Fluorinated Reduced Graphene Oxide as an Efficient Hole-Transport Layer for Efficient and Stable Polymer Solar Cells

Xiaofang Cheng,† Juan Long,† Rui Wu,† Liqiang Huang,‡ Licheng Tan,†‡ Lie Chen,*†‡ and Yiwang Chen†‡

†College of Chemistry and ‡Jiangxi Provincial Key Laboratory of New Energy Chemistry/Institute of Polymers, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

Supporting Information

ABSTRACT: In this work, we have rationally designed and successfully synthesized a reduced graphene oxide (GO) functionalized with fluorine atoms (F-rGO) as a hole-transport layer (HTL) for polymer solar cells (PSCs). The resultant F-rGO has an excellent dispersibility in dimethylformamide without any surfactants, leading to a good film-forming property of F-rGO for structuring a stable interface. The recovery of conjugated C=C bonds in GO oxide after reduction increases the conductivity of F-rGO, which enhances the short-circuit current density of photovoltaic devices from 15.65 to 16.89 mA/cm². A higher work function (WF) (5.1 eV) of F-rGO than that of GO (4.9 eV) is attributed to the fluorine group with a high electronegativity. Naturally, the better-matched WF with the highest occupied molecular orbital level of the PTB7-Th (5.22 eV) donor induces an improved energy alignment in devices, resulting in a superior open-circuit voltage of the device (0.776 vs 0.786 V). Consequently, the device with F-rGO as the HTL achieves a higher power conversion efficiency (8.6%) with long-term stability than that of the devices with GO HTLs and even higher than that of the poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) control device. These results clearly verify that the F-rGO is a promising hole-transport material and an ideal replacement for conventional PEDOT/PSS, further promoting the realization of low-cost, solution-processed, high-performance, and high-stability PSCs.

INTRODUCTION

Polymer solar cells (PSCs) based on bulk-heterojunction structures hold great potential owing to their advantageous properties such as low-cost fabrication, light weight, flexibility, and use of nontoxic elements.1 There has been significant progress in the power conversion efficiency (PCE) of PSCs because of the tremendous efforts in the development of new photoactive materials and fabrication techniques over the past few years.2−4 To date, the PCE of single cells has reached over 11%.5−9 Because the interfaces between the electrodes and the photoactive layer play an important role in improving the overall photovoltaic performance of PSCs, the charge-transport layers between the photoactive layer and electrodes are notably indispensable. The functions of charge-transport layers involved reducing energy barriers for charge carrier transport, forming a selective contact for the corresponding charge carrier at two electrodes, and optimizing the morphology and concentration distribution of the photoactive layer for enhanced device performance.10,11

So far, poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS), a commercial conducting polymer, has been most commonly used as a hole-transport layer (HTL) to increase hole contact and to improve anode collection in PSCs. However, the properties of high acidity and hygroscopicity of PEDOT:PSS limit the further application of devices.12,13 Inorganic materials including NiO, V2O5, and MoO3, as other currently predominant HTLs, are introduced because they could offer a high work function (WF) with good transparency and exhibit favorable durability for long-term device operation. However, it cannot be ignored that the requirement of a thermal treatment and the costly vacuum process have vastly limited their broad applications in PSCs.14,15

