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Title	Graphene oxide as dyestuffs for the creation of electrically conductive fabrics
Author(s)	Fugetsu, Bunshi; Sano, Eiichi; Yu, Hongwen et al.
Citation	Carbon, 48(12), 3340-3345 https://doi.org/10.1016/j.carbon.2010.05.016
Issue Date	2010-10
Doc URL	https://hdl.handle.net/2115/43932
Type	journal article
File Information	Car48-12_3340-3345.pdf



Graphene oxide as dyestuffs for the creation of electrically conductive fabrics

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Abstract

Graphene oxide (GO) was immobilized on the surfaces of acrylic yarns through a conventional dyeing approach. The GO dyed yarns and/or the fabric were immersed in an aqueous sodium hydrosulfite solution at around 363 K for 30 minutes, which converted the GO into graphene. The graphene created a graphitic-coloured and electrically conductive thin layer over each yarn in the fabric. Data on the electrical conductance of the yarns *versus* temperature (30 K ~ 300 K) fit well with the so-called fluctuation-induced tunneling model, which suggests that the graphene layer belong to a continuously interconnected network. Values of the electrical resistivity ranged from 10^2 to 10^{10} ohm/cm, as verified by the content of graphene in the conductive layer.

1. Introduction

Graphene oxide (GO) is heavily oxygenated graphene bearing hydroxyl and epoxide functional groups on the basal planes, and carbonyl and carboxyl groups at the edges [1, 2]. Although GO was first introduced in 1859 [3], it has characteristics which have attracted a great deal of attention in recent years. First, GO belongs to a class of truly sheet-shaped molecules (sometimes ions). A single GO sheet (the fully exfoliated GO), has a length or breadth that is typically larger than micrometers, while its thickness is only one or a few atoms thick. Therefore, it is possible to cover or overlap a substance with an atom-thick molecular sheet. Second, GO is highly dispersible in both aqueous and polar organic solvents; our studies found that the solubility in water or ethylene glycol was as high as 2.0wt% [4]. Compared with carbon nanotubes (CNTs), it is easier to mix GO with other matrixes so that the GO is ideally dispersed. Third, GO can convert to graphene through chemical reductions or with heating. Graphene has many unusual properties. For example, graphene has high in-plane thermal (~ 3000 W/mK) and electrical conductivity ($\sim 10^4 \Omega^{-1} \text{ cm}^{-1}$) and excellent mechanical stiffness (~ 1060 GPa) [5], which enable us to create a broad new class of high-performance materials. Moreover, GO is commonly produced by exfoliating graphite, an abundant material,

through simple chemical reactions [6 ~ 9]; thus, GO has the advantages of low cost and plentiful supply of the starting material.

The applications of GO and/or the reduced GO (namely, graphene) is close to unlimited [10]; however, to realize certain applications, the micro×micro sized molecular sheets need to be linked into macroscopic networks. Two typical strategic starting points have been used for physically linking CNTs, compounding and self assembling. These two essential techniques have also been demonstrated for GO. In a compounding procedure, desirable binders (commonly polymers) are used to glue GO into interconnected macroscopic networks. With this process, chemically functionalized GO (for example, GO after being gratified with compounds having isocyanate groups) was dispersible even in *N,N*-dimethylformamide (DMF). This led to the production of three styrene-based composited polymers (polystyrene, acrylonitrile-butadiene-styrene rubber, and styrene-butadiene rubber), with GO being intimately mixed into the matrixes through a mixing of the solutions [11]. After the GO has been converted into graphene by dimethylhydrazine, the GO-compounded polymers were electrically conductive. Conversely, with the self-assembling method, thin layers of GO can be produced without the need to add binders. In other words, it is possible to obtain a thin layer having GO for its entire constituted elements. For example, methods based on the

Langmuir-Blodgett assembly of GO were capable of producing the thinnest layer possible, with a thickness equal to a single GO [12, 13]. GO layers with this thickness are optically transparent; this allows the production of transparent electrically conductive films by chemically reducing the GO into graphene.

Despite the existence of these methods, the development of a new method for producing graphene-based functional materials in industrial quantities remains a large challenge.

