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Fibrous nanocomposites of carbon nanotubes and graphene-oxide with synergetic mechanical and actuative performance†

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Fibrous nanocomposites of carbon nanotubes, graphene-oxide or graphene were prepared by a simple coagulation spinning technique exhibiting synergetic enhancement of mechanical strength, electronic conductivity and electrical actuation performance.

Carbon nanotubes (CNTs) and graphene have gained extensive interest due to their excellent electrical and mechanical properties.^{1,2} Various applications have been explored based on their unique electrical properties, such as transparent conductive films,³ supercapacitors,⁴ and transistors.⁵ In addition to their excellent electrical properties, carbon nanotubes and graphene exhibit outstanding mechanical properties, such as high tensile strength (> 100 GPa),⁶ and high Young's modulus (~1–2 TPa).⁷ Unfortunately, it is difficult to integrate them into useful mechanical devices due to their small size, although manipulation and even *in situ* measurement of the mechanical property of an individual CNT is possible.⁸ An alternative strategy is to spin CNTs into microfibers⁹ or disperse them within polymers.¹⁰ A number of methods have been proposed to prepare fibers composed entirely of⁷ or a large fraction of carbon nanotubes.¹¹ To the best of our knowledge, spinning graphene into macroscopic fibers has never been reported. Besides, two kinds of carbon allotropes can lead to synergetic enhancement of the mechanical performance of their polymer composites.¹² Therefore, spinning carbon nanotube/graphene composite fibers can be an excellent route to utilize their mechanical performance.

Herein, we report the synthesis of composite fibers containing CNTs, graphene oxide (GO) or graphene by a coagulation spinning technique. Their mechanical and electrical properties were investigated systematically. Synergetic enhancement of their tensile strength and conductivity was found when CNTs and graphene-oxide (GO) were combined to spin fibers. These composite fibers showed excellent electromechanical performance in air. CNT/graphene composite fibers with tunable mechanical and electrical properties were designed.

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GO fibers were prepared by a PVA (poly(vinyl alcohol))-based coagulation spinning technique. The synthesis procedure is similar to that of SWCNT fiber preparation reported by Vigolo *et al.*,¹¹ except that acid was added to the PVA solution to assist the coagulation of GO. It was found that only when the pH of the PVA solution was below 2.0, GO fibers could be spun continuously. As observed from the stress–strain curve (Fig. 1a), the tensile strength of GO fibers is about 240 MPa, which is a little higher than that of SWCNTs fibers (~210 MPa). Interestingly, the mechanical performance is greatly enhanced when SWCNTs and GO solution are mixed to spin fibers. An 80% increase in the tensile strength and 133% increase in the elastic modulus over pure GO fibers are obtained with a 2 : 1 (v/v) ratio of SWCNT to GO. This synergetic enhancement can be attributed to better dispersion of the nanocarbons and stronger interfacial interactions. The nanocarbons, GO or carbon nanotubes are prone to stacking or bundling together when only one of them exists in the fibers, as observed from Fig. 2a and b. This adversely affects their strength since slippage occurs easily between GO sheets and carbon nanotube bundles. After mixing, a well dispersed GO–SWCNT network forms in the PVA matrix as seen from Fig. 2c. That is because GO is amphiphilic and can be used as a dispersing agent for CNTs,¹³ while CNTs can hinder the restacking of GO. The homogeneous intercalation of GO sheets into

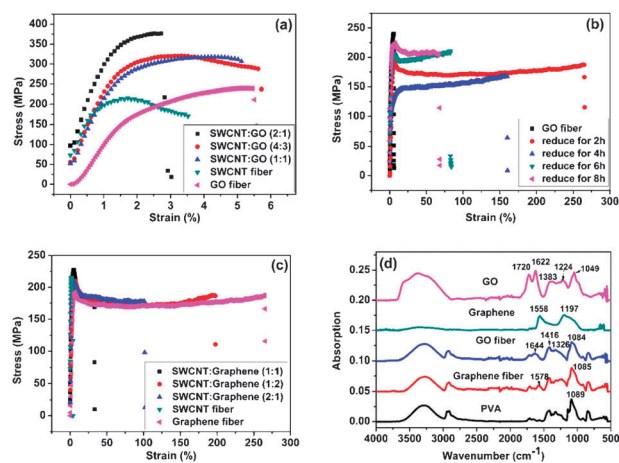


Fig. 1 Stress–strain curves of (a) SWCNT–GO composite fibers; (b) graphene fibers; (c) SWCNT–graphene composite fibers; (d) FTIR spectra of GO, graphene and their fibers.