As a promising alternative to PEDOT:PSS, graphene oxide (GO) possesses numerous advantages, such as tunable electronic structures, low manufacturing cost, and compatibility with roll-to-roll processing. GO is generally prepared from the oxidation of graphite by a strong oxidant concentrated sulfuric acid and potassium permanganate, which was first introduced by Li et al.16 Herein, it is observed that the graphene sheet in graphite oxide is decorated with oxygen functionalities at the edges, including epoxy, hydroxyl, carboxyl, and carbonyl groups. Consequently, the optoelectronic properties of GO, like the van der Waals interactions between the graphene sheets in graphite oxide, could be tuned. In addition, GO (rGO) with oxygen-containing functional groups is endowed with excellent
solubility in water or polar organic solvents. Thus, it is a particularly promising solution-processable interfacial material for application at a large scale. In spite of the aforementioned superiority of GO, it is undisputable that GO
Our team has been working on developing a fluorine-functionalized, reduced GO (F-rGO) using 2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl-hydrazine as a HTL for PSCs. In detail, the developed reductant had seven fluorine atoms, which is less toxic in contrast to the intensively toxic and explosive hydrazine. The resultant F-rGO presents an excellent dispersibility in solution, with a peak intensity ratio of the D and G bands is believed to be proportional to the size of the sp² C domains. The observed result shows that the ratio of I_D/I_G of the F-rGO increases to 1.12 (compared to 0.95 for GO) after reduction, demonstrating that numerous small-size sp² C domains were formed after reduction, further verifying that the GO was reduced and functionalized with fluorine atoms successfully, consistent with the aforementioned result of XPS. The peak intensity ratio of the D and G bands is believed to be proportional to the size of the sp² C domains. The observed result shows that the ratio of I_D/I_G of the F-rGO increases to 1.12 (compared to 0.95 for GO) after reduction, demonstrating that numerous small-size sp² C domains were formed after reduction, further verifying that the GO was reduced and functionalized with fluorine atoms successfully, consistent with the aforementioned result of XPS. The clear chemical structure change is confirmed by Raman spectroscopy measurements. Figure 1d shows the Raman spectra of GO and F-rGO. The peak intensity ratio of the D and G bands is believed to be proportional to the size of the sp² C domains. The observed result shows that the ratio of I_D/I_G of the F-rGO increases to 1.12 (compared to 0.95 for GO) after reduction, demonstrating that numerous small-size sp² C domains were formed after reduction, further verifying that the GO was reduced and functionalized with fluorine atoms successfully, consistent with the aforementioned result of XPS. Figure 1e illustrates the UV-vis absorbance (UV-vis) spectra of GO, which show a strong absorbance peak at 228 nm. However, the absorbance peak of GO is red-shifted to 265 nm and the absorbance in the whole spectral region is enhanced, indicating that the conjugated C=C bonds of GO are restored by reduction. More importantly, the resultant F-rGO shows an excellent dispersibility (Figure S2) of 5 mg/mL in DMF without any surfactants, helpful in forming a film to develop a stable interface. More importantly, F-rGO has both a higher conductivity and a satisfactory WF (5.1 eV) compared to those of GO. Finally, when applied to PSCs, the desirable PCE (8.6%) could be achieved with F-rGO as the HTL. The good device performance contributed to the enhancement of the short-circuit current density (16.89 mA/cm²), open-circuit voltage (0.79 V), and FF (64.8%), meaning that F-rGO is appropriate as a HTL for PSCs.

**RESULTS AND DISCUSSION**

The hole-transport material from reduced GO functionalized with fluorine atoms (F-rGO) was prepared by reduction and simultaneous functionalization of GO using a reductant, 2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl-hydrazine, which possesses seven fluorine atoms, as illustrated in Figure 1a. To confirm that GO has been succeeded in reduction, X-ray photoelectron spectroscopy (XPS) measurements were conducted and the change in the composition and bonding type of GO and F-rGO was explored. The fitting results of the C1s curves of GO and F-rGO are shown in Figure 1b,c. Figure S1 presents the XPS C1s curve. It could be observed that the C1s spectrum of the GO film consists of several components, assigned to C−C (284.7 eV), C−OH (286.5 eV), C−O−C (286.9 eV), and COOH (288.8 eV). However, for F-rGO, the peak intensity of the four components evidently differs from that of GO, especially the enhanced intensity of C−C. This is due to the restoration of the conjugated C=C bonds of the GO sheets after reduction, meaning the successful reduction of GO. Moreover, there occur another two compositions corresponding to C−N (285.8 eV) and C−F (293.1 eV), revealing that the reductant is successfully attached to the basal plane and edges of the GO sheets. The clear chemical structure change is confirmed by Raman spectroscopy measurements. Figure 2a shows the L–V characteristics of GO and F-rGO (the inset represents the structure of the device). (b) AFM micrographs and root-mean-square values of GO and F-rGO on the ITO substrate.

