

Electronic supplementary information for

Water-enabled crystallization of mesoporous SnO₂ as binder-free electrode of enhanced sodium storage

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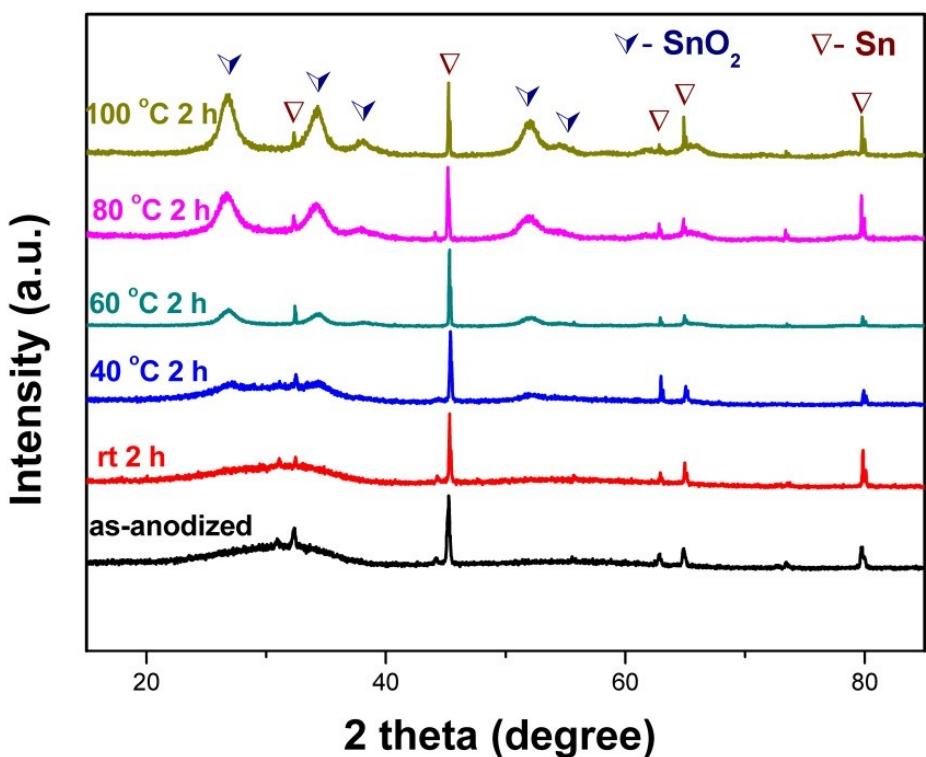


Figure S1. XRD patterns of the as-anodized SnO₂ film before and after water-soaking for 2 hrs at different temperature (rt, 40 °C, 60 °C, 80 °C and 100 °C).

