Layer-by-Layer Assembled Sulfonated-Graphene/Polyaniline Nanocomposite Films: Enhanced Electrical and Ionic Conductivities, and Electrochromic Properties

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(Electronic Supplementary Information)

Synthesis of GO and rGO

2.5 g Graphite and 2.5 g $NaNO_3$ were mixed with 120 ml H_2SO_4 in a 500 mL flask. The mixture was stirred for 30 min in an ice bath and 7.5 g of $KMnO_4$ was slowly added to the suspension under vigorous stirring. The ice bath was removed and the mixture was then stirred at 35°C for 24 h. Afterwards, 150 ml of DI H_2O was slowly added to the pasty mixture still under vigorous stirring. The reaction temperature was observed to rapidly increase to over 90°C with effervescence. After 30 min, another 500 ml DI water was added, and then 1.5 mL of 30 wt.% H_2O_2 aqueous solution. For preliminary purification, the mixture was first washed with 5 wt.% HCl aqueous solution, followed by DI water for five times to remove residual acid and salts. The

yellow mixture is centrifuged 30 min at 11,000 rpm. The obtained GO was freeze-dried for 48 h and stored in a dry cabinet for further use. The rGO was also prepared by reducing the as-prepared GO using a $NaBH_4$ aqueous solution at room temperature.

Calculation for the electrical and ionic conductivities of the conducting polymer films

The electrical and ionic conductivities for the conducting polymer films can be calculated based on a widely used model by solving the following equations.

$$\frac{1}{(R_{high}-R_s)} = \frac{1}{R_e} + \frac{1}{R_{ion}} \quad (1)$$

$$3(R_{low} - R_s) = R_{ion} - R_e \quad (2)$$

$$\sigma = \frac{L}{R \cdot A} \quad (3)$$

The R_s is the solution resistance, which can be obtained by testing the impedance using a bare ITO-coated glass substrate (i.e., without depositing the films) as the working electrode. The R_{high} is the value that is the high frequency real axis intercept minus R_s. The R_{low} is the low frequency limiting real impedance. The R_e and R_{ion} are the electronic resistance and ionic resistance of the films. The σ, R, L and A are the conductivity, resistance, thickness and surface area of the films, respectively. Both R_{high} and R_{low} can be extracted from the EIS curves, so the R_e and R_{ion} can be obtained by solving the Equation (1) and (2). Then the σ_e *and* σ_{ion} can be obtained by solving the Equation (3).

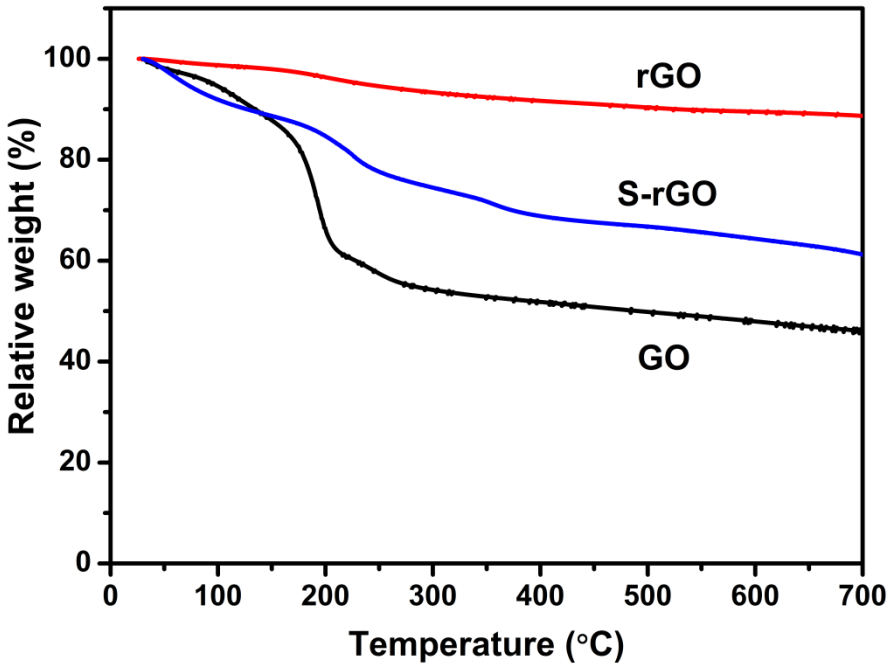

Figure S1. TGA curves of GO, rGO and S-rGO.

