Supporting Information

Optical, Electrochemical, Photoelectrochemical and Electrochromic Properties of Polyamide /Graphene Oxide with Various Feed Ratios of Polyamide to Graphite Oxide

Lina Ma¹, Haijun Niu^{1*}, Jiwei Cai¹, Ping Zhao², Cheng Wang¹, Yongfu Lian¹, Xuduo Bai¹, Wen Wang^{3*}

^{1.}Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, Department of Macromolecular Materials and Engineering, School of Chemical and Chemical Engineering, Heilongjiang University, Harbin 150086, P R China. Tel: 086-0451-86608616, E-mail: haijunniu@hotmail.com (Haijun Niu)

² Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, P R China

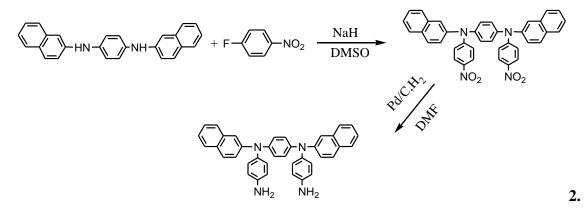
³. School of Material Science and Engineering, Harbin Institute of Technology, Harbin 150080, P R China

*Author to whom correspondence should be addressed

1. Synthesis of Monomers

N,N'-Bis(4-aminophenyl)-N,N'-di-2-naphthalenyl-1,4-benzenediamine was synthesized with modified method according to the literature [1].

Scheme. S1 Synthesis route of Monomers



Synthesis of graphene oxide (GO) and acryl chloride-functionalized graphene oxide (GO)

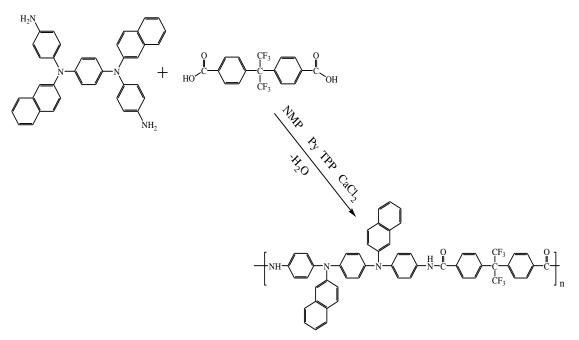
In a typical procedure, graphite (1 g, 325 mesh) and NaNO₃ (0.5 g) were mixed with concentrated H₂SO₄ (25 mL) in a 250 mL flask at 0 °C. The temperature was kept at 5 °C, and the mixture was stirred for 1 h. After that, 3.0 g of KMnO₄ was added in three portions every 10 min with vigorous stirring to prevent temperature rise in excess of 15 °C.Then, the temperature of the reaction mixture was raised to 35 ± 2 °C and the mixture was stirred for 4 h. After completion of the reaction, 100 mL of deionized water was gradually added into the solution. The suspension was reacted further by adding a mixture of H₂O₂ (30 mL, 30%) and water (55 mL). The mixture was centrifuged at 6000 rmp for 8 min. The resulting GO was precipitated at the bottom of the vial. The red-brown solid were repeatedly washed with diluted HCl (3%, 150 mL) and deionized water and centrifuged for 3-4 times, then dried under reduced pressure for 24 h.

Pre-synthesized GO (305.8 mg) was loaded in a 500 mL round bottom flask and water (300 mL) was then added, yielding an inhomogeneous yellow-brown dispersion. This dispersion was sonicated using a DL-720A ultrasonic bath cleaner (500 W) until it became clear with no visible particulate matter. The obtained brown dispersion was then filtered, and dried under reduced pressure overnight.

GO (0.0504 g) was reacted with a large excess of thionyl chloride (10 ml) containing a

catalytic amount of dried DMF under reflux for 24 h under a nitrogen atmosphere, followed by the removal of the residual thionyl chloride under vacuum. The products was dried in vacuum at 40 °C for 48 h which giving acryl chloride-functionalized GO.

