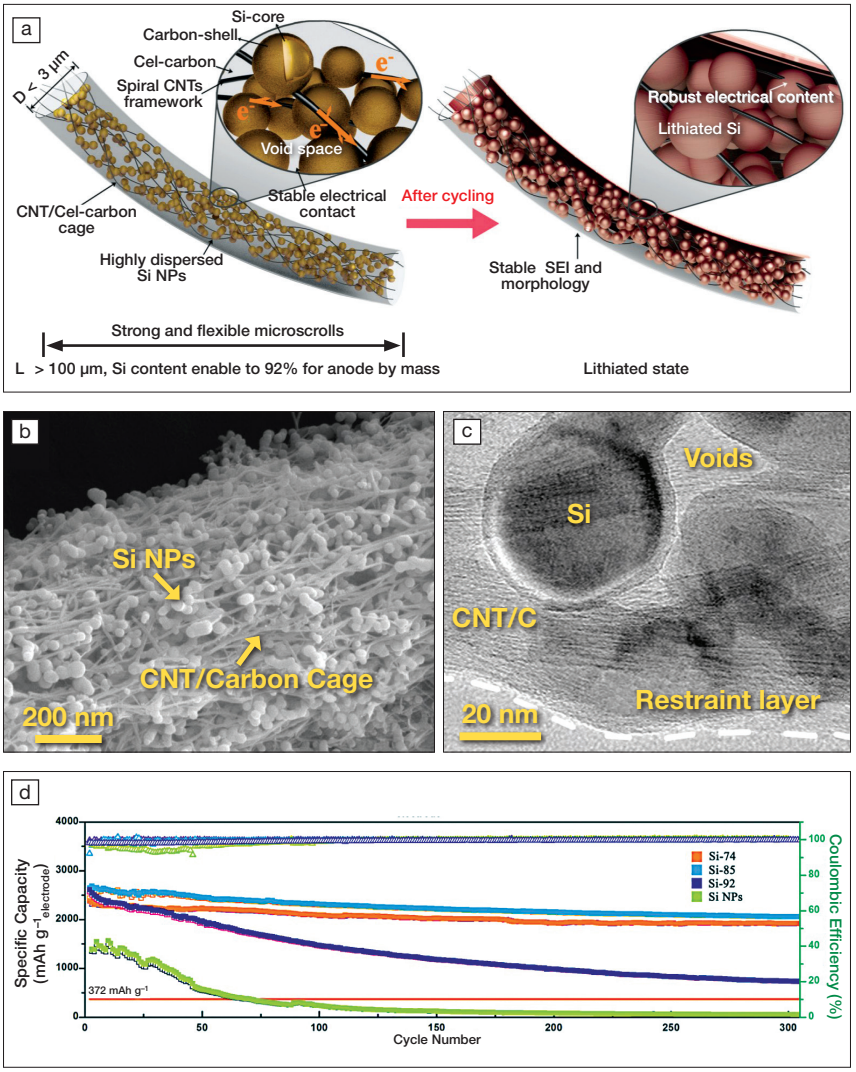
Carbon scrolls stabilize silicon nanoparticles in lithium-ion batteries

A joint research team led by Huiqiao Li of Huazhong University of Science and Technology, Yi Cui of Stanford University, and Qingfeng Sun of Zhejiang A&F University, has developed a carbon-scroll strategy that effectively helps stabilize silicon nanoparticles in Li-ion batteries. Si is a high-capacity, but highly unstable, anode material for Li-ion batteries. With a high Si content of 84.5 wt%, electrodes compromising Si nanoparticles mixed with carbon nanotubes (CNTs) and wrapped in carbon sheets exhibited consistently high capacity above 2000 mAh/g over 300 consecutive charge-discharge cycles. This performance was in sharp contrast to a bare Si nanoparticle electrode that displayed rapid capacity loss. This work was published in *Energy & Environmental Science* (doi:10.1039/c9ee02615k).

