FUNCTIONAL COMPOSITE FIBRES WITH CARBON NANOPARTICLES

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Abstract
A simple 'coffee ring' approach is developed to deposit graphene nanoplatlets (GNPs) and multiwalled carbon nanotube networks (CNTs) onto electrically insulating glass fibre surfaces. We found that the thin networks on a single glass fibre surface exhibit semiconducting properties. This enables us to realise a single carbon nanoparticle-glass fibre with novel multifunctional responsibilities for in situ sensing of surrounding environments, such as temperature, relative humidity (RH) and/or nanoscale liquid-solid phase transitions. We further demonstrate that the sensing behaviors of the single carbon nanoparticle-glass fibres were strongly influenced by the intrinsic surface morphologies of these fibres. Our semiconducting carbon nanoparticle-glass fibre can be developed further as 'nerves' in the fibre reinforced composites.

1. Introduction

As the largest and key organs in mammals, the skin is the interface between an organism and its surrounding world. It plays multifunctional roles, some of which are of current interest, e.g. sensor, colour, superhydrophobicity, or rheological effects. The skin has a sensation function because the skin contains a variety of nerve endings that jump to heat and cold, touch, pressure, vibration, and tissue injury. Therefore, mammals could response to environmental changes to save their life. It provides us with bio-inspired design of skin like composite surfaces for efficiently and economically turning a traditional material to an advanced smart composite.

The bio-inspired composite is considered as an emerging research field that will bring new opportunities to traditional fibre-reinforced polymer composites. An extensive body of research studying the multifunctional composites is associated with nano-reinforcements learned from nature, e.g., nanocomposites with maximum tolerance of flaws [1], solid lubrication coatings [2], smart responsive skins [3], human–like sensing materials [4], coloured polymer films [5] and nanogenerator [6]. While most of the studies are devoted to bulk solids, thin films or powders, the functionalization of traditional fibres (i.e., the most commonly used for micro-diameter- scale reinforcements: glass fibres) or composite interphases are now drawing more and more attention from interdisciplinary fields. The 'smart' coatings on traditional fibres with autonomic nerve-like functionalities have also been developed, which showed abilities for *in situ* detection of failure, strain, stress and temperature. To realise such functional composite fibres, the most important issue is the achievement of the fibre surface with shells of multifunctional nanoparticles. Such shells have electrical sensing ability, high loading capacity and affinity to the polymer matrix. The nanoparticles have to be robust, sensitive to external stimuli, and well dispersed in the coating. As ideal nano-reinforcements, graphene nanoplatlets (GNPs) and multiwalled carbon nanotubes (CNTs) have attracted considerable interest from both academia and industry [7-10].

Here, inspired by the autonomic functionalities of the skin, we report the use of GNPs and CNTs in glass fibre surface coatings to integrate sensation and electrical functionalities along the line of our recent works [11, 12]. Because plastics and their corresponding composites are generally sensitive to changes in their environment and their mechanical properties may vary widely with the absorption of moisture (H_2O in trace amounts), our superior moisture sensitive single fibre has been developed in this work. From a scientific point of view, it is not clear whether our nanoparticle-based fibre surfaces can prevent supercooled trace moisture from icing when the moisture contacts the solid surfaces. We thus report observations of moisture and its liquid-solid phase transition.

2. Materials and test methods

The glass fibres have curved surface as coating substrates at micro-diameter-scale. We use alkali-resistant glass fibres (ARG) with an average diameter of 22 µm made at Leibniz-Institut für Polymerforschung Dresden e. V. by a continuous process. Two kinds of nanoparticles were used for fibre surface coatings. We first used commercially available carboxyl functionalized multi-walled CNTs (NC-3101, Nanocyl S.A., Belgium) produced via the chemical vapor deposition (CVD) process. The average diameter and the average length of CNTs are 9.5 nm and 1.5 µm, respectively. Secondly; we generated GNPs based on a liquid–phase exfoliation graphite method [13] to avoid the inferior effect to electrical conductivity from conventional graphite oxide reduction method. A stable diffusion GNPs in solution is achieved through the bath sonication and centrifugation process, where the sodium dodecyl benzene sulfonate (SDBS) is dissolved in Millipore water. To achieve conducting networks with homogeneous and continuous distribution of carbon nanoparticles (GNPs or CNTs) on the glass fibre surface, the modified dip-coating method is developed. Using the 'coffee ring effect', a layer-by-layer dip coating approach results in the formation of overlapping GNP layers on the glass fibre surface. To make a comparison, the conventional dip-coating method was conducted to deposit conducting CNT networks onto the glass fibre surfaces. The carbon nanotube (MWCNT) aqueous dispersion as reported previously in detail by us [11, 12].

