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COMMUNICATION

Fluorine-functionalized and simultaneously reduced graphene oxide as a novel hole transporting layer for highly efficient and stable organic photovoltaic cells

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A one-step reduction and functionalization of graphene oxide (FrGO) was easily achieved using a novel phenylhydrazine-based reductant containing fluorine atoms, which can induce p-type doping due to the high electronegativity. The FrGO-based OPV exhibited high power conversion efficiency of ~ 6.71% and a superior OPV-stability to commercial PEDOT:PSS.

In recent years, there have been outstanding improvements in the performance of organic based bulk heterojunction photovoltaic cells (OPVs).¹⁻⁵ These outstanding improvements have arisen from the recent progress in small-bandgap conjugated polymers and the development of device processes and architectures.³⁻⁵ As is well known, OPV properties, such as the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF), are highly affected by the inherent optoelectronic characteristics, the work-functions (WF) of the organic or inorganic materials, and the interfacial contact between the photoactive layer and the electrodes.⁶⁻¹² For these reasons, various organic and inorganic interfacial materials have been actively studied, and significant efforts have been devoted to anode interfacial materials due to the inherent problems of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), which include highly acidic, hygroscopic, and non-uniform electrical properties.¹³⁻²⁰

Chemically converted graphene (CCG), including graphene oxide (GO) and reduced graphene oxide (rGO), is one of the most promising interfacial materials for high-performance OPVs.¹⁷⁻²⁰ However, GO is insulating and tends to be affected by the GO thickness;¹⁸⁻²⁰ thus, rGO shows better carrier transporting ability and could be a more efficient graphene-based hole transporting layer (HTL). However, there have been only a few studies on rGO-based interfacial materials for OPVs, most likely due to the difficulties in obtaining a good and uniform film morphology and a high WF that matches the highest occupied molecular orbital (HOMO) of various donor polymers, which could limit the universal and practical application of the CCGs in donor-based OPVs.^{6-9, 20} Recently, the versatile functionalization of graphene has demonstrated the controllability of the electronic properties of graphene sheets, which may lead to higher-efficiency OPVs and their widespread use as hole- and electron-transporting layers in OPVs.^{17, 21} This

functionalization of graphene by tuning the chemical and electronic structures could be highly desirable for HTL applications; however, studies on the development of a functionalized rGO or its practical application in an OPV have hardly been investigated, and to date, there have been no studies on fluorine-functionalized graphene as HTLs in OPVs.

In this study, we introduce a novel rGO functionalized with fluorine atoms (FrGO), and we also demonstrate that the FrGO can be successfully utilized as a hole transporting layer in OPVs. A facile, one-step reduction and functionalization of graphene oxide was achieved using a new reductant, 4-(trifluoromethyl)phenylhydrazine, which contains fluorine atoms and effectively removes oxygen functional groups attached to GO while simultaneously doping fluorine atoms on the basal plane and edges of the graphene sheets, as illustrated in Figure 1(a). A control rGO (CrGO) that contained no fluorine atoms was also synthesized using phenylhydrazine reductants,^{22, 23} and it was used as a reference for rGO-based HTLs in OPVs. The detailed experimental procedures are described in the supporting information. The FrGO dramatically increased the OPV efficiencies due to a better WF, more uniform film surface, and higher conductivity than the unmodified CrGO. In addition, the FrGO-based OPV showed a power conversion efficiency (PCE) comparable to PEDOT:PSS-based OPVs and a superior OPV stability to PEDOT:PSS, indicating that the one-step reduced and functionalized FrGO is a more desirable interfacial material than the conventional PEDOT:PSS HTL for the realization of higher-efficiency and better-stability OPVs.