Scheme. S2 Synthesis route of PA



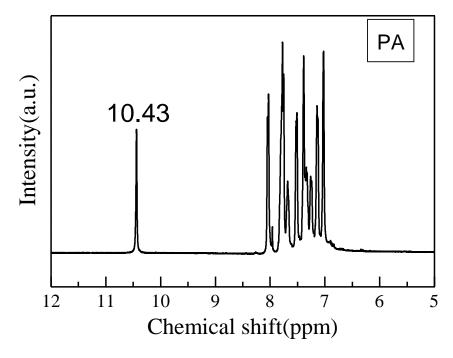
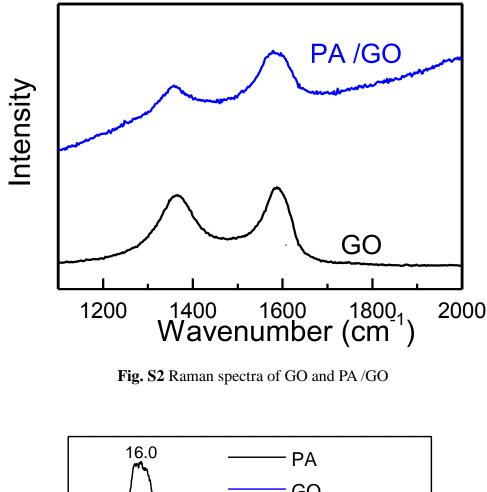


Fig. S1 ¹HNMR spectra of PA



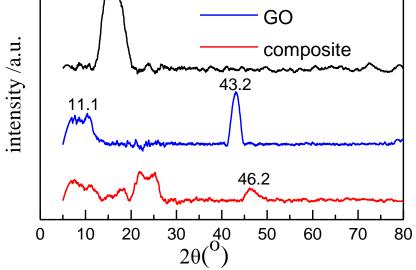


Fig. S3 XRD patterns of PA, GO and PA /GO composite.

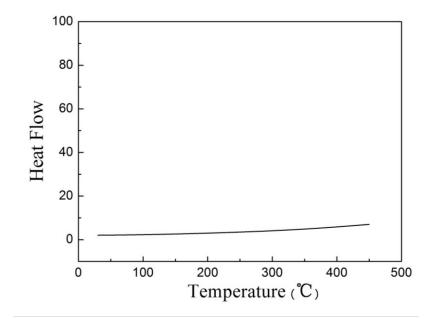


Fig. S4 DSC curve of PA /GO composite.

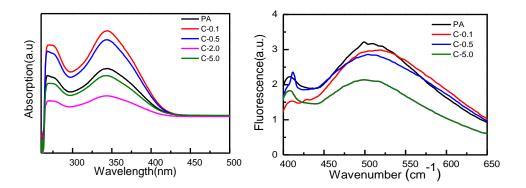


Fig. S5 The UV-visable absorption spectra (a) and fluorescence emission spectra (b) of PA and composites in DMF at room temperature (composite concentration: 1×10^{-6} M).

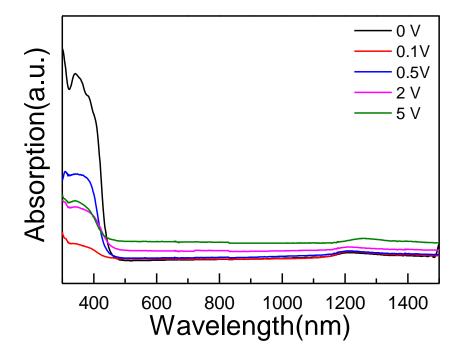
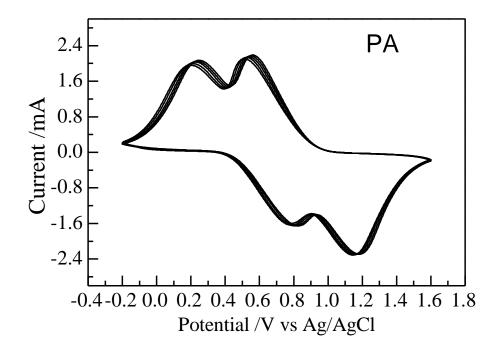
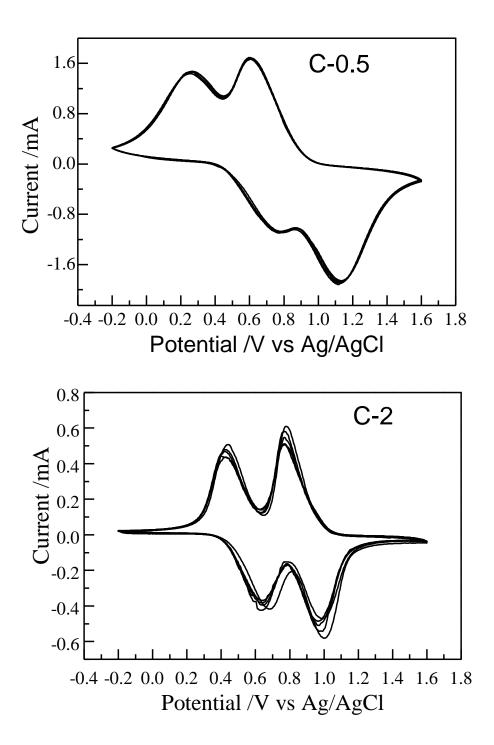