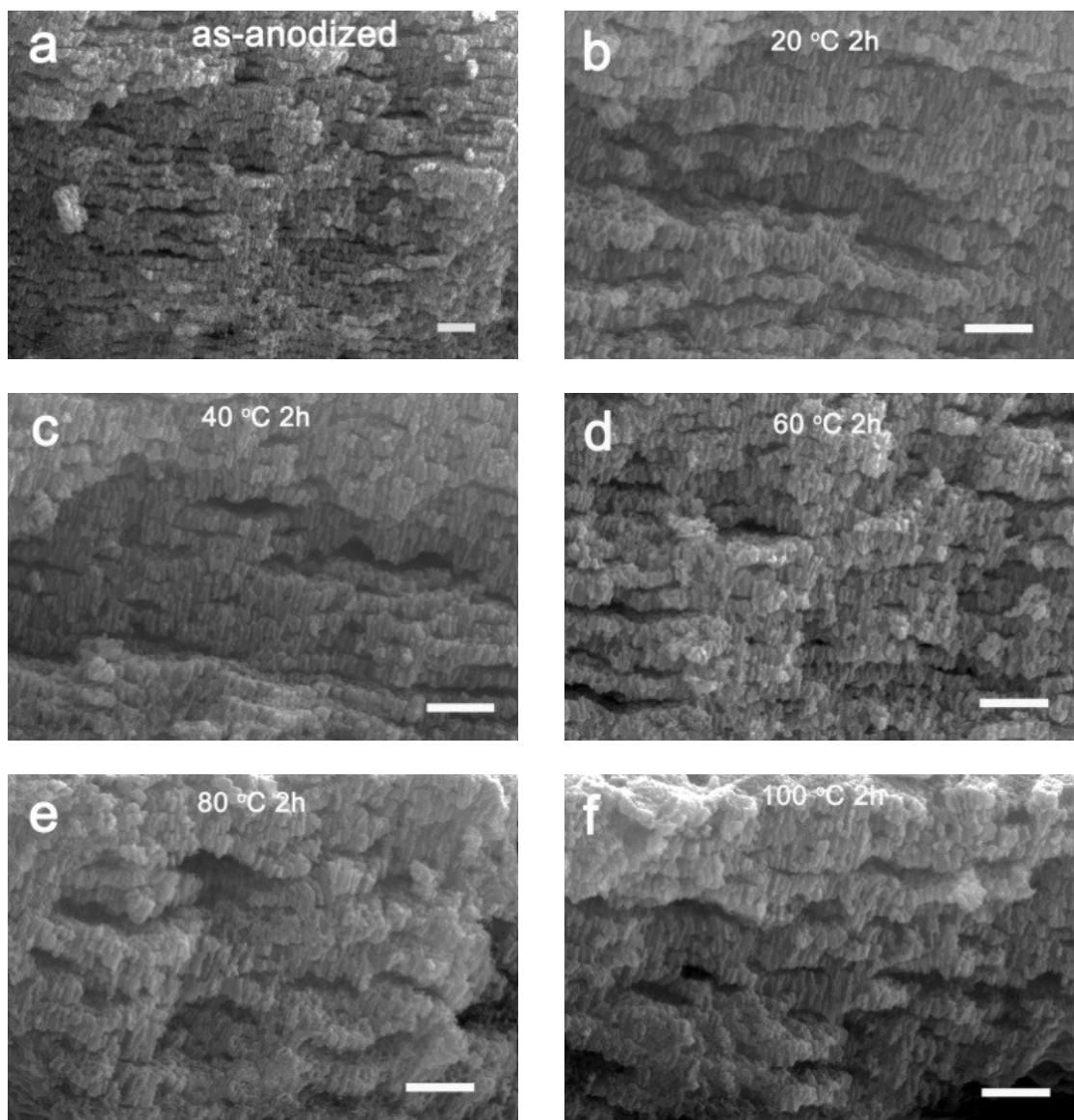


Figure S2. Cross-sectional SEM images of as-anodized SnO₂ samples before (a) and after water-soaking for 2 hrs at different temperatures (rt, 40 °C, 60 °C, 80 °C and 100 °C). Scale bars: 500 nm.

