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**A new facile route to flexible and semi-transparent electrodes based on water exfoliated graphene and their single electrode triboelectric nanogenerator**

*Dong-Wook Shin, Matthew D. Barnes, Kieran Walsh, Dimitar Dimov, Peng Tian, Ana I. S. Neves, C. David Wright, Seong Man Yu, Ji-Beom Yoo, Saverio Russo, and Monica F. Craciun\**

Dr D.-W. Shin, Dr M. D. Barnes, K. Walsh, D. Dimov, Dr P. Tian, Dr A. I. S. Neves, Prof C. D. Wright, Prof S. Russo, Prof M. F. Craciun  
Centre for Graphene Science, College of Engineering, Mathematics and Physical Sciences,  
University of Exeter, Exeter, EX4 4QL, UK  
E-mail: m.f.craciun@exeter.ac.uk

Dr S. M. Yu, Prof J.-B. Yoo  
SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon,  
16419, Republic of Korea

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Flexible and wearable electronics is underpinning the development of future healthcare and communication technologies through seamless, non-invasive remote sensing platforms. Recent advances on wearable energy harvesting technologies are now projecting this research field to the new frontiers of self-powered electronics for which novel high-performance materials and low-cost fabrication processes are highly sought. Graphene, which exhibits remarkably high specific surface area, thermal conductivity, current density, transparency, and impermeability,<sup>[1]</sup> is an ideally suited system for exploring conceptually novel flexible electronics including energy harvesting devices.<sup>[2]</sup> An easy and scalable approach for graphene preparation is the liquid-phase exfoliation of chemically functionalised graphite, such as graphite oxide or graphite intercalated compounds, which allows the separation of the bulk material into individual atomically thin layers in a liquid medium to produce graphene suspensions. However, there are several issues associated with the films deposited from such

suspensions, especially those comprising graphene oxide (GO): they are insulating and need to be converted into reduced graphene oxide (rGO) through harsh chemical or thermal processes,<sup>[3]</sup> which creates defects in the crystallographic structure of graphene, leading to poor electronic performance. Alternatively, pristine graphite (PG) can be directly exfoliated by various techniques such as ball or three-roll milling, sonication, and high-shear mixing to obtain graphene suspensions.<sup>[4,5]</sup> Such suspensions are stabilised by using organic solvents,<sup>[6]</sup> or surfactants to prevent reaggregation of the graphene flakes.<sup>[7]</sup> In particular, PG exfoliation by high-shear mixing leads to a significant improvement in the quality of graphene, when compared with other exfoliation methods, and allows the production of more than 100 litres per hour of defect-free graphene water-based suspension.<sup>[5,8]</sup>

Despite the recent developments in the production of graphene suspensions, the integration of high-quality graphene films obtained from water-based exfoliation of PG in emerging applications, such as flexible electronics, is lagging behind. Specifically, emerging and integrating technologies of water-based exfoliation of PG for harnessing human energy that convert mechanical energy into electricity using various effects are still in its infancy, and more research is needed to develop and implement triboelectric nanogenerators as self-charging devices for flexible and wearable electronics. This is due to several issues associated with the deposition or transfer of the resulting graphene films onto flexible substrates. Deposition methods such as ink-jet, screen and gravure printing have been recently demonstrated. These techniques require the incorporation of additives (e.g. polymers) to adjust the level of viscosity, negatively affecting the electrical and optical properties of the graphene films<sup>[9]</sup>, and requiring annealing at high temperatures to remove them. Furthermore, such high temperatures are not compatible with substrates such as paper, textiles and plastic. Therefore, the development of deposition methods of graphene films on a desired substrate without additives is required for the advancement of graphene based flexible electronics.

Vacuum filtration has been widely utilized to allow the fabrication of flexible and wearable electronics, and it has been used for the deposition of films of carbon nanotubes and graphene.<sup>[9-12]</sup> rGO is usually a target material, and the transfer is done via a “fishing” method, in which the floating film is lifted by the target substrate,<sup>[12]</sup> pressed onto the top of filter,<sup>[9,13,14]</sup> and the filter subsequently dissolved in acetone<sup>[15]</sup>. Despite the advances in the transfer of GO using vacuum filtration, it is challenging to control the thickness and increase the transfer efficiency for graphene thin-films from PG exfoliation. Therefore, it is important to find a versatile way to assemble graphene thin-films using vacuum filtration.

