Electronic Supplementary Information

Low-temperature vapour phase polymerized polypyrrole nanobrushes for supercapacitors

Luciano M. Santino,† Shinjita Acharya,† and Julio M. D’Arcy‡

†Department of Chemistry, ‡Institute of Materials Science & Engineering, Washington University in St. Louis, St. Louis, Missouri 63130, United States
Figure S1. PPy can also be synthesized on glass fiber filter paper.

Figure S2. Three-electrode cyclic voltammetry response of PPy on hard carbon paper and bare hard carbon paper.
**Figure S3.** Purified PPy exhibits a relaxed nanofibrillar structure.

**Figure S4.** SEM shows that nanofibrillar PPy conformally coats the inner architecture of the hard carbon fiber paper substrate.
Figure S5. EDS survey spectra showing dopant region for a film on hard carbon paper after synthesis, after washing in 6 M H$_2$SO$_4$, and after cycling in 1 M LiClO$_4$ (final potential was the open circuit potential). Spectra normalized for the carbon peak.

Figure S6. XPS of the O$_{1s}$ peak before and after cycling ten times at 10 mV/s in 1 M LiClO$_4$ for a 50 °C polymerized PPy sample. Final potential equals the initial open circuit potential for PPy.
Figure Sx. Scanning electron micrographs for syntheses at various temperatures. All scale bars 10 μm.

Figure S8. N₁s XPS spectra of samples synthesized at various temperatures from 30 to 90 °C.
Figure S9. XPS survey scans of unwashed, washed, washed and cycled samples.

Figure S10. FTIR spectrum of a purified PPy sample.
**Figure S11.** EDS maps show the Cl$_{1s}$ signal for unwashed (left) and washed (right) PPy samples.

**Figure S12.** Galvanostatic charge-discharge curve for 1 V PPy supercapacitor at 10 A/g. Inset: Magnification of iR drop.
Table S1. Nyquist equivalent circuit fitting parameters for a single PPy on hard carbon paper electrode in 1 M LiClO₄.

Equivalent circuit: \( R_1 + C_1/R_2 + Q_1/R_3 + C_2 \)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_s )</td>
<td>1.661</td>
<td>Ω</td>
</tr>
<tr>
<td>( C_f )</td>
<td>0.2633</td>
<td>mF</td>
</tr>
<tr>
<td>( R_f )</td>
<td>0.1952</td>
<td>Ω</td>
</tr>
<tr>
<td>( Q_1 )^*</td>
<td>0.3541</td>
<td>Fs^((\alpha-1))</td>
</tr>
<tr>
<td>( A_1 )^*</td>
<td>0.496</td>
<td></td>
</tr>
<tr>
<td>( R_{ct} )</td>
<td>6.07</td>
<td>Ω</td>
</tr>
<tr>
<td>( C_{dl} )</td>
<td>0.09166</td>
<td>F</td>
</tr>
</tbody>
</table>

\[ \frac{\chi^2}{|Z|} = 9.098 \times 10^{-3} \]

*Calculated as \( C_{\text{pseudo}} = 0.7705 \text{ F} \) from constant phase element with an equivalent circuit reduced to \( R_1 + C_1/R_3 + C_1/R_2 + C_2 \) using the equation:

\[ \frac{1}{2\pi(RQ)^{1/\alpha}} = \frac{1}{2\pi R C} \]
Figure S13. Extended cycling stability at 5 A/g shows that a device with a maximum charging voltage of 0.6 V retains roughly 70% initial capacitance over 200 000 cycles.