To confirm the successful FrGO synthesis illustrated in Figure 1(a), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were used as shown in Figure 1(b), S1, and S2. The C 1s spectra of CrGO and FrGO consist of various components assigned to C-C (284.8 eV), C-N (285.9 eV), C-O (286.5 eV), C=O (287.2 eV), O=C-O (289.0 eV), and C-F₃ (292.4 eV) functional groups, as shown in Figure 1(b).²⁴ The C-O, C=O, and O=C-O peak-intensities in CrGO and FrGO were much smaller, as shown in Figure 1(b) and S1, indicating that the oxygen functional groups were effectively eliminated²⁵ and that the phenylhydrazine and 4-(trifluoromethyl)phenylhydrazine are efficient reducing agents for GO reduction. Here, the peak of the C-N bonds of hydrazones (285.9 eV) indicates that the trifluoromethylphenyl and phenyl groups from the 4-(trifluoromethyl)phenylhydrazine and phenylhydrazine

reductants are attached to the CrGO and FrGO graphene sheets, respectively.²² More importantly, as shown in the inset of Figure 1(b), a clear F 1s peak is observed, indicating the presence of fluorine.²⁶ As shown in the AFM images of Figure S1 and S2, the thicknesses of the CrGO and FrGO single sheets were 1.30 nm and 1.44 nm, respectively, which were relatively thicker than generally known GO and r-GO sheets.^{22, 27} This result could be due to the bulky phenyl functional groups grafted onto the CrGO and FrGO sheets.²⁸ The resultant FrGO showed a better conductivity (σ) of ~ 3.5 S/m than the pristine CrGO (~ 1.6 S/m), which were $\sim 10^3$ times higher than the σ of GO.^{20, 21} Furthermore, as shown in Figure 3S, the FrGO showed an excellent dispersibility of ~ 5 mg/ml in polar organic solvents (dimethylformamide, DMF) without any surfactants, which exceeds the CrGO dispersibility of ~ 3 mg/ml and is highly superior to the conventional hydrazine-based rGO, which generally shows a poor dispersibility (~ 1 mg/ml or lower).^{20, 22} There were no large differences between the FrGO and CrGO XPS data (with the exception of fluorine). The FrGO showed a better dispersibility than the pristine CrGO, and the CF₃ groups can reduce the van der Waals interaction due to the bulky unit;²⁹ it is believed that the CF₃ functional groups are responsible for the enhanced dispersibility. More importantly, these results confirm that FrGO has better conductivity and dispersibility than the pristine CrGO, and the novel reductant, 4-(trifluoromethyl)phenylhydrazine, effectively removes various oxygen functional groups attached to GO while simultaneously functionalizing the graphene with fluorine atoms via a one-step reduction process.

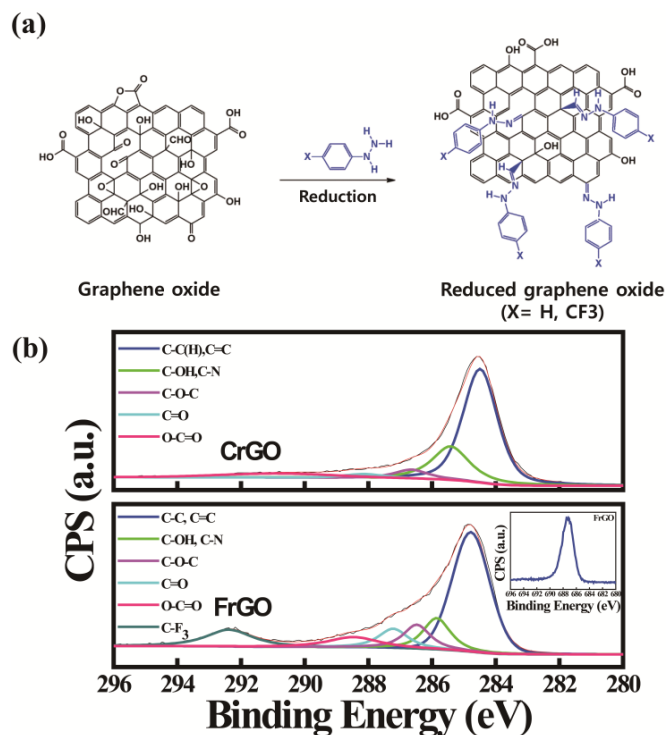


Figure 1 (a) Schematic illustration of CrGO and FrGO reduced by phenylhydrazine based reductants. (b) XPS spectra of C 1s for CrGO and FrGO. The inset shows the F 1s spectrum.

