Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

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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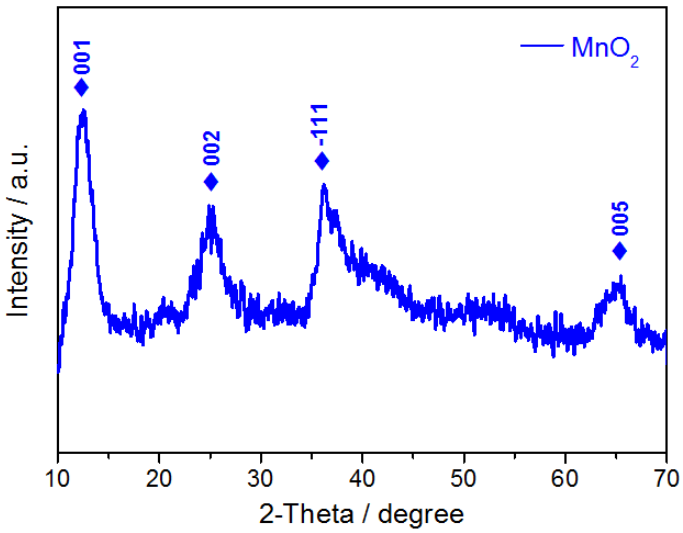

Fig. S1 XRD pattern of MnO_2 nanosheets showing four well-resolved peaks (001, 002, −111 and 005) of δ-MnO_2 (JCPDS card No. 80−1098).

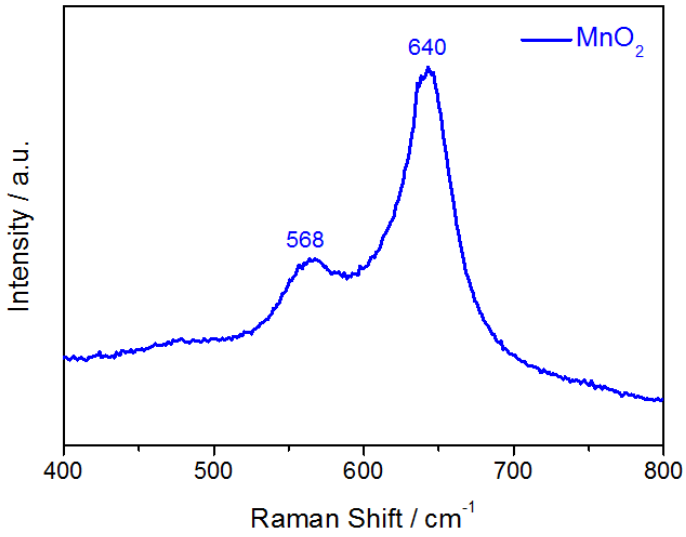

Fig. S2 Raman spectrum of MnO_2 nanosheets showing two well-resolved peaks. Note that the peak at the higher wavenumber can be attributed to the symmetric stretching vibration v_2(Mn−O) of MnO_6 groups, while the peak at the lower wavenumber can be attributed to the v_3(Mn−O) stretching vibration in the basal plane of [MnO_6] sheets.[1–3]

1 J. Zhou, L. Yu, M. Sun, S. Yang, F. Ye, J. He and Z. Hao, *Ind. Eng. Chem. Res.*, 2013, **52**, 9586.

2 C. Julien, M. Massot, R. Baddour-Hadjean, S. Franger, S. Bach and J. P. Pereira-Ramos, *Solid State Ionics*, 2003, **159**, 345.