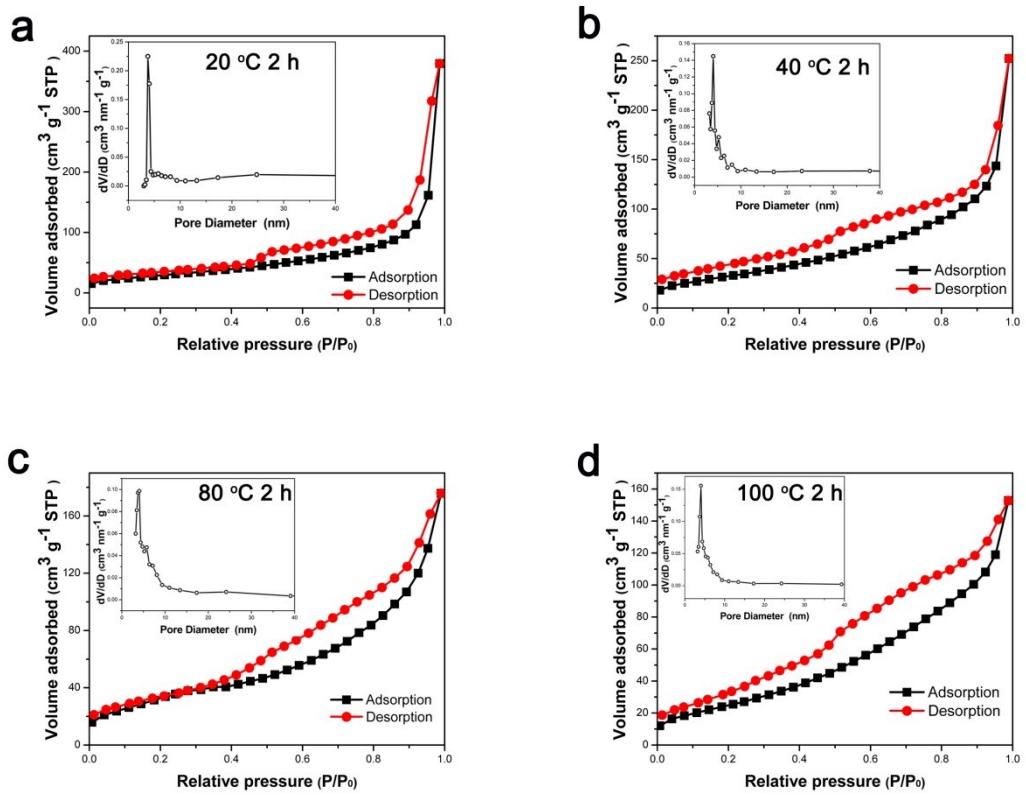


Figure S3. N_2 adsorption and desorption isotherms (measured at 77 K) of water-crystallized anodic SnO_2 at (a) 20 °C, (b) 40 °C, (c) 80 °C and (d) 100 °C. The insets are the corresponding pore-size distribution patterns calculated using the BJH method from the desorption branches.

Table S1. Surface areas and average pore sizes of the as-anodized amorphous SnO₂ and water- or thermal-crystallized SnO₂ samples, calculated from the nitrogen adsorption-desorption isotherms.

^a Average pore size calculated using the BJH model

Treated condition	Surface area (m ² g ⁻¹)	Average pore size ^a (nm)
As-anodized	98.35	3.79
20 °C for 2 hrs in water	108.18	3.76
40 °C for 2 hrs in water	122.553	4.04
60 °C for 2 hrs in water	181.45	3.78
80 °C for 2 hrs in water	133.783	4.34
100 °C for 2 hrs in water	110.918	4.07
400 °C for 2hrs in Ar	54.55	3.89

Table S2. Recent studies on SnO₂-based materials for NIBs.

Structure	Reversible capacity (mA h/g)	Cycles	Voltage (vs.Na ⁺ /Na)	Current rate	W/binder?	Fabrication method	Ref.
Mesoporous SnO ₂	514	100	0.01-2.0	0.1 C	N	anodization method	This work
a-SnO ₂ /GA	380.2	100	0.01-3.0	50 mA/g	Y	hydrothermal method	¹
SnO ₂ @MWCNT nanocomposite	< 400	50	0.01-2.0	0.1 C	Y	solvothermal method	²
SnO ₂ nanoparticle loading onto RGO	330	150	0.005 – 2.5	0.2 C	Y	Solution based percipitation	³
SnO ₂ nanoparticles @ 3D-graphene	432	200	0.01-2.5	100 mA/g	Y	hydrothermal assembly with ice-templated 3-DG	⁴
SnO ₂ / graphene	283	100	0.01-3.0	20 mA/g	Y	hydrothermal method	⁵
SnO ₂ / Carbon	270	200	0.01-1.5	80 mA/g	Y	hydrothermal method	⁶
1-D nanoporous SnO ₂	326	200	0.005-2.0	0.2 C	N	anodization method	⁷
SnO ₂ / graphene nanocomposite	302	100	0-3.0	160 mA/g	Y	hydrothermal method	⁸
Octahedral SnO ₂ nanocrystals	< 200	100	0.01-3.0	160 mA/g	Y	hydrothermal method	⁹
SnO ₂ @ graphene nanocomposite	270	100	0.1-2.5	100 mA/g	Y	wet mechano-chemical process	¹⁰
Mesoporous SnO _x nanosheets	404	100	0.01-2.0	100 mA/g	N	anodization method	¹¹