Fig. S6 UV-Visible absorption spectra of composites (film)





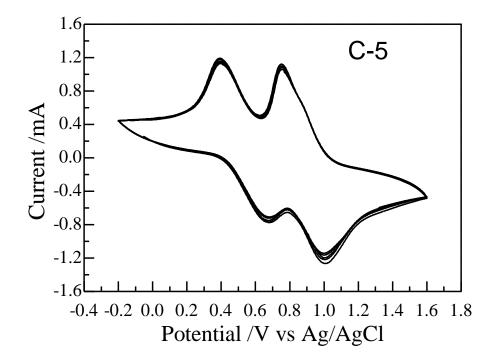
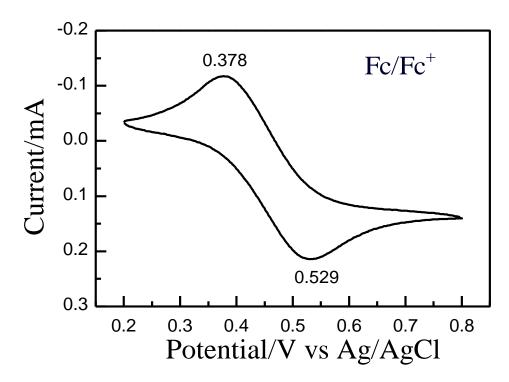


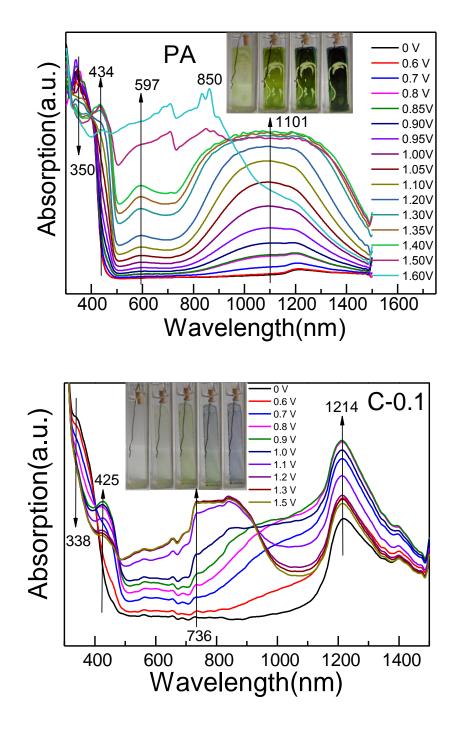
Fig. S7 Cyclic voltammograms for PA and composites in CH₃CN/0.1 M LiClO₄ with Fc/Fc⁺ as an



internal standard, at 50 mV s⁻¹.

Fig. S8 Cyclic voltammograms for ferrocene/ ferrocenium (Fc/ Fc^+) in CH₃CN/ 0.1 mol L⁻¹ LiClO₄ at 50

