

Supplementary Information

Highly conductive and dispersible graphene and its application for P3HT-based solar cells

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Experimental

Synthesis of graphene oxide: Graphene oxides were produced using commercially available graphite (Sigma-Aldrich, Asbury Carbon, 3061) without further purification according to the Hummers method.¹ 15 g of potassium permanganate (KMnO₄, Sigma-Aldrich) was gradually added to the solution containing graphite while maintaining the temperature of the solution at subzero level in an ice bath. The temperature of the solution was then raised to 35 °C and stirred for 2 h. 230 mL of deionized water (DI) was slowly added to the solution while stirring. After 15 min, an additional 700 mL of DI was added to terminate the oxidation reaction. Finally, 12.5 mL of hydrogen peroxide (30 % H₂O₂) was added, which produced a dark yellowish brown solution of oxidized graphene and graphite. A combination of filtration and centrifugation was subsequently employed to remove the graphite, metallic ions, and excess acid. The resultant dark brownish powder was washed three times with centrifuge in water-ethanol mixture solution. The powder was dried in vacuum at 100 °C for 12 h.

Reduction of PCA-grafted graphene oxide: The PCA-grafted GO was reduced by Scheme 1. 5 mg of GO was dispersed in 50 mL DI (a). After 10 min of sonication, to graft GO with PCA (i.e., PCA-GO) a certain quantity of PCA was added into the GO-containing solution and stirred for 1 h at 1500 rpm (b). In order to deoxygenate the PCA-GO, a minimum quantity of N₂H₄ (i.e., 125 µL or 0.25 vol%) was added to the solution at RT and sonicated for 24 h (c). 20 mg of NaOH (or 0.01 M) was then added to the solution under stirring and the resultant solution was kept at RT for 1 h, followed by refluxing at 100 °C for another 1 h (d). Finally, black powders of reduced PCA-grafted graphene oxide (i.e., rGO-PCA) were obtained, washed with DI and collected by vacuum filtration with Anodisc filter (Whatman, pore size 0.1 µm). It is worthwhile to note that more graphene sheets can be stabilized with more adsorption of PCA onto graphene sheets, but the degree of dissociation in functional groups drops considerably, which alters the dispersion and electrostatic forces in the solution. Thus, in this work, to examine the effect of PCA concentration on the solubility and conductivity, the amount of PCA added was varied from 2.5 to 10 mg (i.e., 5 mg rGO/2.5 mg PCA, 5 mg rGO/5 mg PCA, and 5 mg rGO/10 mg PCA). In order to elucidate the effects of chemistry and thermal treatment on the removal of functional groups, four different reduction schemes have been examined (see Table S1); the reduction of GO-PCA with N₂H₄ (125 µL) at RT for 24 h, followed by NaOH (20 mg) treatment at RT for 1 h and refluxing at 100 °C for 1 h (S1; we call this scheme 'standard'), the reduction of GO with N₂H₄ (125 µL) at RT for 24 h, followed by NaOH (20 mg) treatment at RT for 1 h and refluxing at 100 °C for 1 h (S2), the reduction of GO-PCA with N₂H₄ (125 µL) at RT for 24 h, followed by refluxing at 100 °C for 1 h (S3), and the reduction of GO-PCA with N₂H₄ (125 µL) at RT for 24 h, followed by NaOH (20 mg) treatment at RT for 1 h without refluxing (S4). The addition of NaOH to the rGO suspension also improves the solubility of the carboxyl-terminated functionalities.²

