Supporting Information

Strongly Coupled Polypyrrole/Molybdenum Oxide Hybrid Films via Electrochemical Layer–by–Layer Assembly for Pseudocapacitors

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1. CALCULATION METHODS

Specific capacitance calculation: Specific capacitances of different samples according to the constant current charge–discharge profiles are calculated from equation S1:

\[ C = \frac{It}{m\Delta U} \] (S1)

where \( C \) stands for specific capacitance (F g\(^{-1}\)), \( I \) is the discharge current (mA), \( t \) is the discharge time (s), \( m \) is the mass loading of the active materials (mg) and \( \Delta U \) the potential window (V).

Specific capacitances of the ASC device from the constant current charge–discharge profiles are calculated from equation S2:

\[ C = \frac{It}{mU} \] (S2)

where \( C \) is the specific capacitance of the ASC (F g\(^{-1}\)), \( m \) is the mass of both electrodes (mg) and \( U \) is the potential window of the ACS (V).

Energy density and power density calculations for the ASC: Energy density \( (E, \text{ in Wh kg}^{-1}) \) and power density \( (P, \text{ in W kg}^{-1}) \) are calculated according to the equation S3 and S4:

\[ E = \frac{1000}{2 \times 3600} C U^2 \] (S3)
\[ P = \frac{3600 \times E}{t} \] (S4)

where \( C \) is the specific capacitance (F g\(^{-1}\)), \( U \) is the potential window (V) and \( t \) is the discharge time (s) in constant current charge/discharge profiles.

Capacitive and diffusion–controlled capacitance calculations: Specific capacitances were calculated based on CV curves at different scan rates according to the following equation S5:

\[ C = \frac{S}{2 \times \Delta U \times v} \] (S5)

where \( C \) stands for the specific capacitance (F g\(^{-1}\)), \( \Delta U \) is the potential window (V), \( v \) is the scan rate (V s\(^{-1}\)), \( S \) is the integral area of the CV curve (A V g\(^{-1}\)).
Plotting $C^{-1}$ vs. $v^{1/2}$ gives a linear relationship, assuming semi–infinite diffusion of ions, which can be described in the equation S6:

$$C^{-1} = \text{constant} \times v^{1/2} + C_T^{-1} \quad (S6)$$

where $C$, $v$ and $C_T$ are specific capacitance calculated from the corresponding CV curve, scan rate and total capacitance, respectively. Data points collected at larger scan rates deviated from this linear correlation because of the deviation from semi–infinite ion diffusion. Masking the deviated data points, fitting the others and extrapolating the fitting line to $y$–axis can give $C_T^{-1}$. $C_T$ represents the highest possible capacitance because ions can react adequately with active material in enough time. $C_T$ is the sum of $C_C$ and $C_D$. $C_C$ and $C_D$ represent capacitive and diffusion–controlled capacitance, respectively.

Similarly, a linear correlation in $C$ vs $v^{-1/2}$ plot can also be obtained. Fitting the data points at slow scan rates and extrapolating the fitting line to $y$–axis can yield $C_C$, since $C_D$ with slow kinetic can be negligible when reaction time tends to infinitesimal. Subtracting $C_C$ from $C_T$ yields $C_D$. $C_T$, $C_C$ and $C_D$ are calculated to be 413.22 F g$^{-1}$, 303.17 F g$^{-1}$ and 110.05 F g$^{-1}$, respectively.

**EIS analysis method:** The impedance of the electrode material can be described in equation S7:

$$Z(\omega) = \frac{1}{j\omega \times C(\omega)} \quad (S7)$$

where $\omega$ is pulsation [$\omega = 2\pi f$, $f$ is the frequency (Hz)], $C(\omega)$ presents the capacitance as a function of the pulsation $\omega$.