The topological warping of cellulose nanosheets enabled the scrolling strategy. The researchers mixed cellulose nanosheets, commercial Si nanoparticles, and CNTs (electrically conductive scaffolds) in water. The aqueous mixture was then freeze-dried into an aerogel. During freeze-drying, the cellulose nanosheets rolled up and wrapped CNTs and Si nanoparticles inside. The researchers believed that the freeze-drying process dehydrated and rolled up the cellulose nanosheets due to formation of hydrogen bonds, a process similar to wet paper rolling up when dried. Additionally, mechanical simulations revealed that the Si nanoparticles exerted stress that directed the cellulose nanosheets to wrap around them. The as-formed aerogels were subsequently pyrolyzed at 800°C to convert the electrically insulating cellulose into conductive carbon. According to Li, this work was born from an unexpected observation. "Our original plan was combining cellulose nanosheets with silicon to prepare silicon-carbon aerogels. In this process, we were surprised to find a unique scroll structure assembled by silicon and cellulose nanosheets, regardless of the addition of CNTs," Li says.



(a) Scheme showing the stabilization of Si nanoparticles by carbon nanotube/cellulose-derived carbon (CNT/C) wrapping. (b) Scanning electron micrograph and (c) transmission electron micrograph images of CNT/C-wrapped Si nanoparticles. (d) Cycling stability of CNT/C-wrapped Si nanoparticles with 74 wt% (Si-74), 85 wt% (Si-85), and 92 wt% Si (Si-92), in comparison with bare Si nanoparticles (Si NPs). Credit: *Energy & Environmental Science*.

The researchers discovered that the carbon-scrolled Si nanoparticles served as highly stable anode materials in Li-ion batteries. This characteristic is remarkable because Si has notoriously poor stability in Li-ion batteries due to ~300% volumetric expansion upon lithiation (Li^+ incorporation), which leads to structural disintegration. This drawback is exacerbated when the Si content is high. By contrast, the carbon-scrolled Si nanoparticles, having a Si content as large as 84.5 wt%, consistently exhibited charge-storage capacity greater than 2000 mAh/g over 300 charge-discharge cycles. In comparison, the capacity of an anode consisting of bare Si nanoparticles rapidly decayed to 54.6 mAh/g under identical testing conditions.

The excellent cycling stability of the carbon-scrolled Si nanoparticles was attributed to three factors. First, the voids among the highly dispersed Si nanoparticles in the carbon scrolls accommodated the significant volumetric deformation during lithiation, minimizing pulverization and disintegration. Second, the carbon wrapping around the Si nanoparticles, along with the presence of CNTs, formed robust conductive pathways that

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reduced the electrical resistance. Third, the elastic carbon wrapping not only suppressed the structural breakdown of the Si-nanoparticle anode, but also prevented the nanoparticles from detaching from CNTs that caused the loss of active materials.

Guiyin Xu, a battery researcher at the Massachusetts Institute of Technology, says, "The silicon-carbon composite electrodes with the controllable silicon content, excellent flexibility, high initial coulombic efficiency show great potential for flexible and durable electronics." Xu was not involved in this study.

The research team has confirmed that the topological transformation of cellulose is universal. Li says, "Similar results can be achieved with appropriate regulatory parameters when different materials, tin nanoparticles for example, are used to replace silicon nanoparticles, which provides a good opportunity to develop functional composites for different applications."

Tianyu Liu

Tests elucidate high fatigue lifetime of graphene

Graphene is known to be the world's strongest material. Its first commercial uses, in sports equipment and specialty gear, rely on this mechanical resilience. Yet, it is also brittle, fracturing when the load on it passes that maximum strength level.

But what happens to the material when it faces a small mechanical load over and over again? This fatigue life of graphene and associated damage mechanism remain unknown. In a recent study published in *Nature Materials* (doi:10.1038/s41563-019-0586-y), researchers have found that the two-dimensional (2D) material can withstand more than a billion cycles of stress before it breaks. The research should help design next-generation carbon-reinforced composites for aircraft and cars that have high fatigue life.