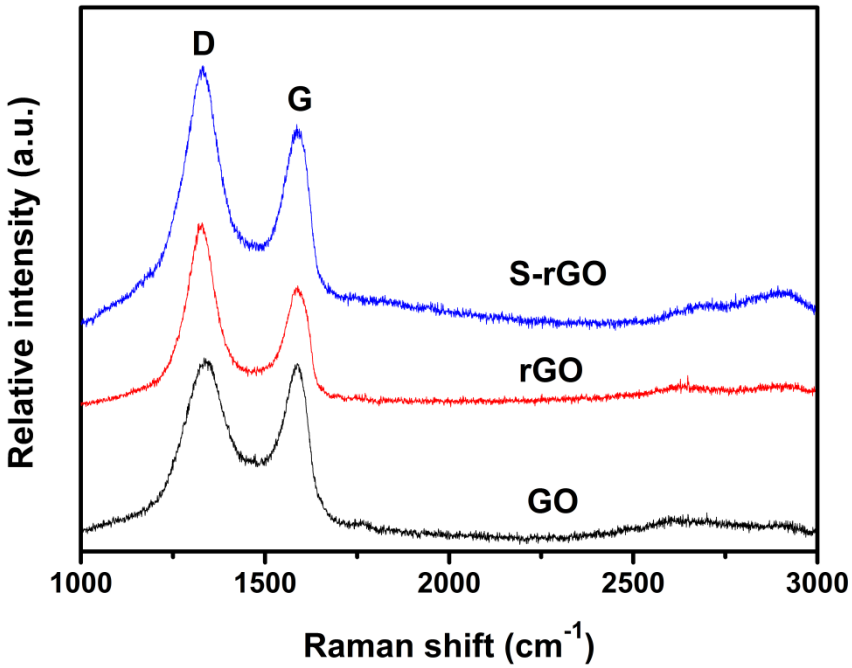

Figure S2. Raman spectra of GO, rGO and S-rGO.

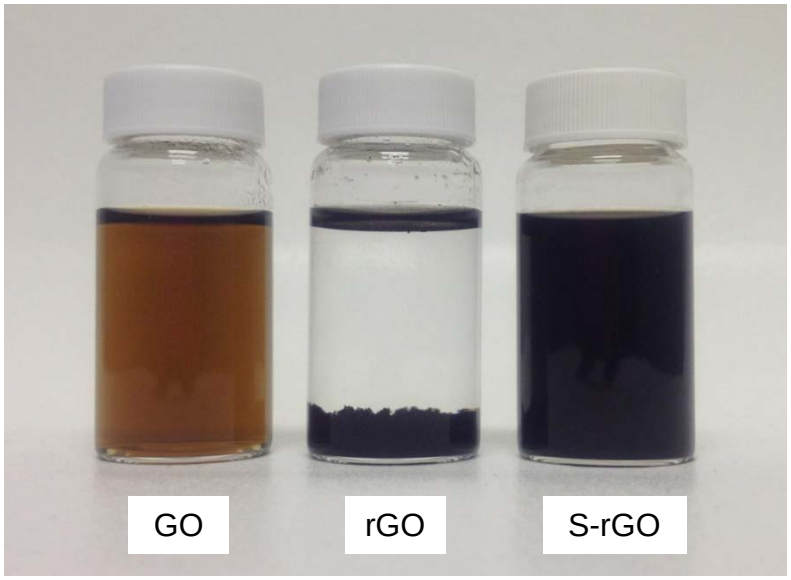

Figure S3. A photograph of the different dispersions after storing for 3 months.