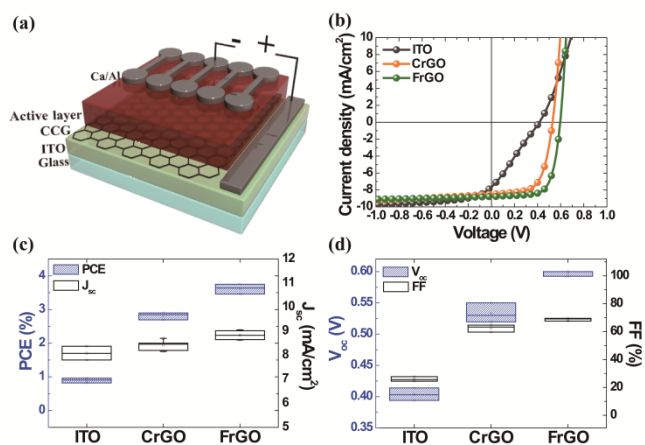


Figure 2 (a) Schematic illustration of the OPV structure. (b) Representative J-V curves of OPVs based on different anode interfacial layers. Influence of the different interfacial layers on the (c) PCE and J_{sc} and (d) V_{oc} and FF of OPVs.

For a feasibility study of FrGOs as an HTL in OPVs, we fabricated FrGO-based OPVs and compared them with other reference OPVs using CrGO or bare indium tin oxide (ITO). Figure 2(a) and (b) show the tested device architecture and representative current density-voltage (J-V) curves of the fabricated OPVs, respectively. As shown in Figure 2(b) and Table S1, the ITO-based OPV with no HTLs exhibited very poor OPV characteristics, but the other OPVs exhibited enhanced device characteristics. In particular, the OPV efficiency was significantly enhanced up to 3.64 % with FrGO. For better comparative studies, changes in the OPV characteristics, including the PCE, J_{sc}, V_{oc}, and FF values that resulted from varying the HTL, are summarized in Figure 2(c) and (d) and Table S2. As shown in Figure 2(c) and (d), all OPV performances were enhanced by the use of rGO-based HTLs, and the enhanced PCEs originated from the dramatic increase in V_{oc} and FF and the relatively small increase in J_{sc}. The OPV with only ITO showed an average PCE of 0.949%, FF of 30.17%, V_{oc} of 0.384 V, and J_{sc} of 8.084 mA/cm², which could result from the large mismatch between the ITO WF and the HOMO of the poly(3-hexylthiophene) (P3HT) donor polymer, leading to inefficient diode characteristics.^{7, 9, 30} With the CrGO, the average V_{oc}, FF, J_{sc}, and PCE increased by 0.53 V, 62.54%, 8.46 mA/cm², and 2.81%, respectively. However, these values did not approach those of conventional P3HT:[6,6]-phenyl-C61 butyric acid methyl ester (PCBM)-based OPVs. In contrast, the FrGOs significantly raised the V_{oc} to 0.6 V, the FF to 68.74%, the J_{sc} to 8.83, and the PCE to 3.62%, approaching the typical cell-parameters shown in the conventional P3HT:PCBM-based OPVs.^{3, 20} These results clearly show that the newly synthesized FrGO can efficiently act as a hole transporting layer to improve the overall performance of solar cells.

To investigate why the FrGO showed enhanced cell performances, various studies on the WF, transmittance and series (R_s) or shunt resistance (R_{sh}) in OPVs, as well as atomic force microscopy (AFM), were performed, as shown in Figure 3 and S4. As shown in the ultraviolet photoelectron spectroscopy (UPS) data of Figure 3(a), there was a significant difference in the WF values, but the corresponding transmittance, which can also have an effect on cell efficiency, showed no large differences, as depicted in Figure S4(a). The WF of ITO was 4.32 eV, while the CrGO showed an increased WF of 4.74 eV, and the FrGO showed a WF of 4.97 eV, larger than that of CrGO and generally known CCGs (4.6–4.8 eV).^{17–21} The larger WF of FrGO could be attributed to the existence of fluorine