The deposition process of nanoparticles onto glass fibres was studied using digital microscope (VHX-1000, Keyence, Japan). The fibre surface morphologies were studied using atomic force microscopy (AFM, a Digital Instruments D3100, USA) and scanning electron microscopy (FE-SEM Ultra 55, Carl Zeiss SMT AG, Germany). The direct current (DC) electrical resistance was measured in direction parallel to the fibre axis at room temperature with a Keithley 2001multimeter. Four-point conductivity measurements were carried out also with a Keithley 2001 multimeter, to *in situ* monitor the DC electrical resistance changes for the single carbon nanoparticle-glass fibre. The experiments of the resistance change with the temperature for the single glass fibre was carried out in a hot–stage (Linkam LTS350 Heating/Freezing, UK) from –150 ℃ to 30 ℃ with a heating rate of 1 K min^{-1} in a nitrogen atmosphere. The experiments of the resistance change with the relative humidity *RH* were carried out by placing single fibre in a desiccator containing drying agent (0.6% *RH*) and saturated solutions of different salts: $CaCl_2 \cdot 6H_2O$ (40% *RH*), $Ca(NO_3)_2 \cdot 4H_2O$ (65% *RH*) and Na_2CO_3 (97% *RH*), in an air-conditioned room at 23.0 ± 1.0 ℃. To demonstrate the extreme sensitivity of the single fibre sensor, that is capable of working stably and operated easily in air, we put the single fibre in front of human's nose with a distance of about 10 cm to monitor human breathing. The electrical resistance change with human's breath was successfully *in situ* recongnised.

3. Results and discussion

3.1 'Coffee ring effect' based layer-by-layer self-assembly of GNPs on fibre

The 'coffee ring effect' is the phenomenon that a drop of coffee dries on a solid surface and in turn rings like deposits along the perimeter, which has attracted much research interest after Thomas A. Witten's work published in Nature [14]. This phenomenon provides potential ways to deposit a novel nano pattern onto a surface [15]. Here, we use this method to deposit carbon nanoparticles onto a glass fibre surface. As the water evaporated causing GNP solution's 'coffee ring effect', the GNPs move to the glass fibre-water interface, layer-by-layer self-assemble to the glass fibre and in turn form multilayer structures. As confirmed by the AFM images (Figure 1), we can see that overlapping GNP layers have overall an ordered arrangement of microstructure.