3 A. K. Sinha, M. Pradhan and T. Pal, *J. Phys. Chem. C*, 2013, **117**, 23976.

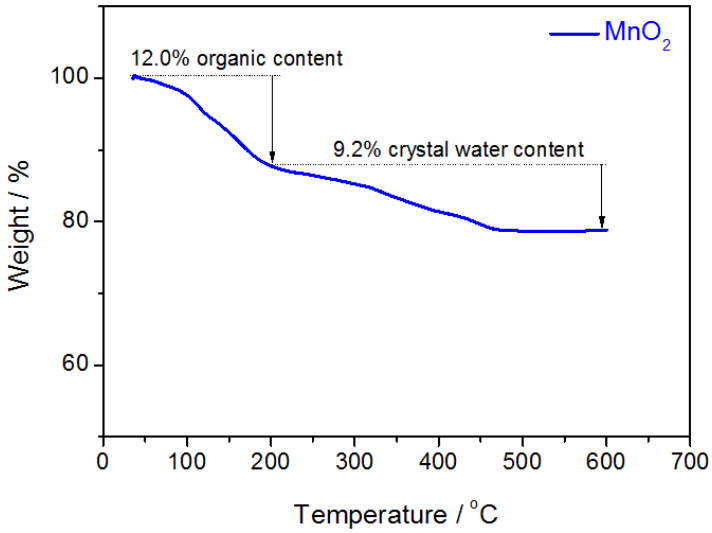

Fig. S3 TGA curve of MnO_2 nanosheets showing 12.0 wt% organic content and 9.2 wt% crystal water content. Note that our K^+-intercalated MnO_2 nanosheets have a chemical formula of $K_{0.46}Mn_{1.54}Mn_{0.46}O_4 \cdot 1.4H_2O$,[1] corresponding to a theoretical crystal water content of 11.6 wt%. The 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.

1 A. K. Sinha, M. Pradhan and T. Pal, *J. Phys. Chem. C*, 2013, **117**, 23976.

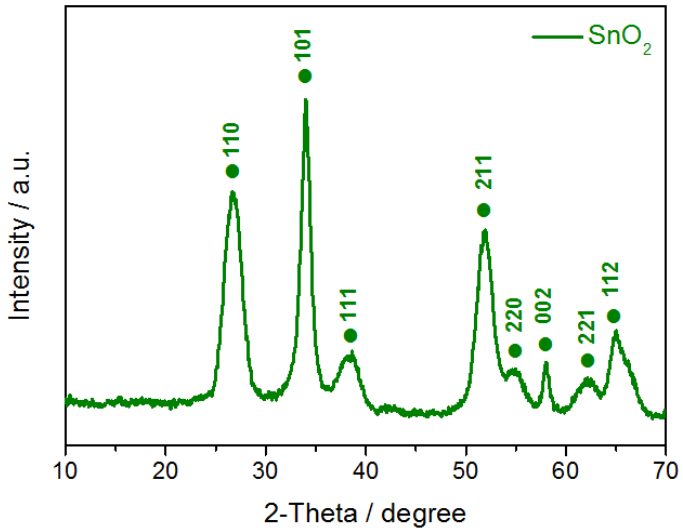

Fig. S4 XRD pattern of SnO_2 nanowires showing eight well-resolved peaks (110, 101, 111, 211, 220, 002, 221 and 112) of rutile SnO_2 (JCPDS card No. 41−1445).

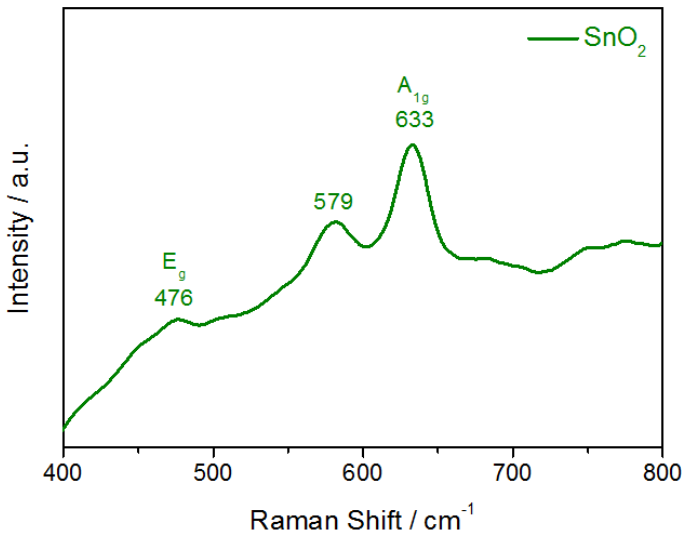

Fig. S5 Raman spectrum of SnO_2 nanowires showing three well-resolved peaks. Note that the peak at 579 nm related to the facet surface area of a crystal arises from nanoscale SnO_2 with small grain sizes.[1]