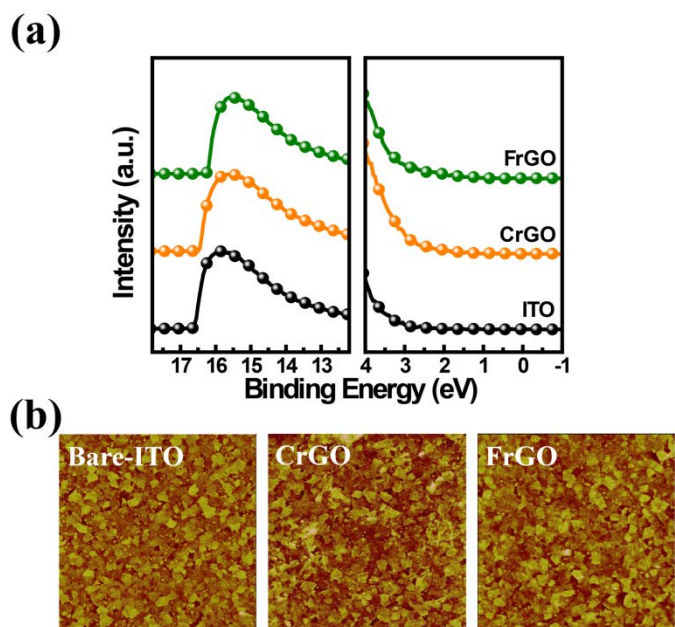


Figure 3 (a) UPS spectra and (b) AFM images of ITO, CrGO, and FrGO.

with a high electronegativity, which induces p-type doping.^{26, 31} Considering that better matching between the WF of ITO and the donor-polymer HOMO by interfacial layers can further improve the built-in potential and the interface resistance, thereby enhancing V_{oc} , FF, and J_{sc} ,⁶⁻¹⁰ the larger WF of FrGO could be responsible for the more improved device characteristics of OPVs with FrGO compared with bare ITO and CrGO.

In addition to the WF, the film morphology of the interfacial materials can influence the FF and PCE,^{8, 9, 20} therefore, AFM analyses were conducted. As shown in Figure 3(b), the root mean square (rms) roughness values of ITO, CrGO, and FrGO were 2.53, 3.11, and 2.70 nm, respectively; the CrGO showed a higher rms value than FrGO. Considering that a non-homogeneous film morphology or a non-uniform film surface can induce poor R_s and R_{sh} values, which result in a poor FF,^{8, 9, 20} and that a lower conductivity (σ) of the HTL materials can also induce poor R_s and FF values,^{10, 20} the smoother film morphology and higher conductivity observed in FrGO films could also be responsible for the better FF and PCE shown in FrGO-based OPVs. These results were also in agreement with the R_s and R_{sh} data shown in Figure S4(b). From these results, it was believed that the enhanced OPV performance observed in the FrGO-based OPVs could be attributed to the larger WF, better film-morphology, and higher σ than those of the pristine CrGO.

To show that the FrGO can be a viable candidate to replace PEDOT:PSS, we directly compared the FrGO-based OPV with the PEDOT:PSS-based OPV. As shown in Figure 4(a), the FrGO-based OPV showed nearly identical cell performances: the PEDOT:PSS-based cell had a PCE of 3.60%, a V_{oc} of 0.60 V, an FF of 66.3%, and a J_{sc} of 9.00 mA/cm². This result is well consistent with the external quantum efficiency (EQE) data depicted in the inset of Figure 4(a). The stability in air of the FrGO OPV based on the ISOS-D-1 protocol³² was also studied and recorded as a function of time. Although the conventional PEDOT:PSS showed a high cell efficiency similar to FrGO, the PEDOT:PSS device showed very poor cell stability compared with the FrGO-based OPV, as demonstrated in Figure 4(b). Considering that the pH value obtained from a 5mg/ml FrGO solution in deionized water is ~ 7.90 and that graphene materials show a good passivation from oxygen and moisture (contact angle = 88.8 degree),^{33, 34} the dramatic changes in

