Bio Focus

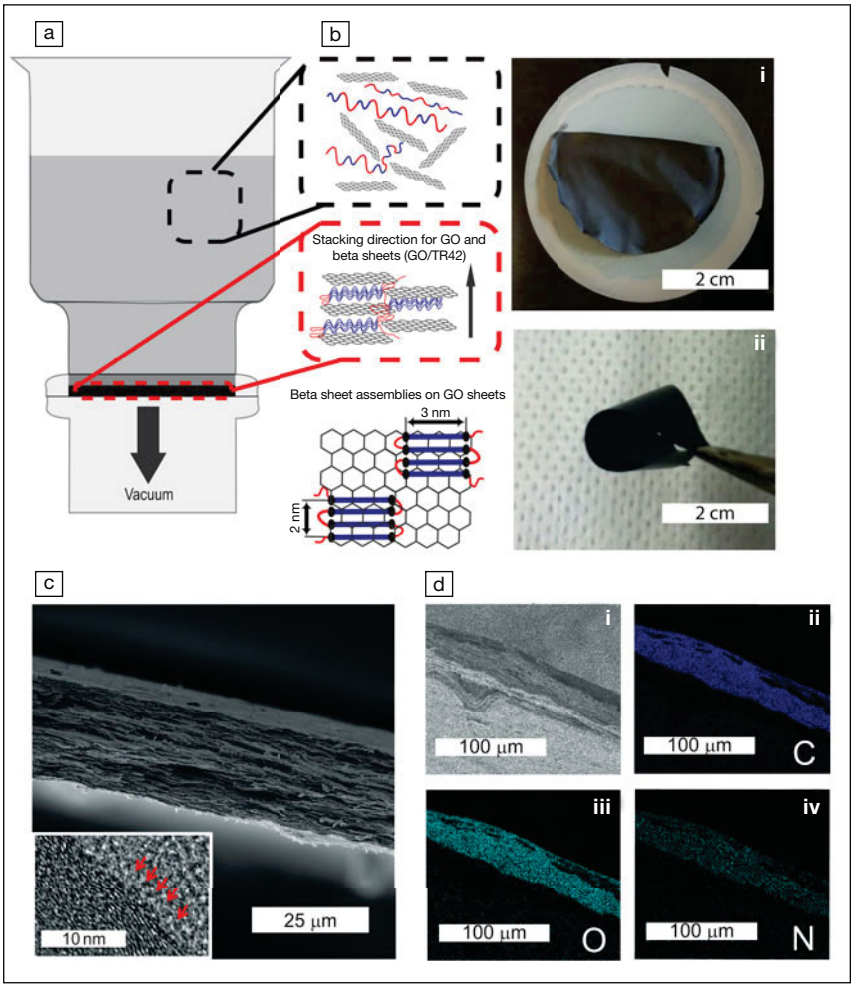
Graphene-based composites achieve microstructural order at atomic scale

Melik Demirel and Mauricio Terrones and their colleagues at The Pennsylvania State University recently published a study in the journal *Carbon* (doi:10.1016/j.carbon.2017.03.053) detailing a novel method for creating a layered graphene-based molecular composite that achieves bulk microstructural order, thus overcoming one of the main obstacles facing two-dimensional (2D) materials utilization. At the heart of their strategy was the ability to tune the spacing between the stacked layers with atomic-level precision, where the resulting composite could be integrated into a highly flexible and efficient thermal actuator.

The combination of strength and high electrical and thermal conductivities of 2D graphene-based materials provides opportunities for engineering materials applications. However, many of these desirable properties are diminished in bulk materials due to a lack of microstructural organization. When precise microstructural control of 2D materials like graphene is achieved in bulk, the extraordinary properties of such materials can be exploited in composites, layered films, and bio-constructs.

With the leaps in performance and efficiency of graphene-based being made in materials like the actuators fabricated by Demirel and Terrones's team, Demirel predicts that future 2D graphene-based materials will be able to "respond to a variety of external stimuli and self-adapt based on the stimuli, thus laying the foundations for truly smart, robust, self-powered, and autonomous systems."

The researchers fabricated the novel molecular composite using graphene oxide and an organic matrix that consisted of tandem repeat (TR) proteins inspired by squid ring teeth. The TR protein matrix self-assembled into a layered structure of antiparallel β-sheets, subsequently providing a template of hydrogen bonding locations for graphene oxide with the TR proteins. Each protein layer was only one β-sheet-thick, thus allowing for ideal intercalation with the graphene oxide.



(a) Schematic illustration of vacuum-assisted self-assembly of 2D molecular composites. (b) Image of freestanding molecular composite consisting of graphene oxide (GO) and tandem repeat (TR) protein with 42 kDa molecular weight. (c) Cross-section scanning electron microscope and transmission electron microscope (inset) image of molecular composite consisting of GO and TR protein with 25 kDa molecular weight. (d)(i) Backscattered-electron image, and energy-dispersive x-ray spectroscopy patterns of (ii) carbon, (iii) oxygen, and (iv) nitrogen for molecular composite consisting of GO and TR protein with 25 kDa molecular weight. Credit: *Carbon*.

By simply altering the molecular weight of the TR proteins, the researchers showed that the spacing between the stacked layers can be controlled. Interlayer spacing of 0.4 nm, 0.6 nm, and 0.9 nm was reported with three different molecular weights of the same TR protein. This atomistic tunability of 2D layer spacing is a major advantage of using TR proteins in graphene-based molecular composites because it allows for precise materials-property selection.

