Electronic Supplementary Information

Three-dimensional graphene oxide/polypyrrole composite electrodes fabricated by one-step electrodeposition for high performance supercapacitors

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Experimental section

Preparation of graphene oxide (GO)

GO used in this work was synthesized by modified hummer method and described in brief as follows: The concentrated 7.5 mL H$_2$SO$_4$ in a 100 mL beaker was heated up to 80 °C. K$_2$S$_2$O$_8$ (2.5 g) and P$_2$O$_5$ (2.5 g) were added in sequence with continuous stirring until the reactants were completely dissolved. Graphite powder (5 g) was then added to above mixture. The resulting mixture was kept at 80 °C for 6 hours, after which the mixture was diluted with distilled water, filtered and washed to remove all soluble substances, and the corresponding pretreated graphite was transferred to a drying dish and left overnight under ambient conditions. Another 115 mL H$_2$SO$_4$ was put into a 500 mL Erlenmeyer flask and then cooled in an ice bath. The pretreated graphite and 15 g KMnO$_4$ were added slowly in sequence and allowed to dissolve completely. The mixture was then allowed to react at 35 °C for 2 hours, after that, 230 mL distilled water was slowly added. After stirring for 15 min, another 700 mL of distilled water was added to the mixture, thereafter 12.5 mL of 30% H$_2$O$_2$ was added to the mixture. The mixture was allowed to stand for at least 12 hours then the clear supernatant was decanted. The remaining mixture was washed with 1.1 L 1:10 HCl solution followed by distilled water. Finally, it was purified by dialysis for at least one week to remove any remaining salt impurities for the following experiments.
Calculation

Three-electrode configuration

For three-electrode configuration, the area capacitance ($C_A$) for the individual electrode (F cm$^{-2}$) is calculated from the CV curves as follows:

$$C_A = \frac{I}{S V (V_c - V_a) \int_{V_a}^{V_c} I(V) dV}$$

(1) where $S$ is the geometric area of the electrode (cm$^2$); $\nu$ is the linear scan rate (V s$^{-1}$); $V_c - V_a$ is the voltage window (V) during discharging (backward scan), $I(V)$ is the resulting current (A).

$C_A$ based on galvanostatic discharge is calculated as follows:

$$C_A = \frac{I \Delta t}{S \Delta V}$$

(2) where $I$ is the discharge current (A), $\Delta t$ is the discharge time (s), $\Delta V$ is the operating potential/cell voltage range exclude with the IR drop (V).

Specific capacitance ($C_S$) of the electrode (F g$^{-1}$) is calculated simply by dividing the $C_A$ with the loading mass ($m$) of GO/PPy composite on the electrode (g cm$^{-2}$):

$$C_S = \frac{C_A}{m}$$

(3)
Two electrode configuration

For two-electrode configuration, the area capacitance ($C_A$) for the individual electrode (F cm$^{-2}$) is calculated from the galvanostatic charge-discharge results as follows:

$$C_A = 2 \frac{I \Delta t}{S \Delta V}$$

(4)

Electrochemical impedance spectroscopy (EIS)

The real ($C'$) and imaginary ($C''$) part of the area capacitance are derived from the impedance data as follows:

$$C' = \frac{-Z''}{S \omega |Z|^2}$$

(5)

$$C'' = \frac{Z'}{S \omega |Z|^2}$$

(6) Where $Z$ is the impedance, $S$ is the geometric area of the electrode, $\omega$ is the angular frequency ($\omega=2\pi f$).

The relaxation time $\tau_0$ is deduced from the knee frequency ($f_0$) as:

$$\tau_0 = \frac{1}{f_0}$$

(7) And $f_0$ can be accurately defined from the peak frequency on $C''-f$ plot.

Energy density and power density

The total energy ($E$) and power ($P$) of the two-electrode supercapacitor device are first calculated from the galvanostatic charge-discharge results as:
\[ E = \frac{1}{2} CV^2 = \frac{1}{2} IV\Delta t \]  \hspace{1cm} (8)

\[ P = \frac{E}{\Delta t} \]  \hspace{1cm} (9)

Where \( C \) is the total capacitance stored in the device, \( V \) is the cell voltage, \( I \) is the discharge current, \( \Delta t \) is the discharge time.

Then the energy density and power density are calculated by dividing \( E \) and \( P \) with the total mass of active materials in the two electrodes, or the geometric area of the supercapacitor (1 cm\(^2\) in this research).
Supplementary Schemes

Scheme S1 Termination reaction.

