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

Jinlin Lu#, Wanshuang Liu#, Han Ling, Junhua Kong, Guoqiang Ding, Dan Zhou, Xuehong Lu*

School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.

Email: asxhlu@ntu.edu.sg

# These authors contributed equally to this work.

(Electronic Supplementary Information)

Synthesis of GO and rGO

2.5 g Graphite and 2.5 g NaNO3 were mixed with 120 ml H2SO4 in a 500 mL flask. The mixture was stirred for 30 min in an ice bath and 7.5 g of KMnO4 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 H2O 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.% H2O2 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 NaBH₄ 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.

\[ \frac{1}{R_{\text{high}} - R_s} = \frac{1}{R_s} + \frac{1}{R_{\text{ion}}} \]  \hspace{1cm} (1)

\[ 3(R_{\text{low}} - R_s) = R_{\text{ion}} - R_s \]  \hspace{1cm} (2)

\[ \sigma = \frac{L}{R \cdot A} \]  \hspace{1cm} (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 \( R_{\text{high}} \) is the value that is the high frequency real axis intercept minus \( R_s \). The \( R_{\text{low}} \) is the low frequency limiting real impedance. The \( R_e \) and \( R_{\text{ion}} \) are the electronic resistance and ionic resistance of the films. The \( \sigma, R, L \) and \( A \) are the conductivity, resistance, thickness and surface area of the films, respectively. Both \( R_{\text{high}} \) and \( R_{\text{low}} \) can be extracted from the EIS curves, so the \( R_e \) and \( R_{\text{ion}} \) can be obtained by solving the Equation (1) and (2). Then the \( \sigma_e \) and \( \sigma_{\text{ion}} \) 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 ($v_{\text{C-O}}$ at 1052 cm$^{-1}$), C-O-C ($v_{\text{C-O-C}}$ at 1226 cm$^{-1}$), C-OH ($v_{\text{C-OH}}$ at 1418 cm$^{-1}$), and C=O in carboxylic acid and carbonyl moieties ($v_{\text{C=O}}$ 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-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 GO, rGO and S-rGO.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (wt.%)</th>
<th>O (wt.%)</th>
<th>H (wt.%)</th>
<th>N (wt.%)</th>
<th>S (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>52.65</td>
<td>43.17</td>
<td>4.08</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>rGO</td>
<td>85.74</td>
<td>13.06</td>
<td>1.20</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>S-rGO</td>
<td>74.63</td>
<td>15.42</td>
<td>2.52</td>
<td>2.26</td>
<td>5.17</td>
</tr>
</tbody>
</table>