wherever it was most energetically favorable to do so.

These results add to this picture, suggesting that ion binding can sometimes overpower energetic favorability.

"Our experiment shows how important these counterions are to the hard system," said De Yoreo, referring to the calcium ions that the organic scaffold soaks up. "Even when you make ordered structures out of proteins, the counterions play a huge role."

Although the idea that ion binding might play a role in the biomineralization process was first suggested by a group of Israeli scientists 30 years ago, the technology to thoroughly test it was only recently developed.

"Liquid-phase TEM makes it possible to view the whole process—from the binding of calcium ions by the matrix, to the formation of amorphous calcium carbonate and its subsequent transformation to crystalline vaterite—at high resolution, as it proceeds in the reaction solution," said Fiona Meldrum, a materials chemist from the University of Leeds who was not involved in the research. "In combination with other experimental methods, the work provides new insight into the mechanisms by which organic molecules control crystallization."

The finding comes at an ideal moment, as concern grows about the impact of excess atmospheric carbon dioxide on the health of the planet. Biomineralization is a natural way to sequester this carbon, removing it from the atmosphere and depositing it elsewhere. Although such technology is a long way from implementation, understanding the process could help researchers recreate it artificially to deliberately remove carbon dioxide from the atmosphere. "Carbon dioxide begs for sequestration," said De Yoreo. "What we're looking at here is a way of promoting this process."

Laurel Hamers

3D-printed structures developed for complex self-evolving deformations

Some technological advances happen by accident. Some happen on purpose. And some are the result of concerted and creative efforts by researchers to explore areas of common interest.

A team of scientists led by Dan Raviv of the Massachusetts Institute of Technology (MIT) has developed a manufacture workflow that combines computationally driven design with printable primitive components, aided by realistic simulations. With this framework, users can design and print non-trivial structures that bend and stretch in response to their environment. They are not unlike the water-capsule children's toys that blow up into dinosaurs in water. However, these active structures extend the process to more sophisticated shapes and functionalities that can exhibit controllable responses to a greater variety of external stimuli, including electric fields, temperature, and light. The team's work is described in the December 2014 issue of *Scientific Reports* (DOI: 10.1038/srep07422).

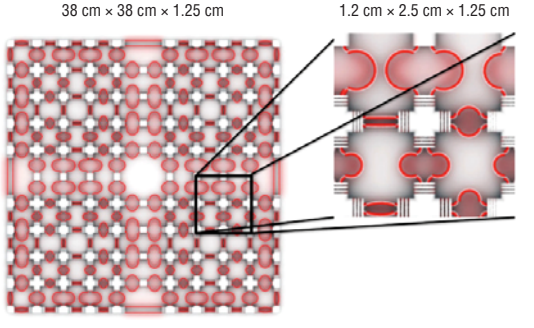
The design step implemented three basic structural units (or primitives): one bending primitive, and two stretching primitives. These primitives are constituent components of the larger, complex shape being manufactured. The bending primitive relies on differential expansion between fused materials. When stimulated, one side expands at a greater rate than the other side, resulting in a curve. The angle and the plane of the curve are controlled by the dimensions and relative position of the two printed materials.

The two stretching primitives use two different schemes. In the first scheme, the mechanism is similar to the bending primitive, except that there is no differential expansion in the printed object, so the growth is linear. The second stretching scheme uses rings. The rings are printed with different materials on the outside and inside; the inner material expands when stimulated so that the ring elongates, resulting in linear stretching. The mathematical models used in the workflow were developed so the user can design the final form of the active structures, and the computer will print the initial configuration.

The team used a Stratasys Connex 500 multi-material three-dimensional (3D) printer in their work, which enabled them to directly integrate the different materials into the printed structures. The expanding materials were acrylated monomers. When activated—in this case, the materials were hydrophilic, but potentially any stimulus could be used—the monomers assembled into linear chains with a few difunctional acrylate molecules. A hydrogel is created with as much as twice the volume of the original material.

Once they achieved their final form, the printed structures were compared to a simulation. The team used the Project Cyborg design platform, enhanced with Autodesk's Nucleus system and some additional functionality for modeling the temporal aspect of the deformations. Simulations were restricted to kinematic behavior and did not model atomic movement.

"This was not a one-(person) job. This was truly a multi-author work," Raviv



A complete example embedding dynamic primitives of stretching and folding on a grid. This grid can accommodate a self-evolving deformation into a complex structure with both convex and concave parts. Reprinted with permission from Nature Publishing Group.