**Figure 2.** (a) L–V characteristics of GO and F-rGO (the inset represents the structure of the device). (b) AFM micrographs and root-mean-square values of GO and F-rGO on the ITO substrate.
To evaluate the conductivity of the GO and F-rGO layers, we fabricated the diodes with a structure of ITO/GO(F-rGO)/Al, as shown in Figure 2a. Note that the different slopes of the current density–voltage (J–V) curves imply that GO(F-rGO) thin films have different electrical conductivities. Normally, the greater the slope, the better the conductivity of thin film. It could be seen from Figure 2a that F-rGO shows a distinct increase in the conductivity compared to that of the pristine GO, which is attributed to the partial restoration of conjugated C=C bonds. Atomic force microscopy (AFM) measurements were also conducted to analyze the morphology of GO and F-rGO (presented in Figure 2b). It could be found that the root-mean-square roughness values of F-rGO increase slightly (from 1.49 to 1.98 nm) after the reduction, probably ascribed to the bulky phenyl functional groups being grafted onto the graphene sheet with disorder.19 However, from AFM topography images of photoactive layers on different substrates (Figure S3), it could be observed that there are no obvious differences in films’ morphologies when the photoactive layers are deposited on different substrates. Furthermore, it is seen from the transmittance of ITO with different HTLs (presented in Figure S4) that the F-rGO has transmittance (>80%) comparable to that of GO and PEDOT after reduction. More importantly, the contact angle measurements depict that the F-rGO/ITO shows a larger contact angle of 71.0° than that of GO/ITO (45.5°) and PEDOT/ITO (13.5°) (given in Figure S5), owing to the decrease of the oxygen-containing groups during reduction. The result indicates that the enhanced hydrophobic surface of the F-rGO-modified ITO is more compatible with the upper active layer in comparison to that of GO-modified ITO. The above results show that the F-rGO is suitable for anode interlayer material.

The ultraviolet photoelectron spectroscopy (UPS) measurements were carried out to explore the WFs of GO and F-rGO. The following equation is used to calculate the WFs of GO and F-rGO deposited onto the ITO substrate

$$WF = h\nu - E_F + E_{cutoff}$$

where \(h\nu\) is the excitation energy of He(I), equals to 21.2 eV, \(E_F\) is the Fermi level, and \(E_{cutoff}\) is the high-binding-energy cutoff.30 It is obvious that, compared to the WFs of bare ITO (4.5 eV), PEDOT (4.9 eV), and GO (4.9 eV), the WF of F-rGO is significantly higher, with the value of 5.1 eV, as shown in Figure 3a. The upshifted WF of F-rGO can be majorly due to the fluorine atoms with a high electronegativity, inducing p-type self-doping of the graphene.1,32 Eventually, the higher WF of F-rGO could match the HOMO of the donor polymer (PTh7-Th, 5.22 eV) better (Figure 3b), leading to a better energy level alignment. Simultaneously, the built-in potential could improve and the interface resistance reduces, thereby enhancing the performance of PSCs.