Herein, we show a facile, effective, and reproducible way to transfer water exfoliated graphene films onto a wide range of flexible and rigid substrates and its single electrode triboelectric nanogenerator (SE-TENG) for the very first time. PG flakes were exfoliated by high shear mixing in water with sodium cholate (NaC - a salt of the naturally occurring cholic acid) as a surfactant, in an industrially and environmentally friendly method (Shear exfoliated graphene, SEG). We developed a novel method for the assembly of SEG films, comprising an isopropyl alcohol (IPA)-assisted direct transfer (IDT) process, deriving from IPA evaporation. We demonstrate that SEG flakes in solution can be easily transferred by IDT to any target substrate such as paper, flexible polymeric sheets and fibres, glass, and Si substrates for further applications. The remaining post-transfer sodium cholate, which is an insulating material, is simply washed out from the surface of SEG by dipping in water, so that it does not affect the electronic properties of graphene. Finally, by combining a single SEG electrode and polydimethylsiloxane (PDMS) as active layer we demonstrate for the first time a flexible and semi-transparent triboelectric nanogenerator (TENG) for harvesting energy. This will pave the way to a new generation of TENG devices, which will benefit from the outstanding physical properties of graphene as well as a scalable, reproducible, environment-friendly and cost-effective route to self-powering wearable devices.

Water-based graphene suspensions were obtained by shear exfoliation of graphite flakes without any chemical treatment<sup>[14,16]</sup>, harsh conditions<sup>[15,17]</sup>, or solvent exchanges<sup>[18]</sup>. Graphite flakes and sodium cholate powder as the surfactant are mixed in deionized water, and then exfoliated by a high-speed rotation of a shear mixer<sup>[5]</sup>, as depicted in Figure 1a (for more details see experimental section in Supporting information). The concentration of the obtained SEG suspensions can be readily varied by controlling the shear exfoliation time (see Figure 1b and Supporting information Figure S1). The obtained SEG sheets have the average lateral size of ~110 nm and average thickness of 4 layers, with about 50% containing 1, 2, or 3 layers (Supporting Information Figure S2). SEG thin-films were obtained by filtrating the water suspensions through a membrane. We have developed the new, facile, effective, and reproducible IDT method to transfer the SEG thin-films from the filtration membrane to other substrates (Figure 1c,d and Experimental Section in Supporting information). The IDT method relies on the evaporation of IPA to separate the film from the membrane, and incomplete evaporation will prevent the release of the film in the wet areas, showing the role of IPA evaporation in the film release process (Supporting information Figure 3S). Additionally, IDT is achieved here from room temperature (RT) to 90 °C, and we have found a logarithmic linear relation between IPA evaporation time and vapor pressure ( $\ln(t)$  vs.  $-\ln(P)$ , Supporting information Figure S4). We suggest that intrinsic properties of IPA such as a low surface tension, high vapor pressure, and high solubility in water<sup>[19]</sup> drive SEG films toward the substrate rather than the membrane. This is because IPA can easily wet every SEG sheet surrounded by NaC and water molecules (second step in Figure 1c)<sup>[20]</sup>, while the initial IPA evaporating near the surface of the target substrate leads to the creation of an intimate contact of the SEG sheets on the substrate (third step in Figure 1c, for more details see Mechanism of IDT in Supporting information). We have successfully transferred SEG films onto flexible and rigid substrates: polyethylene terephthalate (PET), glass, paper, SiO<sub>2</sub>/Si, and polypropylene (PP) textile fibres, as shown in Figure 1e-i, which demonstrates that the IDT method is versatile, quick (under 1

minute at 90 °C), and can even be done at room temperature and be applicable to a transition metal di-chalcogenide (TDMC), such as WS<sub>2</sub> (Supporting information Figure S3c). In particular, both hydrophilic (glass and SiO<sub>2</sub>/Si) and hydrophobic (PET and PP) substrates were coated using this method, with no surface energy modification needed, and only slight discontinuities appearing due to surface roughness, as shown in Figure 1g.