1 B. Cheng, J. M. Russell, W. Shi, L. Zhang and E. T. Samulski, *J. Am. Chem. Soc.*, 2004, **126**, 5972.

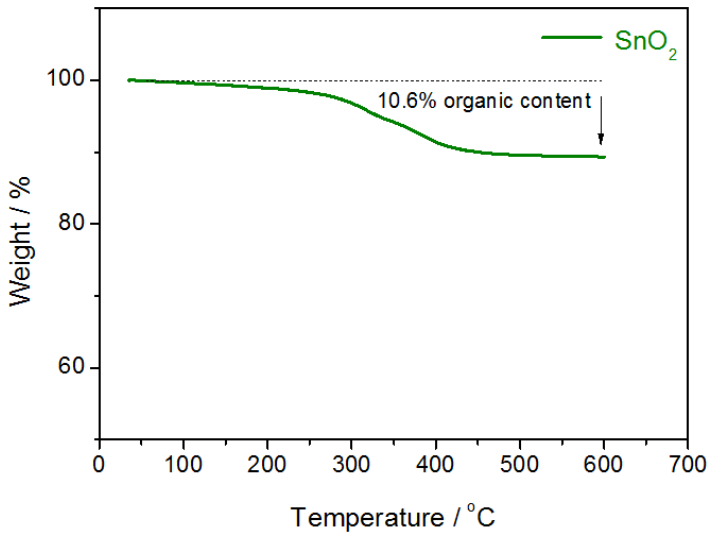

Fig. S6 TGA curve of SnO_2 nanowires showing 10.6 wt% organic content.

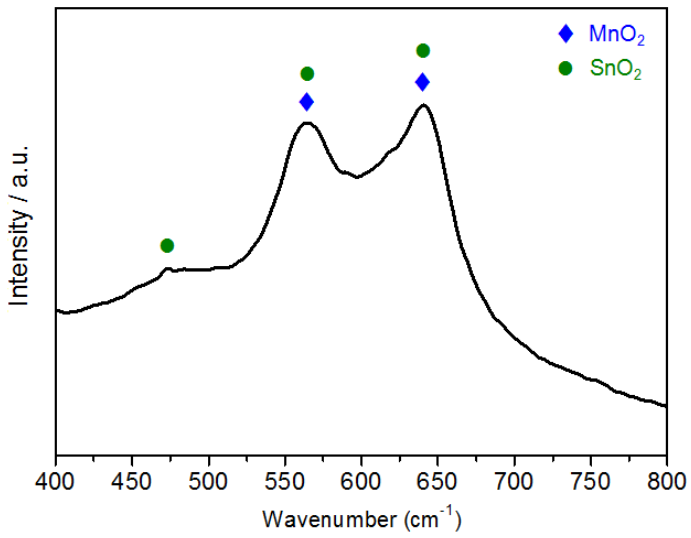

Fig. S7 Raman spectrum of SnO_2/MnO_2 1/2D hybrid architecture. The circles and diamonds indicate the characteristic peaks of SnO_2 nanowires and MnO_2 nanosheets, respectively, with a certain degree of superposition (550−650 cm^{-1}) due to their very close peak positions.