Fabrication of Solar Cells: A hybrid solar cell was fabricated using the mixture of rGO-PCA and poly(3-hexylthiophene) regioregular (P3HT) in the active layer with the structure of glass/ITO/ZnO/rGO-PCA/P3HT:PCA-rGO/GO/Ag. A mixture solution of zinc acetate (0.75 mol/dm³) and monoethanolamine (0.35 mol/dm³) in 100 mL 2-methoxy ethanol was prepared. The solution was spun on ITO glass at 1200 rpm for 30 s and the as-obtained ZnO films (i.e., ITO/ZnO) were annealed at 300 °C for 15 min in air. The PCA-rGO solution in ethanol (1 mg/mL) was spun on the ITO/ZnO at 1200 rpm for 20 s to form ITO/ZnO/ PCA-rGO. Here, the ZnO/PCA-rGO layer acts as electron transport layer (ETL). In order to form the active layer of hybrid electrolyte, 30 mg/mL of P3HT in 2-dichlorobenzene (DCB) was mixed with the PCA-rGO solution (1 mg/mL). The hybrid electrolyte was then spun on the ETL at 800 rpm for 30 s under N₂ atmosphere in a glove box. The deposited samples were kept at RT for 45 min, followed by heating to 150 °C for 10 min in N₂. The GO containing propanol solution (1 mg/mL) was spun on the active layer to be used for HTL. Finally, silver electrode (2×2 mm²) having a thickness of 50 nm was sputter-deposited on the HTL in Ar atmosphere at a working pressure of 1.5×10⁻³ Torr and RF power of 60 W. The effective area of each cell discussed in this work was 0.25 cm².

Characterization: The structural characterization of the rGO and PCA-rGO was performed with transmission electron microscopy (TEM, JEOL JEM-2100F, operated at 200 KV). The as-prepared samples were also subject to characterization by Raman Spectroscopy (Nanofinder 30, Tokyo Instrument) and X-ray photoelectron spectroscopy (XPS) recorded with a Thermo K-α ESCA system with a monochromatic Al-Kα source and a charge neutralizer. The electrical (I –V) measurements were carried out with a probe station (HP 4156C semiconductor parameter analyzer) at different temperatures in the range of 25–200 °C. Based on I –V measurements the conductivity of the PCA-rGO was measured with the graphene films (thickness~1.1 µm) prepared on filter paper under vacuum filtration. A comparison of conductivity between the previously reported

and the as-obtained in this work is summarized in Table S2. For photovoltaic characterization of the solar cell, current density versus voltage (J–V) characteristics in the dark and under white light illumination were measured under simulated AM 1.5 G irradiation (100 mW/cm²).

Scheme 1. Schematic of the reduction process of graphene oxide showing the measured conductivity (σ): (a) graphene oxide, (b) graphene oxide grafted with PCA, (c) reduced graphene oxide with hydrazine, and (d) deoxygenated graphene oxide by NaOH with reflux.