The SEG films fabricated by the IDT method were characterized in terms of their electrical properties, which can be easily tuned by varying the amount of suspension filtered through the membranes.<sup>[9-12,14-16]</sup> Specifically, the sheet resistance of the films (as low as 152.7 ohm/sq) depends on their thickness, which can be confirmed by the change in optical transmittance at 550 nm and the thickness measurement, (Figure 2a and Supporting information Figure S5). The presence of residual NaC in the films will result in an increase of resistance, which is readily overcome by a simple water-dipping treatment. Figure 2b shows that the sheet resistance of SEG films with 73.5, 58.2, and 44.5% transmittance as the function of water treatment time. The sheet resistance of as-prepared SEG films dramatically reduced after the water treatment for 1 h. Above 2 h, their sheet resistance is almost saturated, showing an improvement of over 70%. In particular, regardless of the difference of initial sheet resistance (or transmittance), the same trend observed. To assess the stability of the SEG films after removal of NaC, we measured the sheet resistance upon exposure to air for 15 days following the water treatment, finding that the electrical properties of the film were preserved in air (Supporting information Figure S6). Additionally, we found that the conductivity of SEG film is enhanced by the newly developed IDT method by comparing the film electrical properties deposited on the membrane and after its transfer on glass (Supporting information of Figure S7). We measured the transport characteristics of randomly stacked SEG films with 57% (thin) and 31% (thick) transmittance transferred by IDT to SiO<sub>2</sub>/Si substrates, in a wide range of temperatures (4.5 K to RT), before and after water treatment (Figure 2c). We observed that the thin SEG film has a more markedly semiconducting-like behavior than the thick film. This is

an indication that the electrical transport mechanisms in the films can be changed from semiconducting to metallic by varying the film thickness.<sup>[21]</sup> A detailed study of the temperature dependence of the electrical conductivity revealed that the Mott's two-dimensional variable-range hopping (2D-VRH)<sup>[22]</sup> dominates for low temperatures (4.5-180 K) whilst an Arrhenius-like dependence was found at higher temperatures (180 K to RT). Notably, the extracted characteristic energies indicate that residual NaC does not affect the electronic structure of SEG (section on Transport Properties (Figure S8) on Supporting information).

To further understand the effect of NaC residues and washing procedure, as-prepared and washed films (for 2 and 4 h) were transferred onto SiO<sub>2</sub>/Si and characterized by X-ray photoelectron spectroscopy (XPS). To accurately evaluate the presence of NaC, we looked at the variation of C 1s and Na 1s in the XPS spectra (Figure 2d-f and section on Characterization of washed SEG film by XPS on Supporting information). We observed a minute change in the atomic concentration (at%) of most C 1s species, indicating that the chemical structure of SEG does not change with the water treatment, with the exception of a small change in sp<sup>3</sup> (C–C) and hydroxyl carbons, which are the most abundant carbon species in NaC (Figure 2e and Supporting information Table S1). Additionally, the removal of NaC is confirmed by the Na 1s spectra (Figure 2f and Supporting information Figure S9),<sup>[23]</sup> which show Na at% changes from 1.12 to 0.65 at% after 2 h and to 0.32 after 4 h of water treatment. The quality of SEG flakes can be relatively evaluated by estimating the ratio of sp<sup>3</sup>/sp<sup>2</sup> hybridized carbon via the C 1s spectra, since sp<sup>3</sup> carbon is regarded as a defective site in the honeycomb lattice of sp<sup>2</sup> carbon atoms.<sup>[24,25]</sup> We have obtained a sp<sup>3</sup>/sp<sup>2</sup> ratio of 0.17 (Figure 2e), lower than that of HOPG and graphite, which are 0.18 and 0.33, respectively,<sup>[24,25]</sup> which is an indication that the SEG flakes have an excellent basal plane quality. The tails of C 1s spectra with carbon-oxygen species are related to small undissolved NaC residues between the stacked SEG flakes and their oxidized edge.<sup>[26-28]</sup>