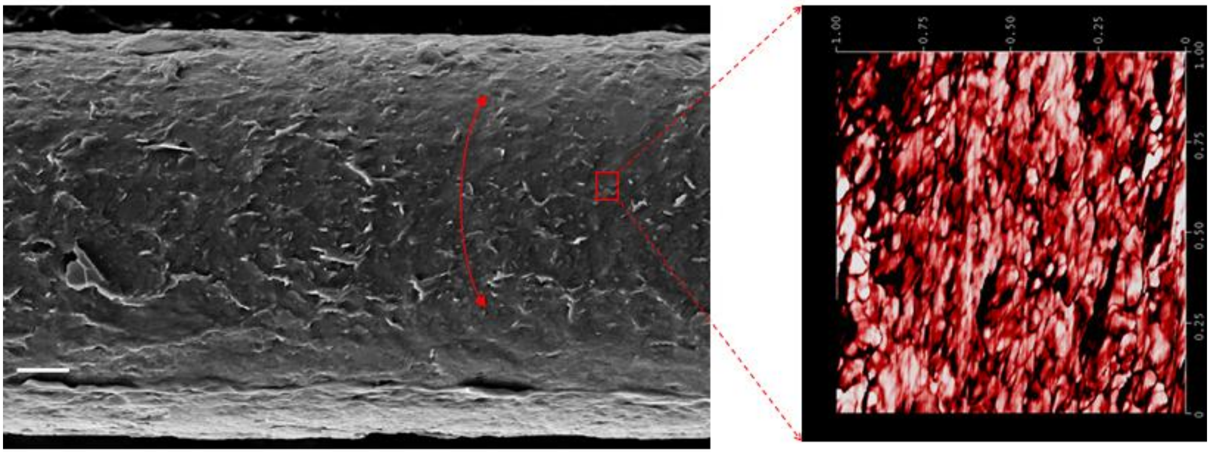

Figure1. The microstructure of GNP coated on glass fibre surface. (Left) SEM image of GNP-glass fibre surface. The arrow shows the direction of 'coffee ring effect'. Scale bar 2 μm. (Right) AFM phase image of GNP-glass fibre surface at a selected area.

3.2 Electrical resistance and surface morphology of a single carbon nanoparticle-glass fibre

To test if the surface microstructures of carbon nanoparticles (GNPs and CNTs) coated glass fibre achieve electrical conducting composite fibre, we measured the DC electrical resistance. Figure 2 shows that the resistance *R* of a single GNP-glass fibre is in range of 10^5 up to 10^7 Ω, and the resistance increases with increasing electrode-electrode distance *L*. Accordingly, we could calculate the specific volume resistance of fibre using the following formula:

$$\rho_{glass} \approx \pi d^2 R / (4L) \qquad (1)$$

where the GNPs and CNTs coated glass fibre have an average diameter of d = 22 μm, the specific volume resistances were approximately 10^0-10^2 Ω·cm and 10^{-1}-10^2 Ω·cm, respectively.

Both value are in the range of carbon nanoparticles based composites (10^{-2}-10^{10} Ω·cm) as summarised in ref. [16]. This reveals that physical paths for charge carrier movement are formed inside both kinds of nanoparticle networks. The carriers are transported by a complex combined electrical conduction mechanism of tunneling and hopping along nanoparticle interconnects. The resistance R is the sum of single nanoparticles' resistance R_{NP} and the contact resistance R_{cont} and tunneling resistance R_{tun}. Although R_{NP} was very small for both individual GNP and CNT, the contact resistance R_{cont} and R_{tun} could be very high since there were many contact points or contact surfaces to form an electrical conductive network in several millimeters long and hundreds micrometers thick. Compare with our previous work [17], we got a relatively better result with a lower specific volume resistances of the single fibres.

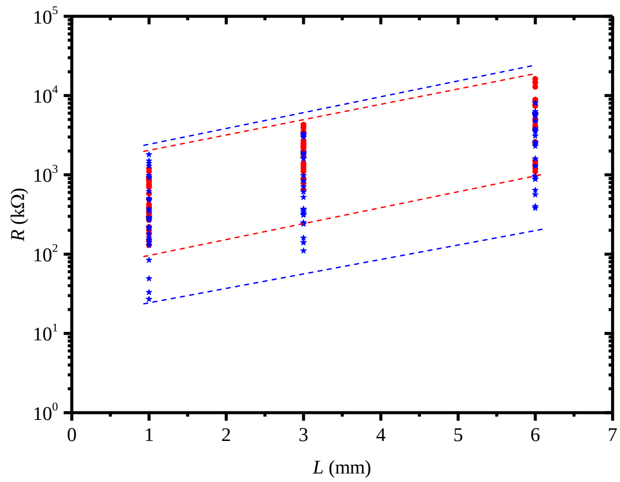

Figure 2. The DC electrical resistances R of a single GNP-glass fibre (red circles) and CNT-glass fibre (blue stars) versus electrode distance L (1 mm, 3 mm and 6 mm).