To assess the viability of F-rGO as a HTL in PSCs, we fabricated the conventional device structure (ITO/HTL/PTB7-Th:PC71BM/PFN/Al, Figure 4a) based on PTB7-Th:PC71BM. Reference devices were also prepared without any modification, with PEDOT:PSS and GO as HTLs. Figure 4a shows the current density–voltage (J–V) characteristics of the devices, and the related device parameters are summarized in Table 1. The device without the HTL shows a poor PCE of 0.650 V, FF of 52.3%, \(J_{SC}\) of 15.02 mA/cm², and PCE of 3.3%, whereas the device with GO as the HTL demonstrates a PCE (7.8%) with a \(V_{OC}\) of 0.776 V, FF of 63.9%, and \(J_{SC}\) of 15.65 mA/cm². It is noteworthy that the device with F-rGO as the HTL displays an obviously improved PCE of 8.6%, with enhanced device parameters including \(V_{OC}\) of 0.786 V, \(J_{SC}\) of 16.89 mA/cm², and FF of 64.8%. The unexceptionable \(J_{SC}\) could be attributed to the higher conductivity of F-rGO after reduction, leading to the better carrier transport property, whereas the slightly increased \(V_{OC}\) is ascribed to the more matched WF (5.1 eV), promoting efficient hole extraction with sufficient built-in potential. In addition, the smaller \(R_s\) (Table 1) of the device with the F-rGO interlayer just confirms the favorable hole-transport property. Figure 4b presents the external quantum efficiency (EQE) of the devices. The \(J_{SC}\) values calculated from the EQE spectra are 14.99, 16.19, 15.52, and 16.59 mA/cm², respectively, for the devices with the bare ITO, PEDOT:PSS, GO, and F-rGO interlayers. The integrated \(J_{SC}\) values are presented in Figure 4b, which are in good accordance with the \(J_{SC}\) values (within 3% mismatch) from the J–V characteristics under light conditions. Furthermore, the dark current densities of the PSCs with PEDOT:PSS, GO, and F-rGO as HTLs (as shown in Figure S6) show that F-rGO is...
more efficient in blocking electrons and collecting holes than PEDOT and GO. We also measured the hole mobility of different HTLs (Figure S7) with space-charge-limited current.\textsuperscript{15} The hole mobilities of F-rGO, GO, and PEDOT are exhibited in Table S1. Obviously, F-rGO has the highest hole mobility among these three HTLs, contributing to the $J_{SC}$ enhancement.

To expand the potential of F-rGO as an outstanding HTL, the device stability of the PSCs with F-rGO was investigated with a function of time of exposure under an ambient environment without encapsulation. As a comparison, the device stability with GO/ITO, PEDOT:PSS/ITO, and bare ITO as anodes was also evaluated. As shown in Figure 4c, a rapid degradation rate could be observed for PCEs with bare ITO. After 4600 min, the device with bare ITO continues to show a very poor PCE due to the poor surface property of ITO. Simultaneously, the device with PEDOT:PSS retains just about 23% of its primal PCE, which originates from the hygroscopic PEDOT:PSS layer by absorbing water from the atmosphere, thus leading to the degradation of hole extraction. In contrast, the devices fabricated with GO and F-rGO HTLs show a greatly enhanced device stability with the PCEs retaining 67 and 63% of their initial PCEs after 4600 min, respectively, which is because of the GO layer, blocking water and oxygen. The result suggests that the conventional PSCs with F-rGO as the HTL could act as an encapsulation at both bottom to obtain a device with high performance and long-term air stability.

\section*{CONCLUSIONS}

In conclusion, we synthesized a fluorine-functionalized, reduced GO with 2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl-hydrazine as a reductant. The resultant F-rGO has an excellent dispersibility, making the subsequent solution processing feasible. Compared with GO, F-rGO has a higher conductivity and higher WF, resulting from the recovery of conjugated C=C bonds in GO after reduction and the grafting of fluorine atoms with a high electronegativity, respectively. Consequently, the F-rGO device acquires a higher efficiency than that of GO device, with the increased short-circuit current density and open-circuit voltage. It is worth noting that the F-rGO device even obtains an ultimately better PCE (8.6\%) in comparison to that of the device with GO. In addition, the F-rGO-based photovoltaic device shows a stability superior to that of the GO-based and PEDOT-based devices. These results clearly demonstrate that the F-rGO is a promising hole-transport material and an ideal replacement for conventional PEDOT, further promoting the realization of low-cost, solution-processed, high-performance, and high-stability PSCs.

\section*{EXPERIMENTAL PROCEDURES}

\textbf{Preparation of GO.} The GO was prepared by a modified Hummer’s method. Briefly, graphite (2.0 g) was added to

| HTL     | $J_{SC}$ [mA/cm$^2$] | $V_{oc}$ [V] | FF [%] | PCE [%] | $R_s$ [Ω cm$^2$] | $R_{sh}$ [Ω cm$^2$] |
|---------|----------------------|-------------|--------|--------|-----------------|------------------|
| bare ITO | 15.02 ± 0.81         | 0.650 ± 0.046 | 52.3 ± 8.5 | 5.1     | 4.06            | 147.45           |
| PEDOT:PSS| 16.43 ± 0.73         | 0.782 ± 0.005 | 61.5 ± 1.7 | 7.9     | 3.33            | 216.26           |
| GO      | 15.65 ± 0.25         | 0.776 ± 0.005 | 63.9 ± 1.4 | 7.8     | 2.27            | 214.56           |
| F-rGO   | 16.89 ± 0.41         | 0.786 ± 0.004 | 64.8 ± 1.1 | 8.6     | 2.07            | 254.53           |