The team further demonstrated the advantageous properties of the TR protein and graphene oxide molecular composites by fabricating two types of bimorph thermal actuators (devices with two active layers): (1) regular TR protein and graphene oxide actuators and (2) molecular composite TR protein and graphene oxide actuators. The regular actuators consisted of a TR protein film and graphene oxide film, while the molecular composite actuators consisted of a TR protein film and the researchers' new molecular composite film. Gold contacts were sputtered onto each type of actuator to allow for testing.

The bimorph actuators with molecular composites outperformed the regular bimorph actuators with respect to the

voltage required to initiate thermal actuation and the curvature achievable for a given power input. Furthermore, increasing the number of TR proteins in the molecular composite extended the range of actuator deformation.

"It is really exciting to see that molecular composites provide energy-efficient actuators," Demirel says. "By altering the number of repeating units in our nanocomposites, thermal actuation efficiencies reaching 1800% of the efficiency of bulk bimorph thermal actuators can be achieved. This is the beginning of a new era of materials science [merging] synthetic biology with advanced 2D materials."

Heather Hunt

Bio Focus

Hierarchical structure of spider dragline silk prevents spinning

Spider dragline silk, which the spider uses for its lifeline when hanging in midair, has long amazed scientists with its high strength and ability to stretch before breaking. A report by researchers in China and the United Kingdom sheds new light on another critical function of the insect's dragline silk: preventing dangling spiders from spinning uncontrollably in midair. "Seeing an abseiling spider descend its dragline silk gracefully instead of spiraling, we simply wanted to know why," says the study's lead author, Dabiao Liu of Huazhong University of Science and Technology.

Liu and the team found that the dragline silk of orb-weaver spiders irreversibly deforms in order to rapidly dissipate most of the energy of twisting, so that a suspended spider quickly stops spinning. "This behavior is quite unlike man-made ropes, whether of hemp or modern synthetics, which tend to twist uncontrollably and unpredictably," says David J. Dunstan of Queen Mary University of London, a co-author on the study.

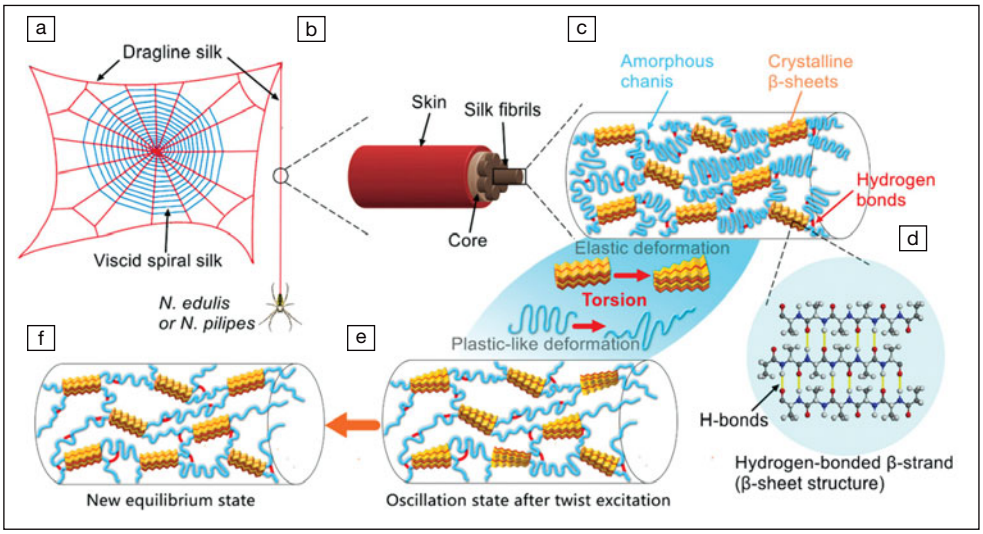
The study's findings, which recently appeared in *Applied Physics Letters* (doi:10.1063/1.4990676), quantified the twisting behavior of the dragline silk using a torsion pendulum and a video camera. Unlike a conventional pendulum that consists of a swinging mass on a string, the torsion pendulum comprises a twisting mass on a string. When conventional fiber materials, such as metal wires or carbon fiber, are twisted, they oscillate around the untwisted equilibrium position.

However, the researchers were surprised to observe that dragline silk immediately oscillated around a deformed position, and that it never relaxed to the original equilibrium position. The researchers rotated the silks to a range of initial twist angles (~20°–3300°) and found that the silks dissipated greater than 75% of the energy of the initial excitation. This strong energy dissipation reduces the amplitude of the subsequent oscillations, preventing the spider from twisting uncontrollably.

The researchers believe that the energy dissipation by torsion deformation is only possible because of the hierarchical structure of the spider's dragline silk. In particular, dragline silk is composed of both crystalline and amorphous components, which each play an important role for the unique torsional properties of the silk. The researchers hypothesize that the plastic-like, irreversible energy dissipation occurs by deformation of amorphous chains. The remainder of the energy is elastically dissipated through the stretching of the hydrogen bonds and the extension and twisting of the crystalline domains. "The authors show the significance of the nanoscale structure of silk, and in particular the [hydrogen]-bonding network, on the macroscopic properties," says Markus J. Buehler of Massachusetts Institute of Technology, a leader in the field of the mechanics of biological materials, including spider silks.

However, "the big issue will be to find out exactly how to engineer these properties in synthetic systems," Dunstan says. "Nature has had four billion years of evolution to find out how to do it by trial-and-error."

Abby Goldman



Hierarchical structure of *Nephila* spider draglines and physical mechanisms for the torsional oscillation. Credit: *Advanced Materials* (doi:10.1002/adma.201104668) (adapted).