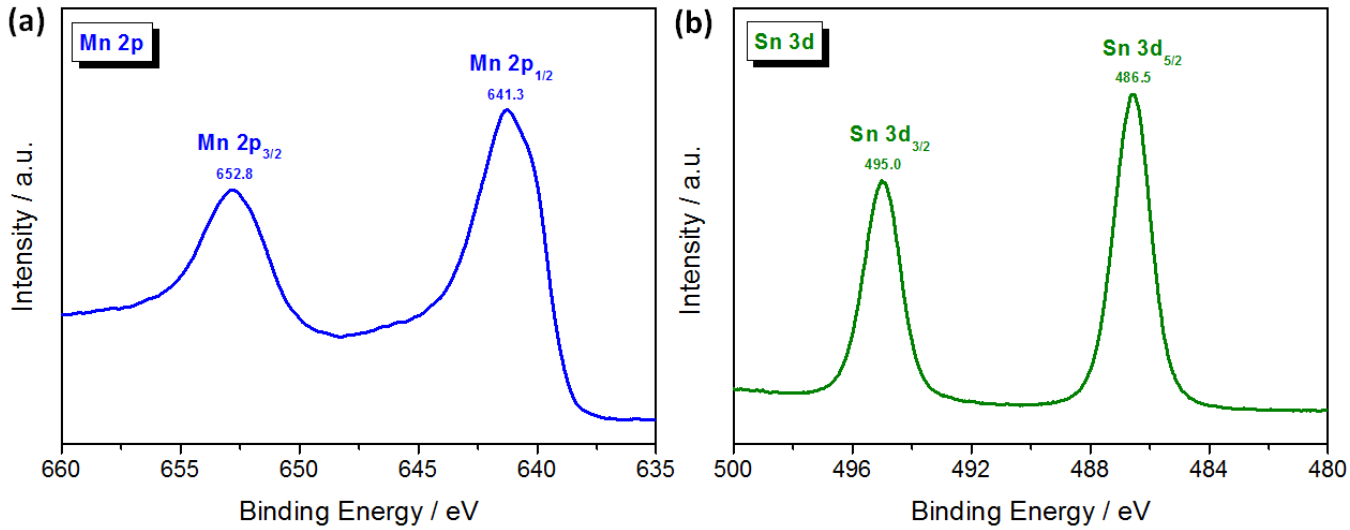

Fig. S8 (a) Mn 2p and (b) Sn 3d XPS spectra of SnO_2/MnO_2 1/2D hybrid architecture. In the binding energy range of 660−635 eV, the two peaks at 652.8 and 641.3 eV are assigned to Mn $2p_{1/2}$ and $2p_{3/2}$ orbitals, indicating the Mn(IV) state in the SnO_2/MnO_2 1/2D hybrid architecture without any alterations.[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.[2–5]

1 A. K. Sinha, M. Pradhan and T. Pal, *J. Phys. Chem. C*, 2013, **117**, 23976.

2 B. Zhang, Q. B. Zheng, Z. D. Huang, S. W. Oh and J. K. Kim, *Carbon*, 2011, **49**, 4524.

3 C. Tan, J. Cao, A. M. Khattak, F. Cai, B. Jiang, G. Yang and S. Hu, *J. Power Sources*, 2014, **270**, 28.

4 X. Wang, X. Cao, L. Bourgeois, H. Guan, S. Chen, Y. Zhong, D.-M. Tang, H. Li, T. Zhai, L. Li, Y. Bando and D. Golberg, *Adv. Funct. Mater.*, 2012, **22**, 2682.