\textsuperscript{a}The structure of the PSC is ITO/HTL/PTB7-Th:PC$_{71}$BM/PFN/Al. All of the values represent average from 12 devices on a single chip. \textsuperscript{b}The best device PCE.
concentrated sulfuric acid (50 mL, 0 °C) under stirring, then sodium nitrate (1.0 g) was added, and the reaction system was stirred for about 0.5 h at 0 °C. Under violent agitation, potassium permanganate (8.0 g) was added slowly to keep the temperature of the mixture lower than 20 °C. Then, the suspension was transferred into a 40 °C water bath and vigorously stirred for about 6.0 h. Subsequently, water (100 mL) was added and the solution was stirred for 20 min at 90 °C. An additional 360 mL of water was added. Then, H2O2 (30%, 0.5 mL) was added slowly, turning the color of the mixture from dark brown to yellow. The suspension was filtered and washed with 1:10 hydrochloric acid aqueous solution (200 mL) to remove metal ions. The precipitate was dispersed into deionized water to form a uniformly dispersed suspension. The suspension was centrifuged (at a low speed) to remove the incompletely oxidized product. The remaining supernatant was centrifuged (at a high speed) to obtain the precipitate, which was freeze-dried for next use.

**Preparation of F-rGO.** First, 0.8 g of the prepared GO was dispersed in 200 mL of deionized water using an ultrasonic bath cleaner. Then, 5.1 g of 2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl-hydrazine was added to the suspension and stirred at 60 °C for 6 h. Finally, the suspension was filtered and washed with methyl alcohol. The filtered product was dried in a vacuum oven at 50 °C for 24 h.

**Characterization of Films.** XPS measurements for GO and F-rGO were performed using a Thermo-VG Scientific ESCALAB 250 system. The morphology of GO, F-rGO, and active layers was investigated using AFM (Agilent 5500). The transmittance spectra and WF of the samples were obtained using UPS (Kratos Analytical Ltd.). The Raman spectra of GO and F-rGO were acquired from LabRam-1B. The transmittance spectra and UV–vis spectrum were analyzed by PerkinElmer Lambda 750. The current–voltage characteristics of the devices under illumination (the light intensity was 100 mW/cm²) and in the dark were tested by a Keithley 2400 Source Meter.

**Device Fabrication.** The photoactive materials, poly[(2,6'-4,8-di-(5-ethylhexylthiophenyl)benzo[1,2-b:3,4-b]dithiophene][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b][thiophenediyl]] (PTB7-Th) and [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM), were purchased from 1-material Inc. and Solarmer Energy, Inc., respectively. The electron transport material, poly[(9,9-bis-(3’-(N,N-dimethylamino)propyl)-2,7-fluorene-alt-2(9,9-dioctyfluorene)] (PFN), was provided by Solarmer Energy, Inc. The device structure is ITO/HTL/PTB7-Th:PC71BM/PFN/Al. The ITO glasses were cleaned by an ultrasonic batch cleaner in acetone, soap water, deionized water, ultrasonic batch cleaner in acetone, soap water, deionized water, and isopropanol, successively. Then, the ITO glasses were dried with nitrogen and treated with O3 plasma for 10 min. The interface layers of the devices were deposited on the ITO glasses using the following spin-cast conditions. The PEDOT layer was spin-cast from the solution at 5000 rpm for 60 s, followed by baking for 20 min at 120 °C. The GO layer was spin-cast from its solution in water (1 mg/mL) using a gradient spin, from 2000 to 5000 rpm for 60 s, followed by baking for 10 min at 150 °C. The F-rGO layer was spin-cast from its solution in DMF (2.0 mg/mL) using a gradient spin, from 2000 to 5000 rpm for 60 s, followed by baking for 10 min at 150 °C. As photoactive layers, PTB7-Th and PC71BM were spin-cast from a mixed solvent of chlorobenzene/1,8-diiodooctane (97:3 v/v) solution (with a total concentration of 25 mg/mL, stirred for at least 12 h at 70 °C) at 1000 rpm for 2 min. The resulting photoactive layer was dried in a glove box with nitrogen before the deposition of the PFN layer. The PFN layer was spin-cast from its solution in methanol (0.4 mg/mL) in the presence of a small amount of acetic acid at 5000 rpm for 60 s. Then, the devices were transferred into a vacuum chamber for thermal deposition of Al (100 nm) at a pressure of 10⁻⁷ Torr. The area of each device was 4 mm², as defined by the overlap of ITO and the evaporated Al.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00408.

