Hierarchical assembly of SnO$_2$ nanowires on MnO$_2$ nanosheets: a novel 1/2D hybrid architecture for high-capacity, reversible lithium storage

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**Fig. S1** XRD pattern of MnO$_2$ nanosheets showing four well-resolved peaks (001, 002, −111 and 005) of δ-MnO$_2$ (JCPDS card No. 80–1098).
Fig. S2 Raman spectrum of MnO$_2$ nanosheets showing two well-resolved peaks. Note that the peak at the higher wavenumber can be attributed to the symmetric stretching vibration $\nu_2$(Mn–O) of MnO$_6$ groups, while the peak at the lower wavenumber can be attributed to the $\nu_3$(Mn–O) stretching vibration in the basal plane of [MnO$_6$] sheets.$^{1-3}$


**Fig. S3** TGA curve of MnO$_2$ nanosheets showing 12.0 wt% organic content and 9.2 wt% crystal water content. Note that our K$^+$-intercalated MnO$_2$ nanosheets have a chemical formula of K$_{0.46}$Mn$_{1.54}$Mn$_{0.46}$O$_4$·1.4H$_2$O, corresponding to a theoretical crystal water content of 11.6 wt%. The actual crystal water content is calculated to be 10.4 wt% when we take into account the 12.0% organic content, which is in agreement with the theoretical value.

**Fig. S4**  XRD pattern of SnO$_2$ nanowires showing eight well-resolved peaks (110, 101, 111, 211, 220, 002, 221 and 112) of rutile SnO$_2$ (JCPDS card No. 41−1445).
Fig. S5  Raman spectrum of SnO$_2$ nanowires showing three well-resolved peaks. Note that the peak at 579 nm related to the facet surface area of a crystal arises from nanoscale SnO$_2$ with small grain sizes.$^1$

Fig. S6  TGA curve of SnO$_2$ nanowires showing 10.6 wt% organic content.
Fig. S7  Raman spectrum of SnO$_2$/MnO$_2$ 1/2D hybrid architecture. The circles and diamonds indicate the characteristic peaks of SnO$_2$ nanowires and MnO$_2$ nanosheets, respectively, with a certain degree of superposition (550–650 cm$^{-1}$) due to their very close peak positions.
Fig. S8 (a) Mn 2p and (b) Sn 3d XPS spectra of SnO$_2$/MnO$_2$ 1/2D hybrid architecture. In the binding energy range of 660–635 eV, the two peaks at 652.8 and 641.3 eV are assigned to Mn 2p$_{1/2}$ and 2p$_{3/2}$ orbitals, indicating the Mn(IV) state in the SnO$_2$/MnO$_2$ 1/2D hybrid architecture without any alterations.\textsuperscript{1} As to the XPS spectrum of SnO$_2$ in the energy range of 500–480 eV, the two peaks at 695.0 and 486.5 eV correspond to Sn 3d$_{3/2}$ and 3d$_{5/2}$ orbitals, demonstrating that the Sn atoms are in the form of SnO$_2$.\textsuperscript{2–5}

Fig.S9  SEM image of SnO$_2$/MnO$_2$ 1/2D hybrid architecture and the corresponding EDS maps showing a homogeneous distribution of Mn, Sn and O elements.
Table S1 – Elemental composition of SnO$_2$/MnO$_2$ 1/2D hybrid architecture.

<table>
<thead>
<tr>
<th></th>
<th>Mn (wt%)</th>
<th>Sn (wt%)</th>
<th>MnO$_2$ (wt%)</th>
<th>SnO$_2$ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual ratio</td>
<td>27.07</td>
<td>1.34</td>
<td>60.78</td>
<td>39.22</td>
</tr>
<tr>
<td>Starting ratio</td>
<td>–</td>
<td>–</td>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>

\(^a\)Note that SnO$_2$ nanowires cannot be completely dissolved in concentrated H$_2$SO$_4$ at ambient temperature, so their accurate composition is calculated by subtracting that of MnO$_2$ nanosheets from 100 wt%. Quantitatively, the content of MnO$_2$ nanosheets is calculated by considering the organic and crystal water contents, and is 60.78 wt%. Therefore, the content of SnO$_2$ nanowires is 39.22 wt%. These values agree well with their starting ratio which again confirm a quite high self-assembly efficiency.
Fig. S11 TEM images of SnO$_2$/MnO$_2$ 1/2D hybrid architecture after 200 charging−discharging cycles at a current density of 200 mA g$^{-1}$. It can be seen that after repeated lithiation/delithiation, the SnO$_2$/MnO$_2$ 1/2D hybrid architecture still preserves its original morphology without stacking or collapsing.
**Fig. S12** Nyquist plots of SnO$_2$/MnO$_2$ 1/2D hybrid architecture as well as neat MnO$_2$ nanosheets and SnO$_2$ nanowires from 100 kHz to 0.01 Hz. The diameter of the semicircle for the SnO$_2$ nanowires, corresponding to the charge transfer resistance ($R_{ct}$), is much smaller than that of the MnO$_2$ nanosheets, demonstrating the higher conductivity of the former.