In this paper, we describe a novel methodology for the massive production of graphene-based networks. This method is established using GO as dyestuffs. GO was immobilized on the surface of each yarn in a fabric through a conventional dyeing approach. The GO dyed fabrics were then chemically reduced. Graphitic-coloured and electrically conductive fabrics with excellent wash fastness were obtained. To the best of our knowledge, this is the first report on the use of GO as dyestuffs for the creation of graphene-based networks over the surface of fabric.

2. Experimental

2.1 Preparation of GO

GO was obtained from natural graphite (SP-1, Bay Carbon), using a modified Hummers and Offeman method [6]. In a typical treatment, 100 g of graphite powder and 20 g of

sodium cholate were mixed in 1000 milliliters of deionized water. The mixture was then milled using a continuously operating bead-milling system, at 40 Hz for 30 minutes.

The wet-milled graphite, after being freeze-dried, was used as the starting material for preparing the GO with the modified Hummers and Offeman method. Briefly, 100 g of the freeze-dried graphite/cholate mixed powders, 50 g of sodium nitrate, and 2000 mL of sulfuric acid were mixed in an ice bath. Next, 100 g of potassium permanganate were slowly added into the sulfuric-acid/graphite/cholate suspension. Once mixed, the suspension was placed in a water bath at 308 ± 3 K and was further mixed for about 30 minutes. Next, approximately five liters of deionized water was added to the suspension, the temperature was increased to 363 ± 3 K, and the suspension was further mixed for about 30 minutes. The suspension was finally diluted to approximately 10 liters using warm deionized water and a small amount (about 50 mL of 30wt% H_2O_2) of hydrogen peroxide. The warm suspension was filtered, producing a yellow-brown filtered cake. The filtered cake was carefully washed with a large amount of warm deionized water, and was then dispersed in deionized water by mechanical mixing to prepare a stock GO aqueous suspension containing approximately 2 wt% GO.

2.2 Dyeing of the fabrics

Woven fabrics consisting solely of polyarylate yarn was obtained from Kuraray, under the trade name Vectran HT0255. The fabric has high tenacity and high elasticity, with a yarn tensile strength of 22.9 cN/dtex (330 kg/mm²). The initial modulus was 530 cN/dtex (7610 kg/mm²), as recommended by the manufacture. The fabrics were dyed at ambient temperature (about 296 K); they were crumpled and soaked for about 15 minutes in a dye vat containing aqueous 0.3 wt% GO (pH 2.13). The liquor ratio was about 100: 1. After drying in ambient conditions (296 K and 53% relative humidity) overnight, the GO dyed fabrics were immersed in an aqueous solution containing 0.5 wt% sodium hydrosulfite, at about 363 for 30 minutes. The fabrics were thoroughly rinsed in warm tap water, then in warm deionized water, and then dried in ambient conditions overnight. To measure the amount of graphene sheets immobilized on the surface of the yarn, the air-dried fabrics were placed in a 378 K oven overnight.

2.3 Characterizations

Atomic force microscopy (AFM) images were performed using an Agilent Series 5500 AFM instrument. The samples were prepared by casting a heavily diluted aqueous GO suspension on the surfaces of mica. The images were obtained using the tapping mode at a scanning rate of 1 Hz. Scanning electron microscopy (SEM) observation of the

surfaces of the initial “as-received” fabrics and the graphitic-coloured fabrics were carried out using a 6500-SEM (JEOL) system. The temperature dependence of conductance was measured using a 2636A source meter (Keithley). The x-ray diffraction (XRD) measurements were performed with a Rigaku RINT Ultima diffractometer with Cu K α radiation (K α 1.54056 Å) and an X-ray power of 40 kV/20 mA.

3. Results and discussion

GO was obtained from graphite powders (Bay carbon, SP-1 graphite) using Hummers and Offeman’s method [6]. Prior to the chemical oxidation reactions, the graphite powders were milled using a wet-milling system to break the particle sizes down to few micrometers. The wet-milled graphite, after being freeze-dried, was the starting material for preparing the GO using Hummers and Offeman’s method. AFM was used to evaluate the morphologies of the resultant GO. The apparent heights of the observed GO were found to be around 1 nm, indicating that the GO was fully exfoliated into individual sheets; a typical AFM image is shown in Figure 1. The length or breadth of each of the 30 pieces of the GO were found to be around 2 ~ 6 micrometers.

