Immoblization of phosphotungstate through doping in polypyrrole for supercapacitors

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Redox reactions of PW_{12}:

\[ [\text{PW}_{12}\text{O}_{40}]^{3-} + e^- \rightleftharpoons [\text{PW}_{12}\text{O}_{40}]^{4-} \quad \text{R. S1} \]
\[ [\text{PW}_{12}\text{O}_{40}]^{4-} + e^- \rightleftharpoons [\text{PW}_{12}\text{O}_{40}]^{5-} \quad \text{R. S2} \]
\[ [\text{PW}_{12}\text{O}_{40}]^{5-} + 2e^- + \text{H}^+ \rightleftharpoons [\text{HPW}_{12}\text{O}_{40}]^{6-} \quad \text{R. S3} \]
\[ [\text{PW}_{12}\text{O}_{40}]^{5-} + e^- \rightleftharpoons [\text{PW}_{12}\text{O}_{40}]^{6-} \quad \text{R. S4} \]
\[ [\text{PW}_{12}\text{O}_{40}]^{6-} + e^- \rightleftharpoons [\text{PW}_{12}\text{O}_{40}]^{7-} \quad \text{R. S5} \]

Calculations

1. Calculation for single electrode:

   The areal \( C_a \) and specific \( C_m \) capacitance of a single electrode can be calculated from galvanostatic charge/discharge profile by the following equations:

   \[
   C_a = \frac{I \times \Delta t}{S \times \Delta U} \quad \text{equ. S1}
   \]

   Where \( C_a \) is the areal capacitance \( \text{(mF cm}^{-2}\text{)} \), \( I \) \( \text{(mA cm}^{-2}\text{)} \) is the galvanostatic charge/discharge current, \( \Delta t \) \( \text{(s)} \) is the discharge time, \( S \) \( \text{(cm}^2\text{)} \) is the geometrical area of the electrode, \( \Delta U \) \( \text{(V)} \) is the charge/discharge potential window.

   \[
   C_m = \frac{I \times \Delta t}{m \times \Delta U} \quad \text{equ. S2}
   \]

   Where \( C_m \) is the specific capacitance \( \text{(F g}^{-1}\text{)} \), \( m \) \( \text{(g)} \) is the mass of active material on the electrode.

2. Charge balance for ASC device:
The charge stored in cathode ($Q^+$) and anode ($Q^-$) should be balanced to maximize the performance of the assembled supercapacitor device by the relationship $Q^+ = Q^-$. The charge stored in each electrode depends on the areal capacitance ($C_a$), the potential window ($\Delta U$) and the geometrical area of each electrode ($S$) by the following equation:

$$Q = C_a \times \Delta U \times S$$

equ. S3

Then the following equation can be deduced:

$$C_a^+ \times \Delta U^+ \times S^+ = C_a^- \times \Delta U^- \times S^-$$

equ. S4

3. Calculations for ASC device:

The volumetric capacitance of an ASC device can also be calculated from galvanostatic charge/discharge profile by the following equation:

$$C_v = \frac{I \times \Delta t}{V \times U}$$

equ. S5

Where $C_v$ is the volumetric capacitance (F cm$^{-3}$), $I$ is the galvanostatic charge/discharge current, $\Delta t$ (s) is the discharge time, $V$ (cm$^3$) is the volume of the whole ASC device and $U$ is the operating voltage.

The volumetric capacitance of an ASC device can be calculated from cyclic voltammetry profile by the following equation:

$$C_{mv}^v = \int_{V \times V \times U}^{i(U)\,dU}$$

equ. S6

Where $C_{mv}^v$ is the volumetric capacitance (F cm$^{-3}$), $V$ (cm$^3$) is the volume of the whole ASC device, $v$ is the scan rate, $U$ is the potential window in the CV curves, and $i(U)$ is the voltammetry current on the profile.
The energy density \( E, \text{mWh cm}^{-3} \) and power density \( P, \text{mW cm}^{-3} \) of an ASC device can be calculated by the following equations:

\[
E = \frac{1000}{2 \times 3600} C_v U^2 \quad \text{equ. S7}
\]

\[
P = \frac{3600 \times E}{t} \quad \text{equ. S8}
\]

Where \( C_v \) is the volumetric capacitance (F cm\(^{-3}\)), \( U \) (V) is the operating voltage and \( \Delta t \) (s) is the discharge time.

**Figures**

**Fig. S1.** CV profiles of PW\(_{12}\) anions in neutral solution (a) and acidic solution (b), together with that of ECNT-PPy/PW\(_{12}\) in neutral solution (c) at a scan rate of 5 mV s\(^{-1}\).
Fig. S2. TEM and elemental mapping images of ECNT-PPy/5PW$_{12}$.

Fig. S3. N 1s XPS core level spectra of UCNT-PPy.
**Fig. S4.** CV profiles of ECNT-PPy/5PW_{12} in the potential window of -1.2 to 0.8 V vs. SCE at a scan rate of 5 mV s\(^{-1}\).

