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*

Flexible and wearable electronics is underpinning the development of future healthcare and communication technologies through seamless, noninvasive 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,[1] is an ideally suited system for exploring conceptually novel flexible electronics including energy harvesting devices.[2] An easy and scalable approach for graphene preparation is the liquid-phase exfoliation of chemically functionalized 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,[3] 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.[4,5] Such suspensions are stabilized by using organic solvents,[6] or surfactants to prevent reaggregation of the graphene flakes.[7] 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 L h⁻¹ of defect-free graphene water-based suspension.[5,8]

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 harvesting 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 (TENGs) 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, and requiring annealing at high temperatures to remove them. Furthermore, such high temperatures are not compatible with flexible 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.\(^\text{[9-12]}\) 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, and the filter subsequently dissolved in acetone.\(^\text{[15]}\) 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 isopropanol 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 fibers, 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 poly(dimethylsiloxane) (PDMS) as active layer we demonstrate for the first time a flexible and semi-transparent 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,\(^\text{[14,16]}\) harsh conditions,\(^\text{[15,17]}\) or solvent exchanges.\(^\text{[18]}\) 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, as depicted in Figure 1a (for more details, see Experimental Section, Supporting Information). The concentration of the obtained SEG suspensions can be readily varied by controlling the shear exfoliation time (see Figure 1b and Figure S1, Supporting Information). The obtained SEG sheets have the average lateral size of \(\approx 110 \text{nm}\) and average thickness of four layers, with \(\approx 50\%\) containing one, two, or three layers (Figure S2, Supporting Information). SEG thin-films were obtained by filtering 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, 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 (Figure S3, Supporting Information). Additionally, IDT is achieved here from room temperature (RT) to \(90^\circ\text{C}\), and we have found a logarithmic linear relation between IPA evaporation time and vapor pressure (\(\text{ln}(t)\) vs \(\text{ln}(P)\), Figure S4, Supporting Information). We suggest that intrinsic properties of IPA such as a low surface tension, high vapor pressure, and high solubility in water\(^\text{[19]}\) 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),\(^\text{[20]}\) 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, Supporting Information). We have successfully transferred SEG films onto flexible and rigid substrates: poly(ethylene terephthalate) (PET), glass, paper, \(\text{SiO}_2/\text{Si}\), and polypropylene (PP) textile fibers, as shown in Figure 1e–i, which demonstrates that the IDT method is versatile, quick (under 1 min at \(90^\circ\text{C}\)), and can even be done at RT and be applicable to a transition metal dichalcogenide (TDMC), such as \(\text{WS}_2\) (Figure S3c, Supporting Information). In particular, both hydrophilic (glass and \(\text{SiO}_2/\text{Si}\)) 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.\(^\text{[9-12,14-16]}\) Specifically, the sheet resistance of the films (as low as 152.7 ohm sq\(^{-1}\)) depends on their thickness, which can be confirmed by the change in optical transmittance at 550 nm and the thickness measurement, (Figure 2a and Figure S5, Supporting Information). 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 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 is 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 (Figure S6, Supporting Information). 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 onto glass (Figure S7, Supporting Information). We measured the transport characteristics of randomly stacked SEG films with 57% (thin) and 31% (thick) transmittance transferred by IDT to SiO₂/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.\[21\] A detailed study of the temperature dependence of the electrical conductivity revealed that the Mott's 2D variable-range hopping (2D-VRH)\[22\] 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 and Figure S8, Supporting Information).

To further understand the effect of NaC residues and washing procedure, as-prepared and washed films (for 2 and 4 h) were obtained on SiO₂/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, 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 sp³ (C=C) and hydroxyl carbons, which are the most abundant carbon species in NaC (Figure 2e and Table S1, Supporting Information). Additionally, the removal of NaC is confirmed by the Na 1s spectra (Figure 2f and Figure S9, Supporting Information), which show Na at% changes from...
1.12 to 0.65 at% after 2 h and to 0.32 at% after 4 h of water treatment. The quality of SEG flakes can be relatively evaluated by estimating the ratio of sp\(^3\)/sp\(^2\) hybridized carbon via the C 1s spectra, since sp\(^3\) carbon is regarded as a defective site in the honeycomb lattice of sp\(^2\) carbon atoms.\(^{[24,25]}\) We have obtained an sp\(^3\)/sp\(^2\) ratio of 0.17 (Figure 2c), lower than that of highly ordered pyrolytic graphite (HOPG) and graphite, which are 0.18 and 0.33, respectively.\(^{[24,25]}\) 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.\(^{[26–28]}\)