"Fundamentally we answered the question, 'can this material fail under fatigue?'" says Tobin Filleter, a mechanical and industrial engineering professor at the University of Toronto. "And the answer is yes, there's a mechanism that will lead to failure at loads below tensile strength. This sets the stage for understanding fatigue life of this general class of 2D materials."

The research team led by Filleter, materials science and engineering professor Chandra Veer Singh and mechanical engineering professor Yu Sun also at Toronto, conducted physical experiments as well as molecular dynamics simulations. In the experiments, they pressed an atomic force microscope (AFM) tip to the center of freestanding films of the graphene and graphene oxide material and then oscillated the tip at a frequency of 100 KHz.

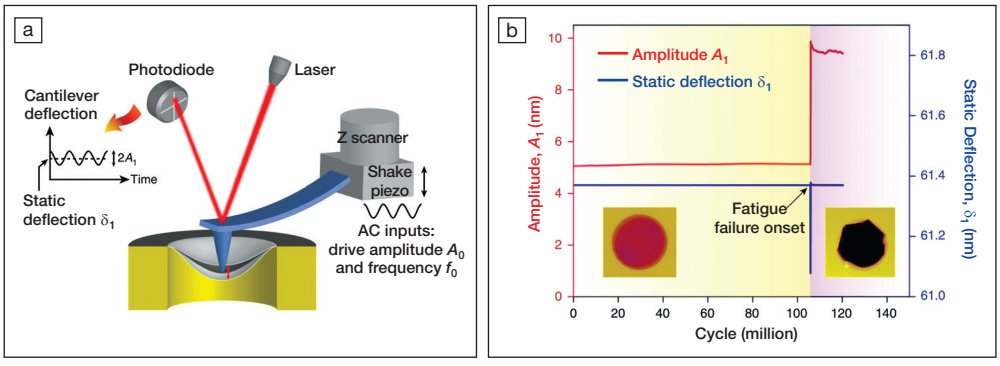
AFM is a widely available technique, but the researchers had to build a special device for the experiments in order to handle these very thin 2D material samples. They etched a silicon chip with half a million holes, each just a few micrometers in diameter, and stretched a graphene sheet over the holes. "There's no commercial approach to do this type of mechanical testing on atomically thin materials where we're controlling static load plus cyclic load," Filleter says.

They used a load that was 50–70% of the material's ultimate tensile strength, the same fraction that is used in studies on metals and alloys. They found that the materials could withstand an average stress of 71 GPa for over a billion cycles before failing.

Computer simulations showed different failure mechanisms for graphene and graphene oxide. In graphene, mechanical loading and thermal fluctuation cause an irreversible bond rotation near the site of a defect, causing the material to abruptly fail without a progressive buildup of cracks or damage as would happen normally in metals.

Graphene oxide simulations, on the other hand, show "progressive damage that's more like traditional fatigue," Singh says. That is because epoxide functional groups present on the material undergo a structural transformation under the mechanical load into ether groups. "In these regions we see small cracks form slowly, which make the material weak." While the billion-cycle fatigue lifetime of graphene is not surprising, the novelty of this research lies in conducting tests on graphene with the test setup used, says Ramesh Talreja, a materials science and engineering professor at Texas A&M University, who was not involved in the study. "The setup is highly specialized, very expensive, and not commonly available," he says.

Prachi Patel



(a) Schematic of the fatigue testing setup for a 2D material. (b) Experimental data showing evolution of the amplitude and DC force signals. Abrupt jumps of the amplitude and DC deflection signals demonstrate the onset of fatigue failure in the film after ~106 million cycles. Insets: Atomic force microscope topographic images before and after fatigue failure. Sample diameter, 2.5 μm. Credit: *Nature Materials*.

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