The crystallinity, doping level, and strain at different locations in the graphene films were evaluated by Raman spectroscopy<sup>[29]</sup> (Supporting information Figure S10). In general, the charge transfer (doping) by physisorption of dopant molecules on graphene can be confirmed by shifts in the G-band position and in the binding energy of C 1s in XPS.<sup>[30,31]</sup> We believe there is no charge transfer between SEG and the residual NaC, since we only observe a  $\sim 1 \text{ cm}^{-1}$  blue shift in the G-band position upon water treatment (Figure 2g), as well as no shift in XPS binding energy. This is consistent with the fact that while the insulating NaC is stabilizing the SEG flakes in water, it is merely adsorbed on the surface of SEG flakes in the films, leading to an increase in the heterogeneous junction resistance and charge trapping from the graphene. The position of introduced defects on graphene can be estimated by the intensities ratio of D and D'-bands.<sup>[5]</sup> Before shear exfoliation, graphite flakes already exhibit basal plane defects ( $I(D)/I(G) = \sim 0.056$ ), and SEG flakes produced from them by shear exfoliation and centrifugation process have an  $I(D)/I(G)$  ratio of  $\sim 0.54$ , which does not change significantly upon water treatment. Plotting  $I(D)/I(G)$  vs.  $I(D')/I(G)$ , we observe a linear behaviour with  $I(D)/I(D') \sim 4.6$ , as shown in Figure 2h, which is just above the expected ratio for edge defects only ( $3 \leq I(D)/I(D') \leq 4.5$ ).<sup>[5]</sup> This suggests some contribution from vacancy defects (see Supporting information Figure S10b), and we believe these come from the starting graphite and are not introduced in the basal plane by the shear exfoliation, which is in agreement with the Raman and XPS data.

Finally, we fabricated a flexible and semi-transparent single electrode triboelectric nanogenerator (SE-TENG) combining a SEG film transferred onto PET by the IDT method and PDMS formed by drop casting. In these devices, the combined action of the triboelectric effect and electrostatic induction enables the conversion of mechanical energy into electrical energy in a reliable and efficient manner even on mechanically flexible substrates.<sup>[32-35]</sup> We show for the very first time the integration of high-quality SEG films obtained from water exfoliated solution processing approaches into TENG devices. Figure 3a shows a schematic that is a

mechanism to generate electricity from SEG SE-TENG device. Surface of PDMS and the fingers (covered with a latex glove<sup>[36]</sup>) as triboelectric layers with a neutral charge in an initial state (I) is charged negatively and positively, respectively, according to triboelectric series<sup>[33,36]</sup> when both surfaces are fully contacted (Full contact, C), which is the contact triboelectrification process. After then, during Releasing (R1) the fingers, SEG electrode can be positively induced by negative charges on the PDMS due to an electrostatic induction, resulting in electrons flow to the ground. After passed process of Full released (R2) that the fingers are away from the PDMS, when the fingers are approaching (A) on the surface of PDMS, electrons flow from the ground to the SEG electrode due to electrostatic induction between fingers and PDMS (See details in Supporting information). Positive and negative open circuit voltage ( $V_{OC}$ ), and short circuit current ( $I_{SC}$ ) pulses of 1.08 V and 0.25  $\mu A$  were registered for the “Approaching (A)” and “Releasing (R1)” modes. (Figure 3b).<sup>[36]</sup> After increasing the electronegativity of the PDMS through the fluorination in  $SF_6$  plasma (see Supporting information Figure S11),<sup>[37,38]</sup> we obtained a  $V_{OC}$  as large as 4.98 V and  $I_{SC}$  of 0.52  $\mu A$ , corresponding to an increase of 461% and 208%, respectively. Additionally, under a flexible state (bent), we obtained a  $V_{OC}$  as large as 4.69 V and  $I_{SC}$  of 0.652  $\mu A$ , and higher performance on fluorinated TENG as a flat fluorinated TENG (Supporting information Figure S12). We seemed to be additional contact and releasing actions between the SEG film and PDMS film under a flexible state by fingers. XPS confirmed the fluorination, with F changing from zero to 12.9 at% following a 60 s plasma treatment (Supporting information Figure S11d). The SE-TENG capability to generate electricity was further demonstrated by connecting it to 5 LEDs under releasing and approaching mode (Figure 3c-e). Our developments for TENG integrated with SEG nanosheets will open new possibilities for a vast scientific and industrial community. Such advancements will have a transformative development in the internet of things and can project flexible electronics to new frontiers, benefitting a wide range of sectors spanning from information