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spoke of the project. There were many parts to the project, across a range of fields: design, mathematics, computation, and materials science. The breadth of the project brought together several laboratories including Raviv's laboratory at MIT, laboratories at Autodesk Inc., Stratasys Ltd., and Singapore University of Technology and Design. Skylar Tibbits at MIT's Self-Assembly Laboratory also contributed significantly. Their work anticipates developments in—and increasing use of—soft robotics, where this has many potential applications *in vivo*. A thermally activated stent, for example, could be printed and inserted into a collapsed artery where it would expand and open the artery on its own. The confluence of materials science, 3D printing technology, and computational engineering heralds a future in which these active, self-evolving structures find many invaluable uses.

Antonio Cruz

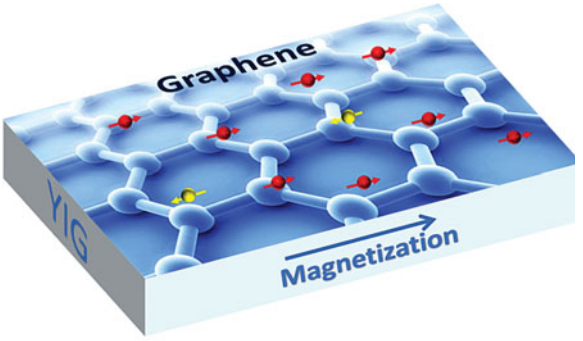
Ferromagnetic thin film induces magnetism in graphene

Over the past decade, graphene has become one of the most intensely investigated materials. Graphene shows high electrical conductivity, and understanding the electrical properties of high-quality graphene under different conditions is a topic of great interest. In an article recently published in the January 7 issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.114.016603), researchers at the University of California–Riverside have determined a way to induce ferromagnetism in graphene, opening a new path of investigation especially into its spintronics applications.

"Graphene has many interesting properties," said Jing Shi, professor of physics at the University of California–Riverside. "It's especially unusual compared to other conducting materials. And now it's even more unusual that we know what it exhibits with an anomalous Hall effect."

The ordinary Hall effect is equivalent to a magnetic field sensor, meaning that it can be used to measure the direction and strength of a magnetic field. A material that shows the anomalous Hall effect is sensitive to the direction of magnetization of a magnetic material. The idea behind the present work is that attaching a magnetic material to graphene can make graphene ferromagnetic, which can induce the anomalous Hall effect. By measuring shifts in the Hall effect, researchers can better understand the properties of a material or the interactions between two materials.

A standalone graphene sheet has been known to exhibit diamagnetism, said Shi. But such magnetism is not very useful for electronic device applications. Attempts to create magnetism in graphene by doping have not been very successful, and would also hurt graphene's excellent electrical transport properties. Shi and his group decided to attempt to induce magnetism by attaching a single layer of graphene to an yttrium iron garnet (YIG) thin film.



A single layer of graphene on top of a ferromagnetic yttrium iron garnet (YIG) thin film. Together, they create an anomalous Hall effect. Credit: Jing Shi.

This film is magnetic up to 550 K. An important aspect of the YIG thin film is that it is an insulator, so it would not divert electric current away and thus affect graphene's conductivity.

A single layer of graphene was first fabricated on top of a traditional SiO_2 substrate. Hall effect measurements were taken at this point to create a baseline. One side of the graphene was spin-coated with poly(methyl methacrylate) (PMMA) that acted as a support during transfer. It was then soaked for two days in a 1 M NaOH solution to completely remove any traces of SiO_2. Once free of the SiO_2, the PMMA-coated graphene was placed on the YIG thin film as a new substrate for the graphene. Then acetone was used to wash away the PMMA, leaving just the graphene and YIG film behind.

Once the graphene was attached, Hall effect measurements were taken again. Since YIG is already magnetized in the film plane, it takes a perpendicular field to rotate the magnetization out of plane; the anomalous Hall effect occurs when such a rotation takes place. It was seen that the Hall effect was indeed present in the graphene, meaning that YIG had induced magnetization in the graphene sheet. The Hall effect senses the magnetization (or electron spin) direction in magnetized graphene that can represent non-volatile information.

"When you put graphene in contact with bulky materials with, say, stronger 'personalities,' it borrows the personality from them," said Antonio Castro Neto, Director of the Centre for Advanced 2D Materials and the Graphene Research Centre at the National University of Singapore. Neto has done similar work with graphene, bulking up the spin orbit interaction of the material by putting it into contact with tungsten disulfide. Three-dimensional materials like YIG and tungsten disulfide have many more atoms than the two-dimensional graphene sheets, he said. "Hence, these three-dimensional materials have billions of atoms more than graphene and, hence, they can 'bully' graphene around. Graphene has no option but to adapt," Neto said.

Meg Marquardt

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