



Reusable encapsulated liquid sorbents rapidly capture CO₂

The need for effective carbon capture is at an all-time high. With over a billion tons of CO₂ produced by coal-burning power plants each year, finding a way to prevent that greenhouse gas from entering the atmosphere is a high priority. But capturing carbon is not always an easy task, especially not at the rate at which it is produced. An article published in the February 5 online edition of *Nature Communications* (DOI: 10.1038/ncomms7124) reports a novel carbon capture material: encapsulated liquid sorbents.

“This is a very neat invention and reverses the usual logic to decouple form from function,” says Stuart Haszeldine, professor of Carbon Capture and Storage at The University of Edinburgh, who is unaffiliated with the work.

Currently, liquid amine sorbents like monoethanolamine are used for carbon capture. They are particularly useful because they are resilient in humid places, such as the flue of a coal factory, and have a rapid uptake and high capacity for CO₂.

However, they are corrosive and potentially toxic, says John Vericella, lead author on the *Nature Communications* article, who began the work as a graduate student at the University of Illinois at Urbana-Champaign. Additionally, removing the carbon from amine solutions during resorption is a high-energy process, says Vericella, who is currently an engineer at Lawrence Livermore National Laboratory (LLNL). As an alternative, the industry has turned to solid sorbents, which have high surface areas for binding CO₂ and are less toxic. However, they are not as robust as liquid sorbents, often failing after a few absorption-resorption cycles.

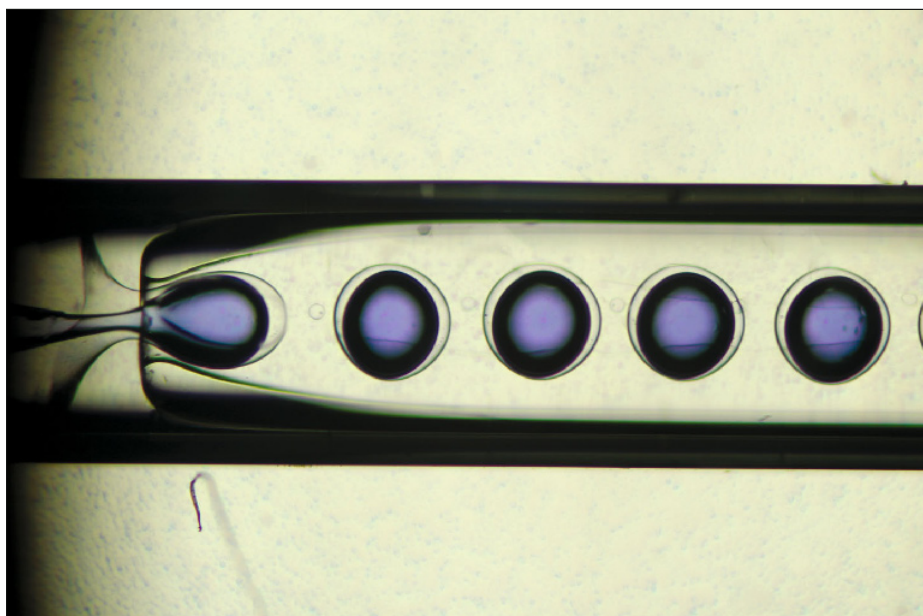
At the heart of the new research was finding a new capture material design. The research was carried out through a collaboration between researchers at LLNL and several universities, including Harvard. Funded in part by the US Advanced Research Projects Agency-Energy (ARPA-E), the pursuit of the ultimate carbon capture material was one of high risk and high reward, says Vericella. “We wanted to make big progress. And for that, we decided to try something a little weird.”

Vericella and co-workers attempted to find a best-of-both-worlds materials

design, which would offer the efficiency and robustness of a liquid sorbent but that would have the lower toxicity and high surface area of a solid sorbent. Vericella and the rest of the team wanted a material comprised of off-the-shelf ingredients so that scale-up would be feasible. “There’s a lot of carbon to capture,” says Vericella. “We will need buckets of this or train cars. It has to be practical.” The team turned to microfluidics, specifically encapsulated liquid sorbents. Microcapsules were an ideal structure because they would provide a large surface area while still being relatively inexpensive to produce.

The microcapsules are comprised of several layers. In the middle lies aqueous potassium or sodium carbonate. A zinc-based catalyst cyclen is incorporated in this interior core to speed up CO₂ absorption. A second, outer layer is made of a liquid version of what will become a solid shell, in this case silicone, which is highly permeable to CO₂. The liquids are fed at different speeds through nested glass capillaries, with the liquid sorbent in an interior capillary. As the silicone flows out first, the liquid sorbent flows into the middle of the forming microcapsule. The silicone liquid eventually encircles all of the liquid sorbent. When exposed to UV light, the silicone hardens and forms the shell.

“The capsules are both highly permeable and highly selective,” says Vericella. The silicone exterior is permeable, allowing CO₂ through at a speed that doesn’t inhibit CO₂ uptake. But the liquid core is highly selective, meaning CO₂ is captured efficiently. With this combination, the microcapsule is capable of capturing CO₂ at a rate comparable if not higher than traditional amine solvent methods, says Vericella, but without the drawbacks of toxicity and corrosion. The microcapsules were stable, even in wet environments, meaning they could be used directly in a flue to capture gas.



