

COLLOIDAL CRYSTALS

Plenty of room at the top

Binary mixtures of nanoparticles of different size and composition can self-assemble in a bewildering variety of lattices. This defies expectations and shows promise for the modular self-assembly of nano-sized building blocks into three-dimensional devices.

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Our brains are three-dimensional, but computer chips, even the most advanced ones, are effectively two-dimensional: they consist of a small number of layers. One reason why we cannot yet compete with the three-dimensional design of living systems is that the latter assemble themselves. In contrast, electronic or mechanical devices have to be deposited or etched, layer-by-layer, by a manufacturer. Now Shevchenko *et al.*, writing in *Nature*, have investigated the many factors that control the structure of binary nanoparticle crystals and made important progress towards the self-assembly of nano-sized components into three-dimensional devices¹.

Self-assembly of ordered structures is common: even atoms and molecules can self-assemble into highly ordered three-dimensional crystals, and the same is true for nanoparticles such as colloids or even proteins. The structure of these crystals is dictated by the interaction between the constituent particles and by external conditions (temperature, pressure or the chemical composition of the solution). Moreover, the crystals that form are not necessarily those that are thermodynamically most stable. Often, a single molecular species can crystallize into an astonishing variety of distinct crystal forms ('polymorphs'). Predicting which crystal structure will form in what circumstances is still largely an unsolved problem that is similar in complexity to the well-known 'protein-folding' problem. But the true challenge in materials science goes beyond predicting the crystal structure of a given material — the aim is to design building blocks that once organized into a structure will have a specific function.

To make progress along this road, we must understand the principles that can be used to guide the self-assembly process. The simplest ordering principle that we know is packing. The structure of a crystal must be compatible with the shape and size of its building blocks. But packing constraints only tell us which crystal structures are possible, not which ones will form. One might think that the specific attractions between the building blocks determine

how molecules pack in a crystal and indeed this is often the case. But in its simplest form, crystal formation is determined not by a minimization of energy but by a maximization of entropy as expressed by the second law of thermodynamics. It is a common misconception to think that for this law a spontaneous change in an isolated system will always lead to more disorder. In fact, many systems increase their entropy on crystallization if this occurs at constant density. The entropy in the crystal phase may be higher than in the liquid phase if the particles can be packed more efficiently in a crystal and consequently have more room to move. As far back as the 1950s, Alder and Wood and colleagues^{2,3} showed by computer simulations that an increase in entropy is at the origin of the crystallization of hard spheres (idealized

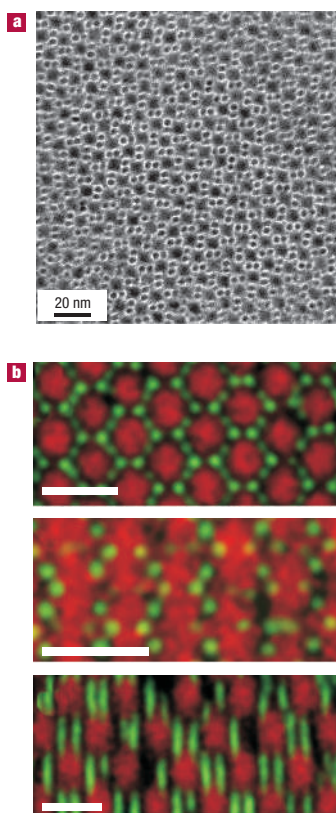


Figure 1 New crystal structures. **a**, Transmission electron micrograph of a binary superlattice structure self-assembled by Shevchenko *et al.* from a suspension of 6.2-nm PbSe and 3.0-nm Pd nanoparticles¹. **b**, Confocal images (of different cuts through the unit cell) of a colloidal 'salt' crystal with LS_6 stoichiometry obtained by Leunissen and co-workers⁸. The crystal contains positive (green, radius 0.36 μm) and negative (red, 1.16 μm) particles of PMMA. All scale bars are 4 μm .

particles that do not attract each other). The value of this observation would have been largely academic were it not for the fact that later experiments demonstrated the feasibility of making suspensions of uncharged colloids that behave like hard spheres in the theoretical prediction⁴. Subsequent experimental work⁵ showed that binary systems of hard colloids can pack into surprisingly complex crystal forms, such as the AB₁₃ structure where icosahedra consisting of 13 B particles are embedded in a simple cubic lattice of large A particles. Again, the high entropy of the AB₁₃ crystal is responsible for the formation of this phase⁶.

But if packing were the only factor determining crystal stability, then the number of distinct binary crystal structures would be small⁷. Shevchenko *et al.* show that it pays to go beyond packing considerations. They obtain a rich variety of binary superlattices by evaporating suspensions containing two types of colloidal particles and demonstrate that these particles can pack in unexpected ways. Not only do they report structures that had not been observed in either intermetallic or ionic crystals, but they also find completely new packing modes for which the transmission electron micrographs could not be related to any known unit cell (these unidentified superlattices are shown in Fig. 1a).

These binary superlattices can be made in a reproducible way by controlling the factors that determine the interactions between colloidal particles at larger distances. Of particular interest is the role played by electrostatic (Coulomb) interactions: the colloidal particles used by Shevchenko *et al.* are slightly charged (typically, no more than a few elementary charges) and these charges can be influenced by additives (such as tri-*n*-octylphosphine oxide or oleic acid). In this respect, colloidal particles are very different from simple ions such as Na⁺ and Cl⁻ that crystallize in a 1:1 stoichiometry to form neutral NaCl crystals. As the charge of colloidal particles can be varied, it becomes possible to make crystals with different stoichiometry from the same building blocks.

A similar phenomenon was recently observed by Leunissen *et al.*⁸ who studied the formation of binary crystals of much larger, weakly charged colloids with opposite charges and obtained colloidal crystals that have no simple molecular counterpart (see Fig. 1b). Intriguingly, Shevchenko *et al.* observe that at the early stages of crystal nucleation, the same solution may yield crystals with different stoichiometries. But because most of these were not electrically neutral they could not grow to macroscopic size. This suggests that it should be possible to design both the structure and the crystallite size of the binary superlattices.

An obvious question is: how do we reach beyond binary lattices? It seems likely that the combined constraints of optimal packing and neutrality of charges will guide the design of crystals with more than two components. Making such structures would be an exciting challenge for combinatorial materials science. The ultimate question is whether there is a limit to the complexity of ordered structures that can be designed. At some point the intrinsically non-specific effects of packing and charge will be insufficient to design a multicomponent crystal. Then we will have to use more selective design principles, for instance by coating the nanoparticles that must be adjacent with complementary strands of DNA⁹. But this may be only part of the solution: for very complex structures, spontaneous self-assembly may simply become too slow to be practical. Then we may have to use 'active' self-assembly, similar to that in living organisms, to build complex devices that are truly three-dimensional.

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