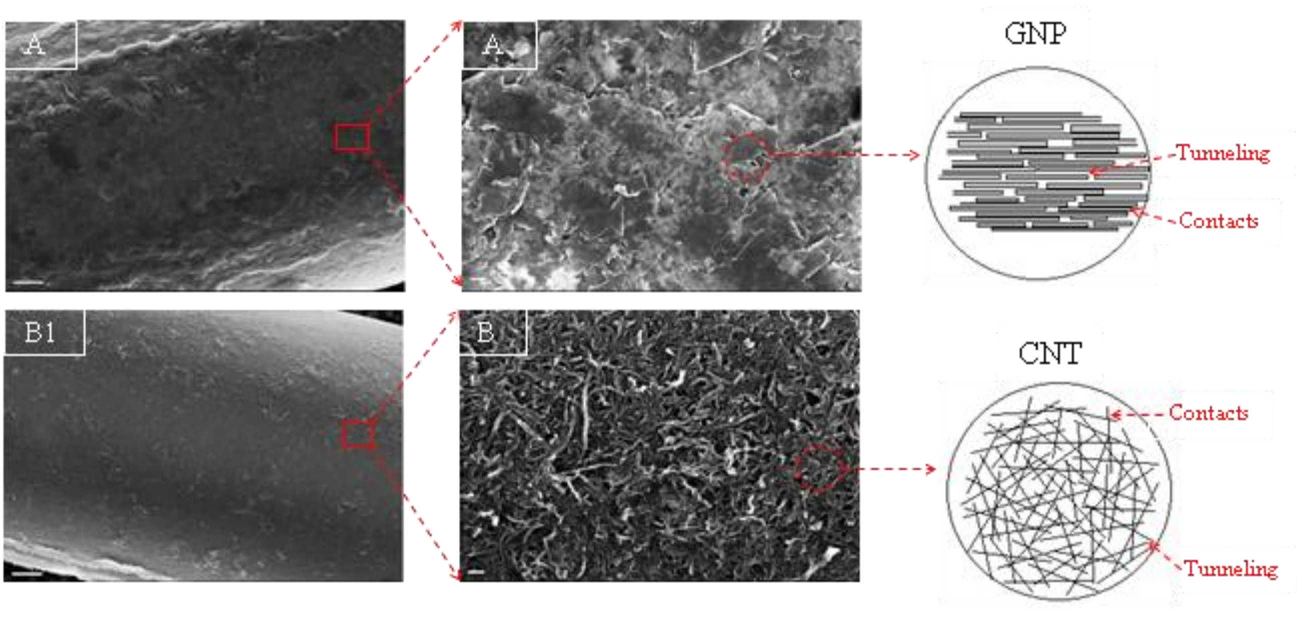

Figure 3. Morphology and schematic electrical conductive network of carbon nanoparticles coated glass fibre. (Left) SEM image of GNP-glass fibre (A1) and CNT-glass fibre (B1), scale bar 2 μm; (Middle) SEM image of the selected area on GNP-glass fibre (A2) and CNT-glass fibre (B2), scale bar 200 nm; (Right) Schematic diagram of electrical conductive network formed by GNPs (top) and CNTs (down).

Compared with that of the GNP-glass fibres, the resistance R of a single CNT-glass fibre has a wider range from 10^4 to 10^7 Ω. We attribute the difference date distribution of resistance R to the surface microstructures formed by GNPs and CNTs. Clearly, the deposition of GNPs onto glass fibre formed quite different morphologies in comparison with the deposition of CNTs (see Figure 3). The thin GNP and CNT interconnected networks on the glass fibre surface possess typical thickness of a few tens to a few hundreds of nanometers, which create physical paths through that charge carriers can flow. The layer-by-layer overlapped GNPs on glass fibre surface look like a brick wall structure. Thus, the GNPs formed relatively uniform electrical conductive network, which is constructed through GNP's point-to-point and face-to-face physical contacts. This structure is responsible for that the resistance variation range of GNP is narrower than that of CNT. In contrast, the electrical conductive network of the CNTs looks like a fishnet structure mainly through point-to-point contacts. As expected, we observe a relative larger resistance variation range due to nonhomogeneous deposited CNTs onto glass fibre. To this end, we obtained two kinds of semiconducting carbon nanoparticle-glass fibres from the originally electrical insulating glass fibres. This was successful first step to develop multifunctional sensing abilities on traditional reinforcement materials.