The impedance $Z(\omega)$ can be written in S8:

$$Z(\omega) = Z'(\omega) + jZ''(\omega) \quad (S8)$$

S7 and S8 lead to S9:
The capacitance $C(\omega)$ can be written in S10:

$$C(\omega) = C'(\omega) - jC''(\omega) \quad (S10)$$

leading to S11 and S12:

$$C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|} \quad (S11)$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|} \quad (S12)$$

where $C'(\omega)$ and $C''(\omega)$ are the real part and imaginary part (ohm) of the capacitance $C(\omega)$.

The mass of PPy and MoO$_x$ in the composite film: The LbL–PPy/MoO$_x$ electrode was first immersed in 50 mL 2 M KOH solution for 24 h to dissolve the MoO$_x$ materials. And then, the electrode was transferred in 100 mL deionized water for 12 h and washed to remove the residues. This electrode was further dried in vacuum oven at 60 °C for 10 h. The weight difference of the electrode is the mass of MoO$_x$ (0.64 mg cm$^{-2}$). The active mass of LbL–PPy/MoO$_x$ is ~1 mg cm$^{-2}$, therefore, the mass of PPy in the composite is ~0.36 mg cm$^{-2}$. We further verified the result using the XPS data. The mass percentage of N and Mo in the composite is ~7.1 % and 5.8 %. Based on their molecular weight, we can estimate that the mass ratio of PPy/MoO$_x$ in the composite is ~0.52, which is agreed with the former experimental results.

Charge balance for cathode and anode: To maximize the performance of a pseudocapacitor, the charge ($Q$) stored in anode and cathode should be balanced, i.e. $Q_+ = Q_-$. The charge stored by each electrode depends on the specific capacitance ($C_s$), potential window ($\Delta U$) and the mass of the active materials ($m$), following equation S13:
\[ Q = C_s \times \Delta U \times m \quad \text{(S13)} \]

In order to get \( Q_+ = Q_- \) at 1 A g\(^{-1}\), the mass ratio of the anode and cathode should follow Equation S14:

\[
\frac{m_+}{m_-} = \frac{(C_{s,-})(\Delta U_-)}{(C_{s,+})(\Delta U_+)} = \frac{398 \times 1.2}{346 \times 1} = 1.38 \quad \text{(S14)}
\]

Where \( C_{s,-} = 398 \text{ F g}^{-1} \) with a potential window of 1.2 V and \( C_{s,+} = 346 \text{ F g}^{-1} \) with a potential window of 1 V. The calculated mass ratio between cathode and anode electrode is about 1.38.
2. SUPPLEMENTARY FIGURES

Figure S1. CV curves of LbL–PPy/MoOₓ films with PPy:MoOₓ ratio of 1:2.5, 1:1.8 and 1:1.4, respectively.

Figure S2. SEM image of films on a 3D electrochemically exfoliated graphite current collector (EG).

Figure S3. The specific capacitance of EG (current collector) as a function of current density.
**Figure S4.** One cycle of CV curve of the electrochemical deposition process of LbL–PPy/MoOₓ.

**Figure S5.** SEM images of (a) PPy, (b) MoOₓ and (c) LbL–PPy/MoOₓ. (d) TEM image of LbL structure of PPy/MoOₓ.
Figure S6. (a) The TEM linear EDX elemental scan of LbL–PPy/MoO$_x$. (b) The magnified signals at the selected area in (a).

Figure S7. SEM images of (a) the as–prepared T–LbL–PPy/MoO$_x$ sample and (b) the sample after KOH etching. (c) EDS spectra collected for the sample after KOH etching, indicating MoO$_x$ was successfully removed.
**Figure S8** Selected area electron diffraction (SAED) pattern of LbL–PPy/MoO$_x$ film. The diffusive rings indicate the amorphous nature of the material.

**Figure S9.** XPS survey spectrum of PPy, MoO$_x$ and LbL–PPy/MoO$_x$. 
Figure S10. CV curves of (a) PPy, (b) MoO\textsubscript{x} and (c) LbL–PPy/MoO\textsubscript{x} at different scan rates. Constant current charge–discharge profiles of (d) PPy, (e) MoO\textsubscript{x} and (f) LbL–PPy/MoO\textsubscript{x} at different current densities.