technology, medical diagnostics, health monitoring, through to manufacturing, high-performance materials, energy and environmental technologies.

In summary, we demonstrated that an environmentally friendly and industrially scalable production of graphene suspensions by shear exfoliation of graphite in water can be used to produce thin films by vacuum filtration. These films can be easily deposited onto arbitrary substrates with a newly developed IPA-assisted direct transfer (IDT) method, with the residual surfactant simply removed by dipping the films in water. We have used these films to fabricate a flexible and semi-transparent triboelectric nanogenerator, in which the SEG film on PET was used as a single electrode and PDMS as the active layer. The performance of these devices can be greatly improved upon a SF<sub>6</sub> plasma treatment of the PDMS, with the devices capable of powering up LEDs from the energy harvested by the motion of a human finger. Our results constitute a new step towards the realisation of energy harvesting devices that could be integrated with a wide range of wearable and flexible technologies, and opens new possibilities for the use of triboelectric nanogenerators in many applications such as electronic skin and wearable electronics.

### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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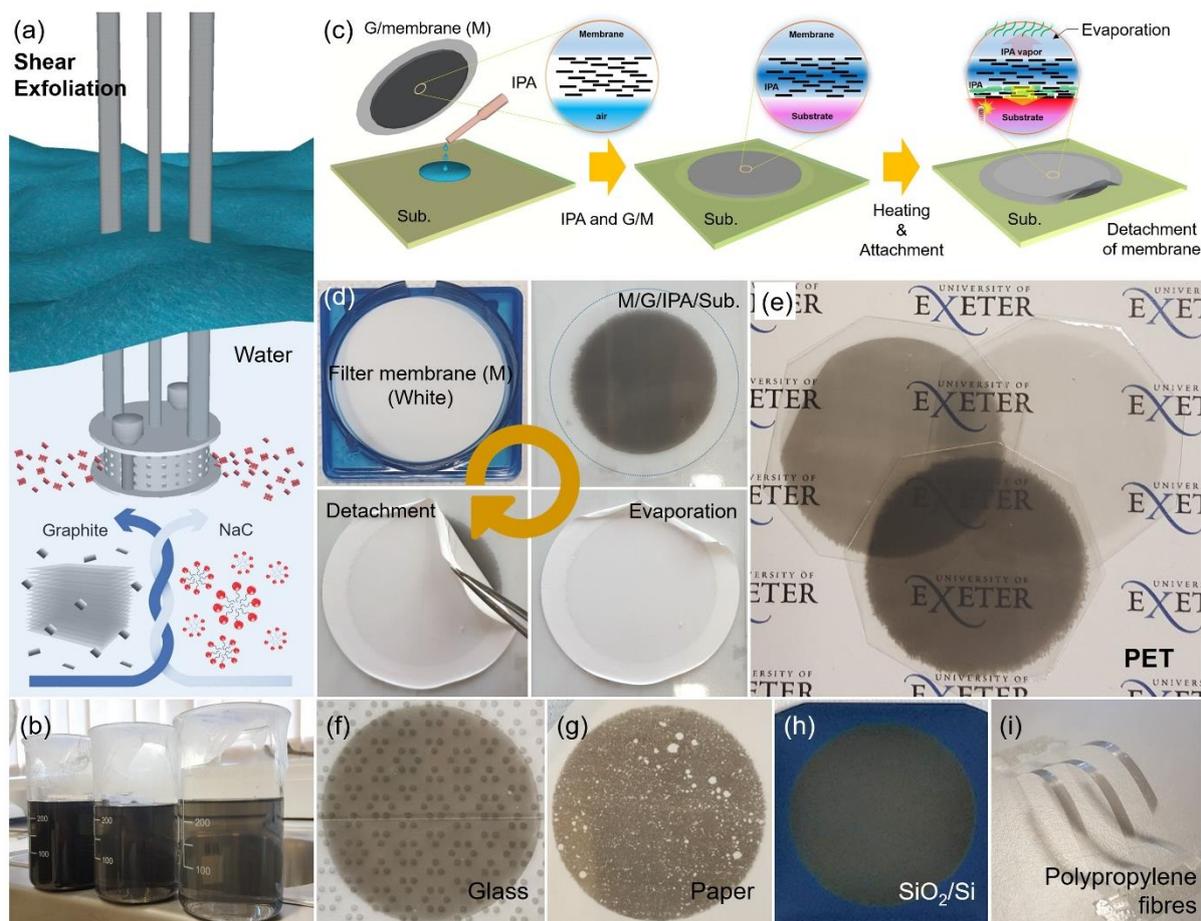
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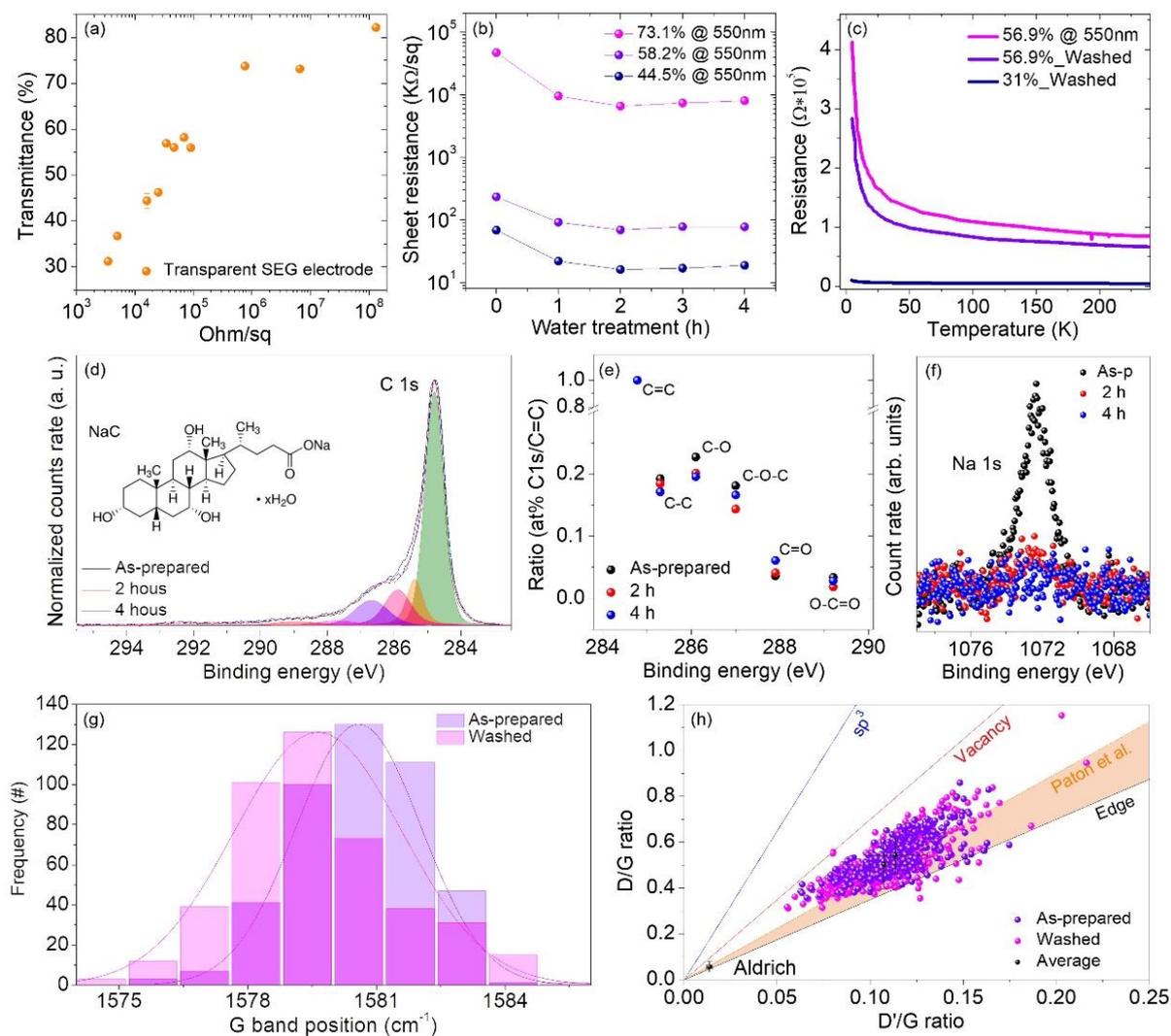
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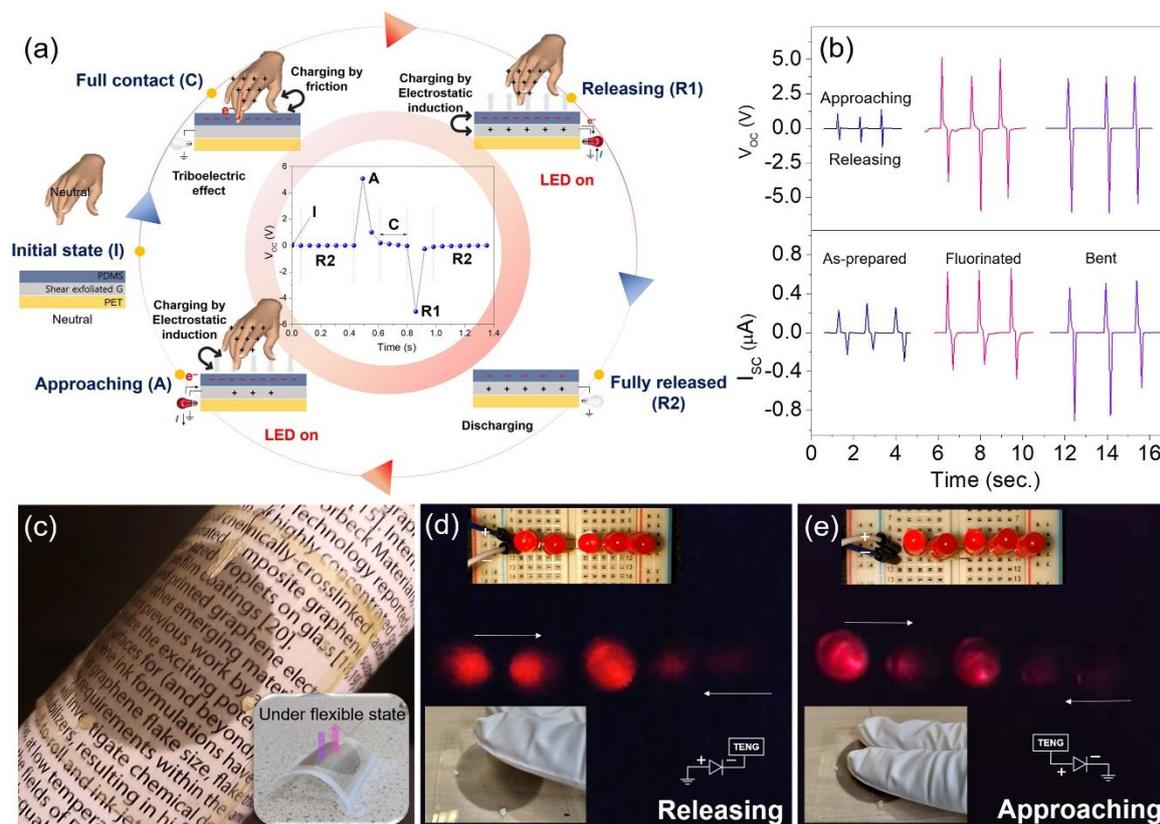
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**Figure 1.** Shear exfoliation of graphite in water and IPA-assisted direct transfer (IDT) method. a) Schematic of shear exfoliation of graphite flakes in water with sodium cholate by high-speed rotation of shear mixer head. b) Photograph of shear-exfoliated graphene (SEG) suspensions with different concentrations, controlled by shear exfoliation time (10, 30, and 60 min). c) Schematics and d) photographs of IDT method. SEG film on filter membrane (hydrophilic PTFE) is simply put on a substrate wetted with IPA (“M/G/IPA/Sub.” in c and d), and heated at 90°C. When IPA between membrane/graphene and substrate evaporates the membrane becomes white (“Evaporation” in d). The membrane is detached from graphene/sub. (“Detachment” in c and d), leaving the SEG film on different substrates such as: e) PET, f) glass, g) paper, h) SiO<sub>2</sub>/Si, and i) PP fibres.



