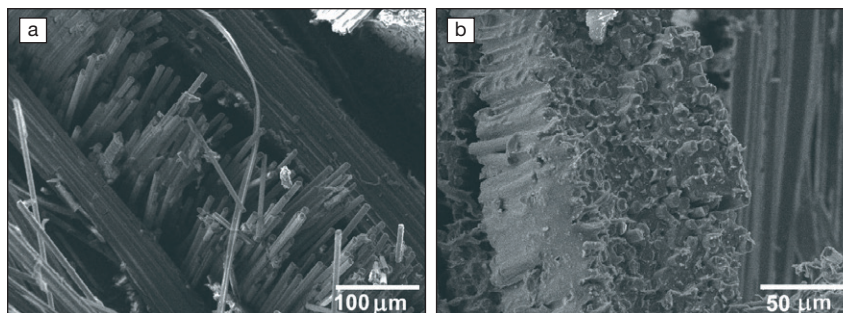


Thermal oxidation toughens carbon fiber/polysulfone composites

Due to their high strength and lightweight characteristics, carbon fibers are frequently used as reinforcement materials for polymer resins. However, the degree of enhancement of mechanical robustness due to the carbon fibers still has room for improvement. The smooth surfaces and limited surface functional groups in commercially available carbon fibers are such that the adhesion between the fibers and polymer matrices is weak, leading to weak interfaces and compromised strength. A potential solution to this problem has been provided by a research team led by Victor Tcherdyntsev at the National University of Science and Technology, Russia, who has shown that heating carbon fibers in air prior to their use in the composite materials effectively tackled the problem. Their work was published recently in *Results in Physics* (doi:10.1016/j.rinp.2019.102634).

Increasing the number of oxygen-containing moieties on carbon fiber surfaces could boost the fiber-matrix interfacial interaction. To realize this goal, the researchers adopted a thermal oxidation process to introduce oxygen-containing functional groups onto the carbon fiber surface. They heated the carbon fibers in a furnace to 500°C for 30 min in air. X-ray



Scanning electron microscope images of fracture cross sections of (a) pristine carbon fiber/polysulfone and (b) oxidized carbon fiber/polysulfone. Credit: *Results in Physics*.

photoelectron spectroscopy revealed that the heating process introduced hydroxyl ($-C-OH$), ether or epoxy ($-C-O-C-$), carboxyl ($-COOH$), and carbonyl ($-C=O$) groups onto the carbon fiber surface. They showed that these functional groups could form chemical bonds with polysulfone when used as the matrix, and strengthen the fiber/polymer composite.

The shear strength of the oxidized carbon fiber/polysulfone was found to be enhanced by 47% compared to that of the pristine carbon fiber/polysulfone, reaching 62.9 ± 2.7 MPa. The scanning electron microscope image of the fracture surface of pristine carbon fiber/polysulfone showed multiple carbon fibers with clean and smooth surfaces, indicating that breakdown of the fiber/matrix interfaces was the reason for the mechanical failure. In contrast, the fracture surface of oxidized carbon fiber/polysulfone contained carbon fibers

bundled with polysulfone. The attachment of polysulfone onto carbon fibers marked the reinforced fiber/matrix interfaces.

Juan Guan, professor of materials science and engineering at Beihang University, China, suggests a different mechanism for the enhancement in the shear strength: “Typically, oxidation in air appreciably decreases the strength of carbon fibers, which could lead to a different failure model that alters the composite’s shear strength.” Guan was not involved in this study.

The facile strategy of improving polysulfone adhesion to carbon fibers demonstrated in this work could potentially be applied to other oxygen-containing polymers such as poly(methyl methacrylate) and poly(dimethylsiloxane), thus creating opportunities for diversifying carbon fiber-reinforced polymers.

Tianyu Liu

3D carbon nanotubes and graphene sheets grown simultaneously on copper

Graphene and carbon nanotubes (CNTs) are promising materials for many applications due to their chemical, mechanical, and electrical properties. There is an emerging research area that is focused on combining CNTs and graphene for applications such as sensors, solar cells, supercapacitors, and optoelectronic devices. This is achieved by growing a three-dimensional (3D) network of CNTs on graphene or ultrathin

graphite layers (CNTs/G). The great potential of the 3D CNTs/G composite structure in such devices is due to its efficient charge transfer and carrier collection superior to 2D ultrathin graphite sheets alone.

In practice, the growth of 3D CNTs/G is challenging for two reasons: first, graphene and CNTs have different growth conditions, and second, controlling the density and length of CNTs is challenging. Current growth techniques necessitate complicated multistep processes that limit the applicability of CNTs/G hybrid structures in devices. A research team at KU Leuven led by

Jin Won Seo has simplified the growth techniques into a one-step process where CNTs and ultrathin graphite layers are grown simultaneously.