Figure S11. (a) CV curves of PPy@MoO\textsubscript{x}, MoO\textsubscript{x}@PPy and LbL–PPy/MoO\textsubscript{x} at 40 mV s\textsuperscript{-1}. (b) Constant current charge–discharge profiles of PPy@MoO\textsubscript{x}, MoO\textsubscript{x}@PPy and LbL–PPy/MoO\textsubscript{x} at 10 A g\textsuperscript{-1}. (c) Specific capacitance of PPy@MoO\textsubscript{x}, MoO\textsubscript{x}@PPy and LbL–PPy/MoO\textsubscript{x} as a function of current density.
Figure S12. $i(V)/v^{1/2}$ vs. $v^{1/2}$ plot collected for LbL–PPy/MoO$_x$ using the anodic current at a selected potential of $-0.2$ V vs. SCE.

**Dunn Method:** According to Dunn method, the current response at a fixed potential comes from two separate mechanisms, capacitive–controlled and diffusion–controlled processes:

$$i(V) = k_1 v + k_2 v^{1/2}$$  \hspace{1cm} (15)

Where $k_1 v$ stands for the current contributions from the capacitive effects, and $k_2 v^{1/2}$ corresponds to the current contributions from the diffusion–controlled process. Dividing $v^{1/2}$ on both sides of the equation yields:

$$i(V)/v^{1/2} = k_1 v^{1/2} + k_2$$ \hspace{1cm} (16)

By reading the $i(V)$ at a selected potential from CV curves collected at different scan rates followed by plotting $i(V)/v^{1/2}$ vs. $v^{1/2}$, in the linear fitting line, $k_1$ equals the slope and $k_2$ equals the $y$–intercept. Figure S12 shows an example of $i(V)/v^{1/2}$ vs. $v^{1/2}$ plots collected for LbL–PPy/MoO$_x$ at a fixed potential of $-0.2$ V vs. SCE in the anodic process. Using the $k_1$ and $k_2$ obtained above, current contributions from the capacitive effect ($k_1 v$) and diffusion–controlled process ($k_2 v^{1/2}$) at the specific potential are obtained according to Equation (15).

Through conducting the same steps for other potentials, the capacitive/diffusion contribution is shown in Figure 3d.
Figure 13. SEM images of LbL−PPy/MoOₓ electrodes with mass loading of (a) 3 mg cm⁻² and (b) 1 mg cm⁻².

Figure S14. SEM images of (a) Mn₃O₄ and (b) Na₀.₅MnO₂. Magnified SEM images of (c) Mn₃O₄ and (d) Na₀.₅MnO₂. (e) XRD patterns of Mn₃O₄ and Na₀.₅MnO₂. (f) EDS spectra of Na₀.₅MnO₂.

Figure S14a and c show the SEM images of Mn₃O₄ nanoflakes grown on 3D porous EG base. The magnified SEM image reveals the Mn₃O₄ nanoflakes are nearly vertically aligned on the base. After cyclic voltammetry scan, Na₀.₅MnO₂ nanoflakes are obtained (Figure S14b and d). Figure S14e shows
the XRD patterns of the Mn$_3$O$_4$ and Na$_{0.5}$MnO$_2$ materials deposited on EG. For the XRD pattern of Mn$_3$O$_4$, except for the diffraction peaks of carbon from EG, all the diffraction peaks can be well indexed to the tetrahedral hausmannite Mn$_3$O$_4$ (JCPDS No. 24–0734). After cyclic voltammetry scan, the diffraction peaks of Mn$_3$O$_4$ disappear while the new diffraction peaks can be indexed to monoclinic Birnessite (JCPDS No. 43–1456), revealing the phase transition from Mn$_3$O$_4$ to Na$_{0.5}$MnO$_2$. Moreover, Na signal was detected for Na$_{0.5}$MnO$_2$, which further indicates the transition to Na$_{0.5}$MnO$_2$. These observations are highly consistent with the results reported before.$^1$

**Figure S15.** (a) CV curves of Na$_{0.5}$MnO$_2$ at different scan rates. (b) Constant current charge–discharge profiles of Na$_{0.5}$MnO$_2$ at different current densities. (c) Specific capacitance of Na$_{0.5}$MnO$_2$ as a function of current density.