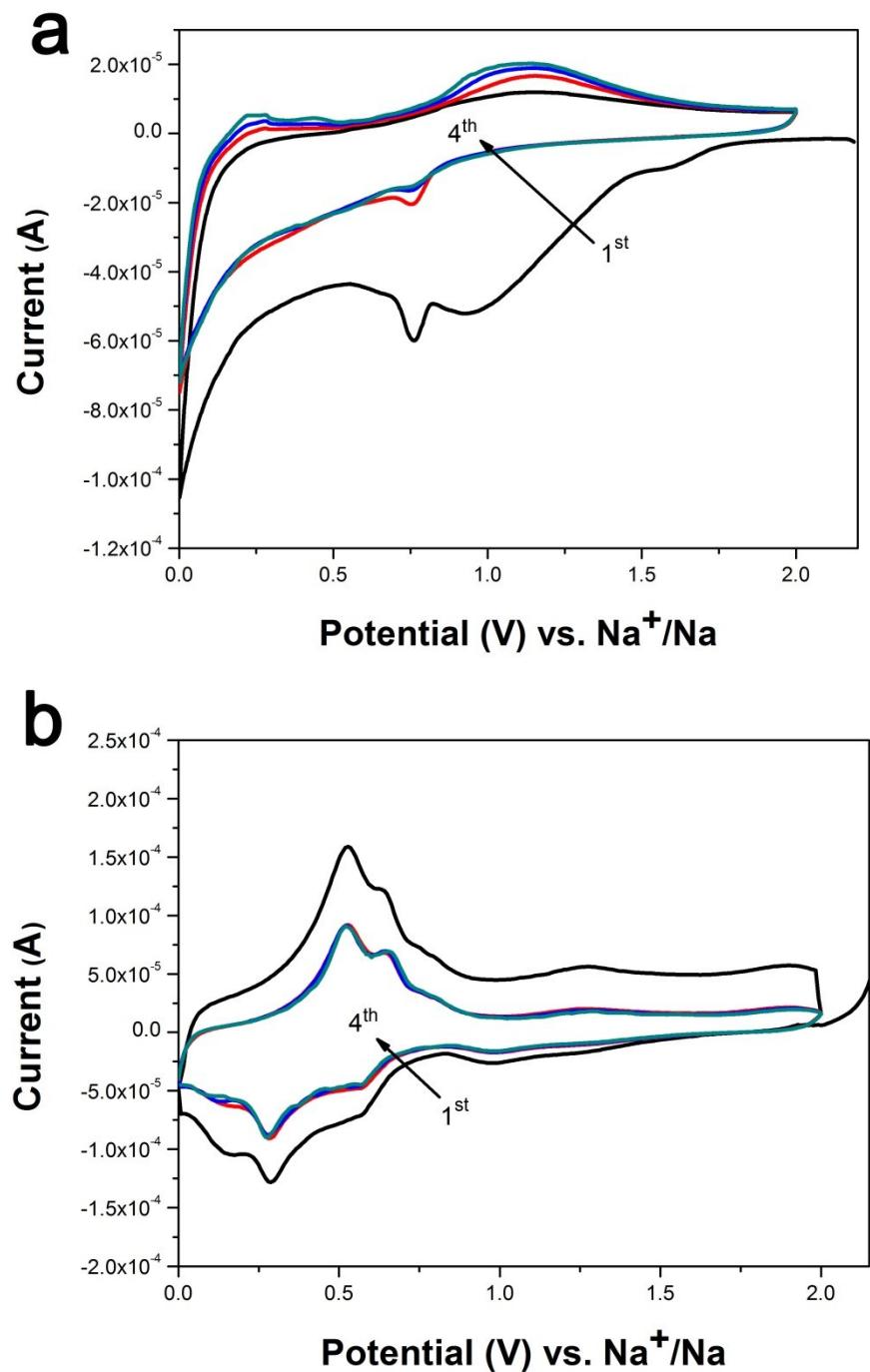


Figure S4. Cyclic voltammetry curves of a) as-anodized and b) thermally-crystallized (400 °C for 2 hrs) SnO_2 electrodes at 0.1 mV s⁻¹ between 0 and 2.0 V vs. Na^+/Na .