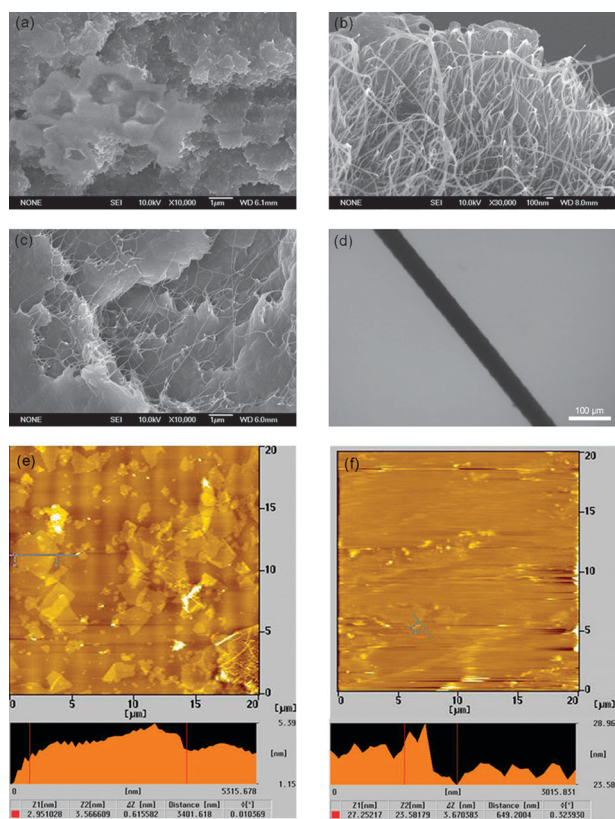


Fig. 2 SEM images of the cross-section of (a) GO fibers; (b) SWCNT fibers; (c) SWCNT–GO (2 : 1) composite fibers; (d) optical microscope image of the SWCNT–GO (2 : 1) composite fiber; (e) AFM image of GO sheets; (f) AFM image of graphene sheets which were reduced for 2 h.

SWCNT networks greatly increases the interfacial contact area which is conducive to the stress transfer between the nanocarbons and PVA molecules. The addition of GO also introduces more carboxyl and hydroxyl groups, which form hydrogen bonds with surrounding CNTs and PVA molecules. This enhances interfacial interactions, which increases the strength of the fibers.

In addition to strength, a better dispersion state enhances the conductivity of the fibers. As seen from Table S1 in the ESI†, SWCNT–GO (2 : 1) hybrid fibers are more conductive than SWCNT fibers, although the content of the conductive SWCNTs was lower than that of the latter ones. When concentrated hydrochloric acid was added to the coagulation bath, the conductivity of the composite fibers greatly increased, by about 18 times. This can be attributed to an acid induced doping effect,¹⁴ but needs to be investigated further.

Based on the above investigations, it has been found that SWCNT–GO (2 : 1) composite fibers coagulated from acidic PVA solution have both high strength and high conductivity, and are promising candidates for actuators. Therefore, actuators based on them have been designed and their electromechanical performance has been measured by applying a sine wave voltage. Fig. 3 shows that the actuated displacement vibrates exactly in line with the input voltage and hence perfect sine curves with the same frequencies are obtained. These curves indicate the fibers' sensitive and controllable response to the

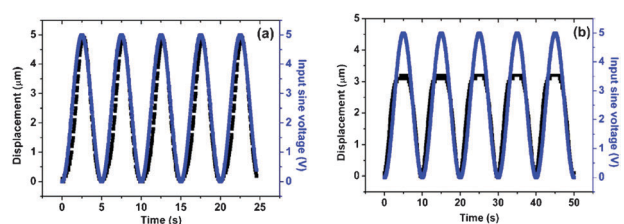


Fig. 3 Displacement vibration of SWCNT–GO fibers under input sine voltage (a) 0–5 V, 0.2 Hz; (b) 0–5 V, 0.1 Hz.

applied electrical signals, and imply their excellent actuation capabilities. When the voltage frequency was reduced, the actuation amplitude decreased, and a steady state was observed. This can be attributed to the combination of the electric heating and rapid cooling of the GO–SWCNT networks, which will be discussed later.

In previous reports, PVA was always pyrolyzed to improve their conductivity, and the left SWCNT fibers were immersed in the electrolytes to be actuated. However, the low flexibility of the annealed fibers and the necessity of employing a liquid electrolyte limited their applications.¹⁵ Our work is the first to report actuation performance of SWCNT–GO–PVA composite fibers in air and shed light on a new application of SWCNTs or graphene-based composite fibers.