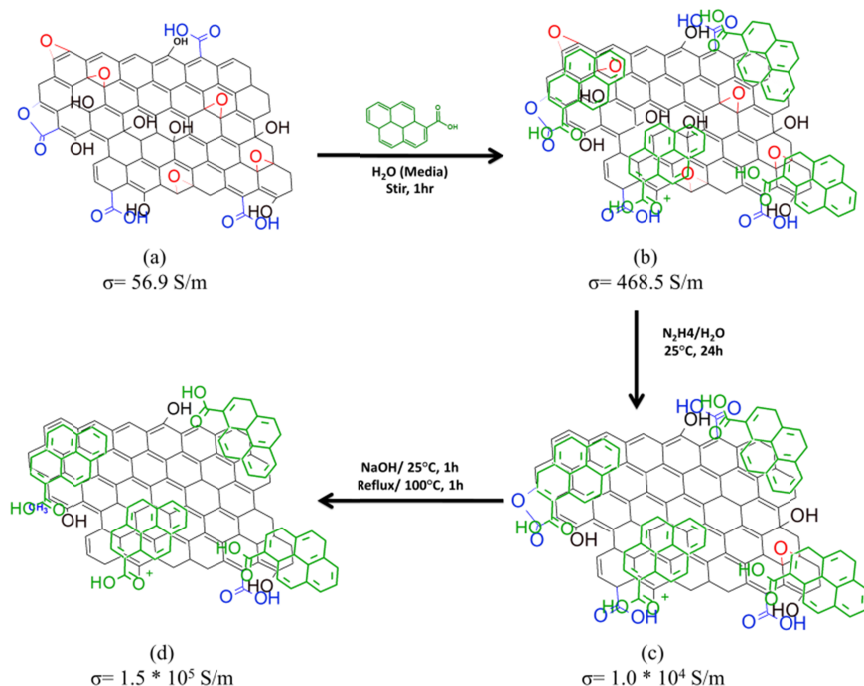


Table S1. Four different reduction schemes numbered as S1, S2, S3 and S4 with conductivity measurements.

Scheme number	Description	Remark	Conductivity (S/m)
S1	Reduction of PCA(10mg)/GO with N ₂ H ₄ (125 μ L) at RT for 24 h, followed by NaOH (20mg) treatment at RT for 1 h with refluxing at 80 °C for 1 h	standard	1.52x10 ⁵
S2	Reduction GO with N ₂ H ₄ (125 μ L) at RT for 24 h, followed by NaOH (20mg) treatment at RT for 1 h with refluxing at 80 °C for 1 h	w/o PCA grafting	1.34x10 ⁴
S3	Reduction of PCA(10mg)/GO with N ₂ H ₄ (125 μ L) at RT for 24 h, followed by refluxing at 80 °C for 1 h	w/o NaOH addition	1.41x10 ⁴
S4	Reduction of PCA(10mg)/GO with N ₂ H ₄ (125 μ L) at RT for 24 h, followed by NaOH (20 mg) treatment at RT for 1 h	w/o refluxing	3.25x10 ⁴

Table S2. Comparison of conductivity between the reported and as-obtained in this work.

Method	Annealing temperature	Reducing agent	Product	Conductivity (S/m)	Ref.
			Pristine graphene	1.59×10^5	3
Solution	RT	Hydrazine/NaOH	rGO	1.52×10^5	this work
Solution	1050 °C	-	rGO	1000-2300	4
Solution	1000 °C	-	rGO	$374-5.73 \times 10^4$	5
Solution	1100 °C	NaBH ₄ / H ₂ SO ₄	rGO	$40.8-2.20 \times 10^4$	6
Solution	800 °C	-	rGO	2.72×10^4	7
Solution	-	Hydrazine	rGO	2.98×10^4	8
CH ₄ plasma	575 °C	-	G-monolayer	1.59×10^5	9
CH ₄ /H ₂ plasma	1000 °C	-	G- monolayer	$3.5 \times 10^4-4.2 \times 10^4$	10
C ₂ H ₂ /H ₂ plasma	1000 °C	-	G-monolayer	1.4×10^5	11
Solution	-	-	Intercalated graphite	9.3×10^4	12

Table S3. Hall measurements results.

Sample	Field (G)	Resistivity (cm)	Hall coefficient (cm ³ /C)	Carrier density (1/cm ³)	Type
PCA/rGO (10mg/10mg)	2.00E+03	6.07E-04	3.13E+00	1.99E+18	p
GO	2.00E+03	1.64E+03	-2.64E+07	2.37E+11	n