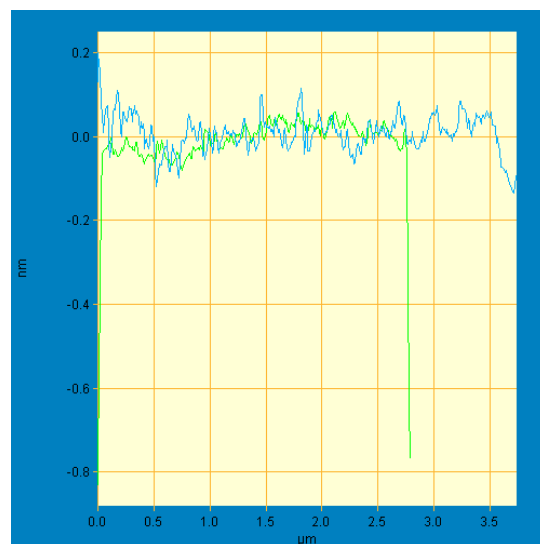
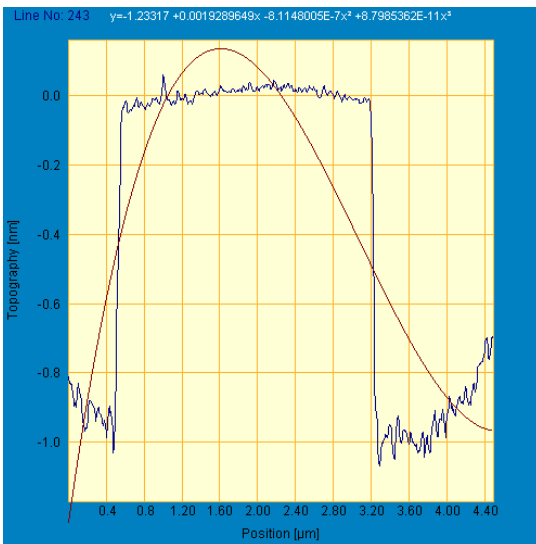
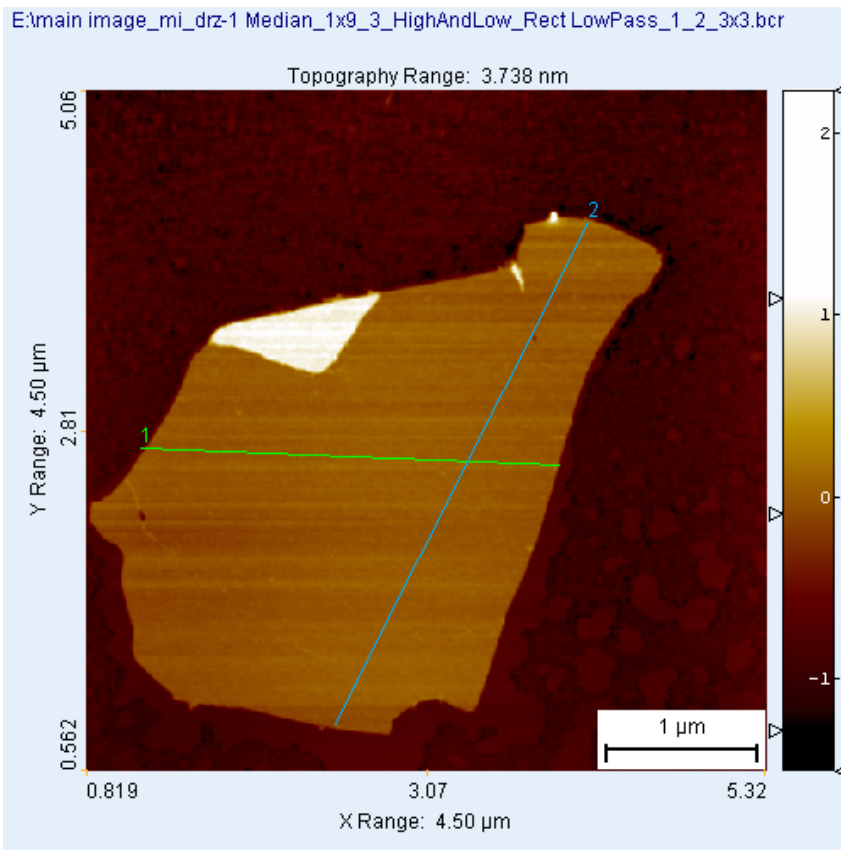