Figure S15a shows the CV curves of Na$_{0.5}$MnO$_2$ at different scan rates. The shape of CV curves maintains nearly rectangular without distortion even at a scan rate of 100 mV s$^{-1}$, revealing the ideal capacitive behavior and good rate capability. Constant current charge–discharge profiles of Na$_{0.5}$MnO$_2$ exhibit an approximately symmetric triangle shapes with negligible IR drops, indicating pseudocapacitive behavior and the small resistance of the electrode. Figure S15c shows the specific capacitance of Na$_{0.5}$MnO$_2$ as a function of current density. The Na$_{0.5}$MnO$_2$ electrode achieves a good specific capacitance of 346 F g$^{-1}$ at 1 A g$^{-1}$. At a high current density of 20 A g$^{-1}$, it can still achieve a high capacitance of 240 F g$^{-1}$.
<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Potential Window (V)</th>
<th>Specific Capacitance (maximum)</th>
<th>Specific Capacitance (minimum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂MoO₃₋ₓ²</td>
<td>Sea Water</td>
<td>−0.9—0.1</td>
<td>250 F g⁻¹ @ 1 A g⁻¹</td>
<td>122 F g⁻¹ @ 20 A g⁻¹</td>
</tr>
<tr>
<td>K₂MoO₃₋ₓ³</td>
<td>5 M LiCl</td>
<td>−0.9—0.1</td>
<td>325 F g⁻¹ @ 0.5 A g⁻¹</td>
<td>186 F g⁻¹ @ 100 A g⁻¹</td>
</tr>
<tr>
<td>MoO₃₋ₓ/CNT⁴</td>
<td>5 M LiCl</td>
<td>−0.9—0.1</td>
<td>337 F g⁻¹ @ 0.5 A g⁻¹</td>
<td>214 F g⁻¹ @ 10 A g⁻¹</td>
</tr>
<tr>
<td>Graphene/MoO₃⁵</td>
<td>1 M Na₂SO₄</td>
<td>−1—0</td>
<td>291 F g⁻¹ @ 2 mV s⁻¹</td>
<td>75 F g⁻¹ @ 50 mV s⁻¹</td>
</tr>
<tr>
<td>α-MoO₃⁶</td>
<td>0.5 M Li₂SO₄</td>
<td>−1.0—0.3</td>
<td>369 F g⁻¹ @ 0.1 A g⁻¹</td>
<td>207 F g⁻¹ @ 1 A g⁻¹</td>
</tr>
<tr>
<td>m-MoO₂⁷</td>