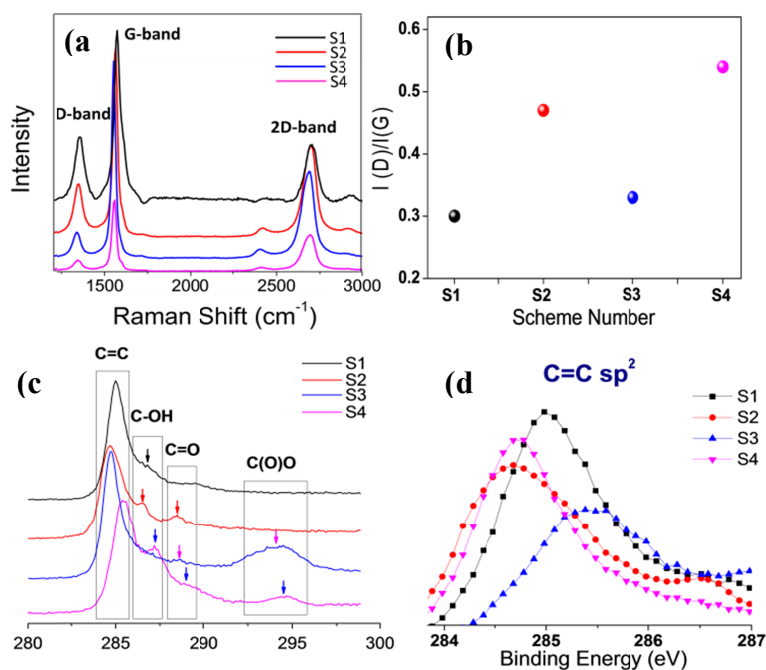


Figure S1. (Top) (a) Raman spectra of the rGO obtained from S1-S4 samples and (b) their I(D)/I(G) ratio. (Bottom) (c) XPS measurements of the C1s from S1-S4 samples and (d) comparison of C1s peaks of C=C bond.

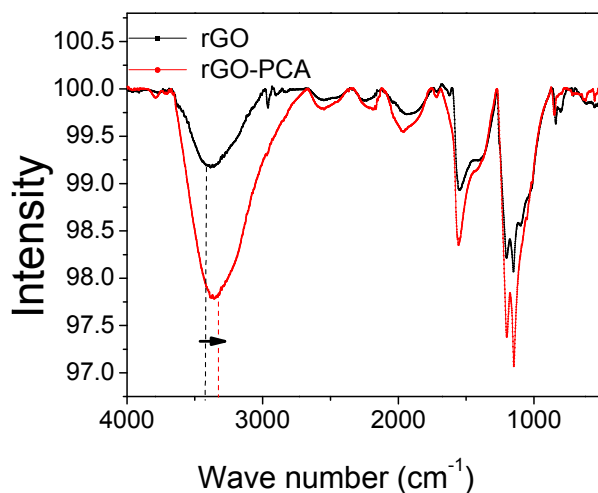


Figure S2. FTIR spectra of rGO (black line) and PCA-rGO (red line), in which, peaks in wave number 3300 cm⁻¹ relate to O-H vibration bond which shows higher intensity by PCA grafting and a blue shift to lower wave numbers which confirms involving the hydroxyl bond into hydrogen bonding between PCA and rGO moieties. The other peaks are: 1780 cm⁻¹ (C=O), 1200 cm⁻¹ (C-OH), 1400 cm⁻¹ (C-H) and 1100 cm⁻¹ (C-O-C).

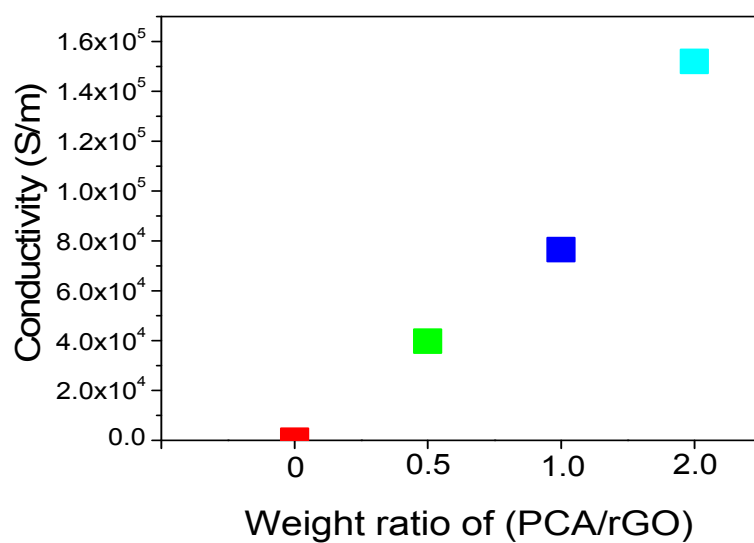


Figure S3. Conductivities of PCA-rGO films with different loadings of PCA.