Figure 1 A typical AFM image showing the fully exfoliated graphitic oxide (FE-GO) with a folded edge on mica (left figure). The thickness of the GO was estimated to be

about 1 nm (right figure); the length and breadth were 3.75 μm and 2.72 μm , respectively.

Woven fabrics consisting entirely of polyarylate yarn (aromatic backboned, high tenacity, and high elasticity yarn) were dyed through an exhaustion procedure with a liquor ratio of 100: 1. The dye vat contained GO at an optimized concentration of 0.3 wt% and a pH value of 2.13. The fabric dyeing was carried out in ambient conditions for 15 minutes by crumpling and soaking the fabrics in the dye vat. After drying overnight at ambient conditions (296 K and 53% relative humidity), the GO dyed fabrics were immersed for 30 minutes in an aqueous solution containing 0.5 wt% sodium hydrosulfite, at a temperature of about 363 K. The GO was chemically converted into graphene and the resulting fabrics exhibiting a shiny metallic luster (we describe this colour as a graphitic or “graphene” colour). Figure 2 shows a typical graphene-coloured fabric, compared with an initially identical fabric that was coated with CNTs. Note that a graphene-coloured fabric can be obtained without the addition of any binders to the GO based dyestuffs; however, for the CNT-coloured fabrics, a certain amount of binder (in this study, a polyurethane-based polymer) has to be added into the

CNT-based dyestuffs in order to firmly immobilize the CNTs on the surface of the fabric yarn [14].



Figure 2 Photos of a section of a typical graphene-coloured fabric (right photo), together with a section of a typical CNT-coloured fabric (left photo).

The GO is highly dispersible in water. After dispersion in the aqueous dye vat, it interacts with the polyarylate-based yarn through the so-called π - π stacking interactions occurring between the aromatic backbones of the yarn and the skeleton of the basal planes of the GO. For the fabrics used in our study, one gram of fabric was able to

uptake about 8 mg of the GO. In the resulting graphene-coloured fabrics, the ratio of graphene to fabric was found to be approximately 7/1000. The graphene-coloured fabrics were observed using scanning microscopy (SEM). The fabric consisted of 40 filaments of the yarn, and changes in its surface morphologies were not recognized (Supporting Information, Figure S1).

The graphene-coloured fabrics are electrically conductive. Using a current/voltage plot, the average value of electrical resistivity for the graphene-coloured fabric shown in Figure 2 was calculated to be 92.52 Ω/cm (Supporting Information, Figure S2).

Moreover, the electrical resistivity (and the shiny metallic luster) remained almost unchanged ($< 3.2\%$, $n = 30$), even after 30 water washings in warm (308 K) tap water. Thus, the graphene-coloured fabric showed excellent wash fastness properties.

About 30 lengths of yarn were disassembled from the graphitic-coloured fabrics (Supporting Information, Figure S3) and were used to evaluate the conductive mechanisms. The so-called variable-range hopping (VRH) [15] and fluctuation-induced tunneling (FIT) [16] mechanisms are two typical conduction mechanisms involved in conducting polymers [17] or in CNT-based networks [18]. VRH is commonly encountered in disordered systems, such as bundles of CNTs or defective CNTs, while FIT is commonly encountered in systems composed of highly conductive regions

connected through tunneling barriers [18]. Only a few studies have focused on the conduction mechanism of graphene-based composites. Gómez-Navarro et al [19] demonstrated that graphene sheets obtained by chemically reducing GO exhibit VRH conduction. Conversely, Eda et al [20] observed an anomalous temperature (T) dependence of the conductivity in their graphene-based thin-film transistors. However, a definitive explanation for these anomalous characteristics was not provided in the previously reports. Kaiser et al [21] also observed the VRH conduction mechanism in individual chemically-reduced graphene mono-layers. These results indicate that a meaningful quantity of defects exist in graphene-based materials. VRH conductions were also observed in individual hydrogenated graphene ($10 < T < 300$ K) [22] and in bi-layered graphene thin films ($T < 5$ K) [23].