Using nested glass capillaries, microcapsule layers are created at the same time, with UV exposure hardening the exterior, leaving the interior liquid. Credit: LLNL.

“Exposure to flue gas is enhanced to increase the speed of capture with a huge surface area across millions of spheres,” says Haszeldine. “Circulation can be reproducible and reliable using normal industrial processes—the same spheres irrespective of contents. The chemical capture filling, simple or toxic, can be

changed, tailored, and specified to the application without affecting handling, corrosion, or leakage.”

The exterior and interior materials could also be tuned, created with materials that target specific molecules in the gas, such as CO₂. Also important is the fact that the microcapsules can be used

multiple times. Tests showed that in 10 absorption-desorption cycles, the capsules maintained a 90% absorption rate. Scaling the process up to an industrially stable level is a next step in making these novel capsules a viable form of carbon capture.

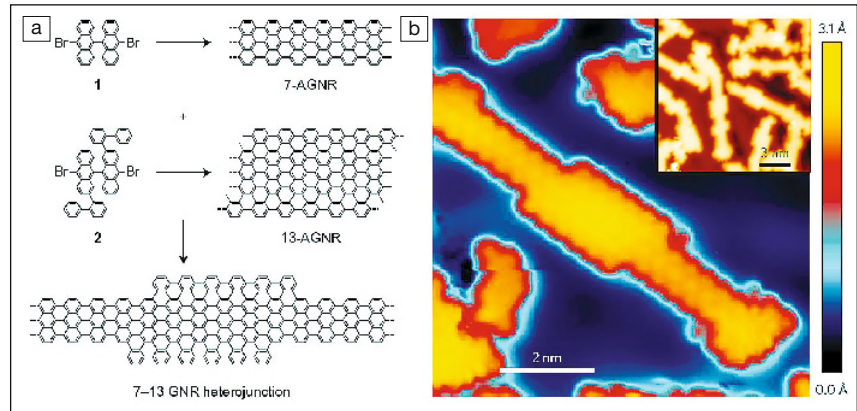
Meg Marquardt

Nano Focus

Bandgap engineering in graphene nanoribbons sets the stage for next-generation electronic devices

Miniaturization of consumer electronics has put pressure on the industry to develop semiconductor devices that operate at smaller length scales. An increase in recent demand coupled with more advanced synthesis techniques has led to breakthroughs in semiconductor design and development. From three-dimensional chip stacking to the fabrication of a junctionless transistor, researchers are making great strides every day to push this industry to the brink of its dimensional limits. However, the shrinking of current semiconductor devices often leads to performance loss. Graphene-based electronics have the potential to outshine current technology with greater scalability, more control over dopants, and higher charge-carrier mobility. Graphene-based electronics would benefit from ballistic electron transport; much like a carefully aimed shot will arrive at its target in the shortest possible time, the scattering of electrons from atomic sites is limited in materials on very small length scales. With the electrons experiencing minimal obstruction, these devices could operate at much faster speeds, leading to improved performance.

Utilizing a novel bottom-up synthesis strategy, researchers from the University of California–Berkeley, Lawrence Berkeley National Laboratory, and the Kavli Energy NanoSciences Institute have fabricated molecular-scale graphene-based heterojunctions with widths less than 1.5 nm. As the researchers describe in their January *Nature Nanotechnology* publication



(a) Synthesis strategy of nonuniform graphene nanoribbon (GNR) heterostructures from basic molecular building blocks. (b) High-resolution scanning tunneling microscope image showing topography of a GNR on a gold surface. Inset: Larger-scale image showing multiple GNRs. AGNR is armchair graphene nanoribbon. Reproduced with permission from *Nature Nanotech.* **10** (2) (2015), DOI: 10.1038/nnano.2014.307; p. 156. © 2015 Macmillan Publishers Limited.

(DOI: 10.1038/NNANO.2014.307), graphene nanoribbon (GNR) heterojunctions were fabricated by combining precision-designed molecular building blocks. By altering the shape of the molecular building blocks, the researchers generated ribbons with nonuniform widths that display position-dependent local densities of states (LDOS).

The researchers took a twofold approach when it came to investigating the local electronic structure of these GNRs. First, the researchers used scanning tunneling microscopy to spatially map electron behavior at various points on these ribbons to obtain a picture of the energy-dependent LDOS. They then explained their findings by simulating the electronic structure of the ribbons using first-principles density functional theory within the local density approximation. Both experimental and theoretical results confirmed that controlling the width of the GNRs in subnanometer increments allowed for

explicit manipulation of the bandgap, a technique the researchers called “molecular-scale bandgap engineering.”

“We can’t go on working with silicon” said Felix Fischer, a contributing author to this work. “It might be two or three more generations of silicon chips in the pipeline right now, but even big manufacturers are searching for new alternatives. Whether this is going to be graphene or other types of materials, that’s still open for debate. What we’re doing is laying the fundamental groundwork.” The researchers have demonstrated that the synthesis of GNR structures with enhanced functional effects is possible through the combined efforts of theorists, physicists, and chemists. As Fischer says, “Right now it turns more into kind of a dialogue between experiment and theoretical prediction of what the most exciting material properties are going to be.”

Ian J. McDonald