

COLLOIDAL SELF-ASSEMBLY

Interlocked octapods

Suspensions of octapod-shaped nanocrystals are seen to spontaneously interlock into chains, which in turn aggregate side-by-side to form three-dimensional crystals. The observed hierarchical self-assembly can be explained by the octapod's shape and the solvent-tunable van der Waals interactions.

Sara M. Rupich and Dmitri V. Talapin

Progress in the self-assembly of nanoscale particles into ordered structures is directly related to advances in synthetic techniques. For instance, self-assembly puts stringent requirements on the nanoparticles' maximum polydispersity. As a consequence, most research in the field has revolved around the study of the self-assembly of easy-to-synthesize spherical particles in single, binary and sometimes ternary combinations¹⁻³. More recently, the crystallization of simple anisotropic particles such as nanorods, nanocubes and occasionally more complex structures such as nanostars⁴ has been reported. Writing in *Nature Materials*, Miszta *et al.* report that monodisperse, octapod-shaped nanocrystals spontaneously assemble into chains, which in turn interlock into three-dimensionally ordered porous superlattices⁵ (Fig. 1). The demonstration of such hierarchical self-assembly is an important milestone on the way towards the realization of precise packings of engineered building blocks into macroscopic assemblies, on which components and functionalities can be added, tuned or combined in a predictable and controllable manner.

Through the impressive refinement of a synthetic protocol⁶, the authors were able to prepare octapod semiconductor nanoparticles (Fig. 1a) with an unprecedentedly narrow distribution of size and shape. The octapods remained as isolated individual particles when dispersed in chloroform due to a proper surface treatment that minimized attractive interactions between them. To induce self-assembly, the authors decreased the stability of the colloidal suspension by varying the composition of the solvent, which according to the authors' computer simulations tunes the strength of the van der Waals interactions between the octapods. In toluene, the octapods slowly aggregated into chains, and electron-microscopy analysis of the structure revealed that all of the octapods had assembled in an interlocked configuration with neighbouring octapods rotated by 45° with respect to each other (Fig. 1b,c). After addition of the highly polar solvent acetonitrile, and as a result

of the increased van der Waals attraction, the octapod chains self-assembled (Fig. 1d) into three-dimensional superlattices with a tetragonal structure (Fig. 1e,f).

Finding such distinctive 45°-tilted packing motifs in the assemblies of octapods is unexpected because nanoparticles often tend to simultaneously form mixtures of structures. (In fact, in single-component self-assembly, closely related structures with very similar free energies are usually observed: for instance, in experiments

hard spheres crystallize in a mixture of face-centred cubic and hexagonally close-packed stackings.) To some extent, the number of accessible structures can be minimized through the addition of site-specific linkers such as DNA⁷. However, no such additional guiding was necessary for the octapods to obtain a single most energetically favourable configuration. By using geometrical arguments and calculating the solvent-mediated van der Waals energy between the octapods, the authors were

