Reduced Graphene Oxide Grafted by Polymer of Polybromopyrroles to Nanocomposites with Superior Performance for Supercapacitors

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Electronic Supplementary Information

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S1. Preparation of graphene oxide (GO)

1 g of expanded graphite (10–30 μm; Nanjing, China) was added into 10 mL of concentrated sulfuric acid (H\textsubscript{2}SO\textsubscript{4}, 98.3 wt.%), followed by ultrasonic treatment at room temperature for 2 min. Then, 1 g of potassium persulfate (K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}, A. R.) and 1 g of phosphorus pentoxide (P\textsubscript{2}O\textsubscript{5}, A.R.) were slowly added into the above mixture under constant ultrasonic treatment. The mixture was allowed to stand at room temperature for 12 h after agitation at 80 °C for 6 h.

After that, the mixture was diluted to 500 mL by slowly adding distilled water, followed by filtration to obtain the precipitate. The precipitate was transferred into 50 mL of concentrated H\textsubscript{2}SO\textsubscript{4}, and dispersed by ultrasonication for 2 min. Then, 6 g of potassium hypermanganate (KMnO\textsubscript{4}, A.R.) was added into the mixture. The mixture was vigorously stirred at room temperature for 4 h, followed by addition of 20 mL of distilled water to elevate the mixture temperature to be above 95 °C. After incubation for 15 min, 400 mL of distilled water and 10 mL of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, 30 wt.%) were slowly added into the mixture under mild agitation, respectively. The mixture turned out to be saffron yellow after addition of H\textsubscript{2}O\textsubscript{2}. The saffron-yellow mixture was allowed to stand for 12 h, and then subjected to centrifugal separation several times. The precipitate was thoroughly washed with distilled water until the supernate was neutral. The precipitate was collected by filtration, and finally dried in a freeze-drier to obtain GO.

S2. Synthesis of polybromopyrroles (PBPs)

PBPs were synthesized through electrophilic bromination of pyrrole with bromine
(Br₂) in absolute ethanol, according to previous report. In brief, 60 mL of absolute ethanol and 5 mL of Br₂ were added into a three-neck flask with capacity of 250 mL. The flask was transferred into a low-temperature reaction bath with temperature kept at 0 °C. The flask was bubbled with Ar for 0.5 h, followed by dropwise addition of 30 mL of absolute ethanol containing 1.67 mL of redistilled pyrrole. The reaction was conducted at 0 °C for 4 h with constant agitation under Ar atmosphere to produce PBPs ethanol solution. The components in PBPs ethanol solution were determined to be 2,5-dibromopyrrole (1) (86%), 2,3,5-tribromopyrrole (2) (7%), and 2,3,4,5-tetrabromopyrrole (3) (7%), respectively.

S3. SEM images of the electrode film

![Figure S1. SEM of the electrode film: (a) Low magnification; (b) High magnification.](image-url)
S4. Results of Lorentzian fittings of the Raman spectra

Table S1. Results of Lorentzian fittings of the Raman spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(D_1) (cm(^{-1}))</th>
<th>(D_3) (cm(^{-1}))</th>
<th>(D_4) (cm(^{-1}))</th>
<th>(G + D_2) (cm(^{-1}))</th>
<th>(I_{D_1}/I_{G+D_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO/PPBP-1</td>
<td>1347</td>
<td>1484</td>
<td>1250</td>
<td>1585</td>
<td>0.798</td>
</tr>
<tr>
<td>RGO/PPBP-2</td>
<td>1344</td>
<td>1473</td>
<td>1243</td>
<td>1584</td>
<td>0.797</td>
</tr>
<tr>
<td>RGO/PPBP-3</td>
<td>1345</td>
<td>1493</td>
<td>1219</td>
<td>1587</td>
<td>0.783</td>
</tr>
<tr>
<td>RGO</td>
<td>1348</td>
<td>1502</td>
<td>1229</td>
<td>1589</td>
<td>0.866</td>
</tr>
</tbody>
</table>
### S5. XPS analysis