3.3 Multifunctional sensor of a single carbon nanoparticle-glass fibre

We then investigated the sensing behavior of the carbon nanoparticles coated single fibres as a function of *RH*. Figure 4 shows that $\Delta R/R_o$ increases with increasing *RH*. The moisture, which is absorbed on the carbon nanoparticles surface, changes the electrically conductive networks for both GNP-glass fibres and CNT-glass fibres. Specifically, $\Delta R/R_o$ increases exponentially with increasing *RH* values: $\Delta R/R_o \propto \exp(bRH)$, where b is a positive constant. Notably, the b value of CNT-glass fibre (0.08) is about two times higher than that of GNP-glass fibre (0.03), suggesting a higher moisture sensitivity, especially at high *RH* levels (>50%). We assume that this finding is most likely related to the carboxyl functional group of CNT and the surface structure. The carboxyl functional groups are hydrophilic group, which can absorb moisture. In addition, the overlapping multilayer microstructure of GNPs is hindering the moisture to diffuse into the internal layers (see Figure 4). Therefore, the interconnected networks of CNTs absorb moisture much easier than those of GNPs.

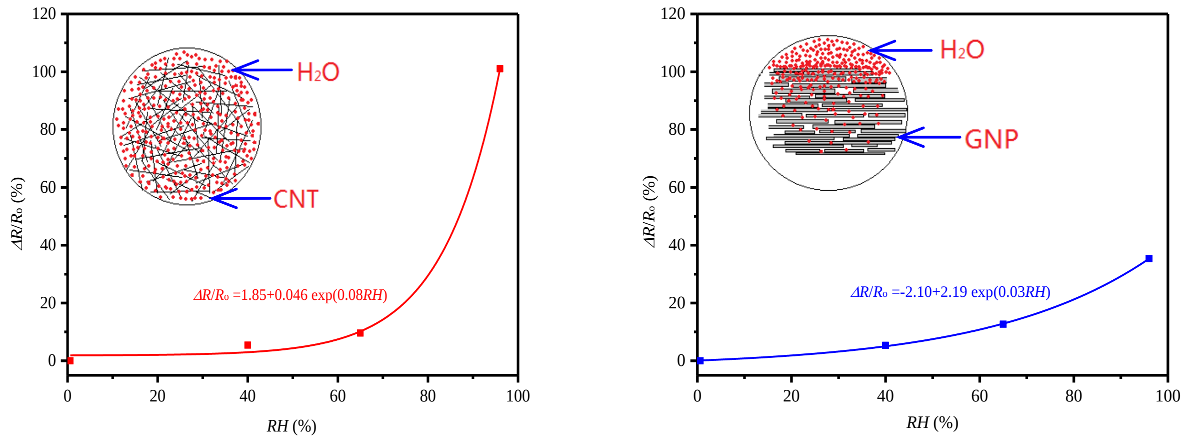

Figure 4. Dependence of fractional resistance $\Delta R/R_o$ on relative humidity *RH* for single CNT-glass fibre (left) and GNP-glass fibre (right).

Next, it would be interesting to find out whether our single fibre can be used to test the dynamic response of flow with variable *RH*. Figure 5 shows that our sensor can effectively real time monitor human breathing by recording the resistance *R*. The reversible cycles show excellent repeatability, extremely fast response time and short recover time.

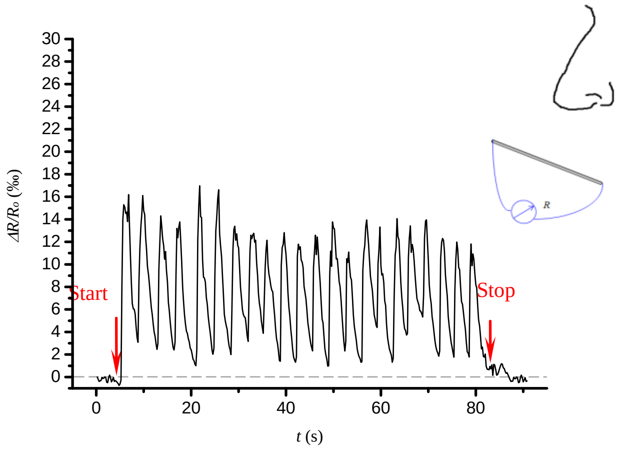

Figure 5. Dependence of fractional resistance $\Delta R/R_o$ on time *t* for a single GNP-glass fibre to monitor human breathing.