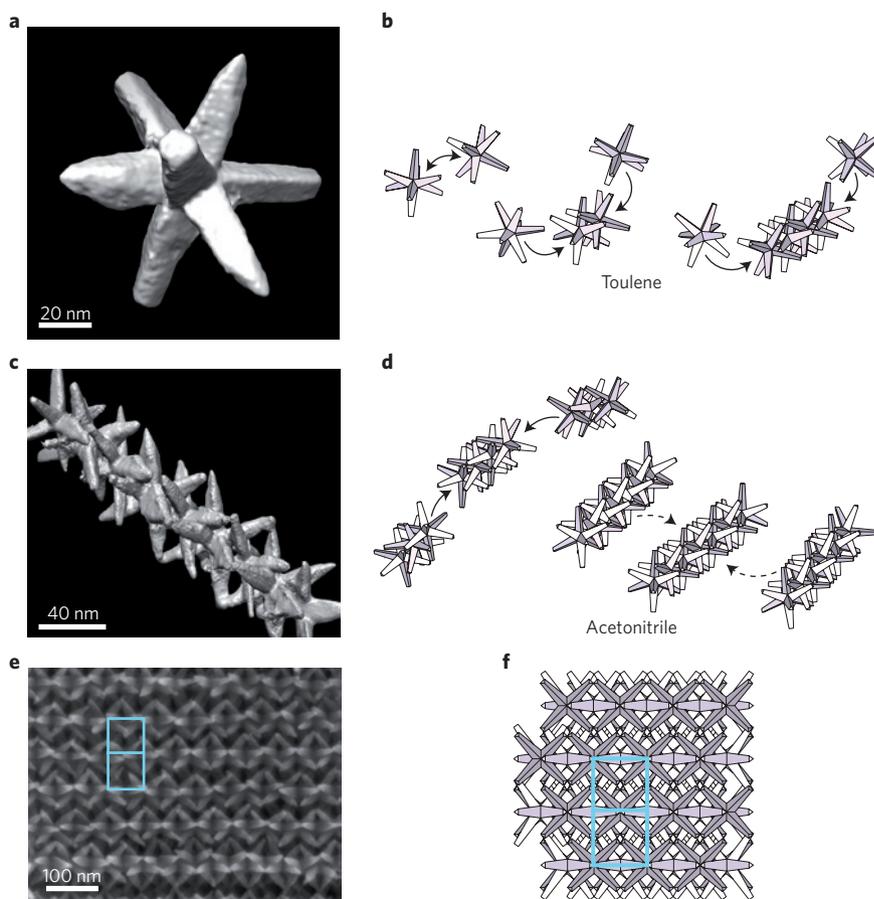


Figure 1 | Hierarchical self-assembly of nanometre-sized octapods⁵. **a-c**, Individual octapods (**a**), which remain separated in a chloroform solution, form on dissolution in toluene chains of interlocked octapods (**b,c**). **d-f**, On the addition of acetonitrile, these chains aggregate side-to-side (**d**) into three-dimensional ordered porous crystals (**e,f**). Both the interlocked (a 45° tilt between neighbouring pairs) and side-to-side (pod-pod interactions between neighbouring chains) configurations result from van der Waals attractions between the octapods, the strength of which is tuned by the composition of the solvent.