#### Table S2. XPS results of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (at.%)</th>
<th>N (at.%)</th>
<th>O (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO/PPBP-1</td>
<td>84.65</td>
<td>9.06</td>
<td>6.29</td>
</tr>
<tr>
<td>RGO/PPBP-2</td>
<td>81.61</td>
<td>9.66</td>
<td>8.73</td>
</tr>
<tr>
<td>RGO/PPBP-3</td>
<td>81.29</td>
<td>11.66</td>
<td>7.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component (eV)/content (at.%)</th>
<th>Component (eV)/content (at.%)</th>
<th>Component (eV)/content (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO/PPBP-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>284.7/46.6</td>
<td>285.7/42.9</td>
<td>287.0/10.5</td>
</tr>
<tr>
<td>398.5/25.3</td>
<td>400.3/49.4</td>
<td>401.0/10.3</td>
</tr>
<tr>
<td>405.4/15.0</td>
<td>531.4/48.1</td>
<td>533.4/38.7</td>
</tr>
<tr>
<td>536.1/13.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RGO/PPBP-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>284.5/12.8</td>
<td>285.1/43.3</td>
<td>286.7/32.0</td>
</tr>
<tr>
<td>290.9/11.9</td>
<td>398.4/22.4</td>
<td>400.4/59.5</td>
</tr>
<tr>
<td>401.9/4.4</td>
<td>403.9/13.7</td>
<td>530.2/30.6</td>
</tr>
<tr>
<td>532.3/62.2</td>
<td>536.6/7.2</td>
<td></td>
</tr>
<tr>
<td>RGO/PPBP-3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>284.7/42.0</td>
<td>285.8/31.8</td>
<td>286.3/26.2</td>
</tr>
<tr>
<td>–</td>
<td>398.5/19.8</td>
<td>400.5/53.4</td>
</tr>
<tr>
<td>402.6/11.3</td>
<td>404.0/15.5</td>
<td>531.2/44.9</td>
</tr>
<tr>
<td>533.3/44.3</td>
<td>536.0/10.8</td>
<td></td>
</tr>
<tr>
<td>Assignment</td>
<td>C=C</td>
<td>C–C</td>
</tr>
<tr>
<td></td>
<td>C–O/C–N</td>
<td>O–C=O</td>
</tr>
<tr>
<td></td>
<td>N-6</td>
<td>N-5</td>
</tr>
<tr>
<td></td>
<td>N-Q</td>
<td>N-X</td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td>COH/C–O–C</td>
</tr>
<tr>
<td></td>
<td>O2/H2O</td>
<td></td>
</tr>
<tr>
<td>refs.</td>
<td>2,3</td>
<td>1,2,4</td>
</tr>
</tbody>
</table>

refs. 2,3, 1,2, 4
S6. SEM images of individual RGO and PPBP

Figure S2. SEM images of: (a,b) RGO; (c,d) PPBP. a and c are the low-magnification images; b and d are the high-magnification images corresponding separately to a and c.
S7. Scanning probe microscopy images of RGO/PPBP-2

Figure S3. (a,b) SPM images of different regions for RGO/PPBP-2; (c,d) Height distribution diagrams corresponding to a and b, respectively.
S8. GC/MS analysis

Table S3. GC/MS results of the resulting products after microwave irradiation of individual NMP.

<table>
<thead>
<tr>
<th>Intermediate</th>
<th>( t_R ) (min)</th>
<th>( M_W )</th>
<th>Structure</th>
<th>Main fragment ions (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrrolidone (1)</td>
<td>8.0</td>
<td>85</td>
<td></td>
<td>85, 57/56, 29/28</td>
</tr>
<tr>
<td>1-methyl-1H-pyrrol-2(5H)-one (2)</td>
<td>9.7</td>
<td>97</td>
<td></td>
<td>97, 69/68, 40, 29/28</td>
</tr>
<tr>
<td>N-methylsuccinimide (3)</td>
<td>11.2</td>
<td>113</td>
<td></td>
<td>113, 85/84, 57/56, 29/28</td>
</tr>
</tbody>
</table>

S9. BET analysis

Table S4. BET analysis results of the samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>( S_{BET} ) (m(^2) g(^{-1}))</th>
<th>( V_{total} ) (cm(^3) g(^{-1}))</th>
<th>( V_{micro} ) (cm(^3) g(^{-1}))</th>
<th>( V_{meso} ) (cm(^3) g(^{-1}))</th>
<th>( S_{micro} ) (m(^2) g(^{-1}))</th>
<th>( S_{micro}/S_{BET} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO/PPBP-1</td>
<td>378.4</td>
<td>0.4375</td>
<td>0.0171</td>
<td>0.4204</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>RGO/PPBP-2</td>
<td>390.6</td>
<td>0.3448</td>
<td>0.0114</td>
<td>0.3334</td>
<td>174.1</td>
<td>44.6%</td>
</tr>
<tr>
<td>RGO/PPBP-3</td>
<td>259.6</td>
<td>0.1846</td>
<td>0.0054</td>
<td>0.1792</td>
<td>104.1</td>
<td>40.1%</td>
</tr>
<tr>
<td>RGO</td>
<td>173.1</td>
<td>0.1669</td>
<td>0.0000</td>
<td>0.1669</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure S4. Fitted EIS spectrum obtained by Zsimpwin software using the data from the original EIS spectrum of RGO/PPBP-2||RGO/PPBP-2 supercapacitor cell.

Table S5. Fitting report of Figure S4 based on a R(C(RW))C equivalent circuit.

<table>
<thead>
<tr>
<th>index</th>
<th>fixed</th>
<th>symbol</th>
<th>start</th>
<th>end</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>R</td>
<td>3.32</td>
<td>3.32</td>
<td>1.47</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>C</td>
<td>0.7756</td>
<td>7.756E-5</td>
<td>5.963</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>R</td>
<td>3.989</td>
<td>3.989</td>
<td>3.111</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>W</td>
<td>0.06378</td>
<td>0.0638</td>
<td>3.674</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>C</td>
<td>0.07506</td>
<td>0.07505</td>
<td>3.114</td>
</tr>
</tbody>
</table>

References


