Directed self-assembly of graphene oxide on an electrospun polymer fiber template

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Development of self-assembly routes for long-range organization of graphene oxide (GO) is an active field of research due to the enormous potential and diverse applications of this carbonaceous material. We present a simple strategy for producing anisotropic GO assemblies through utilizing electrospun polymer fibers as a physical template. We demonstrate that intertwined uniform electrospun microfibers comprising a mixture of polyethylenimine (PEI) and polyvinylpyrrolidone (PVP) constituted docking sites for GO flakes through electrostatic attraction between the negatively-charged GO and positive amine-displaying polymer fibers. The reduced GO (r-GO) network formed after chemical reduction exhibited electrical conductivity and optical transparency, opening the way for varied electro-optical applications.

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1. Introduction

Graphene, an atomic scale honey-comb lattice of sp2 hybridized carbon atoms, has attracted significant interest due to its unique electronic, optical, mechanical, and chemical properties [1–6]. Graphene-based materials display novel and improved functionalities compared to other substances and exhibit potential for a wide variety of applications [7,8]. Transparent conductive films (TCFs) in particular, which are essential components in varied electronic and photonic applications, have been prepared from graphene using varied strategies [7,9–11]. TCF applications benefit from the excellent charge carrier mobility of graphene and the feasibility of producing flexible films [7,12].

High quality graphene sheets can be prepared through varied methods such as exfoliation, chemical vapor deposition (CVD), epitaxial growth, and others [13–16]. While those techniques have been widely used for graphene fabrication, synthesis of water-soluble graphene oxide (GO) and its subsequent reduction (through thermal or chemical means) to reduced graphene oxide (r-GO) is considered a promising route towards production of graphene and its use in practical applications and devices. The advantages of GO emanate from the use of inexpensive reagents, simple procedures not requiring sophisticated instrumentation, scalability, and wide range of potential applications [17–20]. An essential prerequisite for utilizing GO in TCFs and other applications is the development of methods for arranging the GO sheets in two- and three-dimensions [21]. Varied methodologies have been proposed to achieve this goal, including self-assembly of GO at the liquid–liquid and liquid–air interfaces [22], electrophoretic deposition [23,24], spin coating [25,26], dip coating [27,28], transfer printing [29,30] and others.

Fibers and nanowires of metals have been employed as platforms for TCFs, primarily due to the long-range conductivity achieved through linkage among individual wire elements, as well as the abundant empty spaces within the conductive network, enabling optical transparency [12,31–33]. Electrospun polymer fibers constitute useful templates or etch masks for metal assemblies and construction of TCFs exhibiting excellent electrical conductivity and optical transparency [34–36]. Electrospinning is a powerful generic technology for production of uniform fibers, particularly using polymer blends [37,38]. Previous studies have reported incorporation of GO inside or outside electrospun fibers and their applications in sensing [39,40], and for improving physical scaffolding of the fibers [41]. Here we show that electrospun fibers comprising polyethylenimine (PEI) and polyvinylpyrrolidone (PVP) served as a versatile template for construction of transparent conductive GO films. Importantly, the assembly process was based upon the electrostatic attraction between the negatively-charged GO and the PEI/PVP fibers (which are positively-charged due to the surface-
2.2. Synthesis of graphene oxide

6 g of KMnO₄ were successively added very slowly (within 15 min). The reaction mixture was stirred for 3 h. 50 mL of deionized water was then added to the reaction mixture, followed by 5 mL H₂O₂. The reaction mixture was stirred for another 10 min. The reaction mixture was then centrifuged (5000 rpm, 20 min) to separate the precipitate. Stirring was continued for another 10 min. The reaction mixture was then centrifuged (5000 rpm, 20 min) to separate the precipitate. Stirring was continued for another 10 min. The reaction mixture was then centrifuged (5000 rpm, 20 min) to separate the precipitate.

2.3. Electrospinning of PEI/PVP fibers

A solution of the polymers was prepared in ethanol such that the combined weight percentage of polymers in the solution was 8% and the ratio of weight percentages of PEI to PVP was 3:1. Electrospinning was carried out using an experimental setup shown in Fig. 1. The polymer solution was placed in a syringe, on which pressure was applied from a syringe pump. High voltage was applied between the syringe needle and a grounded metallic collector. Glass substrates were placed on the substrate to collect the electrospinning fibers. We observed that uniform and continuous fiber formation were obtained when we use a flow rate of 0.5 mL/h in the syringe pump, 13 kV voltage between the needle and collector, and 15 cm separation between them. Thickness of the fibers can be varied by using needles of different diameters and the amount of fiber deposited on the substrates can be controlled by using different deposition times. Typically, electrospinning times of between 30 s and 2 min were used to prepare samples with different densities of fibers on the surface.

