~90 nanoparticles, each of which has an average negative charge of 0.6 on account of a small excess of OH^- or SH^- ligands at the surface. The role of electrostatics is critical and intuitive — the nanoshells implode when repulsions between particles are screened, which can be triggered by increasing the ionic strength of the solution.

The structures of the CdS nanoshells can be rationalized by considering the interactions between the randomly oriented constituent nanoparticles. As was noted above, van der Waals attractions are approximately balanced by electrostatic repulsions. However, molecular dynamics calculations fail to predict nanoshell formation if they only take these two types of interaction into account, as is the case when coarse-grained models are used. It is only when hydrogen bonding between surfaces and hydrostatic osmotic pressure inside the nanoshells are considered that the balance is tipped in favour of the observed nanoshells. Importantly, the forces are cooperative and interdependent on each other, invalidating our previous understanding of such systems, whose interactions were modelled additively.

The porosity and electronic properties of CdS nanoshells may lend themselves to challenging photocatalytic processes, such as the reduction of carbon dioxide or dinitrogen. More broadly, parallels can be drawn between the assembly of inorganic nanoshells in the laboratory and organic vesicles in nature: "The spontaneous formation of capsule-like shells sheds light on the potential origin of life. A big question regarding the origin of life is compartmentalization, and these data indicate that it can be achieved in the absence of lipids or other high molecular weight organics," explains Kotov. It is then suggested that inorganic nanoshells might well have served as cauldrons for prebiotic mixtures — witches brews from which life grew.

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> "The spontaneous formation of capsule-like shells sheds light on the potential origin of life"

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