<td>1 M LiOH</td>
<td>−1.2—0.5</td>
<td>146 F g⁻¹ @ 5 mV s⁻¹</td>
<td>69 F g⁻¹ @ 500 mV s⁻¹</td>
</tr>
<tr>
<td>MoO₃/PPy⁸</td>
<td>1 M Na₂SO₄</td>
<td>−0.5—0.5</td>
<td>123 F g⁻¹ @ 0.27 A g⁻¹</td>
<td>104 F g⁻¹ @ 2.67 A g⁻¹</td>
</tr>
<tr>
<td>SnO₂/PPy⁹</td>
<td>1 M Na₂SO₄</td>
<td>−0.8—0.0</td>
<td>260 F g⁻¹ @ 1 A g⁻¹</td>
<td>189 F g⁻¹ @ 50 A g⁻¹</td>
</tr>
<tr>
<td>V₂O₅/PPy¹⁰</td>
<td>1 M Na₂SO₄</td>
<td>−0.4—0.5</td>
<td>344 F g⁻¹ @ 0.2 A g⁻¹</td>
<td>189 F g⁻¹ @ 10 A g⁻¹</td>
</tr>
<tr>
<td>Fe₂O₃/FGS¹¹</td>
<td>1 M Na₂SO₄</td>
<td>−1—0</td>
<td>347 F g⁻¹ @ 10 mV s⁻¹</td>
<td>140 F g⁻¹ @ 1.6 V s⁻¹</td>
</tr>
<tr>
<td>H–TiO₂@C¹²</td>
<td>5 M LiCl</td>
<td>−1—0</td>
<td>253 F g⁻¹ @ 10 mV s⁻¹</td>
<td>178 F g⁻¹ @ 400 mV s⁻¹</td>
</tr>
<tr>
<td>VN¹³</td>
<td>5 M LiCl</td>
<td>−1.2—0.0</td>
<td>299 F g⁻¹ @ 10 mV s⁻¹</td>
<td>213 F g⁻¹ @ 100 mV s⁻¹</td>
</tr>
<tr>
<td>PPy/V₂O₅¹⁴</td>
<td>0.5 M K₂SO₄</td>
<td>−0.9—0.1</td>
<td>308 F g⁻¹ @ 0.1 A g⁻¹</td>
<td>Not reported</td>
</tr>
<tr>
<td>TiN@C¹⁵</td>
<td>1 M KOH</td>
<td>−1—0</td>
<td>159 F g⁻¹ @ 0.25 A g⁻¹</td>
<td>125 F g⁻¹ @ 5 A g⁻¹</td>
</tr>
<tr>
<td>Fe₂O₃/PPy¹⁶</td>
<td>1 M Na₂SO₄</td>
<td>−0.8—0.0</td>
<td>316 F g⁻¹ @ 0.5 mA cm⁻²</td>
<td>100 F g⁻¹ @ 6 mA cm⁻²</td>
</tr>
<tr>
<td>CNT–rGO¹⁷</td>
<td>1 M Na₂SO₄</td>
<td>−0.8—0.0</td>
<td>280 F g⁻¹ @ 1 A g⁻¹</td>
<td>190 F g⁻¹ @ 20 A g⁻¹</td>
</tr>
<tr>
<td>Fe₂N¹⁸</td>
<td>1 M LiCl</td>
<td>−0.8—0.0</td>
<td>168 F g⁻¹ @ 10 mV s⁻¹</td>
<td>129 F g⁻¹ @ 100 mV s⁻¹</td>
</tr>
<tr>
<td>PPy/MoO₃x⁴</td>
<td>5 M LiCl</td>
<td>−1.2—0.0</td>
<td>398 F g⁻¹ @ 1 A g⁻¹</td>
<td>282 F g⁻¹ @ 20 A g⁻¹</td>
</tr>
</tbody>
</table>