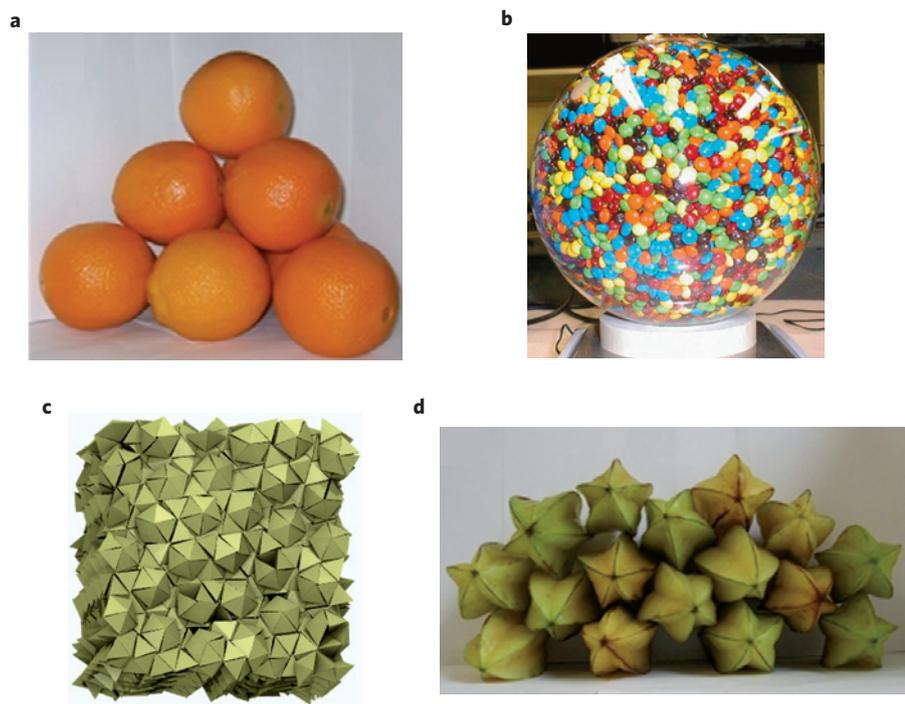


Figure 2 | Predicting the self-assembly and densest configurations of simple objects is hard. **a**, A proof of the densest packing of hard spherical objects, the face-centred cubic lattice, was only achieved as recently as 1998. **b,c**, The unusually dense disordered packings of simple hard objects such as M&M's sweets⁸ (**b**) and tetrahedra (**c**), which form dodecagonal quasicrystals⁹, have been demonstrated more recently. **d**, The packing of objects with complex shapes is among the oldest and most challenging problems in mathematics. Figures reproduced with permission from: **b**, ref. 8 © 2004 AAAS; **c**, ref. 10, © 2011 Annual Reviews.

able to explain their observed hierarchical arrangement⁵, thus showing that it is possible to encode structural driving forces into the building blocks.

However, a more difficult problem is to design *a priori* such driving forces and assembly conditions. Indeed, figuring out the rules linking the shape and interactions of individual building blocks with the symmetry of the structures that they self-assemble into may seem to be a simple problem, especially in view of the sophistication of modern mathematics and available computer power. However, it is not. In fact, although in 1611 Johannes Kepler proposed that the densest packing of hard

spherical objects is the face-centred cubic lattice (Fig. 2a), it was not until 1998 that Thomas C. Hales succeeded in proving this conjecture. In 2004, Chaikin and co-workers found that ellipsoids with the shape of M&M's sweets randomly packed much more densely than spheres (Fig. 2b)⁸. In 2009, the computer simulations of Glotzer and colleagues revealed that hard tetrahedra can self-assemble into a zoo of amazingly complex structures, including dodecagonal quasicrystals (Fig. 2c)⁹. These examples illustrate how even the assembly of simple nonspherical objects pushes the limits of our ability to predict the resulting structure. As for objects with more complex

shapes, such as those in Fig. 2d, we can only guess what structure represents the energetically most favourable arrangement. Indeed, computational attempts to predict superlattice structures such as those that the octapods of Miszta and colleagues self-assemble into are expensive. The reason lies in the vast volume of the configurational phase space available to the particles — which increases with particle anisotropy — that the simulation algorithms would have to explore. Still, the combination of experiment and simulation creates a powerful approach to understanding self-assembly of nanoscale objects with complex shapes.

A unique feature of the octapod superlattices is their high porosity, which permits the diffusion of ions in and out of the structure. To demonstrate this, the authors used copper ions to replace most of the cadmium ions in the superlattice of cadmium chalcogenide octapods, while retaining its structural integrity. Subsequent exposure to oxygen plasma resulted in the formation of a copper oxide layer on the octapods' surface that fused the tips of neighbouring octapods, thus generating a rigid, continuous framework. Such combination of electrical connectivity and structural rigidity may open up opportunities for the use of these highly porous superlattices in photovoltaic and photonic devices. □

Sara M. Rupich and Dmitri V. Talapin are in the Department of Chemistry, University of Chicago, Chicago 60637, USA.

e-mail: dvtalapin@uchicago.edu

References

- Murray, C. B., Kagan, C. R. & Bawendi, M. G. *Science* **270**, 1335–1338 (1995).
- Shevchenko, E. V., Talapin, D. V., Kotov, N. A., O'Brien, S. & Murray, C. B. *Nature* **439**, 55–59 (2006).
- Evers, W. H., Friedrich, H., Fillion, L., Dijkstra, M. & Vanmaekelbergh, D. *Angew. Chem. Int. Ed.* **48**, 9655–9657 (2009).
- Quan, Z. & Fang, J. *Nano Today* **5**, 390–411 (2010).
- Miszta, K. *et al. Nature Mater.* **10**, 872–876 (2011).
- Deka, S. *et al. Nano Lett.* **10**, 3770–3776 (2010).
- Park, S. Y. *et al. Nature* **451**, 553–556 (2008).
- Donev, A. *et al. Science* **303**, 990–993 (2004).
- Haji-Akbari, A. *et al. Nature* **462**, 773–777 (2009).
- Keys, A. S., Iacovella, C. R. & Glotzer, S. C. *Annu. Rev. Condens. Matter Phys.* **2**, 263–285 (2011).