The temperature dependence of the conductance in our graphene-coloured yarn was measured to investigate their conduction mechanism. Two samples were prepared. The two ends of each length of the graphene-coloured yarn were attached to copper electrodes on a small printed circuit board using silver paste. The distances between the contacts for the two samples were approximately 4 and 8 mm, respectively. Figure 3 shows a typical plot obtained using a source meter. Our data were not at all consistent with the VRH mechanism. However, we did observe good agreement between the

measured data and the FIT model, with $T_0 = 503$ K and $T_1 = 1631$ K for sample 1, and $T_0 = 940$ K and $T_1 = 3489$ K for sample 2. Here, the conductance is expressed by equation (1):

$$\sigma = \sigma_{FIT} \exp[-T_1 / (T + T_0)], \quad (1)$$

where T is the temperature and σ_{FIT} is a constant. The extracted T_0 and T_1 were rather high compared with the temperatures observed in single-walled [24-26] and in multi-walled [27-31] CNT networks. The probability of tunneling at the Fermi energy through a junction between two conductors is proportional to $\exp(-T_1/T_0)$. Despite the high values of T_0 and T_1 , the T_1/T_0 ratios for our samples were almost identical to those reported for the single-walled carbon nanotube (SWCNT) networks. A possible conduction mechanism for the graphene-coloured fibers was investigated within the FIT model framework [16]. We assumed that the graphene-based network, in our study, is composed of huge numbers of interconnected few-layered and/or multi-layered graphene, having an average tunneling width of w and an average junction area of A . The tunneling barrier height V_0 and the relative permittivity of the barrier region ε_r were

estimated to be 4.4 eV (work function of graphene) and 1.0 (vacuum), respectively.

These values were calculated rigorously using equations (8 ~ 27) in previous work [16].

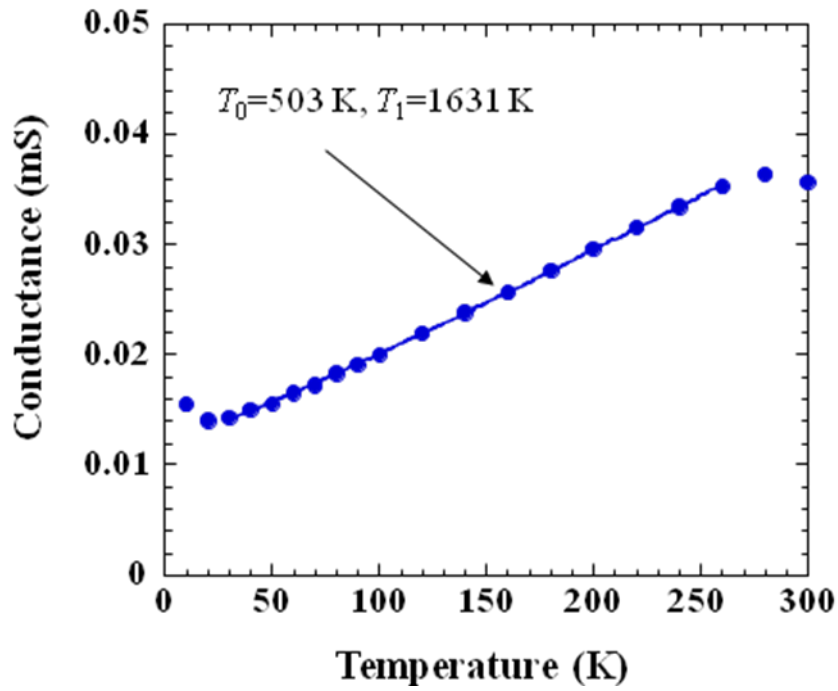


Figure 3 Temperature dependence of the conductance for a length of yarn, disassembled from the graphene-coloured fibers. Symbols: measured data. Lines: fitted with FIT model.