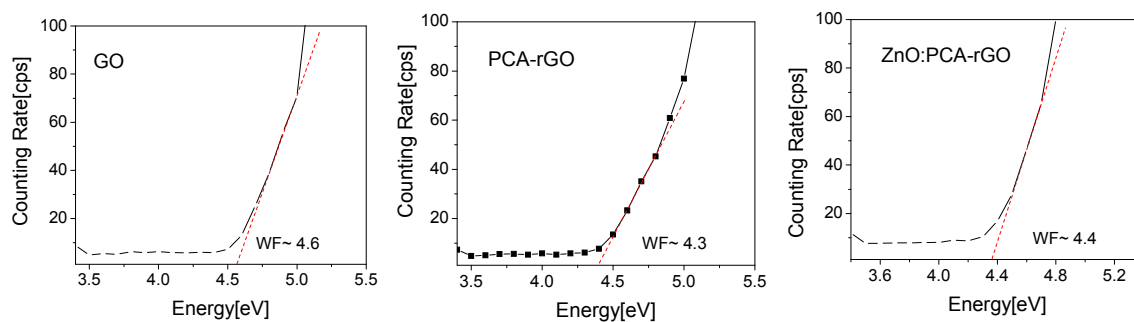


Figure S4. Work function measurements of GO, PCA-rGO and ZnO/PCA-rGO films.

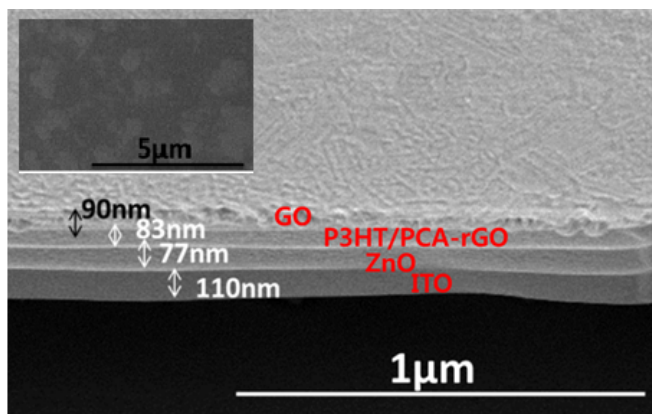


Figure S5. Cross-sectional FESEM image of glass/ITO/ZnO/(P3HT/PCA-rGO/GO). Inset is FESEM image of P3HT:PCA-rGO film. The FESEM images show a smooth and uniform distribution of PCA-rGO in P3HT (inset) and a well-defined interface between active layer (i.e., P3HT/PCA-rGO/GO) and electron transport layer (i.e., ZnO) without showing any vertical segregation and/or phase separation.

Discussion

In the hetero-nuclear bond of carboxyl group in PCA the electrons are not shared equally between two atoms and thus an asymmetrical bond is formed leading to polar feature. By calculation of electronegativity of the atoms attached to carbon in PCA we can explain the effect of the grafted polar molecule on an electron rich material like graphene. The difference in electronegativity ($\Delta\chi$) between atoms A and B is given by equation:¹³

$$\chi_A - \chi_B = (eV)^{-\frac{1}{2}} \sqrt{E_d(AB) - \frac{[E_d(AA) + E_d(BB)]}{2}} \quad (1)$$

where E_d is the dissociation energies of the A–B, A–A and B–B bonds in electron volt (eV). In PCA, the electronegativity for aromatic rings which have equal atoms with equal strength and shared electrons is zero. For the functional groups of C=O and O–H, dissociation energies (E_d) are 3.340 and 4.813 eV, respectively, thus $\Delta\chi$ for each bond is 2.26 and 1.34 (see Table S2). The electronegativity of PCA is then calculated as ~ 0.92 , indicating that the polar functional group in the molecule attached to pyrene rings will induce a dipole to the entire PCA molecule with total electronegativity of 0.92. Besides, due to the π - π interaction between pyrene rings and graphene, the polar nature of the PCA molecule withdraws the π - electrons from the graphene sheets.