2.4. Assembly of GO on PEI/PVP fibers

GO solution was prepared by dissolving GO flakes (8 mg/mL) in a solvent mixture of DMF and water (9:1) [44]. The mixture was sonicated for 3 h to ensure effective exfoliation and dispersion. Glass substrates containing electrospun PEI/PVP fibers on the surface were then kept immersed in the GO solution for 12 h. The substrates were subsequently rinsed with water two times to remove unbound GO and dried in air.

2.5. Reduction of GO on the PEI/PVP fiber template

Reduction of GO was based upon a published method [45] with minor modifications. Specifically, substrates containing GO on PEI/PVP fibers were placed inside a closed container along with hydrazine hydrate. The container was then heated in low pressure at 100 °C for 3 h, as these conditions were found to produce the most optimal reduction. After cooling, the substrates were rinsed with water and dried in air.

2.6. Instruments and characterization

Scanning electron microscopy (SEM) experiments were conducted with a JEOL (Tokyo, Japan) JSM-7400F scanning electron microscope. X-ray photoelectron spectroscopy (XPS) analysis was conducted using a Thermo Fisher ESCALAB 250 instrument with a basic pressure of 2 × 10⁻⁹ mbar. The samples were irradiated in two different areas using monochromatic Al Kα, 1486.6 eV X-rays, using a beam size of 500 μm. Conductivity measurements were performed on a Keithley 2400 sourcemeter in a two-probe configuration. For the sample preparation of electrical measurements, the substrate containing the gold film was mounted in a thermal evaporator with a stainless steel shadow mask attached. Cr (10 nm) and Au (90 nm) displayed amine residues). Following chemical reduction, an interspersed r-GO network was produced, yielding transparent/conductive films.

Fig. 1. Experimental scheme. Schematic representation of (a) Electrospinning and (b) assembly and reduction of GO on PEI/PVP fibers. (A colour version of this figure can be viewed online).
were evaporated onto the substrates to obtain the electrode patches at a predefined spacing. Raman spectroscopy measurements were carried out on a Jobin-Yvon LabRam HR 800 micro-Raman system, equipped with a Synapse CCD detector. The excitation source was an Argon laser (514.5 nm) with a power of 3 mW on the sample. In most of the measurements, the laser power was reduced by 10 using ND filters. The laser was focused with an ×100 objective to a spot of about 1 μm. The grating used was a 600 g mm⁻¹ and the measurement was done using a confocal hole of 100 μm with an exposure time of 1 min. Atomic force microscopy (AFM) and conductive-AFM (c-AFM) were conducted on MFP-3D-Bio setup from Asylum Research. A dual-gain ORCA holder (10⁶ and 10⁹ V/A), suitable for current sensing in the range of 1 pA to 1 and the circuit is closed when the tip is in contact with the conductive regions of the sample. Current from this circuit is measured for current mapping and I–V measurements.

3. Results

The new GO template-deposition strategy, designed to produce a fiber network enabling electronic transport and optical transparency, is depicted in Fig. 1. A polymer mixture comprising PEI and PVP was used to generate uniform microfibers through electrospinning (Fig. 1a). The rationale for using both PEI and PVP in this work was our observation that this particular polymer blend was PVP was used to generate uniform microfibers through electrospinning (Fig. 1a). The rationale for using both PEI and PVP in this work was our observation that this particular polymer blend was PEI/PVP template. Indeed, previous studies have demonstrated that PEI could induce self-assembly of GO through the electrostatic attraction between the polymer amine groups and the carboxylic acid moieties of GO [44].

Following the electrospinning procedure, the fibers were placed upon a transparent substrate, and subsequently immersed in a solution of GO flakes synthesized by modified Hummer’s method [42,43] (Fig. 1b). The GO flakes exhibited lateral dimensions of between 100 nm and 10 μm, thickness of 1 nm–1.5 nm, as is generally the case in chemical exfoliation procedures for GO synthesis [16] and their consistency and purity were confirmed through application of microscopy and Raman spectroscopy (Fig. S1, supplementary information). As depicted in Fig. 1b, since GO has negative surface charge due to the carboxylic groups present at the edges [22], the GO flakes are electrostatically attracted to the positive functional groups (amines and other nitrogen-containing units) upon the PEI/PVP fibers. In the final stage, the fiber-attached GO underwent chemical reduction upon brief exposure to hydrazine vapor, producing a conductive network of reduced-GO (r-GO) attached to the electrospun polymer template.