**Fig. S5.** Galvanostatic discharge profile of ECNT-PPy/5PW_{12} at a current density of 1 mA cm\(^{-2}\).
Fig. S6. CV profiles at 5 mV s⁻¹ of ECNT-PPy/5PW₁₂, UCNT-PPy/5PW₁₂ and ECNT/PPy.

Fig. S7. Galvanostatic charge/discharge curves of ECNT-PPy/5PW₁₂ and UCNT-PPy/5PW₁₂ at different current densities.

Table. S1. Capacitive performances of recently reported PW₁₂ based composite materials and electrochemically fabricated composites of PPy and CNT film

<table>
<thead>
<tr>
<th>Materials</th>
<th>Capacitance</th>
<th>Rate capability</th>
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<tbody>
<tr>
<td>Cu-MOF/PPy/PW₁₂¹</td>
<td>1.09 F cm⁻² (0.5 mA cm⁻²)</td>
<td>68.8% (0.5-2.5 mA cm⁻²)</td>
</tr>
<tr>
<td>biochar carbon/PW₁₂²</td>
<td>1.19 F cm⁻² (10 mV s⁻¹)</td>
<td>70% (10-200 mV s⁻¹)</td>
</tr>
<tr>
<td>PW₁₂/PPy/rGO³</td>
<td>295 F g⁻¹ (1 A g⁻¹)</td>
<td>55% (1-20 A g⁻¹)</td>
</tr>
<tr>
<td>Polypyrrole nano-pipes/PW₁₂⁴</td>
<td>434 mF cm⁻² (2 mA cm⁻²)</td>
<td>63% (2-20 mA cm⁻²)</td>
</tr>
<tr>
<td>CNT/PPy⁵</td>
<td>637 mF cm⁻² (1 mA cm⁻²)</td>
<td>75% (1-40 mA cm⁻²)</td>
</tr>
<tr>
<td>CNT/PPy⁶</td>
<td>280 mF cm⁻² (1.4 mA cm⁻²)</td>
<td>43% (1.4-14 mA cm⁻²)</td>
</tr>
<tr>
<td>This work</td>
<td>1300.0 mF cm⁻² (1 mA cm⁻²)</td>
<td>78.6% (1-40 mA cm⁻²)</td>
</tr>
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</table>
Fig. S8. Galvanostatic charge/discharge curves of ECNT-PPy/2.5PW₁₂ (a) and ECNT-PPy/10PW₁₂ (b) at different current densities and areal capacitance of ECNT-PPy/2.5PW₁₂, ECNT-PPy/10PW₁₂ and ECNT-PPy/10PW₁₂ at various current densities ranging from 1 to 40 mA cm⁻² (c).
Fig. S9. SEM images of CNT-MnO$_2$ (a), Mn 3s (b) and Mn 2p (c) XPS core level spectra of CNT-MnO$_2$ and XRD patterns of CNT and CNT-MnO$_2$ (d).

Fig. S10. (a) CV profiles of CNT-MnO$_2$ at 30 mV s$^{-1}$; (b) Galvanostatic charge/discharge curves of CNT/MnO$_2$ at different current density; (c) Areal capacitance of CNT-MnO$_2$ at various current densities ranging from 1 to 20 mA cm$^{-2}$.

From SEM images of CNT-MnO$_2$ shown in Fig. S9a, it could be seen that MnO$_2$ existed in assembled nanosheets. This could facilitate the penetration of electrode in the active materials for fast faradic reactions. The oxidation state of manganese could be estimated from the spin-energy separation (DE) of Mn 3s signal in XPS spectrum. CNT-MnO$_2$ displayed a DE of 4.78 eV in its
Mn 3s XPS core level spectrum (Fig. S9b), indicating that the manganese exists in its +4 oxidation state.\(^7,8\) In the Mn 2p XPS core level spectrum of CNT-MnO\(_2\), Mn 2p\(_{3/2}\) and Mn 2p\(_{1/2}\) signals appeared at 642.3 and 654.0 eV, respectively with a DE of 11.7 eV (Fig. S9c). This was in accordance with previously reported MnO\(_2\).\(^9,10\) The crystal structure of MnO\(_2\) was characterized by XRD. The characteristic diffractions in the XRD pattern (Fig. S9d) could be indexed to (021) and (061) planes of the birnessite-type MnO\(_2\) (JCPDS 14-0644)\(^11\), respectively.

To investigate the electrochemical performances of CNT-MnO\(_2\), electrochemical measures were conducted in a three-electrode system containing 5 M LiCl electrolyte (Fig. S10). Galvanostatic charge/discharge profiles at different current densities are shown in Fig. S10b. The charge profiles were quite symmetric to the discharge ones, demonstrating a good rate capability for CNT-MnO\(_2\). The areal capacitances could be calculated through equ. S1-2, based on the galvanostatic charge/discharge experiments. CNT-MnO\(_2\) displayed an areal capacitance of 1380 mF cm\(^{-2}\) at a current density of 1 mA cm\(^{-2}\), and a specific capacitance of 336.58 F g\(^{-1}\) at 0.24 A g\(^{-1}\), 60% of its capacitance can be retained when the current density increases 20 times to 20 mA cm\(^{-2}\) (Fig. S10c).

**References**