Table S2. Standard chemical bonds, bond dissociation energies (E_d), and electronegativity ($\Delta\chi$) calculated by Eq. (1)

Bond	E_d (eV)	$\Delta\chi$
C=O	3.340	2.26
O-H	4.813	1.34
C=C	6.331	0
H-H	4.519	0
C-C	3.60	0
O-O	1.52	0

The phenomenon effectively induces instability in the immobilized π -electrons and significantly boosts electron transport which eventually supports straightforward chemical reduction in presence of the PCA molecules. In addition, the PCA as an electron withdrawer makes free electrons more accessible for bond reduction of C-sp³ to C-sp², which is confirmed by the Raman spectra as shown in Figure 1 (c) and (d). The intensity of the C-sp² (G-band) in PCA-rGO is much higher than that of C-sp³ (D-band) as compared to that of rGO. The attraction of π -electrons of PCA not only plays a significant role in good electrical conductance but also causes a blue shift in peak position of G-band in Raman spectra due to PCA insertion. Despite the presence of the strong double bond, the existence of such electron puller can reduce the concentration of the π -electrons from p-orbital and renders it a weaker bond which can show resonance in lower frequencies thus giving rise to a blue shift in peak position.

References

1. W. S. Hummers Jr and R. E. Offeman, *Journal of the American Chemical Society*, 1958, **80**, 1339-1339.
2. X. Fan, W. Peng, Y. Li, X. Li, S. Wang, G. Zhang and F. Zhang, *Advanced Materials*, 2008, **20**, 4490-4493.
3. Z. Shi, R. Yang, L. Zhang, Y. Wang, D. Liu, D. Shi, E. Wang and G. Zhang, *Advanced Materials*, 2011, **23**, 3061-3065.
4. H. C. Schniepp, J.-L. Li, M. J. McAllister, H. Sai, M. Herrera-Alonso, D. H. Adamson, R. K. Prud'homme, R. Car, D. A. Saville and I. A. Aksay, *The Journal of Physical Chemistry B*, 2006, **110**, 8535-8539.
5. S. Dubin, S. Gilje, K. Wang, V. C. Tung, K. Cha, A. S. Hall, J. Farrar, R. Varshneya, Y. Yang and R. B. Kaner, *Acs Nano*, 2010, **4**, 3845-3852.
6. W. Gao, L. B. Alemany, L. Ci and P. M. Ajayan, *Nature chemistry*, 2009, **1**, 403-408.
7. D. Li, M. B. Mueller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nature nanotechnology*, 2008, **3**, 101-105.
8. S. Pei, J. Zhao, J. Du, W. Ren and H.-M. Cheng, *Carbon*, 2010, **48**, 4466-4474.
9. M. Cheng, R. Yang, L. Zhang, Z. Shi, W. Yang, D. Wang, G. Xie, D. Shi and G. Zhang, *Carbon*, 2012, **50**, 2581-2587.
10. B. Dai, L. Fu, L. Liao, N. Liu, K. Yan, Y. Chen and Z. Liu, *Nano Research*, 2011, **4**, 434-439.
11. Y. Liang, J. Frisch, L. Zhi, H. Norouzi-Arasi, X. Feng, J. P. Rabe, N. Koch and K. Müllen, *Nanotechnology*, 2009, **20**, 434007.
12. K. H. Park, B. H. Kim, S. H. Song, J. Kwon, B. S. Kong, K. Kang and S. Jeon, *Nano letters*, 2012, **12**, 2871-2876.
13. L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*, Cornell University Press, 1960.