**Figure 2.** Removal of NaC by water treatment and crystallinity of SEG film. a) Sheet resistance vs. transmittance at 550 nm for SEG films treated with water for 2 h. b) Sheet resistance as a function of water treatment for films with different thickness, saturating after 2 h. c) Resistance dependence with temperature for thin and thick SEG films before and after water treatment. d) XPS spectra of SEG films as-prepared and washed for 2 h and for 4 h. The C 1s peak consists of six components:  $sp^2$  carbon (C=C) at 284.78 eV,  $sp^3$  carbon (C-C) at 285.3 eV, hydroxyl carbon (C-O) at 286.1 eV, epoxy carbon (C-O-C) at 287.0 eV, carbonyl carbon (C=O) at 287.9 eV, and carboxylate carbon (O-C=O) at 289.2 eV. The inset shows the molecular structure of NaC. e) Ratio of  $sp^3/sp^2$  hybridized carbon for the various C bond configuration extracted from the peaks of the C 1s spectra in (d) before and after water treatment (note that for the C=C bonds the black, red, and blue dots overlap). f) XPS spectra of Na 1s before and after water treatment. g) Dispersion of G band positions for all samples before and after water treatment, with a shift of  $1\text{ cm}^{-1}$ . h)  $I(D)/I(G)$  vs.  $I(D')/I(G)$  ratio to estimate the defect position on SEG flakes.