The crystallinity, doping level, and strain at different locations in the graphene films were evaluated by Raman spectroscopy\(^{[29]}\) (Figure S10, Supporting Information). 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.\(^{[30,31]}\) We believe there is no charge transfer between SEG and the residual NaC, since we only observe an ≈1 cm\(^{-1}\) blueshift 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.\[5\] Before shear exfoliation, graphite flakes already exhibit basal plane defects (I(D)/I(G) \approx 0.056), and SEG flakes produced from them by shear exfoliation and centrifugation process have an I(D)/I(G) ratio of \approx 0.54, which does not change significantly upon water treatment. Plotting I(D)/I(G) versus I(D')/I(G), we observe a linear behaviour with I(D)/I(D') = 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).\[5\] This suggests some contribution from vacancy defects (see Figure S10b, Supporting Information), 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 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,\[32–35\] 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\[36\]) as triboelectric layers with a neutral charge in an initial state (I) is charged negatively and positively, respectively, according to triboelectric series\[33,36\] when both surfaces are fully contacted (Full contact, C), which is the contact triboelectrification process. Afterward, 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 μA were registered for the “Approaching (A)” and “Releasing (R1)” modes. (Figure 3b).\[36] After increasing the electronegativity of the PDMS through the fluorination in SF$_6$ plasma (see Figure S11, Supporting Information),\[37,38] we obtained a $V_{OC}$ as large as 4.98 V and $I_{SC}$ of 0.52 μA, 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 μA, and higher performance on fluorinated TENG as a flat fluorinated TENG (Figure S12, Supporting Information).

It seemed to be additional triboelectrification process between the SEG and PDMS film under a flexible state by fingers. XPS confirmed the fluorination, with F changing from 0 to 12.9 at% following a 60 s plasma treatment (Figure S11d, Supporting Information). The SE-TENG capability to generate electricity was further demonstrated by connecting it to five 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 have 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 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 TENG, 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$_6$ 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 toward the realization of energy harvesting devices capable of powering up LEDs from the energy harvested by the motion of a human finger. Our results constitute a new step toward the realization of energy harvesting devices capable of powering up LEDs from the energy harvested by the motion of a human finger.

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

Acknowledgements
The authors acknowledge financial support from the European Commission (H2020-MSCA-IF-2015-704963), the UK Engineering and Physical Sciences Research Council (EPSRC) (Grant no. EP/K017160/1, EP/K010050/1, EP/M001024/1, and EP/M002438/1), the EPSRC Centre for Doctoral Training in Metamaterials (EP/L015331/1), the Royal Society International Exchanges Scheme 2016/R1, and the Leverhulme Trust (Grant “Quantum Revolution”).

Note: The definition of $V_{OC}$ on this page was added on September 21, 2018, after initial publication online.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
shear exfoliated graphene, sodium cholate, transfer, triboelectric nanogenerator, water

Received: May 8, 2018
Revised: July 23, 2018
Published online: August 23, 2018

[1] a) A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Xiao, C. N. Lau, Nano Lett. 2008, 8, 902; b) R. Murali, Y. Yang, K. Brenner, T. Beck, J. D. Meindl, Appl. Phys. Lett. 2009, 94, 243114; c) R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, A. K. Geim, Science 2008, 320, 1308; d) J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. van der Zande, J. M. Parpia, H. G. Craighead, P. L. McEuen, Nano Lett. 2008, 8, 2458.

[2] Y. Zhu, S. Muriali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, Adv. Mater. 2010, 22, 3906.

[3] a) W. S. Hummers, R. E. Offeman, J. Am. Chem. Soc. 1958, 80, 1339; b) J. Zhao, S. Pei, W. Ren, L. Gao, H.-M. Cheng, ACS Nano 2010, 4, 5245; c) S. Tian, J. Sun, S. Yang, P. He, S. Ding, G. Ding, X. Xie, RSC Adv. 2015, 5, 69854.

[4] R. Raccicini, A. Varzi, S. Passerini, B. Scrosati, Nat. Mater. 2015, 14, 271.