Complementary XPS spectra, AFM measurements, transmittance spectra, and surface contact angle; dark J–V characteristic curves and hole mobilities of hole-only devices with different interlayers (PDF)

**AUTHOR INFORMATION**

*Corresponding Authors*  
- E-mail: chenlie@ncu.edu.cn (L.C.).  
- E-mail: ywchen@ncu.edu.cn. Tel: +86 791 83968703. Fax: +86 791 83969561 (Y.C.).

**ORCID**

Yiwang Chen: 0000-0003-4709-7623

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Y.C. thanks support from the National Science Fund for Distinguished Young Scholars (51425304) and the National Natural Science Foundation of China (NSFC) (51673091). L.C. thanks support from the NSFC (51473075 and 51673092). L.T. thanks support from the NSFC (51672121).

**REFERENCES**

(1) Hu, X.; Chen, L.; Zhang, Y.; Hu, Q.; Yang, J.; Chen, Y. Large-Scale Flexible and Highly Conductive Carbon Transparent Electrodes via Roll-to-Roll Process and its High Performance Lab-Scale Indium Tin Oxide-Free Polymer Solar Cells. *Chem. Mater.*, 2014, 26, 6293–6302.

(2) Liao, X.-F.; Wang, J.; Chen, S.-Y.; Chen, L.; Chen, Y. Diketopyrrolopyrrole-Based Conjugated Polymers as Additives to Optimize Morphology for Polymer Solar Cells. *Chin. J. Polym. Sci.*, 2016, 34, 491–504.

(3) Zhang, H.; Yao, H.; Zhao, W.; Ye, L.; Hou, J. High-Efficiency Polymer Solar Cells Enabled by Environment-Friendly Single-Solvent Processing. *Adv. Energy Mater.*, 2016, 6, No. 1502177.

(4) Ma, W.; Yang, G.; Jiang, K.; Carpenter, J. H.; Wu, Y.; Meng, X.; McAfee, T.; Zhao, J.; Zhu, C.; Wang, C.; et al. Influence of Processing Parameters and Molecular Weight on the Morphology and Properties of High-Performance P3BT4T-2OD: PC71BM Organic Solar Cells. *Adv. Energy Mater.*, 2015, 5, No. 1501400.

(5) He, Z.; Xiao, B.; Liu, F.; Wu, H.; Yang, Y.; Xiao, S.; Wang, C.; Russell, T. P.; Cao, Y. Single-Junction Polymer Solar Cells with High Efficiency and Photovoltage. *Nat. Photonics*, 2015, 9, 174–179.

(6) Zhao, J.; Li, Y.; Yang, G.; Jiang, K.; Lin, H.; Ade, H.; Ma, W.; Yan, H. Efficient Organic Solar Cells Processed from Hydrocarbon Solvents. *Nat. Energy*, 2016, 1, No. 15027.
(7) Yang, Y.; Zhang, Z.-G.; Bin, H.; Chen, S.; Gao, L.; Xue, L.; Yang, C.; Li, Y. Side-Chain Isomerization on an N-Type Organic Semiconductor ITIC Acceptor Makes 11.77% High Efficiency Polymer Solar Cells. J. Am. Chem. Soc. 2016, 138, 15011–15018.