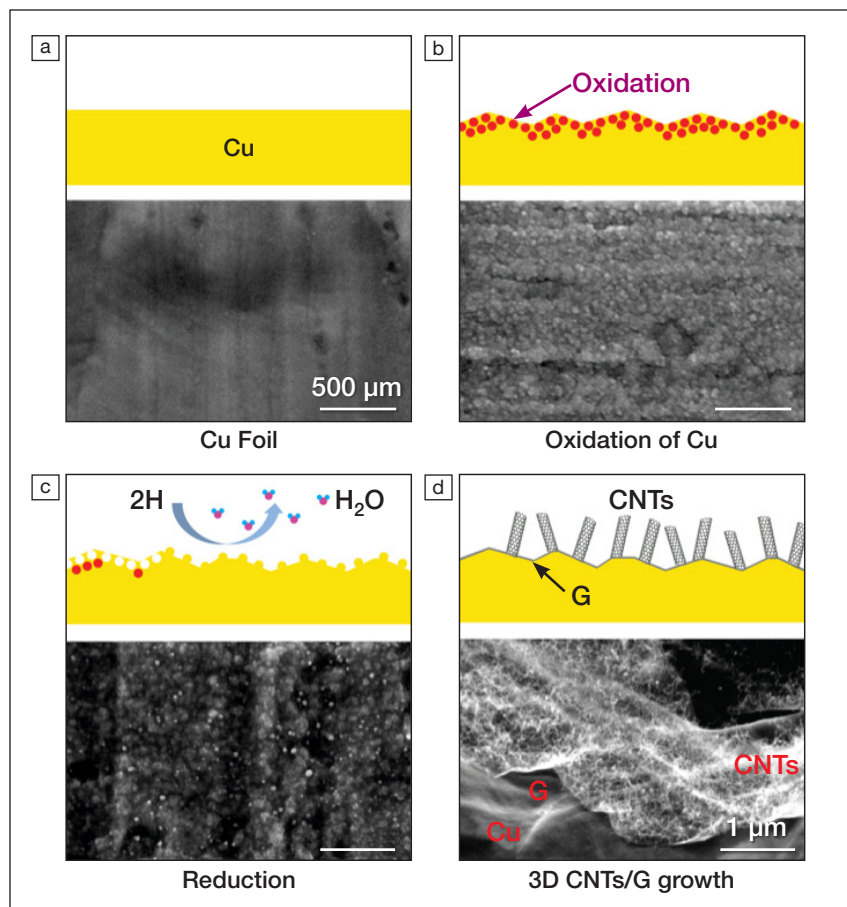
The technique utilizes copper (Cu) nanoparticles, formed by first oxidizing a Cu foil at 190°C for 10 min, which causes the surface to roughen, then annealing under hydrogen flow, thereby reducing the oxide layer and generating a Cu surface roughened by Cu nanoparticles. Ultrathin graphite layers grow from absorbed carbon atoms on the flat surface of Cu foil after introducing CO_2 and acetylene into the chamber, while CNTs form from C atoms concentrated at the nanoparticles.

Both the graphite layer and CNTs thus grow simultaneously in one step rather than the conventional multistep process.

“Although the ideal growth conditions for graphene and CNTs are totally different, their growth is competitive. Therefore, as soon as the 2D growth is established, it is difficult to initiate CNT growth. However, the Cu nanoparticles formed by the oxidation/reduction are able to locally promote CNT growth and to form 3D CNTs/G,” says Lee-Woon Jang of KU Leuven, the first author of the research recently reported in *Scientific Reports* (doi:10.1038/s41598-019-48725-w).

The research team characterized the structural quality of the 3D CNTs/G hybrid by using Raman spectroscopy and transmission electron microscopy (TEM). TEM showed that CNTs had a diameter of ~25 nm, while graphite layers were ~10 nm thick corresponding to ~20 layers of graphene. Conductive atomic force microscopy (AFM) embedded inside a scanning electron microscope was used to study the electrical properties. A network of CNTs/G produced 0.71 mA at 2 V compared to 0.62 mA for bare ultrathin graphite proving that the CNTs/G hybrid has better conductivity, due to increased contact area with the AFM. “Comparing the electrical properties of bare ultrathin graphite, a single and multiple CNTs/G network was the ultimate proof of better conductivity,” Seo says.

As proof of concept, the researchers fabricated perovskite optoelectronic devices using the hybrid 3D CNTs/G and a bare ultrathin graphite layer to compare their electrical properties. Time-resolved photoluminescence measurements showed that the lifetime of carriers in the 3D CNTs/G structure is 41% shorter than that in bare ultrathin graphite (10 ns and 17 ns) due to additional carrier transport by CNTs, and a high nonradiative recombination rate of



Schematic drawing illustrating the growth procedure of the three-dimensional carbon nanotubes/graphene (3D CNTs/G) networks and respective scanning electron microscope images demonstrating the change of the Cu surface after each step. (a) Pristine Cu foil, (b) oxidized Cu surface after annealing on a hot plate, (c) surface after the reduction step in H₂-rich atmosphere, and (d) grown 3D CNTs/G network. Credit: *Scientific Reports*.

photogenerated holes and electrons by defects. Both high carrier recombination and easier carrier collection are key to the better performance of the 3D CNT/G-based devices for applications, such as in solar cells, detectors, batteries, piezoelectric generators, and membranes.

László Forró, a professor at École Polytechnique Fédérale de Lausanne, Switzerland, and an expert in the physics of nanomaterials and novel electronic

materials, says, “3D CNTs/G hybrid structures allow extending the excellent electrical conductivity of graphene and CNTs to three dimensions. The KU Leuven team has succeeded to develop a simple and efficient one-step growth procedure for 3D CNTs/G hybrid, which gives opportunities to significantly improve the performance of various devices through efficient carrier collection.”

Nora M. Hassan

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