has afforded an impressive 21 g of few-layer graphene at a rate of 5.3 g h⁻¹, and projections of 100 g h⁻¹ are suggested. That is indeed reaching industrial utility for applications such as thin films where only milligram or sub-milligram quantities of graphene are required per unit of product. More concerning, however, is the low yield of the overall process: <0.1%. Most of the material remains as a graphitic sediment. Although recycling of the sediment can increase the yield to ultimately 3%, this extends the hurdle for industrial utility, if it is indeed solvable at all. Additionally, the average flake size being <1 µm in diameter could either mean that the shear-exfoliation process will fragment larger sheets into smaller sizes, or that efficient exfoliation will only work on smallerdiameter graphite flakes. It is known that small-diameter flakes of graphite intercalate faster than larger ones⁵. And although this

shear-exfoliation method is touted to be independent of solvent pre-intercalation, avoiding this graphite pre-treatment step might limit the effectiveness of this approach to submicrometre-diameter graphene.

Coleman and colleagues' process of shear exfoliation to generate few-layer two-dimensional materials solutions is ambitious and characteristic of the detailed studies that are needed to proceed from discovery to a commercialized technology. While not yet ready for deployment, a few more insightful and industrious teams can probably proceed along the path projected here to complete the exciting technology-readiness climb to large-scale production of few-layer graphene and related two-dimensional nanomaterials.

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References

- http://www.acq.osd.mil/chieftechnologist/publications/ docs/TRA2011.pdf (accessed 22 March 2014).
- 2. Peplow, M. Nature 503, 327-329 (2013).
- 3. Paton, K. R. et al. Nature Mater. 13, 624-630 (2014).
- 4. James, D. K. et al. Acc. Chem. Res. 46, 2307-2318 (2013).
- Dimiev. A. M. et al. ACS Nano 8, 3060–3068 (2014).

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Correction

In the version of the News & Views article Nanoparticle crystallization: DNA-bonded 'atoms' originally published (*Nature Mater.* **13**, 121-122; 2014), in the affiliation for Shawn J. Tan, 'A*STAR' was missing. Corrected in the online versions after print 16 April 2014.

IN THE FOOTSTEPS OF THE SEA STARS

For sea creatures, adhesion is a way of life. Limpets are the proverbial example, but their skill at sticking is not always what the situation requires. In a hydrodynamically turbulent environment where friction counts for little, locomotion, or simply grasping objects, demands a more temporary glue than that which cements bivalves to rocks and ship hulls1. The 'peelable' adhesive mechanism used by geckos relies on purely physical attractions that have already proved fertile for bioinspired artificial systems². But a study of the adhesive used underwater by sea stars reveals that here chemistry, not physics, seems to be the operative principle.

Hennebert et al. have previously reported that the organic component of the adhesive secreted by the tube-like feet of the sea star Asterias rubens is predominantly protein³. Using mass spectrometry, they found that these socalled sea-star footprint proteins (Sfps) are diverse — no fewer than 43 peptide sequences were identified after the material was treated with the digestive enzyme trypsin — and have no known homologues. Now the researchers have characterized the sequence of one of the main protein bands of this extract, and find it discloses a whole new strategy for biological adhesion4.

This protein, designated Sfp1, is large — 3,833 amino-acid residues —

and turns out to be the second most abundant constituent of the sea star's adhesive footprint. This material is not itself used to bind directly to the substrate. Rather, the creature initially secretes a film of other proteins that coats the surface, and Sfp1 then mediates contact between this film and the proteoglycan coating of the foot itself. In doing so, Sfp1 and the other components of the adhesive apparently self-assemble into a fibrillar reticular mesh, although what role (if any) this morphology plays in determining the properties of the bond remains to be explored.

But Sfp1 has additional layers of complexity. More than half of the peptide sequences identified previously can be found in this protein, suggesting that they are fragments produced by degradation in the analysis — perhaps in the detachment process, which, in the wild, involves secretion of a kind of anti-adhesive to break the bond. However, Sfp1 seems to have an intrinsic propensity to fragment into four large subunits before it is secreted from the foot (the largest of these might be further broken down). Inside the foot's adhesive cells these four fragments are linked by disulphide bonds, and the researchers suspect that this association is maintained in the adhesive footprint too.

Each of these subunits contains several domains known already to



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engage in chemical binding of other proteins, carbohydrates and metals, offering the Sfp1 complex a range of options for sticking to itself, to the primary adhesive film and to the foot cuticle. Bearing in mind that this complex is still only a part of the adhesive material, the implication is that the sea star's adhesion is a multivalent. hierarchical and heterogeneous affair, within which there is doubtless plenty of scope for fine-tuning the specificity, strength and permanence. If there is potential here for biomimicry, it may prove to be versatile but also challenging to master.

References

- Lee, B. P., Messersmith, P. B., Israelachvili, J. N. & Waite, J. H. Annu. Rev. Mater. Res. 41, 99–132 (2011).
- Mengüç, Y., Röhrig, M., Abusomwan, U., Hölscher, H. & Sitti, M. J. R. Soc. Interface 11, 20131205 (2014).
- Hennebert, E., Wattiez, R., Waite, J. H. & Flammang, P. Biofouling 28, 289–303 (2012).
- Hennebert, E. et al. Proc. Natl Acad. Sci. USA 111, 6317–6322 (2014).