device stability shown in the PEDOT:PSS-based OPV could be due to the inherent material properties of PEDOT:PSS with high acidity (pH = ~ 1) and hydrophilicity (contact angle = 31.7 degree), as shown in Figure S5.¹³ To expand the potential of FrGO as HTLs in OPVs, we fabricated two different OPV systems based on a blend of thieno[3,4-*b*]thiophene/benzodithiophene:[6,6]-phenyl C_{71} -butyric acid methyl ester (PTB7:PC₇₁BM) and P3HT:indene- C_{60} bisadduct (ICBA). As shown in Figure 5 and Table S3, the FrGO OPV based on PTB7:PC₇₁BM exhibited excellent device-performances: a PCE of 6.71%, a V_{oc} of 0.70 V, an FF of 65.1%, and a J_{sc} of 14.84 mA/cm², closely approaching PEDOT:PSS OPVs based on PTB7:PC₇₁BM, which have a PCE of 6.85%, a V_{oc} of 0.71 V, an FF of 63.76%, and a J_{sc} of 15.05 mA/cm². A similar trend and result were also observed in P3HT:ICBA-based OPVs, as shown in Figure 5 and Table S3. This result clearly shows that the FrGO can be effectively utilized in various donor or acceptor-based OPV systems.

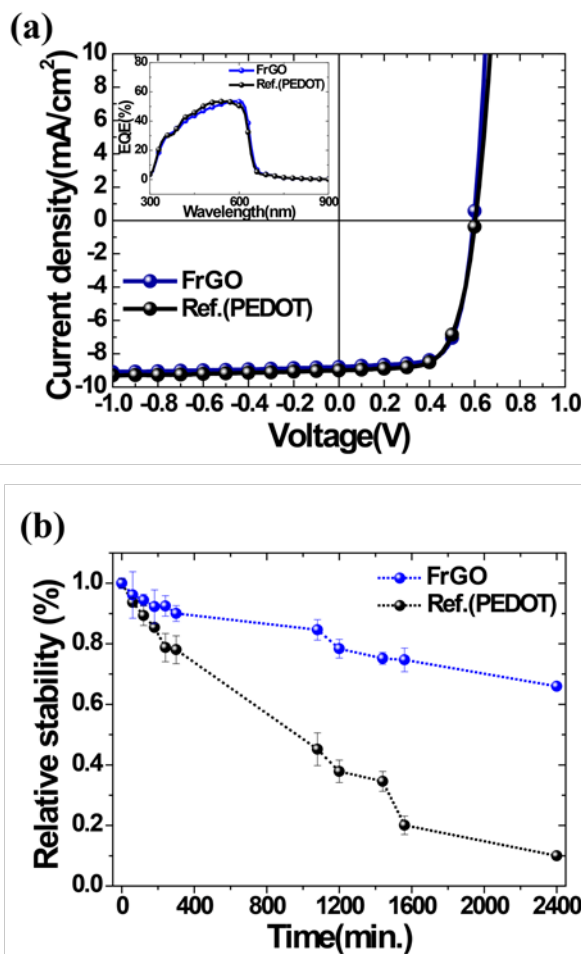


Figure 4 (a) The representative J-V curves for OPVs with FrGO and PEDOT:PSS. The inset shows EQE data. (b) Changes in the PCEs of FrGO-based OPVs and PEDOT:PSS based OPVs under an ambient atmosphere.

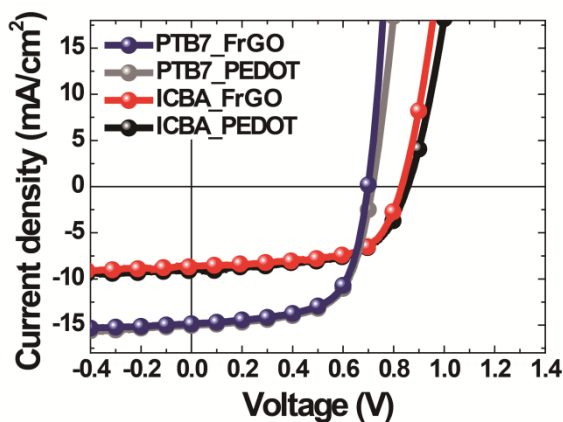


Figure 5 The representative J-V curves for PTB7 or ICBA-based OPVs with FrGO and PEDOT:PSS.

