Controlling Chemistry Improves Potential of Carbon Nanotubes

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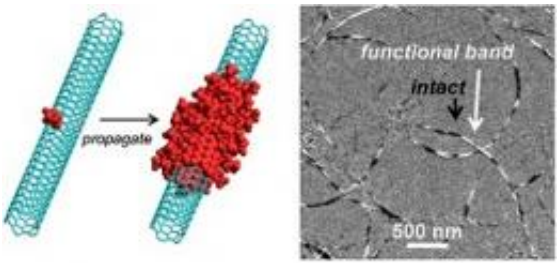

Left: The Billups-Birch alkylcarboxylation reaction allows functional groups to propagate down the CNT from points of pre-existing defects. Right: Electron microscopy shows "banded" CNTs with distinct functionalized and intact regions along their lengths. Photo credits: Nature Communications.

(PhysOrg.com) -- A team of University of Maryland nanotechnology researchers has solved one of the most vexing challenges hindering the use of carbon nanomaterials for better electrical energy storage or enhancing the fluorescence sensing capabilities of biosensors. The findings are published in the July 12 issue of *Nature Communications*.

The breakthrough research was led by Professor Yu Huang Wang of the Department of Chemistry and Biochemistry and conducted in the university's Nanostructures for Electrical Energy Storage Center (an Energy Frontier Research Center of the Department of Energy), Northwestern University, and the Maryland NanoCenter.

Carbon nanotubes (CNTs) are recognized has having enormous potential. They are some of the most conductive structures ever made-highly efficient electrodes with enormous surface area. To take full advantage of these properties, however, CNTs must be soluble-that is, have the ability to be dispersed in a liquid environment or to evenly coat a solid composite material. Unfortunately, in their raw state CNTs are insoluble; they clump together rather than disperse.

For more than a decade, researchers have been developing new chemical processes to address this challenge. One idea has been to create permanent defects on the surfaces of CNTs and "functionalize" them so they are soluble. Unfortunately, this also has the undesired side effect of quickly destroying the CNTs' electrical and optical properties.

Wang and his team have developed a new functionalization process for CNTs that delivers solubility and preserves electrical and optical properties. They purposefully functionalize defects on the tubes in useful-not random-places, creating strategic "functional groups." These carefully placed molecular groups allow CNTs to readily disperse while retaining their optical properties and ability to conduct electric current in large regions along the tube.

The challenge has been to control the chemical reactions that produce the functional groups on the CNTs. By using a chemical process called Billups-Birch reductive alkylcarboxylation, Wang's team found they could progressively add new functional groups to the CNT wall in a controlled way without introducing unintended new defects.

When the CNTs are immersed in a chemical solution for a specific length of time, the functionalized groups on the nanotubes lengthen by a predictable amount. Each time the process is repeated, or as the time in the solution increases, the sections grow longer. When the CNTs are viewed under a special, high magnification electron microscope, it is

evident that the functionalization has progressed lengthwise along the tube.

The propagation can initiate from either naturally occurring or intentionally introduced defects. Because the propagation mechanism confines the reaction and strategically controls where the functional groups grow, Wang's team can produce clustered functional groups at a controlled, constant propagation rate. It is the first clearly established wet chemistry process that does so.

The breakthrough makes it possible to create new functional structures such as "banded" nanotubes with alternating segments of functionalized and intact regions. The functionalized regions keep the CNTs from clumping, making them among the most water-soluble CNTs known. At the same time, the bands of intact, non-functionalized regions of the CNTs allow electrical and optical properties to be retained.

"This is important for the future use of these materials in batteries and solar cells where efficient charge collection and transport are sought," Wang explains. "These CNTs also could be used as highly sensitive biochemical sensors because of their sharp optical absorption and long-lived fluorescence in the near infrared regions where tissues are nearly optically transparent."

"This is a major step towards building the controlled nanostructures needed to understand electrochemical science and its value for energy solutions," says University of Maryland NanoCenter Director, Professor Gary Rubloff, a collaborator on the project.

More information: Confined propagation of covalent chemical reactions on single-walled carbon nanotubes, *Nature Communications* 2, Article number: 382 doi:10.1038/ncomms1384

Abstract

Covalent chemistry typically occurs randomly on the graphene lattice of a carbon nanotube because electrons are delocalized over thousands of atomic sites, and rapidly destroys the electrical and optical properties of the nanotube. Here we show that the Billups–Birch reductive alkylation, a variant of the nearly century-old Birch reduction, occurs on single-walled carbon nanotubes by defect activation and propagates exclusively from sp3 defect sites, with an estimated probability more than 1,300 times higher than otherwise random bonding to the 'π-electron sea'. This mechanism quickly leads to confinement of the reaction fronts in the tubular direction. The confinement gives rise to a series of interesting phenomena, including clustered distributions of the functional groups and a constant propagation rate of 18±6 nm per reaction cycle that allows straightforward control of the spatial pattern of functional groups on the nanometre length scale.

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