

Graphene oxide gets green

EurekaAlert

"We can make you and we can break you." If Rice University scientists wrote country songs, their ode to graphene oxide would start something like that. But this song wouldn't break anybody's heart.

A new paper from the lab of Rice chemist James Tour demonstrates an environmentally friendly way to make bulk quantities of graphene oxide (GO), an insulating version of single-atom-thick graphene expected to find use in all kinds of material and electronic applications.

A second paper from Tour and Andreas Lüttge, a Rice professor of Earth science and chemistry, shows how GO is broken down by common bacteria that leave behind only harmless, natural graphite.

The one-two punch appears online this week in the journal *ACS Nano*.

"These are the pillars that make graphene oxide production practical," said Tour, Rice's T.T. and W.F. Chao Chair in Chemistry as well as a professor of mechanical engineering and materials science and of computer science. The GO manufacturing process was developed as part of a research project with M-I SWACO, a Houston-based producer of drilling fluids for the petrochemical industry that hopes to use graphene to improve the productivity of wells. (Read about that here.)

Scientists have been making GO since the 19th century, but the new process eliminates a significant stumbling block to bulk production, Tour said. "People were using potassium chlorate or sodium nitrates that release toxic gases ? one of which, chlorine dioxide, is explosive," he said. "Manufacturers are always reluctant to go to a large scale with any process that generates explosive intermediates."

Tour and his colleagues used a process similar to the one they employed to unzip multiwalled nanotubes into graphene nanoribbons, as described in a Nature paper last year. They process flakes of graphite ? pencil lead ? with potassium permanganate, sulfuric acid and phosphoric acid, all common, inexpensive chemicals.

"Many companies have started to make graphene and graphene oxide, and I think they're going to be very hard pressed to come up with a cheaper procedure that's this efficient and as safe and environmentally friendly," Tour said.

The researchers suggested the water-soluble product could find use in polymers, ceramics and metals, as thin films for electronics, as drug-delivery devices and for hydrogen storage, as well as for oil and gas recovery.

Though GO is a natural insulator, it could be chemically reduced to a conductor or

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semiconductor, though not without defects, Tour said.

With so many potential paths into the environment, the fate of GO nanomaterials concerned Tour, who sought the advice of Rice colleague Lüttge.

Lüttge and Everett Salas, a postdoctoral researcher in his lab and primary author of the second paper, had already been studying the effects of bacteria on carbon, so it was simple to shift their attention to GO. They found bacteria from the genus *Shewanella* easily convert GO to harmless graphene. The graphene then stacks itself into graphite.

"That's a big plus for green nano, because these ubiquitous bacteria are quickly converting GO into an environmentally benign mineral," Tour said.

Essentially, Salas said, *Shewanella* have figured out how to "breathe" solid metal oxides. "These bacteria have turned themselves inside out. When we breathe oxygen, the reactions happen inside our cells. These microbes have taken those components and put them on the outside of their cells."

It is this capability that allows them to reduce GO to graphene. "It's a mechanism we don't understand completely because we didn't know it was possible until a few months ago," he said of the process as it relates to GO.

The best news of all, Lüttge said, is that these metal-reducing bacteria "are found pretty much everywhere, so there will be no need to 'inoculate' the environment with them," he said. "These bacteria have been isolated from every imaginable environment ? lakes, the sea floor, river mud, the open ocean, oil brines and even uranium mines."

He said the microbes also turn iron, chromium, uranium and arsenic compounds into "mostly benign" minerals. "Because of this, they're playing a major role in efforts to develop bacteria-based bioremediation technologies."

Lüttge expects the discovery will lead to other practical technologies. His lab is investigating the interaction between bacteria and graphite electrodes to develop microbe-powered fuel cells, in collaboration with the Air Force Office of Scientific Research and its Multidisciplinary University Research Initiative (MURI).

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