Fan *et al.*¹⁰ and Hu *et al.*¹⁶ have investigated the actuation mechanism of CNT–polymer composites. They drove the actuation between -5 and $+5$ V, and found that the displacement was always in the same direction, independent of the direction of the applied voltage. This proved that the actuation mechanism was purely resistive and an electrothermal mechanism was proposed. When an alternating current passed through the fiber, periodic heating took place, which resulted in cycling thermal expansion and contraction. SWCNT–GO networks acted as conductive paths in the polymer matrix. The higher the electrical conductivity, the larger the current that passed through the fibers, and therefore more heat was generated, which led to larger displacement. The rapid response of our fibers is mainly attributable to the high conductivity, originating from the homogeneous SWCNT–GO networks. In addition to their role in enhancing conductivity, SWCNT–GO networks also worked as active cooling systems due to their excellent thermal conductivity.¹⁶ When the voltage frequency was reduced, the current increased more slowly resulting in lower heating efficiency. Besides, more heat dissipates to the surroundings during longer cycles. That is why the actuation amplitude decreased when the voltage frequency was reduced. The steady state observed in Fig. 3b was due to an equilibrium between electrically generated heating and rapid cooling.

In our research, SWCNT, GO and their hybrid fibers all have high strength and low toughness. However, graphene fibers, discussed in the following section, show completely different performance (Fig. 1b). GO fibers are brittle and their elongation at break is only about 5–6%, while that of graphene fibers reaches 270%. The major factor responsible for this difference is the interfacial interactions between the nanocarbons and PVA molecules. There are a lot of carboxyl and hydroxyl groups on GO sheets, which formed hydrogen bonds with surrounding PVA molecules as deduced from the

more than 100 cm^{-1} shift of C–O groups (Fig. 2d). The hydrogen bond formation greatly enhances interfacial interactions and hinders the slippage of GO sheets and PVA molecules, which leads to high tensile strength and low strain to break. After reduction, carboxyl and hydroxyl groups on GO sheets were removed as shown from the FT-IR spectra (Fig. 1d) and Raman spectra (S1, ESI†), which greatly weakens interfacial interactions. Additionally, sheet thickness increased after reduction as seen from the AFM image (Fig. 2e and f), indicating the restacking of graphene sheets. Slippage easily occurs between the stacking graphene sheets, which also leads to the higher elongation of the fibers. Once GO was reduced for a longer time, the fiber toughness decreased. This is because graphene clusters formed with reduction and hindered elongation of the polymer chains. The morphology difference between carbon nanotubes and graphene is also a crucial factor. In CNT fibers, PVA molecules are apt to wrap around carbon nanotubes, making slippage more difficult. By comparison, PVA molecules can adsorb on graphene sheets only through van der Waals force. Therefore, slippage of PVA molecules in graphene fibers is much easier. That is why graphene fibers exhibited such high elongation, while elongation of CNT fibers was low even when their functional groups were removed.

When SWCNTs and graphene were combined, fibers with tunable mechanical performance, from brittle to high toughness, were prepared. As seen from Fig. 1c, fibers tend to have high toughness when graphene dominates, but turn brittle when SWCNTs dominate. Therefore, the toughness of the fibers can be regulated conveniently by adjusting the ratio of SWCNTs to graphene, with minimal change in their strength. The SWCNT–graphene hybrid fibers have lower strength and conductivity compared to SWCNT–GO fibers, which can be attributed to their worse dispersion in the polymer matrix. Therefore, their actuation response is not as good as SWCNTs–GO hybrid fibers. However, they still have potential in a wide range of applications considering their tunable mechanical performance. To our knowledge, this is the first report of fibers with tunable toughness based on SWCNTs and graphene.

In this communication, SWCNT, GO, graphene and their hybrid fibers were prepared. Mixing SWCNTs and GO improves dispersion of both in the polymer matrix and leads to the synergetic enhancement of the strength of the fibers. The conductivity of the fibers was also increased by mixing SWCNTs and GO together at the ratio of 2:1. Adding concentrated HCl into the coagulation bath enhances the conductivity of the fibers significantly. SWCNT–GO (2:1) fibers coagulated from acid PVA solutions have both

high strength and conductivity, and show excellent actuation performance. Contrary to GO fibers, graphene fibers exhibit high toughness upon the removal of carboxyl and hydroxyl groups. Fibers with tunable toughness were designed by mixing SWCNTs with graphene in different ratios. These tunable fibers have potential in a wide range of applications.

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