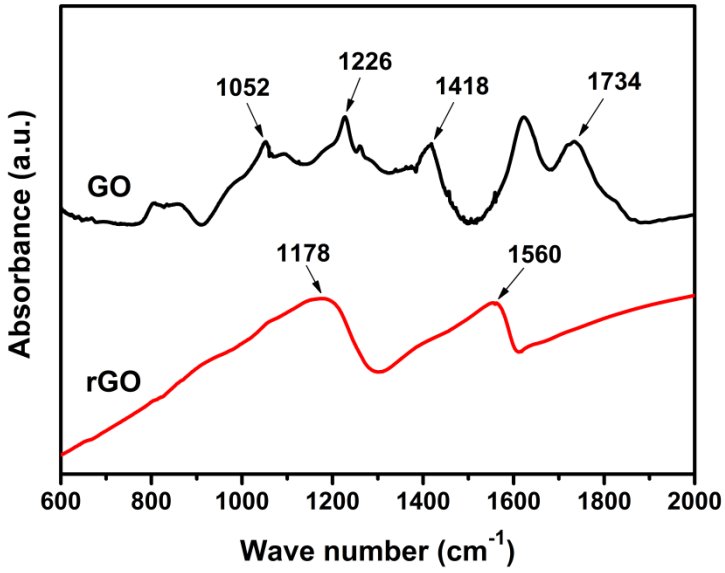

Figure S4. FTIR spectra of GO and rGO. The spectrum of GO illustrates the presence of C-O ($\nu_{C\text{-}O}$ at 1052 cm^{-1}), C-O-C ($\nu_{C\text{-}O\text{-}C}$ at 1226 cm^{-1}), C-OH ($\nu_{C\text{-}OH}$ at 1418 cm^{-1}), and C=O in carboxylic acid and carbonyl moieties ($\nu_{C=O}$ at 1734 cm^{-1}). For the rGO, there are only two peaks at 1178 and 1560 cm^{-1}, indicating the GO has been effectively reduced by $NaBH_4$ in the mild condition.

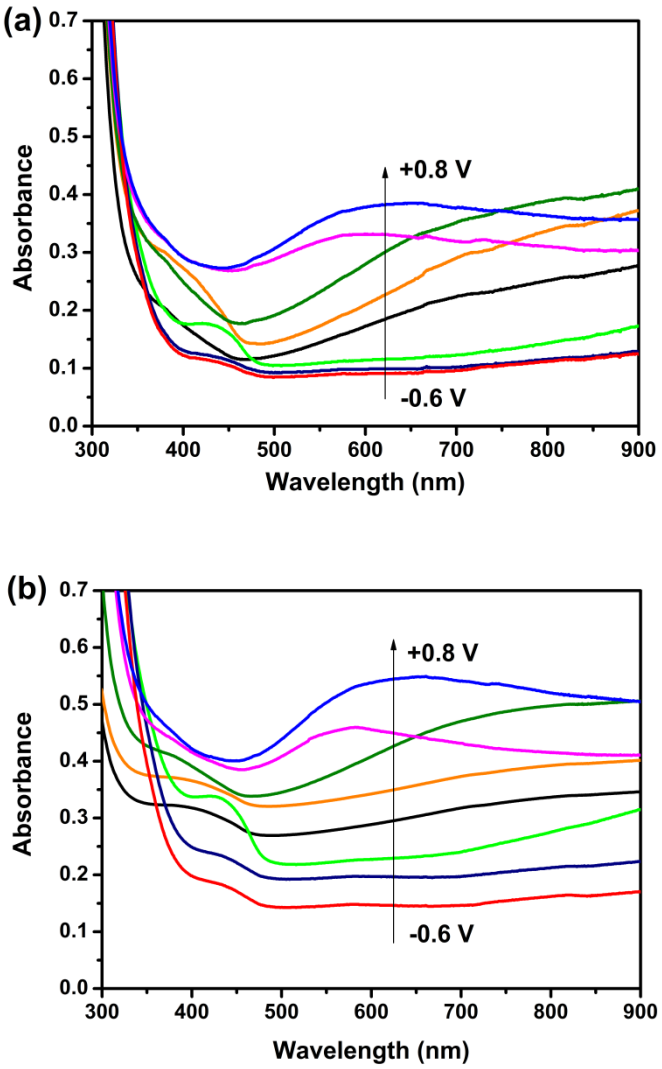

Figure S5. UV-vis absorbance spectra of (a) spin-coated PANI film and (b) $(S\text{-}rGO/PANI)_{25}$ film under different potentials between -0.6 V and 0.8 V with a 0.2 V increase from bottom to up.

Table S1. Elemental analysis of of GO, rGO and S-rGO.

Sample	C (wt.%)	O (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)
GO	52.65	43.17	4.08	<0.10	<0.10
rGO	85.74	13.06	1.20	<0.10	<0.10
S-rGO	74.63	15.42	2.52	2.26	5.17