antiferromagnetically coupled to one another through the LNO layer. This ferromagnetic coupling at the LNO/LMO interface in turn contributes to stabilizing the antiferromagnetism in the LNO layer.

The researchers also demonstrated the exchange bias effect in the LNO/LMO heterostructures, a phenomenon that finds tremendous use in applications such as magnetic recording media. This unique effect, which originates from a balance between anisotropy energy (keeping magnetic moments aligned in a preferred direction) and exchange energies (coupling magnetic moments to one another) at an interface, produces a shift along the field axis of the magnetic hysteresis measurement. At low temperature ($T < 15$ K), a negative shift occurs in the LNO/LMO superlattice. However, at slightly higher temperatures (15 K < T < 30 K), there is a sign reversal of the exchange bias field that shifts the magnetic hysteresis measurement toward the positive field axis. Finally, at T > 30 K, this effect makes way for the antiferromagnetically coupled state described earlier.

This complex magnetic behavior is explained through an asymmetry in the interfacial energy terms at the top and bottom LNO/LMO interfaces that arises from the intermixing of Ni and Mn atoms. The competition between the anisotropy energy of the LNO layer and the interfacial energies at each of the LNO/LMO interfaces, all of which vary with temperature, leads to the complex evolution of the exchange bias phenomena.

These results demonstrate that the restriction of dimensionality that occurs at oxide interfaces can promote unique magnetic phenomena in a material that is typically nonmagnetic.

Ian McDonald

Proteins link up to form dynamic 2D materials

Two-dimensional (2D) materials like graphene are highly attractive due to their unique electronic and mechanical properties. However, flexible methods for bottom-up assembly of such planar structures remain to be developed. The ability to customize the chemistry or structure of 2D crystals through assembly would be very valuable, expanding the potential of these materials for practical applications. Recent work by investigators at the University of California, San Diego and Purdue University suggest that a biological approach to 2D crystal synthesis, using engineered proteins as lattice elements, offers unprecedented flexibility for tuning self-assembly. This study is described in a recent publication of *Nature* (doi:10.1038/nature17633).

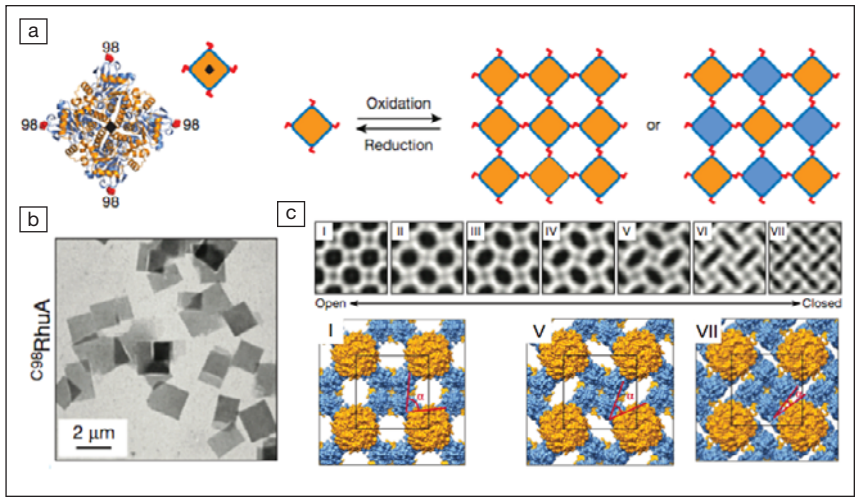
The researchers worked with the protein L-rhamnulose-1-phosphate aldolase, or "RhuA," a model system which has previously been used as a building block for protein crystal self-assembly. In contrast to previous efforts to engineer protein crystal formation by merging multiple protein units or utilizing computational design strategies, the approach utilized in the current work is remarkable in its simplicity.

RhuA is a homotetramer, that is, a protein complex, with C4 symmetry. This provides the tetramer with a square-like geometry suitable for checkerboard-like lattice assemblies; see part (a) in the Figure. To achieve 2D structures, the researchers inserted either single or double amino acid mutations at the tetramer corners that could serve as linkage sites that drive assembly. Three variants were created, including either single or double cysteine mutations, or double histidine mutations at tetramer corners.

Once obtained, the purified RhuA variants were induced to assemble by adding a reducing reagent (such as β-mercaptoethanol) to drive disulfide bridge formation or a soluble metal (e.g., Zn^{2+}) to initiate metal bridge linkages.

Initial evidence of protein assembly could be easily observed by the eye as a cloudy precipitate, allowing a wide variety of potential assembly buffer chemistries to be rapidly explored. Once initial conditions were identified, transmission electron microscopy analysis was used to further characterize potential crystalline materials.

All three RhuA variants yielded crystalline assemblies. Products from the single cysteine variant, ^{C98}RhuA, were most interesting, forming near defect-free single crystals up to several micrometers in



(a) Schematic of RhuA tetramer structure and possible modes of two-dimensional assembly; (b) transmission electron microscope image of ^{C98}RhuA crystals; and (c) seven conformations assumed by the coherently dynamic ^{C98}RhuA crystals, with three structural schematics further illustrating the structural changes. Credit: *Nature*.

https://doi.org/10.1557/mrs.2016.146 Published online by Cambridge University Press

size and exhibiting square shapes that reflected the molecular unit-cell geometry; see part (b) in the Figure.

Furthermore, ^{C98}RhuA crystals relaxed over a period of several days into one of seven different conformational states; see part (c) in the Figure. This state conversion was reversible—lattices could be opened back up through mechanical agitation—and unit-cell strain analysis between the initial and relaxed conformations showed the crystals to be auxetic (see Figure). This means that when stretched in one planar direction, the materials *thicken* in the perpendicular planar direction (whereas most non-auxetic materials become thinner in the perpendicular direction). In fact, the degree of transverse thickening matched the theoretical limit postulated for a 2D lattice of rotating rigid squares with flexible hinges. The fact that such a unique material property can emerge from a self-assembly process is striking, suggesting that proteins can serve as valuable building blocks in bottom-up material fabrication.

"This work represents a significant advance in the design of synthetic self-assembling macromolecular systems," says Jim De Yoreo of Pacific Northwest National Laboratory, who is an expert in the field and was not involved in the work. De Yoreo was particularly impressed with two aspects from the ^{C98}RhuA system: "The first is the high fidelity of assembly; the error rate reminiscent of inorganic crystals. The second is the conformational flexibility of the lattice; the extreme negative value of the Poisson ratio suggests the potential for application as a high-performance stimulus responsive material."

According to Akif Tezcan of UC San Diego, senior author of the article, "From our perspective as synthetic chemists, what most excites us is that a single chemical modification can give rise to such interesting emergent properties. Disulfides typically cause proteins to crash out of solution, but if judiciously placed they become a useful tool for driving hierarchical assembly."

Indeed, this material outcome which emerged from one point mutation in one protein system suggests a wealth of tantalizing possibilities for further applications across a myriad of other proteins that could be harnessed from nature. Genetic tunability and the prospect of templating mineral phases on the protein crystals strengthen the links between protein assembly and a dynamic future for 2D materials.

Lukmaan Bawazer

https://doi.org/10.1557/mrs.2016.146 Published online by Cambridge University Press

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