[This work]
Table S2  Energy density and cycling stability of energy storage devices assembled by using PPy or MoO\textsubscript{x} as the electrode materials.

<table>
<thead>
<tr>
<th>Device</th>
<th>Energy Density</th>
<th>Cycling Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO\textsubscript{3}/MoO\textsubscript{3}\textsuperscript{19}</td>
<td>22.9 Wh kg\textsuperscript{-1} @ 0.69 kW kg\textsuperscript{-1}</td>
<td>96.5% in 20000 cycles</td>
</tr>
<tr>
<td>MoO\textsubscript{3}@PPy/LiMn\textsubscript{2}O\textsubscript{4}\textsuperscript{20}</td>
<td>45.0 Wh kg\textsuperscript{-1} @ 0.35 kW kg\textsuperscript{-1}</td>
<td>90% in 150 cycles</td>
</tr>
<tr>
<td>SnO\textsubscript{2}/PPy//SnO\textsubscript{2}/MnO\textsubscript{2}\textsuperscript{9}</td>
<td>27.2 Wh kg\textsuperscript{-1} @ 0.85 kW kg\textsuperscript{-1}</td>
<td>80% in 2000 cycles</td>
</tr>
<tr>
<td>MnO\textsubscript{2}@PPy//AC\textsuperscript{21}</td>
<td>25.8 Wh kg\textsuperscript{-1} @ 0.90 kW kg\textsuperscript{-1}</td>
<td>90.3% in 6000 cycles</td>
</tr>
<tr>
<td>CNT@MnO\textsubscript{2}/CNT@PPy\textsuperscript{22}</td>
<td>40.0 Wh kg\textsuperscript{-1} @ 0.52 kW kg\textsuperscript{-1}</td>
<td>85% in 5000 cycles</td>
</tr>
<tr>
<td>NiMoO\textsubscript{4}·xH\textsubscript{2}O//H\textsubscript{2}MoO\textsubscript{3}\textsuperscript{23}</td>
<td>55.6 Wh kg\textsuperscript{-1} @ 0.64 kW kg\textsuperscript{-1}</td>
<td>81% in 5000 cycles</td>
</tr>
<tr>
<td>Graphene/MnO\textsubscript{2}//Graphene/MoO\textsubscript{3}\textsuperscript{5}</td>
<td>42.6 Wh kg\textsuperscript{-1} @ 0.28 kW kg\textsuperscript{-1}</td>
<td>~81.1% in 1000 cycles</td>
</tr>
<tr>
<td>PANI//MoO\textsubscript{3}\textsuperscript{24}</td>
<td>71.9 Wh kg\textsuperscript{-1} @ 0.25 kW kg\textsuperscript{-1}</td>
<td>78% in 1000 cycles</td>
</tr>
<tr>
<td>MgCo\textsubscript{2}O\textsubscript{4}@PPy//AC\textsuperscript{25}</td>
<td>33.4 Wh kg\textsuperscript{-1} @ 0.32 kW kg\textsuperscript{-1}</td>
<td>91% in 10000 cycles</td>
</tr>
<tr>
<td>Co\textsubscript{3}O\textsubscript{4}@PPy@MnO\textsubscript{2}//AC\textsuperscript{26}</td>
<td>34.3 Wh kg\textsuperscript{-1} @ 0.08 kW kg\textsuperscript{-1}</td>
<td>100.4% in 11000 cycles</td>
</tr>
<tr>
<td>CoO@PPy//AC\textsuperscript{27}</td>
<td>43.5 Wh kg\textsuperscript{-1} @ 0.09 kW kg\textsuperscript{-1}</td>
<td>91.5% in 20000 cycles</td>
</tr>
<tr>
<td>PPy//PPy\textsuperscript{28}</td>
<td>32.9 Wh kg\textsuperscript{-1} @ 0.65 kW kg\textsuperscript{-1}</td>
<td>80.1% in 5000 cycles</td>
</tr>
<tr>
<td>PPy@MoO\textsubscript{3}//AC\textsuperscript{29}</td>
<td>28.0 Wh kg\textsuperscript{-1} @ 0.46 kW kg\textsuperscript{-1}</td>
<td>93% in 1800 cycles</td>
</tr>
<tr>
<td>NNA@MnO\textsubscript{2}//NNA@PPy\textsuperscript{30}</td>
<td>48.9 Wh kg\textsuperscript{-1} @ 1.28 kW kg\textsuperscript{-1}</td>
<td>106.6% in 20000 cycles</td>
</tr>
<tr>
<td>LbL–PPy/MoO\textsubscript{3}//Na\textsubscript{0.5}MnO\textsubscript{2}\textsuperscript{31}</td>
<td>72.7 Wh kg\textsuperscript{-1} @ 0.34 kW kg\textsuperscript{-1}</td>
<td>92.3% in 10000 cycles</td>
</tr>
<tr>
<td><strong>This work</strong></td>
<td><strong>72.7 Wh kg\textsuperscript{-1} @ 0.34 kW kg\textsuperscript{-1}</strong></td>
<td><strong>92.3% in 10000 cycles</strong></td>
</tr>
</tbody>
</table>
3. REFERENCES