Figure 4 shows the calculated contours in the w - A plane that reproduce T_0 and T_1 from the samples. The intersection of the two lines for each sample provides a possible combination of w and A . From these plots, the average values for the tunneling width and the junction areas were estimated to be 0.44 nm and 0.114 nm², respectively.

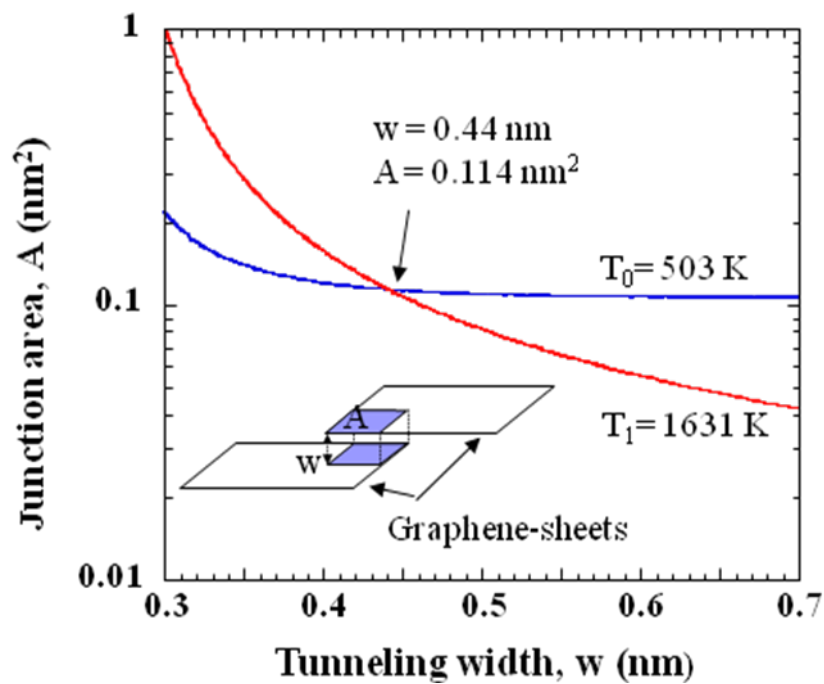


Figure 4 Calculated relationships between w and A to reproduce the extracted T_0 and T_1 for the two samples. Inset: junction geometry model.

We have further measured the tunneling width using X-ray diffraction (Supporting Information, Figure S4). The graphene-coloured fabrics displayed a strong X-ray diffraction peak around 19.44° , corresponding to a layer-to-layer distance (which in this study corresponds to the major w value) of about 0.456 nm. There were three additional weak and broad peaks at around 16.18° ($w = 0.574$), 22.34° ($w = 0.398$), and 27.66° ($w = 0.322$ nm); these are possible minor w values. Note that the layer-to-layer distance for the graphene found for the graphene-coloured fabrics is slightly larger than the layer-to-layer distance in the pristine graphite. This can be attributed to the inability of hydrosulfite to completely reduce the carboxyl groups located at the edges of the GO. In fact, some carboxyl groups remained in the reduced graphene was confirmed by analyzing the graphene-coloured fabrics using FT-IR (data not shown). In Figure 2, the graphene-coated fabric is not black but dark-brown; this might also implies a small amount of oxygen containing functional groups is included in this sample. Nevertheless, the chemically reduced GO has constructed an infinite network of connected paths over the surface of each yarn in the fabric. Studies focusing on the reduction behaviors of graphene oxide by hydrosulfite are undertaking by our groups. The resulting graphene-based network functioned as a single piece of large-sized, few- or multi-layered graphite; this opens up wide areas of research that could be performed with the large-

sized graphene sheet-based networks, with graphene sheets composing the entire element.

The values of the electrical resistivity ranged from 10^2 to 10^9 ohm/cm, as verified by the overall graphene content in the conductive thin layer of the graphene-coloured fabrics.