mV s⁻¹



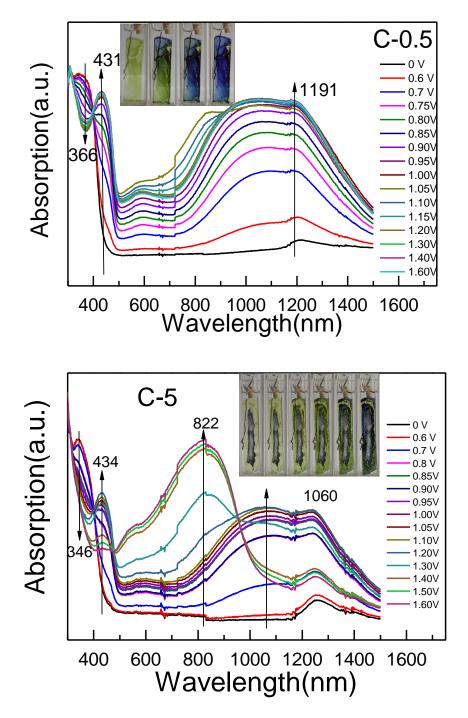
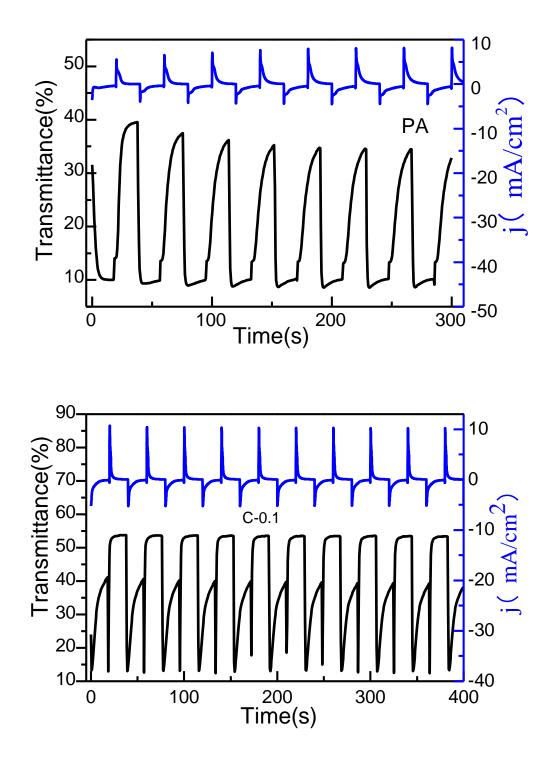


Fig. S9 Electrochromic behavior of C-0.1, C-0.5 and C-5 thin films (in CH₃CN with 0.1 M LiClO₄ as the supporting electrolyte) between 0.0 and 1.6 V (V vs. Ag/AgCl). (insets are the pictures of doped composites).



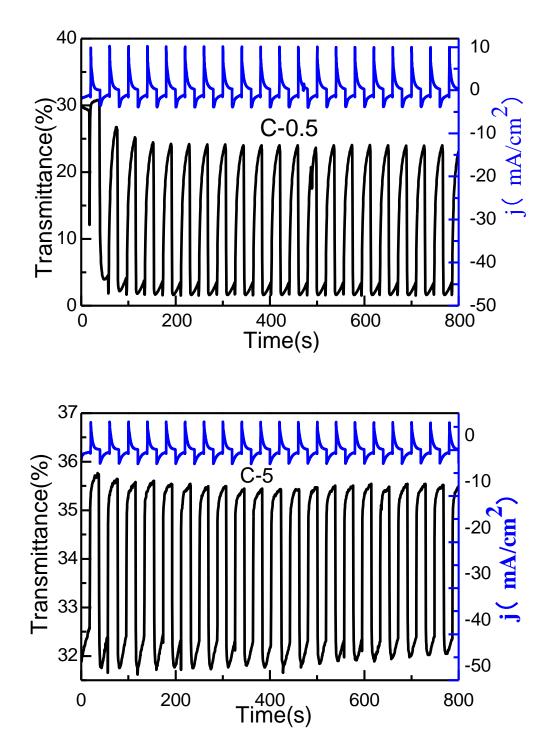


Fig. S10 Dynamic changes of the transmittance and current upon switching the potential between -0.2 ↔ 0.9 V (vs. Ag / AgCl) with a pulse width of 40 s applied to the cast film of PA on the ITO-coated glass slide in MeCN containing 0.1 M LiClO₄. The absorption was recorded at 470 nm.