**Figure 3.** Flexible and semi-transparent single electrode triboelectric nanogenerator (SE-TENG) device comprising a PDMS and SEG-coated PET film by IDT. a) Schematic of the working principle of a SE-TENG device. b) Open circuit voltage ( $V_{OC}$ ) and short circuit current ( $I_{SC}$ ) of as-prepared,  $SF_6$  plasma-treated for 60s, and bent device, showing significant improvement. c) Photograph of flexible and semi-transparent device and the bent device in the inset. d) and e) Photographs of LEDs turning on upon "Releasing (R1)" and "Approaching (A)" actions. Blue and white wires are connected to ground and TENG device, respectively. "+" and "-" are the direction of LED and photographs of each action by fingers with latex on the SE-TENG device (inset).

**Table of contents (TOC)**

**Shear exfoliated graphene integrated into flexible and semi-transparent triboelectric nanogenerator is developed by using a new facile isopropanol-assisted direct transfer method.** Environmentally and industrially preferred graphene solutions in water are obtained by shear exfoliation. Their graphene flakes are transferred onto a wide range of substrates such as PET, paper, fibers, glass, SiO<sub>2</sub>/Si driven by the transition of isopropanol liquid to vapor.

**Keyword: shear exfoliated graphene, transfer, sodium cholate, water, triboelectric nanogenerator**

D.-W. Shin, M. D. Barnes, K. Walsh, D. Dimov, P. Tian, A. I. S. Neves, C. D. Wright, S. M. Yu, J.-B. Yoo, S. Russo, M. F. Craciun\*

**Title: A new facile route to flexible and semi-transparent electrodes based on water exfoliated graphene and their single electrode triboelectric nanogenerator**