Conclusions

In conclusion, we showed a simple way to reduce graphene oxide and simultaneously introduce fluorine functionalization, yielding FrGO. In addition, the FrGO was successfully utilized as an anodic interfacial material in OPVs. A facile one-step reduction and functionalization of graphene oxide was achieved using a novel phenylhydrazine-based reductant containing fluorine atoms, 4-(trifluoromethyl)phenylhydrazine, which effectively removed oxygen functional groups attached to GO and simultaneously doped fluorine atoms on the basal plane and edges of the graphene sheets. A control rGO with no fluorine was also synthesized using phenyl hydrazine reductants, and it was investigated as a reference for rGO-based HTLs in OPVs. The FrGO showed desirable properties for use as HTLs in OPVs, such as a high dispersion concentration (~5 mg/ml) and work-function (4.97 eV), a uniform film-morphology with a 2.7 nm rms roughness, and a good conductivity (~3.5 S/m). As a result, the FrGO dramatically raised the OPV efficiencies up to 3.62% for P3HT:PCBM, 4.57% for P3HT:ICBA, and 6.71% for PTB7:PC₇₁BM, thus successfully demonstrating the excellent performance of FrGOs as HTLs and the feasibility of their use in various OPVs. In addition, the FrGO-based OPV showed a similar PCE to PEDOT:PSS-based OPVs and a superior OPV stability to PEDOT:PSS. This one-step reduction and functionalization of graphene could be highly desirable and beneficial for the future development of OPVs with excellent efficiencies and stabilities.

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Notes and references

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- 1 C. Brabec, U. Scherf and V. Dyakonov, *Organic photovoltaics: materials, device physics, and manufacturing technologies*, Wiley, com, 2011.
- 2 K. Norrman, M. V. Madsen, S. A. Gevorgyan and F. C. Krebs, *Journal of the American Chemical Society*, 2010, **132**, 16883-16892.
- 3 S.-I. Na, S.-S. Kim, J. Jo and D.-Y. Kim, *Adv. Mater.*, 2008, **20**, 4061-4067.
- 4 R. F. Service, *Science*, 2011, **332**, 293.
- 5 J. You, C.-C. Chen, Z. Hong, K. Yoshimura, K. Ohya, R. Xu, S. Ye, J. Gao, G. Li and Y. Yang, *Adv. Mater.*, 2013, **25**, 3973-3978
- 6 H. Ma, H.-L. Yip, F. Huang and A. K. Y. Jen, *Adv. Funct. Mater.*, 2010, **20**, 1371-1388.
- 7 S.-I. Na, T.-S. Kim, S.-H. Oh, J. Kim, S.-S. Kim and D.-Y. Kim, *Appl. Phys. Lett.*, 2010, **97**, 223305.
- 8 R. Steim, S. A. Choulis, P. Schilinsky and C. J. Brabec, *Appl. Phys. Lett.*, 2008, **92**, 093303.
- 9 L.-M. Chen, Z. Hong, G. Li and Y. Yang, *Adv. Mater.*, 2009, **21**, 1434-1449.
- 10 R. Steim, F. R. Kogler and C. J. Brabec, *J. Mater. Chem.*, 2010, **20**, 2499-2512.
- 11 L.-M. Chen, Z. Xu, Z. Hong and Y. Yang, *J. Mater. Chem.*, 2010, **20**, 2575-2598.
- 12 H.-L. Yip, S. K. Hau, N. S. Baek, H. Ma and A. K. Y. Jen, *Adv. Mater.*, 2008, **20**, 2376-2382.
- 13 M. Jørgensen, K. Norrman and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2008, **92**, 686-714.
- 14 S. Shao, J. Liu, J. Bergqvist, S. Shi, C. Veit, U. Würfel, Z. Xie and F. Zhang, *Adv. Energy Mater.*, 2013, **3**, 349-355.
- 15 G. Li, C.-W. Chu, V. Shrotriya, J. Huang and Y. Yang, *Appl. Phys. Lett.*, 2006, **88**, 253503.
- 16 M. D. Irwin, J. D. Servaites, D. B. Buchholz, B. J. Leever, J. Liu, J. D. Emery, M. Zhang, J.-H. Song, M. F. Durstock, A. J. Freeman, M. J. Bedzyk, M. C. Hersam, R. P. H. Chang, M. A. Ratner and T. J. Marks, *Chem. Mater.*, 2011, **23**, 2218-2226.
- 17 J. Liu, Y. Xue, Y. Gao, D. Yu, M. Durstock and L. Dai, *Adv. Mater.*, 2012, **24**, 2228-2233.

