Malleable and bounces back

Foam consisting of graphene oxide and boron nitride is lightweight and tough and returns to its original shape after compression

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When associated with other molecules, the sheets of carbon atoms that form graphene can attain surprising properties. A team of researchers at Rice University collaborated with physicists at the University of Campinas (Unicamp) to develop a type of sponge that is extremely light, tough, and malleable. They made use of a chemical reaction that bonds graphene oxide (GO), a variant of graphene, to the hexagonal form of boron nitride (BN), a synthetic compound used as a lubricant and additive in cosmetics. When small samples of this sponge were compressed with one or two pennies, they easily bounced back to their original shape. The nanometric structure of the new material, known as GO-0.5BN, is similar to the framework of a building under construction, with floors and walls that are self-assembled from a base of graphene oxide sheets reinforced with boron nitride platelets. GO-0.5BN is 400 times less dense than graphite.

Composed solely of boron and nitrogen atoms, boron nitride molecules are arranged in a hexagonal configuration similar to that of graphene. The two compounds combine seamlessly, which produces a tougher material with greater mechanical malleability. "The new material is chemically and thermally stable and can be used in energy-storing systems, such as supercapacitors and battery electrodes, and it can also absorb gases," says Douglas Galvão of the Gleb Wataghin Physics Institute at Unicamp, who participated in the study. "Boron nitride reinforces the structure of graphene oxide, which has a few gaps and can become brittle in certain points," explains theoretical physicist Pedro Alves da Silva Autreto, who is conducting post-doctoral research at Unicamp on a FAPESP fellowship and has spent time at Rice, where he performed computer simulations to predict the characteristics of GO-0.5BN. The process used to obtain the sponge and its properties was presented in a scientific paper published on July 29, 2014 in *Nature Communications*.

Graphene oxide has essentially the same properties as pure graphene but is simpler and less expensive to produce, which explains why researchers prefer to use this variant of graphene in their experiments. It can be produced in large amounts by chemically exfoliating oxidized graphite. The presence of oxygen atoms in the hexagonal lattice of the graphene carbons provides the compound with an additional advantage: compared with pure graphene, it is easier to stack graphene oxide sheets and thus create layers that are both extremely tough and extremely thin. "We expected that adding boron nitride to graphene oxide would generate a new structure but not exactly one that had the ordered layered structure that we ended up with," says electrical engineer Soumya Vinod from Rice University, first author of the report published in *Nature Communications*.

The hexagonal boron nitride platelets are uniformly distributed across the walls and floors that compose the internal structure of the sponge. The platelets bind together the graphene oxide sheets that serve as a type of skeleton for GO-0.5BN. According to Vinod, the platelets absorb stress from compression and stretching and prevent the graphene oxide floors from crumbling or becoming cracked, in addition, they increase the compound's thermal stability.

NO PATENT

Before discovering the chemical formulation of the sponge described in the paper, the researchers tested other versions of the new material containing different percentages of the two ingredients. Whereas the group at Rice University combined different quantities of powdered graphene oxide and boron nitride, Autreto ran computer simulations to predict the properties of the materials under development in order to provide parameters that could be used by his colleagues to refine their experiments. "I was the only theoretical physi-