This was achieved by controlling the total amount of the GO that was immobilized on the surface of the initial untreated fabric. We produced three levels of electrical conductivity for the graphene-coloured fabrics. Fabrics with an electrical resistivity of 10^2 Ω /cm could be used to create soft and flat electrical heaters. With 10^5 Ω /cm resistivity, fabrics may be used for anti-static clothing, and with 10^9 Ω /cm resistivity, fabrics can be used as brushes in photocopying machines.

4. Conclusions

We demonstrated experimentally that soft, durable, and large-sized graphene -based networks can be obtained by immobilizing chemically reduced graphenes on the individual surfaces of fabric yarn or fabric fiber. We used a traditional dyeing approach with the graphene oxide as the dyestuffs. The directly employing graphene oxide in dyeing opens new possibilities for the massive production of graphene-based functioning materials, and thus their use in a variety of industrial applications.

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Supporting Information

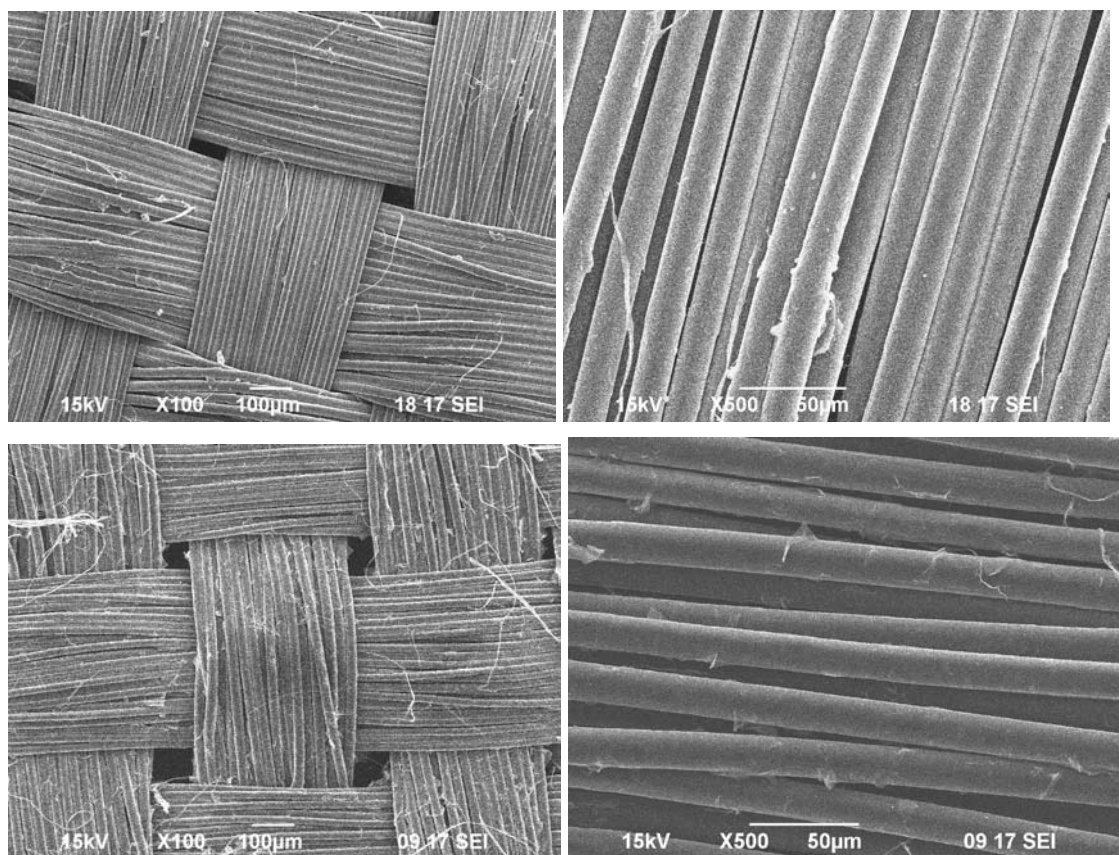


Figure S1 SEM images of the as-received fabrics (upper two images) and the graphene-coloured fabrics (lower two images).