The GO/fiber network was microscopically and spectroscopically characterized (Figs. 2–3). Fig. 2 depicts representative scanning electron microscopy (SEM) images of the PEI/PVP electrospun fibers before and after r-GO assembly. Fig. 2a shows the bare polymer fibers, exhibiting diameters of between 500 nm and 2 μm. Selective attachment of GO to the fibers is evident in the SEM image presented in Fig. 2b (additional SEM results are shown in Fig. S2, supplementary information). While the GO particulates exhibit varied sizes, Fig. 2b demonstrates that the GO flakes trace the fiber template and almost no GO is present in the empty areas in between fibers. The dark appearance of the coated fibers in the SEM image in Fig. 2b and interfacial contacts between adjacent GO sheets indicates that a continuous GO network was formed upon the fibers. Specific attachment of GO to the polymer fiber template is further confirmed by AFM analysis (Fig. S3, supplementary information).

Fig. 3 presents spectroscopic data confirming the transformation of GO to r-GO on the polymer fiber template. Fig. 3a depicts Raman spectroscopy data displaying the characteristic G band corresponding to the first order scattering of the E₂g at 1590 cm⁻¹ and the D band corresponding to the lattice distortions at 1350 cm⁻¹ [46,47]. The increase in the ratio between the D and G peaks (i.e. increase in the intensity ratio I_D/I_G), apparent in Fig. 3a, is indicative of the reduction of GO to r-GO [46,47]. Raman analysis further confirmed that GO/r-GO flakes were present exclusively upon the polymer fibers (Fig. S4, supplementary information).

X-ray photoelectron spectroscopy (XPS) data (Fig. 3b) provide additional evidence for the reduction of GO upon the PEI/PVP fiber template. Specifically, the C 1s spectrum of the PEI/PVP/GO fiber system (Fig. 3b, left spectrum) can be deconvoluted into four components [48] corresponding to C–C (284.8 eV), C–O (286.3 eV), C=O (287.6 eV), and C(O)O (289.0 eV). Similarly, as depicted in Fig. 3b (right spectrum), the C 1s spectrum of PEI/PVP/r-GO was deconvoluted to five components [48] corresponding to C–C (284.8 eV), C=N (285.4 eV), C–O (286.4 eV), C=O (287.9 eV), and C(O)O (288.9 eV). Importantly, the XPS spectral analysis demonstrates that the relative intensities of the peaks corresponding to oxygen-bonded C atoms were lower compared to the deconvoluted C–C XPS peak, consistent with the reduction of GO to r-GO [46,48]. Indeed, significant increase in carbon-to-oxygen ratio, calculated

![Fig. 2. Selective attachment of GO to the polymer fibers. SEM images of (a) PEI/PVP fibers, and (b) r-GO on PEI/PVP fibers. The scale bars represent 20 μm in both images.](image-url)
Fig. 3. Spectroscopic characterization. (a) Raman spectra of PEI/PVP coated with GO (red) and r-GO (black). (b) XPS spectra of the C 1s region of PEI/PVP/GO and PEI/PVP/r-GO. The black spectra were the experimental results and the colored component peaks correspond to the carbon atoms in C–C (blue), C–O (red), C=O (magenta), C(O)O (green) and C=N (purple). (A colour version of this figure can be viewed online).

Fig. 4. Electrical conductivity of a single r-GO/polymer fiber. Conductive atomic force microscopy (C-AFM) measurements depicting current mapping of r-GO assembled upon PEI/PVP fibers (top image), and I–V curves measured at two locations indicated by arrows (bottom). (A colour version of this figure can be viewed online).
from the intensities of C1s peaks and O1s peaks in the XPS experiments, further confirms the reduction of GO to r-GO (Table S1, supplementary information). XPS spectra of bare PEI/PVP fibers (without attached graphene) show distinct positions of the carbon atoms in PEI and PVP that were different than in the GO-attached fiber samples (Fig. S5, supplementary information). Notably, the fact that no underlying polymer peaks were recorded in the GO/PEI/PVP samples (Fig. 3b) implies that the graphene coating is relatively thick. This conclusion is further supported by the absence of polymer peaks in the Raman spectrum (Fig. 3a).