(8) Bin, H.; Gao, L.; Zhang, Z.-G.; Yang, Y.; Zhang, Y.; Zhang, C.; Chen, S.; Xue, L.; Yang, C.; Xiao, M.; Li, Y. 11.4% Efficiency Non-fullerene Polymer Solar Cells with Trialkylsilyle Substituted 2D-Conjugated Polymer as Donor. Nat. Commun. 2016, 7, No. 13651.

(9) Zhao, W.; Qian, D.; Zhang, S.; Li, S.; Inganis, O.; Gao, F.; Hou, J. Fullerene-Free Polymer Solar Cells with Over 11% Efficiency and Excellent Thermal Stability. Adv. Mater. 2016, 28, 4734–4739.

(10) Yip, H.-L.; Jen, A. K.-Y. Recent Advances in Solution-Processed Interfacial Materials for Efficient and Stable Polymer Cells. Energy Environ. Sci. 2012, 5, 5994–6011.

(11) Zhou, H.; Zhang, Y.; Mai, C. K.; Collins, S. D.; Nguyen, T. Q.; Bazan, G. C.; Heeger, A. J. Conductive Conjugated Polyelectrolyte as Hole-Transporting Layer for Polymer Bulk Heterojunction Solar Cells. Adv. Mater. 2014, 26, 780–785.

(12) Wang, Y.; Zhu, H.; Shi, Z.; Wang, F.; Zhang, B.; Dai, S.; Tan, Z. Engineering the Vertical Concentration Distribution Within the Polymer: Fullerene Blends for High Performance Inverted Polymer Solar Cells. J. Mater. Chem. A 2017, 5, 2319–2327.

(13) Park, H.; Kong, J. An Alternative Hole Transport Layer for Both ITO-and Graphene-Based Organic Solar Cells. Adv. Energy Mater. 2014, 4, No. 1301280.

(14) Shrotriya, V.; Li, G.; Yao, Y.; Chu, C.-W.; Yang, Y. Transition Metal Oxides as the Buffer Layer for Polymer Photovoltaic Cells. Appl. Phys. Lett. 2006, 88, No. 073508.

(15) Irwin, M. D.; Buchholz, D. B.; Hains, A. W.; Chang, R. P.; Marks, T. J. p-Type Semiconducting Nickel Oxide as an Efficiency-Enhancing Anode Interfacial Layer in Polymer Bulk-Heterojunction Solar Cells. Proc. Natl. Acad. Sci. U.S.A. 2008, 105, 2783–2787.

(16) Li, S.-S.; Tu, K.-H.; Lin, C.-C.; Chen, C.-W.; Chhowalla, M. Solution-Processable Graphene Oxide as an Efficient Hole Transport Layer in Polymer Solar Cells. ACS Nano 2010, 4, 3169–3174.

(17) (a) Wang, D. H.; Kim, J. K.; Seo, J. H.; Park, I.; Hong, B. H.; Park, J. H.; Heeger, A. J. Transferable Graphene Oxide by Stamping Nanotechnology: Electron-Transport Layer for Efficient Bulk-Heterojunction Solar Cells. Angew. Chem., Int. Ed. 2013, 52, 2874–2880.

(b) Gao, Y.; Yip, H.-L.; Hau, S. K.; O’Malley, K. M.; Cho, N. C.; Chen, H.; Jen, A. K.-Y. Anode Modification of Inverted Polymer Solar Cells Using Graphene Oxide. Appl. Phys. Lett. 2010, 97, No. 203306.

(18) (a) Yang, D.; Zhou, L.; Chen, L.; Zhao, B.; Zhang, J.; Li, C. Chemically Modified Graphene Oxides as a Hole Transport Layer in Organic Solar Cells. Chem. Commun. 2012, 48, 8078–8080. (b) Yang, D.; Zhou, L.; Yu, W.; Zhang, J.; Li, C. Work-Function-Tunable Chlorinated Graphene Oxide as an Anode Interface Layer in High-Efficiency Polymer Solar Cells. Adv. Energy Mater. 2014, 4, No. 1403591.