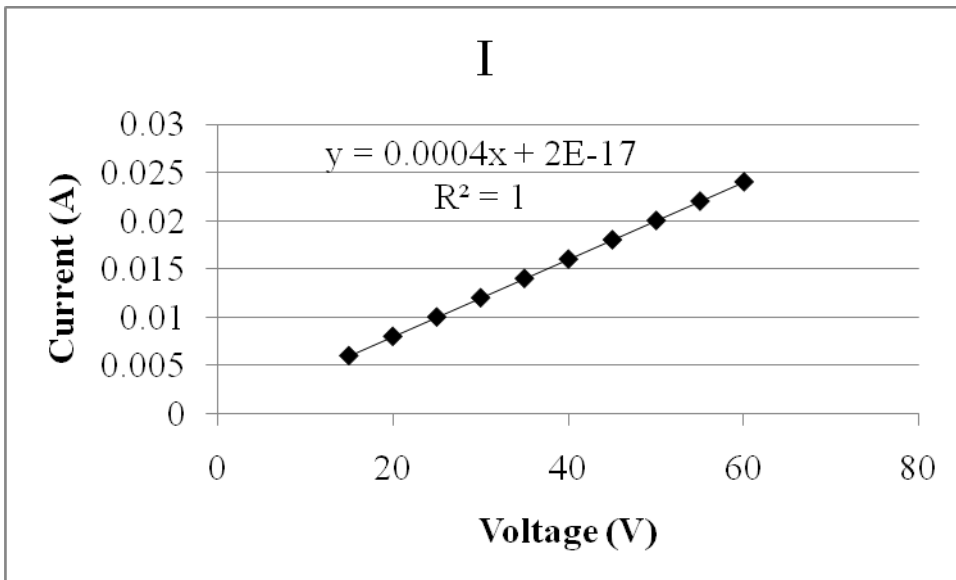


Figure S2 The current/voltage plot of the graphene-coloured fabric sample; each of the two opposite edges of the fabric sample was sandwiched using two pieces of copper plates (electrodes). The distance between the electrodes was 27 cm.



Figure S3 Photos of the graphene-coloured yarn (the dark-black colour) and the pristine yarn obtained by disassembling them from the graphene-coloured fabric and the pristine fabric, respectively.

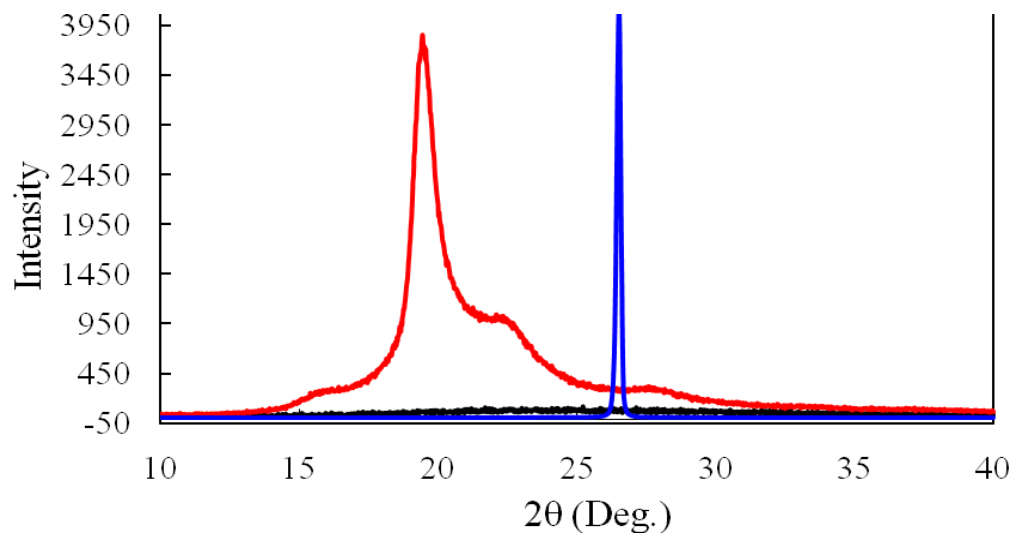


Figure S4 XRD patterns of the graphene-coloured fabric sample (red line), the precursory fabric sample (black line), and the pristine graphite powder sample (blue line).