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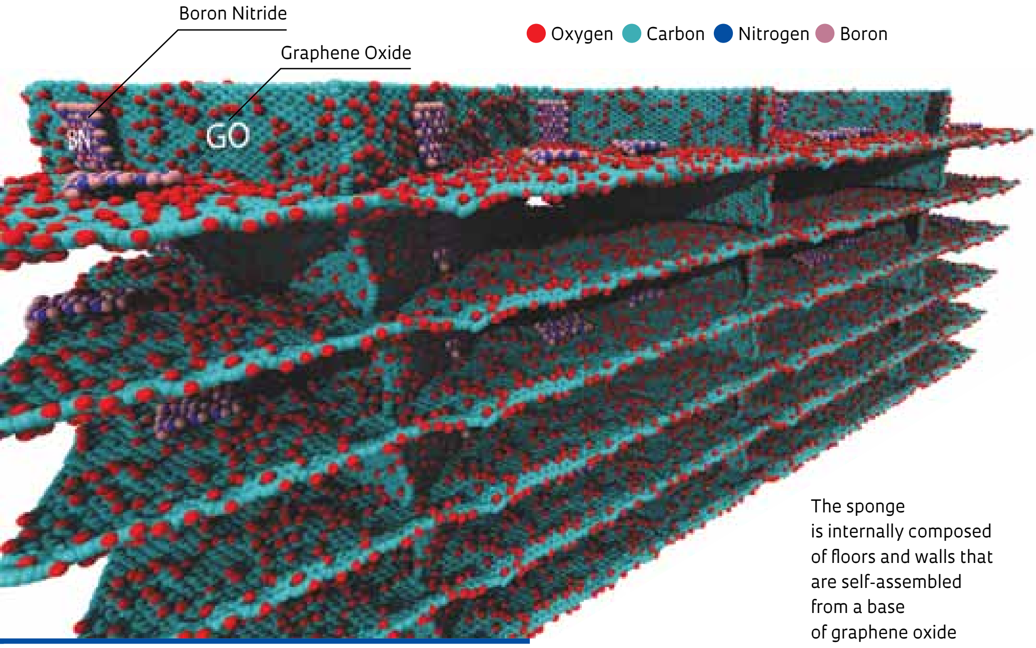
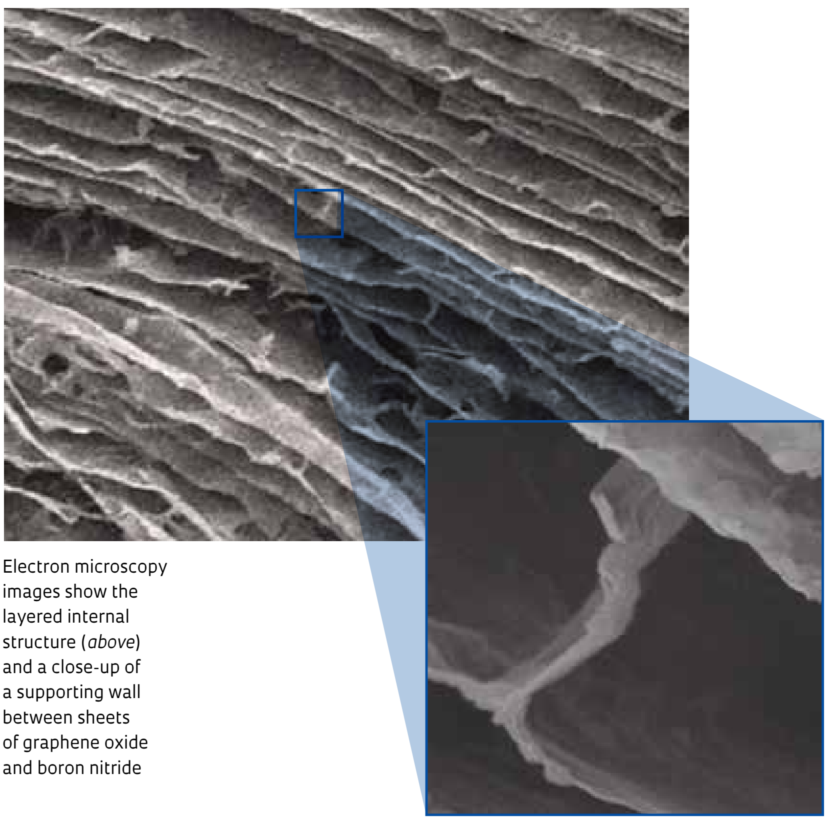


The sponge is internally composed of floors and walls that are self-assembled from a base of graphene oxide layers reinforced with sheets of boron nitride

Structural reinforcement

Hexagonal boron nitride makes the graphene oxide sheets less brittle and prevents the inner layers of the material from crumbling



Electron microscopy images show the layered internal structure (*above*) and a close-up of a supporting wall between sheets of graphene oxide and boron nitride

cist among 50 experimental researchers in Professor Pulickel Ajayan's group," says Autreto, referring to his stint at the American university. The most stable version of the sponge was the one that had boron nitride accounting for half its final weight. The graphene oxide interacts with boron nitride via the action of chemical catalysts. The spongy material produced by the reaction is freeze-dried, and it loses its moisture through sublimation. The resulting foam takes the shape of its container. "Once we had the necessary amounts of graphene oxide and hexagonal boron nitride in hand, we took two or three days to produce the foam," Vinod explains.

The nanostructured sponge, which retains its shape and can be used to store energy or absorb gas, has not yet been protected by a commercial patent. The partnership between Unicamp and Rice is expected to continue and to generate new projects. "Two post-doctoral researchers from our group will join Professor Ajayan's team in order to continue the collaboration," says Galvão, who advised Autreto in his master's and doctorate work and is now supervising his post-doctoral research. ■

Project

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Scientific article

VINOD, S. *et al.* Low-density three-dimensional foam using self-reinforced hybrid two-dimensional atomic layers. **Nature Communications**. 29 Jul. 2014.