Scheme S2 Secondary reaction.
Fig. S1 SEM surface morphologies of the GO/PPy composite electrodes deposited in electrolyte with GO concentration of 0.1 mg mL\(^{-1}\) for different times: (a) 1200 s; (b) 1800 s; (c) 2400 s; (d) 2700 s. Enlarged images of area A and B are shown in Fig. S2.
Fig. S2 High magnification SEM surface morphologies of the GO/PPy composite electrodes deposited in electrolyte with GO concentration of 0.1 mg mL$^{-1}$ for different time: (a) 1200 s; (b) 2700 s.
Fig. S3 SEM surface morphology of the pure PPy-1200 s electrode deposited in 5 vol.% (72 mmol L\(^{-1}\)) pyrrole aqueous solution containing 20 mmol L\(^{-1}\) LiClO\(_4\) as supporting electrolyte: (a) low magnification; (b) high magnification.
Fig. S4 SEM surface morphologies of the GO/PPy composite electrodes deposited with various GO concentrations (the deposition time is 1200 s for all the electrodes): (a) 0.05 mg mL\(^{-1}\); (b) 0.1 mg mL\(^{-1}\); (c) 0.2 mg mL\(^{-1}\); (d) 0.4 mg mL\(^{-1}\); (e) 0.8 mg mL\(^{-1}\); (f) 1.2 mg mL\(^{-1}\).
Fig. S5 Cl2p spectra of the original GO/PPy composite and GO/PPy composites after keeping in 1 M KCl solution for at least one day.
Fig. S6 Comparison of plots of area capacitance vs. scan rate for GO/PPy-2400, -2700 and -3000 s composite electrodes.
Fig. S7 CV curves of aqueous supercapacitor with cell voltage of 0.8 and 1.0 V (scan rate: 10 mV s⁻¹).
Fig. S8 Photos for the LED powered by four unit solid-state capacitors in series at different times.
## Supplementary Tables

### Table S1 Comparison of the mass loading, area and specific capacitances of various graphene/PPy composite electrodes.

<table>
<thead>
<tr>
<th>Composites</th>
<th>Mass loading (mg cm(^{-2}))</th>
<th>Area capacitance (mF cm(^{-2}))</th>
<th>Specific capacitance (F g(^{-1}))</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Graphene/PPy</td>
<td>-</td>
<td>-</td>
<td>165 at 1 A g(^{-1})</td>
<td>1</td>
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<tr>
<td>Graphene/PPy</td>
<td>0.16</td>
<td>-</td>
<td>424 at 1 A g(^{-1})</td>
<td>2</td>
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<td>Graphene/PPy</td>
<td>-</td>
<td>-</td>
<td>248 at 0.3 A g(^{-1})</td>
<td>3</td>
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<tr>
<td>Graphene/PPy</td>
<td>1.7</td>
<td>175 at 10 mV s(^{-1})</td>
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<td>4</td>
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<tr>
<td>Graphene/PPy</td>
<td>-</td>
<td>-</td>
<td>345 at 1 A g(^{-1})</td>
<td>5</td>
</tr>
<tr>
<td>GO/PPy</td>
<td>-</td>
<td>-</td>
<td>332.6 at 0.25 A g(^{-1})</td>
<td>6</td>
</tr>
<tr>
<td>GO/PPy</td>
<td>-</td>
<td>-</td>
<td>356 at 0.5 A g(^{-1})</td>
<td>7</td>
</tr>
<tr>
<td>GO/PPy</td>
<td>0.26</td>
<td>152.5 at 10 mV s(^{-1})</td>
<td>-</td>
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<tr>
<td>GO/PPy</td>
<td>1.02</td>
<td>116 at 10 mV s(^{-1})</td>
<td>481.1 at 0.77 A g(^{-1})</td>
<td>Present</td>
</tr>
<tr>
<td></td>
<td></td>
<td>94 at 200 mV s(^{-1})</td>
<td>410.4 at 38.5 A g(^{-1})</td>
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<tr>
<td></td>
<td></td>
<td>350 at 10 mV s(^{-1})</td>
<td>380.0 at 0.2 A g(^{-1})</td>
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<tr>
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<td></td>
<td>173 at 200 mV s(^{-1})</td>
<td>315.9 at 10 A g(^{-1})</td>
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All the capacitances are single electrode capacitance.

### Table S2 Elemental analysis results of GO/PPy composite electrodes deposited in electrolyte with different GO concentration (the deposition time is 2100 s).

<table>
<thead>
<tr>
<th>Concentration of GO (mg mL(^{-1}))</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>PPy</th>
<th>GO</th>
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<tr>
<td>0.1</td>
<td>15.31</td>
<td>53.05</td>
<td>3.400</td>
<td>28.24</td>
<td>72.90</td>
<td>27.10</td>
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<tr>
<td>0.4</td>
<td>14.56</td>
<td>50.16</td>
<td>3.166</td>
<td>32.11</td>
<td>69.33</td>
<td>30.67</td>
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<tr>
<td>0.8</td>
<td>14.43</td>
<td>50.07</td>
<td>3.172</td>
<td>32.32</td>
<td>68.71</td>
<td>31.29</td>
</tr>
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References