- 18 S.-S. Li, K.-H. Tu, C.-C. Lin, C.-W. Chen and M. Chhowalla, *ACS Nano*, 2010, **4**, 3169-3174.
- 19 Y. Gao, H.-L. Yip, K.-S. Chen, K. M. O'Malley, O. Acton, Y. Sun, G. Ting, H. Chen and A. K. Y. Jen, *Adv. Mater.*, 2011, **23**, 1903-1908.
- 20 J.-M. Yun, J.-S. Yeo, J. Kim, H.-G. Jeong, D.-Y. Kim, Y.-J. Noh, S.-S. Kim, B.-C. Ku and S.-I. Na, *Adv. Mater.*, 2011, **23**, 4923-4928.
- 21 J. Liu, Y. Xue and L. Dai, *J. Phys. Chem. Lett.*, 2012, **3**, 1928-1933.
- 22 V. H. Pham, T. V. Cuong, T.-D. Nguyen-Phan, H. D. Pham, E. J. Kim, S. H. Hur, E. W. Shin, S. Kim and J. S. Chung, *Chem. Comm.*, 2010, **46**, 4375-4377.
- 23 P.-G. Ren, D.-X. Yan, X. Ji, T. Chen and Z.-M. Li, *Nanotechnology*, 2011, **22**, 055705.
- 24 D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228-240.
- 25 V. H. Pham, T. T. Dang, K. Singh, S. H. Hur, E. W. Shin, J. S. Kim, M. A. Lee, S. H. Baeck and J. S. Chung, *J. Mater. Chem. A*, 2013, **1**, 1070-1077.
- 26 A. L. Walter, K.-J. Jeon, A. Bostwick, F. Speck, M. Ostler, T. Seyller, L. Moreschini, Y.-S. Kim, Y. J. Chang, K. Horn and E. Rotenberg, *Appl. Phys. Lett.*, 2011, **98**, 184102-184103.
- 27 J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang and S. Guo, *Chem. Comm.*, 2010, **46**, 1112-1114.
- 28 B. Levrard, Y. Ruff, J.-M. Lehn and A. Herrmann, *Chem. Comm.*, 2006, **28**, 2965-2967.
- 29 Y. Si and E. T. Samulski, *Nano Lett.*, 2008, **8**, 1679-1682.
- 30 A. W. Hains, J. Liu, A. B. F. Martinson, M. D. Irwin and T. J. Marks, *Adv. Funct. Mater.*, 2010, **20**, 595-606.
- 31 I. Gierz, C. Riedl, U. Starke, C. R. Ast and K. Kern, *Nano Letters*, 2008, **8**, 4603-4607.
- 32 M. O. Reese, S. A. Gevorgyan, M. Jørgensen, E. Bundgaard, S. R. Kurtz, D. S. Ginley, D. C. Olson, M. T. Lloyd, P. Morvillo, E. A. Katz, A. Elschner, O. Haillant, T. R. Currier, V. Shrotriya, M. Hermenau, M. Riede, K. R. Kirov, G. Trimmel, T. Rath, O. Inganäs, F. Zhang, M. Andersson, K. Tvingstedt, M. Lira-Cantu, D. Laird, C. McGuinness, S. Gowrisanker, M. Pannone, M. Xiao, J. Hauch, R. Steim, D. M. DeLongchamp, R. Rösch, H. Hoppe, N. Espinosa, A. Urbina, G. Yaman-Uzunoglu, J.-B. Bonekamp, A. J. J. M. van Breemen, C. Girotto, E. Voroshazi and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 1253-1267.
- 33 H. Kim, Y. Miura and C. W. Macosko, *Chem. Mater.*, 2010, **22**, 3441-3450.
- 34 Z. Liu, J. Li and F. Yan, *Adv. Mater.*, 2013, **25**, 4296-4301.