Metastable material: Study shows availability of hydrogen controls chemical structure of graphene oxide

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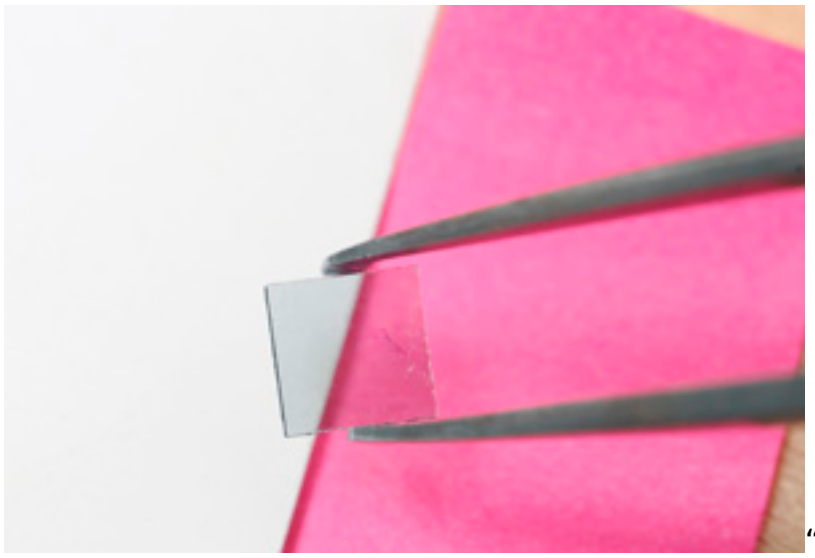
A new study shows that the availability of hydrogen plays a significant role in determining the chemical and structural makeup of graphene oxide, a material that has potential uses in nano-electronics, nano-electromechanical systems, sensing, composites, optics, catalysis and energy storage.

The study also found that after the material is produced, its structural and chemical properties continue to evolve for more than a month as a result of continuing chemical reactions with hydrogen.

Understanding the properties of graphene oxide – and how to control them – is important to realizing potential applications for the material. To make it useful for nano-electronics, for instance, researchers must induce both an electronic band-gap and structural order in the material. Controlling the amount of hydrogen in graphene oxide may be the key to manipulating the material properties.



“Graphene oxide is a very interesting material because its mechanical, optical and electronic properties can be controlled using thermal or chemical treatments to alter its structure,” said Elisa Riedo, an associate professor in the School of Physics at the Georgia Institute of Technology. “But before we can get the properties we want, we need to understand the factors that control the material’s structure. This study provides information about the role of hydrogen in the reduction of graphene oxide at room temperature.”

The research, which studied graphene oxide produced from epitaxial graphene, was reported on May 6 in the journal Nature Materials. The research was sponsored by the National Science Foundation, the Materials Research Science and Engineering

Center (MRSEC) at Georgia Tech, and by the U.S. Department of Energy.

Graphene oxide is formed through the use of chemical and thermal processes that mainly add two oxygen-containing functional groups to the lattice of carbon atoms that make up graphene: epoxide and hydroxyl species. The Georgia Tech researchers began their studies with multilayer expitaxial graphene grown atop a silicon carbide wafer, a technique pioneered by Walt de Heer and his research group at Georgia Tech. Their samples included an average of ten layers of graphene.

After oxidizing the thin films of graphene using the established Hummers method, the researchers examined their samples using X-ray photo-emission spectroscopy (XPS). Over about 35 days, they noticed the number of epoxide functional groups declining while the number of hydroxyl groups increased slightly. After about three months, the ratio of the two groups finally reached equilibrium.

“We found that the material changed by itself at room temperature without any external stimulation,” said Suenne Kim, a postdoctoral fellow in Riedo’s laboratory. “The degree to which it was unstable at room temperature was surprising.”

Curious about what might be causing the changes, Riedo and Kim took their measurements to Angelo Bongiorno, an assistant professor who studies computational materials chemistry in Georgia Tech’s School of Chemistry and Biochemistry. Bongiorno and graduate student Si Zhou studied the changes using density functional theory, which suggested that hydrogen could be combining with oxygen in the functional groups to form water. That would favor a reduction in the epoxide groups, which is what Riedo and Kim were seeing experimentally.

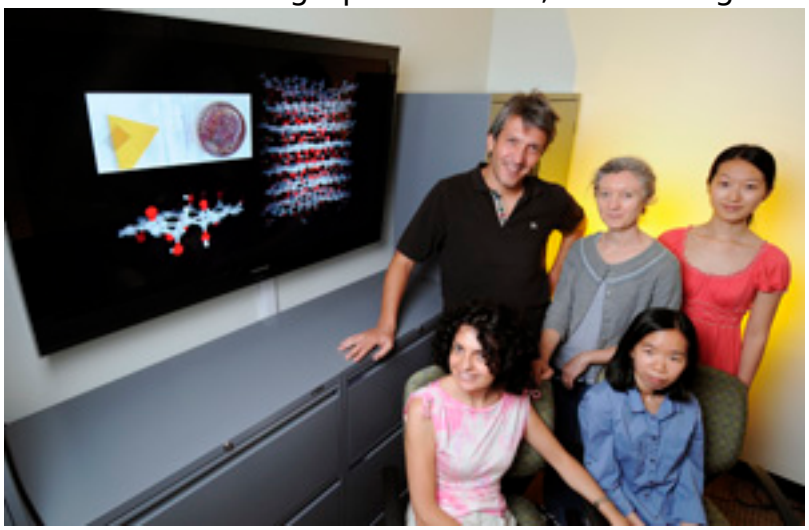
“Elisa’s group was doing experimental measurements, while we were doing theoretical calculations,” Bongiorno said. “We combined our information to come up with the idea that maybe there was hydrogen involved.”

The suspicions were confirmed experimentally, both by the Georgia Tech group and by a research team at the University of Texas at Dallas. This information about the role of hydrogen in determining the structure of graphene oxide suggests a new way to control its properties, Bongiorno noted.

“During synthesis of the material, we could potentially use this as a tool to change the structure,” he said. “By understanding how to use hydrogen, we could add it or take it out, allowing us to adjust the relative distribution and concentration of the epoxide and hydroxyl species which control the properties of the material.”

Riedo and Bongiorno acknowledge that their material – based on epitaxial graphene – may be different from the oxide produced from exfoliated graphene. Producing graphene oxide from flakes of the material involves additional processing, including dissolving in an aqueous solution and then filtering and depositing the material onto a substrate. But they believe hydrogen plays a similar role in determining the properties of exfoliated graphene oxide.

“We probably have a new new form of graphene oxide, one that may be more useful commercially, although the same processes should also be happening within the other form of graphene oxide,” said Bongiorno.



The next steps are to understand how to control the amount of hydrogen in epitaxial graphene oxide, and what conditions may be necessary to affect reactions with the two functional groups. Ultimately, that may provide a way to open an electronic band gap and simultaneously obtain a graphene-based material with electron transport characteristics comparable to those of pristine graphene.

“By controlling the properties of graphene oxide through this chemical and thermal reduction, we may arrive at a material that remains close enough to graphene in structure to maintain the order necessary for the excellent electronic properties, while having the band-gap needed to create transistors,” Riedo said. “It could be that graphene oxide is the way to arrive at that type of material.”

Beyond those already mentioned, the paper’s authors included Yike Hu, Claire Berger and Walt de Heer from the School of Physics at Georgia Tech, and Muge Acik and Yves Chabal from the Department of Materials Science and Engineering at the University of Texas at Dallas.

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