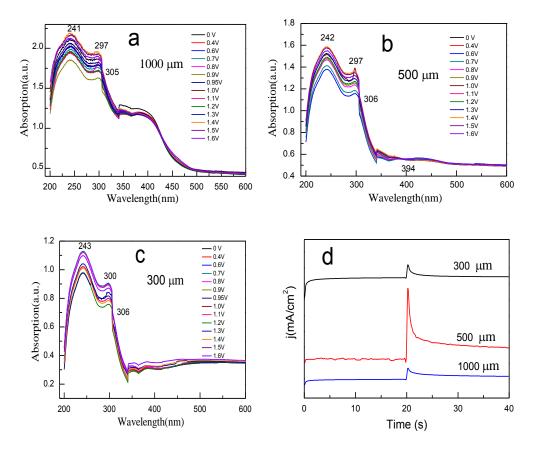
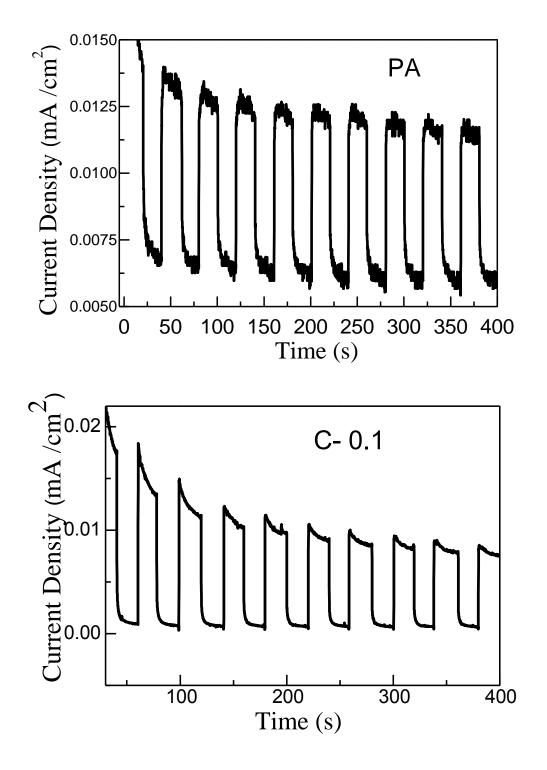


Fig. S11 Electrochromic behavior of C-2 from 0.0 to 1.6 V with 0.05 V potential intervals (V vs. Ag/AgCl) at different thickness (a, b, c), and the dynamic changes of the current upon switching the potential between $-0.2 \leftrightarrow 0.9$ V (vs. Ag/AgCl) with a pulse width of 40 s applied to the cast film of C-2 with

different thickness (d). The absorption was recorded at 434 nm.



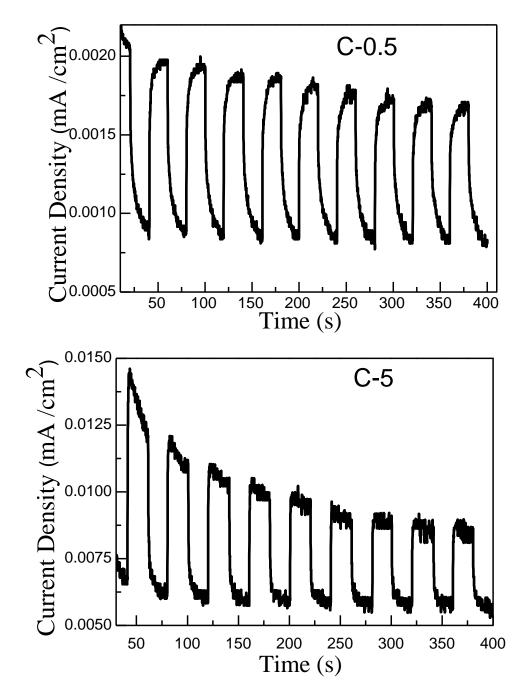


Fig. S12 Typical photocurrent responses for composites immobilized ITO glass upon exposure to on/off light at room temperature.

| | $R_s(\Omega)$ | $R_{ct}(\Omega)$ | CPE (F) |
|-------|---------------|------------------|-----------|
| PA | 73.24 | 28411 | 0.0002473 |
| C-0.1 | 89.15 | 3553 | 0.005133 |
| C-0.5 | 107.6 | 3044 | 0.00699 |
| C-2 | 64.94 | 397.8 | 2.303E-6 |
| C-5 | 139.7 | 1332 | 3.802E-9 |

Table S1 Electrochemical impedance data for PA and composite

[1] Cai, J. W.; Niu, H. J.; Wang, C.; Ma, L. N.; Bai, X. D.; Wang, W. Electrochim Acta 2012, 76, 229–241.