Since r-GO is electrically conductive, the r-GO/fiber network is conducive to production of transparent/conductive films. Figs. 4 and 5 explores the electrical and optical properties of the films. Fig. 4 depicts results of conductive atomic force microscopy (C-AFM) experiment. To record the C-AFM image, the tip and the sample were electrically linked, providing simultaneous current and topography mapping in the contact mode. The representative C-AFM image together with linear $I-V$ curve reflecting Ohmic behavior of electron transport, which was recorded at the indicated location upon the fiber (Fig. 4i), indicate that the r-GO assembly upon the polymer scaffold endows conductivity to the individual r-GO/fiber. Note the lack of electrical conductivity outside of the r-GO/fiber ($I-V$ curve in Fig. 4ii); Current mapping experiment done on PEI/PVP fibers (Fig. S6, supplementary information) showed negligible contrast between the background and the fibers, providing further evidence that the conductivity in our samples is due to the presence of r-GO on the fibers.

While the C-AFM analysis in Fig. 4 reveals electrical conductivity at the level of single r-GO/polymer fibers, we also examined the macroscopic electrical and optical properties of the r-GO/fiber network (Fig. 5). Fig. 5a presents current–voltage ($I-V$) curves measured after evaporating gold contacts at a distance of 100 μm (through a shadow mask) on r-GO/polymer fiber film deposited on a glass substrate. The linear appearance of the $I-V$ curves indicates continuous electron pathways and effective electric conductance through the fiber-template r-GO network (i.e. Ohmic properties). Linear $I-V$ curves were recorded even in case of longer electrode distances (Fig. S7, supplementary information). Electrical conductivity of the films varied according to the density/coverage of fibers present. Films with greater concentrations of fibers exhibited higher conductivity due to more abundant electron transport pathways. Sheet resistances in the range of 10 kΩ/sq to 100 kΩ/sq were recorded in films having different densities of r-GO/fibers.

Fig. 5b depicts transmittance spectra recorded for samples prepared with different fiber concentrations. Representative photographs of r-GO/fiber films spectra are provided in Fig. S8, supplementary information. The transmittance spectra and images in Fig. 5b reveal that denser r-GO/fiber films gave rise to lower transparency (e.g. 65% transmittance at 550 nm). Overall, we recorded transmittance of between 65% and 90% (at 550 nm) in the r-GO/PEI/PVP films having different fiber concentrations. These results are ascribed to the fact that higher concentrations of the fibers attenuated light passage through the film and correspondingly limited transparency, as apparent in Fig. 5b. Table S2 correlates sheet resistance and transmittance in several films exhibiting different fiber densities. To investigate the influence of the GO flakes’ sizes upon conductivity, we carried out size separation of GO (dissolved in DMF:H2O at a 9:1 ratio) using centrifugation. Smaller GO flakes in the supernatant and bigger GO flakes in the residue were separately incubated with the polymer fibers. Notably, while the fibers coated with the larger GO sheet fraction were electrically conductive, samples prepared using the smaller GO sheet exhibited...
negligible conductivities. This result is attributed to the reported observations that smaller r-GO display low conductivity [49,50].

The new r-GO/polymer fiber films can be readily used for practical uses. The photographs in Fig. 5c depict a closed electrical circuit in which the r-GO/fiber film was positioned as a component within the circuit. A switch was then used to turn on/off an external voltage and a red LED bulb (top right) was employed to report passage of current in the circuit. The right photograph in Fig. 5c nicely demonstrates that the bulb could be turned on by applying voltage to the electrical circuit (i.e. turning on an electric switch), confirming effective charge transport through the r-GO/fiber film.

4. Discussion

We present a new approach for self-assembly of graphene oxide, using a physical template comprising electrospun polymer fibers. The thrust of the assembly process is the electrostatic attraction between the negatively-charged GO sheets and positive residues upon the polymer fibers. The fiber-template GO sheets can be easily and effectively reduced, producing a network of conductive r-GO network. Importantly, optical transparency of the r-GO films was directly related to the specific attachment of GO to the polymer fiber framework (rather than randomly upon the film surface) – generating abundant empty regions within the films which enable light transmission.