5 L. Wang, D. Wang, Z. Dong, F. Zhang and J. Jin, *Nano Lett.*, 2013, **13**, 1711.

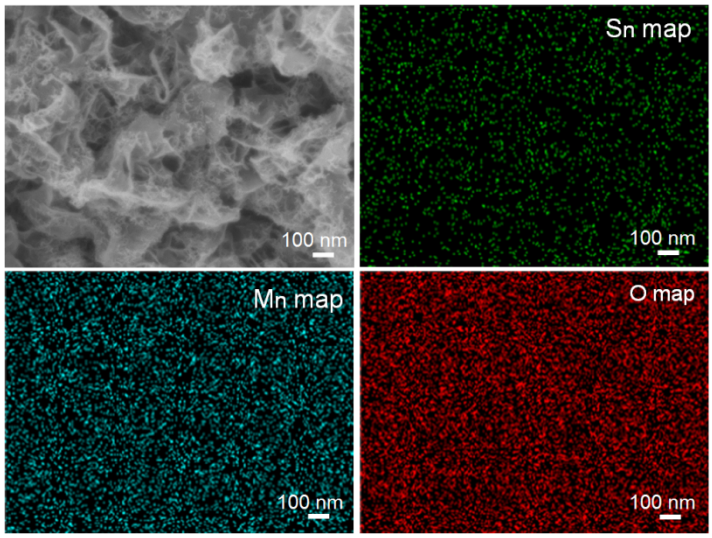

Fig. S9 SEM image of SnO_2/MnO_2 1/2D hybrid architecture and the corresponding EDS maps showing a homogeneous distribution of Mn, Sn and O elements.

Table S1 − Elemental composition of SnO_2/MnO_2 1/2D hybrid architecture.

	Mn (wt%)	Sn (wt%)	MnO_2 (wt%)	SnO_2 (wt%)
Actual ratio	27.07	1.34	60.78	39.22
Starting ratio	–	–	60	40

[a)]Note that SnO_2 nanowires cannot be completely dissolved in concentrated H_2SO_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.

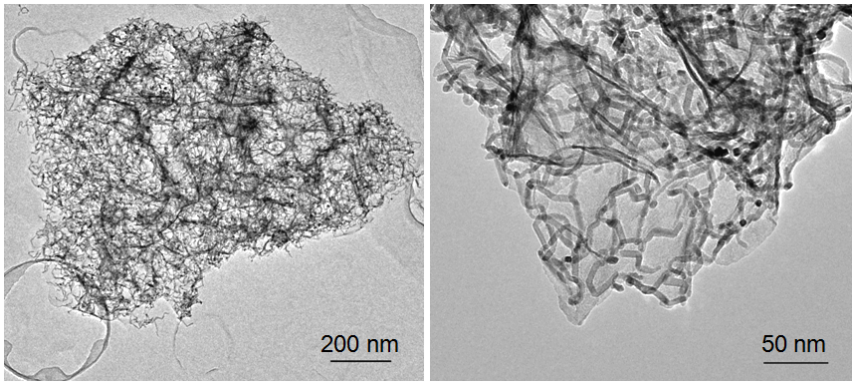

Fig. S11 TEM images of SnO_2/MnO_2 1/2D hybrid architecture after 200 charging−discharging cycles at a current density of 200 mA g^{-1}. It can be seen that after repeated lithation/delithation, the SnO_2/MnO_2 1/2D hybrid architecture still preserves its original morphology without stacking or collapsing.

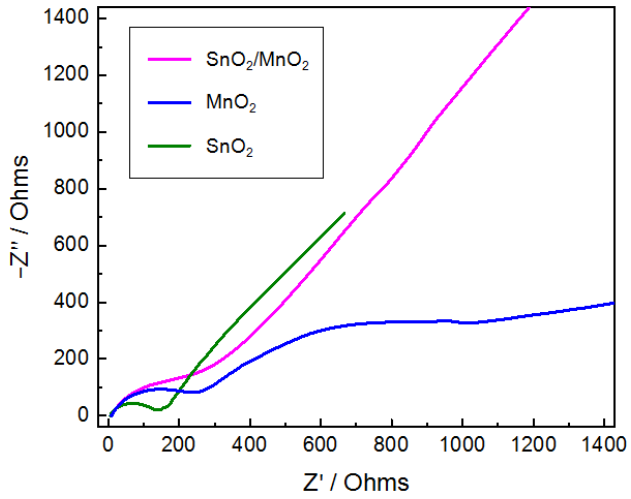

Fig. S12 Nyquist plots of SnO_2/MnO_2 1/2D hybrid architecture as well as neat MnO_2 nanosheets and SnO_2 nanowires from 100 kHz to 0.01 Hz. The diameter of the semicircle for the SnO_2 nanowires, corresponding to the charge transfer resistance (R_{ct}), is much smaller than that of the MnO_2 nanosheets, demonstrating the higher conductivity of the former.