[5] K. R. Paton, E. Varila, C. Backes, R. J. Smith, U. Khan, A. O’Neill, C. Boland, M. Lotya, O. M. Istrate, P. King, T. Higgins, S. Barwich, P. May, P. Puczkarski, I. Ahmed, M. Moebius, H. Pettersson, E. Long, J. Coelho, S. E. O’Brien, E. K. McGuire, B. M. Sanchez, G. S. Duesberg, N. McEvoy, T. J. Pennycook, C. Downing, A. Crossley, V. Nicolosi, J. N. Coleman, Nat. Mater. 2014, 13, 624.

[6] Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighè, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun’Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchinson, V. Scardaci, A. C. Ferrari, J. N. Coleman, Nat. Nanotechnol. 2008, 3, 563.

[7] M. Lotya, P. J. King, U. Khan, S. De, J. N. Coleman, ACS Nano 2010, 4, 3155.

[8] P. G. Karagiannidis, S. A. Hodge, L. Lombardi, F. Tomarchio, N. Dettorre, S. Milana, I. Goykhman, Y. Su, S. V. Mesite, D. N. Johnstone, R. K. Leary, P. A. Midgley, N. M. Pugno, F. Torrisi, A. C. Ferrari, ACS Nano 2017, 11, 2742.

[9] L. Baptista-Pires, C. C. Mayorga-Martínez, M. Medina-Sánchez, H. Montón, A. Merkoçi, ACS Nano 2016, 10, 853.

[10] D.-W. Shin, J. H. Lee, Y.-H. Kim, S. M. Yu, S.-Y. Park, J.-B. Yoo, Nanotechnology 2009, 20, 475703.

[11] J. H. Lee, D.-W. Shin, V. G. Makotchenko, A. S. Nazarov, V. E. Fedorov, Y. H. Kim, J.-Y. Choi, J. M. Kim, J.-B. Yoo, Adv. Mater. 2009, 21, 4383.

[12] X. Wang, Z. Xiaong, Z. Liu, T. Zhang, Adv. Mater. 2015, 27, 1370.

[13] W. J. Hyun, O. O. Park, B. D. Chin, Adv. Mater. 2013, 25, 4729.
[14] K. Parvez, Z.-S. Wu, R. Li, X. Liu, R. Graf, X. Feng, K. Müllen, J. Am. Chem. Soc. 2014, 136, 6083.
[15] G. Eda, G. Fanchini, M. Chhowalla, Nat. Nanotechnol. 2008, 3, 270.
[16] K. Parvez, R. Li, S. R. Puniredd, Y. Hernandez, F. Hinkel, S. Wang, X. Feng, K. Müllen, ACS Nano 2013, 7, 3598.
[17] H. Yamaguchi, G. Eda, C. Mattevi, H. Kim, M. Chhowalla, ACS Nano 2010, 4, 524.
[18] G. Bepete, E. Anglaret, L. Ortolani, V. Morandi, K. Huang, A. Pénilcaud, C. Drummond, Nat. Chem. 2017, 9, 347.
[19] H. Mishima, T. Yasui, T. Mizuniwa, M. Abe, T. Ohmi, IEEE Trans. Semicond. Manuf. 1989, 2, 69.
[20] S. Lin, C.-J. Shih, M. S. Strano, D. Blankschtein, J. Am. Chem. Soc. 2011, 133, 12810.
[21] A. Salehi-Khojin, D. Estrada, K. Y. Lin, K. Ran, R. T. Haasch, J.-M. Zu, E. Pop, R. I. Masel, Appl. Phys. Lett. 2012, 100, 033111.
[22] B. Muchharla, T. N. Narayanan, K. Balakrishnan, P. M. Ajayan, S. Talapatra, 2D Mater. 2014, 1, 011008.
[23] H.-Z. Geng, K. K. Kim, K. P. So, Y. S. Lee, Y. Chang, Y. H. Lee, J. Am. Chem. Soc. 2007, 129, 7758.
[24] K. Haubner, J. Murawski, P. Olk, L. M. Eng, C. Ziegler, B. Adolphi, E. Jaehne, ChemPhysChem 2010, 11, 2131.
[25] J.-W. P. Chen, C.-Y. Huang, S.-H. S. Jhou, Y.-W. Zhang, Sci. Rep. 2014, 4, 3928.
[26] A. Lerf, H. He, M. Forster, J. Klinowski, J. Phys. Chem. B 1998, 102, 4477.