While diverse methodologies for production of “bottom-up” (i.e. self-assembled) graphene films have been reported, most such techniques face significant hurdles, particularly with regard to the tradeoff between electrical conductivity and optical transparency [25,51–53]. Specifically, to attain good conductivity - i.e. useful sheet resistances - multiple layers of r-GO have been usually required, resulting in significant reduction of light transmittance. For example, in a widely-cited publication reporting fabrication of self-assembled r-GO films through spin coating and subsequent reduction, sheet resistances in the range of $10^3 \ \Omega \ \text{sq}^{-1}$ were recorded for samples of maximal 40% transparency at 550 nm [25,51]. Indeed, in that study sheet resistance increased by approximately two orders-of-magnitude for films exhibiting transmittance of around 90% [25,51]. This conundrum highlights the fact that conductivity can be improved by increasing the thickness of r-GO while severely compromising the optical transparency. The system reported here, however, partly surmounts this conductivity/transparency tradeoff since graphene does not uniformly coat the surface but rather the GO sheets only trace the polymer fiber network, thereby generating abundant empty spaces that enable light passage (i.e. optical transparency). Indeed, the use of electrospun polymer fibers as a physical template for GO assembly provides a means for conductivity/transparency modulation through varying the density of deposited fibers.

An additional notable feature of the fiber-template graphene films is the simplicity of the assembly process, both conceptually and technically. Essentially, the technique utilizes conventionally-synthesized GO sheets that are electrostatically-targeted to the surface of polymer fibers produced through electrospinning – a powerful and easy to apply technology for generating large quantities of elongated fibers. Utilization of electrospinning for assembling the GO template points to potential applications of the technique for construction of transparent and conductive films even upon non-planar surfaces, since electrospun polymer fibers can be deposited on such substrates [54,55]. As a consequence of the use of readily available building blocks, which furthermore involve coating only a fraction of the surface area, very small reagent quantities are needed. The GO solution, in fact, can be reused several times as only a small concentration of the material is required for effective deposition upon the fibers.

Very few studies successfully integrated polymer fibers and graphene systems [22]. While electrospun polymer fibers have been previously used as templates for graphene [39,41], such fibers have been used as physical scaffolds for GO, not as a platform for creating transparent, conductive films. Recent studies reporting the use of electrospun fibers for generating GO-based conductive films required chemical derivatization of the fiber surface [40] or GO [56], both constitute significantly more complex and elaborate schemes compared to the assembly approach presented here.

Several important aspects in the GO/polymer self-assembly process should be highlighted. Specifically, the absence of PEI/PVP-associated peaks in the Raman and XPS data in Fig. 2, complemented by the AFM analysis in Fig. S3, indicate a relatively thick GO coating upon the polymer fibers, likely comprising several layers of GO sheets. Such multi-layered coating might appear surprising since electrostatic attraction (which is inversely proportional to distance) is presumed to induce GO attachment. It has been reported, however, that PEI, which comprises of the amine-displaying component within the electrospun polymer fibers, gave rise to diffusion-induced self-assembly of GO, similarly giving rise to multiple layers of GO upon the polymer surface [44]. We hypothesize that this mechanism also plays a significant role in the assembly process of GO upon the polymer fibers.

Several experimental parameters were shown to affect the conductivity and transparency of the GO/polymer fiber films. The degree of GO coating, determined by both graphene concentration and incubation time of GO with the polymer fibers, intimately affected the conductivity, likely due to the extent of coating and thickness of the GO layer attached to the polymer surface. Furthermore, the conductivity/transparency profiles of the GO films (e.g. Fig. 5) highlight the significance of electrospinning time as a primary parameter. Specifically, the duration of electrospinning affects fiber density which constitutes a major factor responsible for both enabling electron transport (i.e. inducing conductivity), as well as optical transparency (as light can be transmitted through the empty spaces between the surface-deposited fibers).

5. Conclusions

In conclusion, we present a new methodology for directed self-assembly of graphene oxide (GO), using electrospun polymer fibers as a physical template. Driving the assembly process is the electrostatic attraction between the negatively-charged GO (specifically the carboxylic moieties displayed upon the GO edges) and the positive surface charge upon the polymer fibers (through amines and nitrogen-containing groups). Following chemical reduction of the fiber-templated GO assembly, we demonstrated formation of a continuous network of reduced GO (r-GO) which traced the electrospun polymer fibers. The r-GO network exhibited electrical conductivity from the level of single r-GO-coated fibers to the macroscale – yielding large area conductive films. Such films were furthermore transparent, on account of the fiber organization displaying sizeable empty surface areas enabling light transmittance. Importantly, both conductivity and transparency could be modulated by the density of deposited polymer fibers. The new template-directed self-assembly approach is easy to apply, does not require expensive reagents nor sophisticated instrumentation, and could open the way to varied electro-optic applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbonyl.2015.09.021.

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