Finally, we investigated the sensing ability of the GNP- and CNT-glass fibres on temperature and moisture's liquid-solid phase transitions. The single fibre sensor was based on monitoring of resistance change by scanning temperature from +30℃ to –150℃. Figure 6 shows negative temperature coefficient (NTC) effect on both GNP-glass fibre and CNT-glass fibre. The $\Delta R/R_o$ curves decrease with increasing temperature, exhibiting a rather non–metallic behavior. The negative electrical temperature coefficient β can be computed using the following formula:

$$\frac{\Delta R}{R_o} = \beta T + b \quad (2)$$

where the negative electrical temperature coefficient β reflects the temperature sensitivity of the fibre. The β value of a GNP-glass fibre is almost two times higher than that of a CNT-glass fibre. It indicates that the GNP interconnect electrical networks have a much higher temperature sensitivity than CNT interconnect electrical networks. We attributed such variation to the electrical pathways formed by different aforementioned surface structures. Importantly, the absorption of water vapor as a result of ambient humidity at temperatures close to freezing conditions (0°C) leads to a specific non–monotonous temperature dependence of the resistance. We could see an abnormal resistance change of GNP and CNT near the temperatures of -18°C and -5°C, respectively. Obviously, this change is caused by the phase change of the trace moisture which was absorbed onto carbon nanoparticles. The trace moisture absorbed on surface of carbon nanoparticles would freeze through a heterogeneous nucleation mechanism during cooling, and the freezing temperature will decease for heterogeneous nucleation. It has been reported that graphitic layer of soot play a great variability of ice nucleation ability: freezing temperatures ranging from -34℃ to -18℃ [18]. Our values (-18°C and -5°C) agree well with the freezing temperature range (-20℃ to -4℃) of water freezing on solid material surface [19]. Thus, the fibre surfaces with nanoparticles have anti-icing effect, especially for GNPs. Based on this approach, our fibre sensor can help to understand the absorption of trace moisture in the fibre reinforced composites.

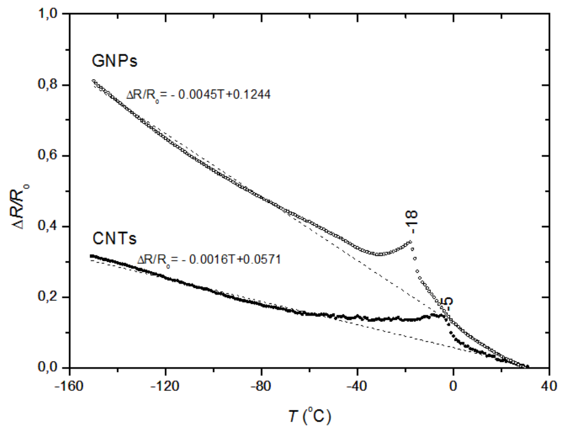

Figure 6. Dependence of fractional resistance $\Delta R/R_o$ of a single GNP-glass fibre and CNT-glass fibre versus temperature together with linear regressions (dotted line).

4. Conclusions

In this study we used the ‘coffee ring effect’ to deposit carbon nanoparticles (GNPs and CNTs) onto electrical insulating glass fibres surface to introduce novel semiconducting microstructures. Firstly, the GNPs deposited onto the glass fibre form overlapping multilayer microstructures, whereas the CNTs form fishnet like microstructures. Secondly, owing to the distinctive features of microstructures formed by carbon nanoparticles, the single glass fibres with GNPs and CNTs show quite different DC electrical resistance values. Thirdly, both GNP- and CNT-glass fibres achieve multifunctional sensing abilities to temperature and relative humidity *RH*. Comparing GNP-glass fibres with CNT-glass fibres, their sensing behaviors are strongly depended on their interconnected electrically conductive networks. The GNP’s microstructures results in higher temperature sensitivity than the CNT’s. We find a linear dependence of the electrical resistance on temperature in the test range, except the range involved moisture’s liquid-solid phase transition. The microstructures of the nanoparticles result ice formation temperature decreasing, thus they have anti-icing effect. Besides, the microstructures of GNPs hinder the moisture to diffuse into the internal GNP layers. This explains the effect that the GNP-glass fibre show lower *RH* sensitivity than the CNT-glass fibre. Finally, the single GNP-glass fibre can effectively monitor human breathing with an excellent repeatability, an extremely fast response time and short recovery time. Overall, our glass fibre coated with carbon nanoparticles possess multifunctional sensing abilities within a surrounding environment, and provide a potential way to use such fibres as ‘nerves’ for detection of trace moisture absorption in fibre reinforced composites.

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