(19) Stratakis, E.; Savva, K.; Konios, D.; Petridis, C.; Kymakis, E. Improving the Efficiency of Organic Photovoltaics by Tuning the Work Function of Graphene Oxide Hole Transporting Layers. Nanoscale 2014, 6, 6925–6931.

(20) Kim, J.; Tung, V. C.; Huang, J. Water Processable Graphene Oxide: Single Walled Carbon Nanotube Composite as Anode Modifier for Polymer Solar Cells. Adv. Energy Mater. 2011, 1, 1052–1057.

(21) Yeo, J.-S.; Yun, J.-M.; Jung, Y.-S.; Kim, D.-Y.; Noh, Y.-J.; Kim, S.-S.; Na, S.-I. Sulfonic Acid-Functionalized, Reduced Graphene Oxide as an Advanced Interfacial Material Leading to Donor Polymer-Independent High-Performance Polymer Solar Cells. J. Mater. Chem. A 2014, 2, 292–298.

(22) Yun, J. M.; Yeo, J. S.; Kim, J.; Jeong, H. G.; Kim, D. Y.; Noh, Y. J.; Kim, S. S.; Ku, B. C.; Na, S.-I. Solution-Processable Reduced Graphene Oxide as a Novel Alternative to PEDOT: PSS Hole Transport Layers for Highly Efficient and Stable Polymer Solar Cells. Adv. Mater. 2011, 23, 4923–4928.

(23) Pham, V. H.; Cuong, T. V.; Nguyen-Phan, T.-D.; Pham, H. D.; Kim, E. J.; Hur, S. H.; Shin, E. W.; Kim, S.; Chung, J. S. One-Step Synthesis of Superior Dispersion of Chemically Converted Graphene in Organic Solvents. Chem. Commun. 2010, 46, 4375–4377.

(24) Hunter, B.; Schoene, D. Sulfoxyl Hydrazide Blowing Agents for Rubber and plastics. Ind. Eng. Chem. 1952, 44, 119–122.

(25) Bednarski, M.; Lyssikatos, J. Comprehensive Organic Synthesis: Selectivity, Strategy and Efficiency in Modern Organic Chemistry; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 2, p 661.

(26) Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. Synthesis of Graphene-Based Nanosheets via Chemical Reduction of Exfoliated Graphite Oxide. Carbon 2007, 45, 1558–1565.

(27) Ma, J.; Wang, X.; Liu, Y.; Wu, T.; Liu, Y.; Guo, Y.; Li, R.; Sun, X.; Wu, F.; Li, C.; Gao, J. Reduction of Graphene Oxide with I-Lysine to Prepare Reduced Graphene Oxide Stabilized with Polysaccharide Polyelectrolyte. J. Mater. Chem. A 2013, 1, 2192–2201.

(28) Zhang, J.; Yang, H.; Shen, G.; Cheng, F.; Zhang, J.; Guo, S. Reduction of Graphene Oxide via L-Ascorbic Acid. Chem. Commun. 2010, 46, 1112–1114.

(29) Si, Y.; Samulski, E. T. Synthesis of Water Soluble Graphene. Nano Lett. 2008, 8, 1679–1682.

(30) Ishii, H.; Sugiyama, K.; Ito, E.; Seki, K. Energy Level Alignment and Interfacial Electronic Structures at Organic/Metal and Organic/Organic Interfaces. Adv. Mater. 1999, 11, 605–625.

(31) Walter, A. L.; Jeon, K.-J.; Bostwick, A.; Speck, F.; Ostler, M.; Seyller, T.; Moreschini, L.; Kim, Y. S.; Chang, Y. J.; Horn, K.; Rothenberg, E. Highly p-Doped Epitaxial Graphene Obtained by Fluorine Intercalation. Appl. Phys. Lett. 2011, 98, No. 184102.

(32) Giera, I.; Riedl, C.; Starke, U.; Ast, C. R.; Kern, K. Atomic Hole Doping of Graphene. Nano Lett. 2008, 8, 4603–4607.