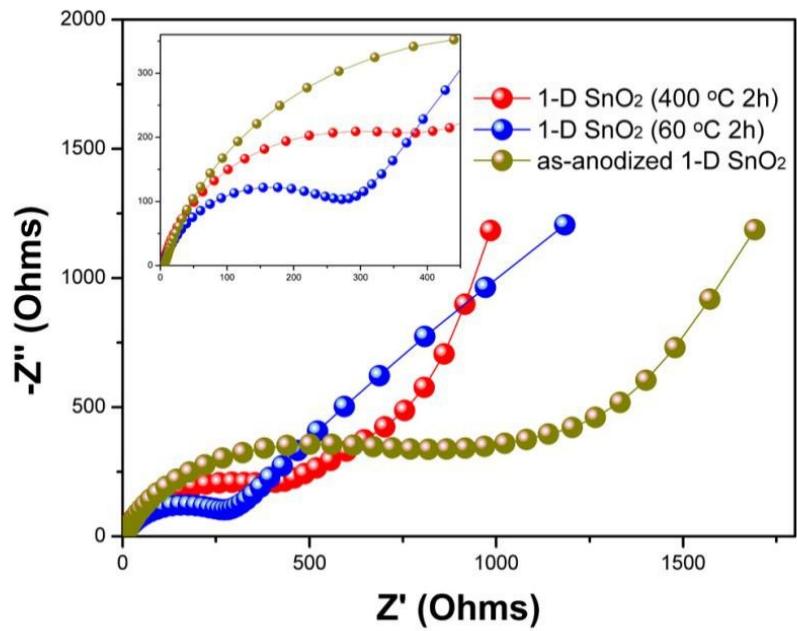


Figure S5. Nyquist plots of the as-anodized SnO_2 , water-crystallized SnO_2 (60 °C for 2 hrs) and thermal-crystallized SnO_2 (400 °C for 2 hrs), measured at an amplitude of 5 mV over a frequency range from 100 kHz to 0.01 Hz.

Reference

- 1 L. Fan, X. Li, B. Yan, J. Feng, D. Xiong, D. Li, L. Gu, Y. Wen, S. Lawes and X. Sun, *Adv. Energy Mater.*, 2016, **6**, 1502057.
- 2 Y. Wang, D. Su, C. Wang and G. Wang, *Electrochem. Commun.*, 2013, **29**, 8-11.
- 3 Y.-X. Wang, Y.-G. Lim, M.-S. Park, S.-L. Chou, J. H. Kim, H.-K. Liu, S.-X. Dou and Y.-J. Kim, *J. Mater. Chem. A*, 2014, **2**, 529-534.
- 4 L. Pei, Q. Jin, Z. Zhu, Q. Zhao, J. Liang and J. Chen, *Nano Res.*, 2015, **8**, 184-192.
- 5 X. Xie, D. Su, J. Zhang, S. Chen, A. K. Mondal and G. Wang, *Nanoscale*, 2015, **7**, 3164-3172.
- 6 J. Ding, Z. Li, H. Wang, K. Cui, A. Kohandehghan, X. Tan, D. Karpuzov and D. Mitlin, *J. Mater. Chem. A*, 2015, **3**, 7100-7111.
- 7 H. Bian, J. Zhang, M.-F. Yuen, W. Kang, Y. Zhan, D. Y. W. Yu, Z. Xu and Y. Y. Li, *J. Power Sources*, 2016, **307**, 634-640.
- 8 D. Su, H.-J. Ahn and G. Wang, *Chem. Commun.*, 2013, **49**, 3131-3133.
- 9 D. Su, C. Wang, H. Ahn and G. Wang, *PCCP*, 2013, **15**, 12543-12550.
- 10 S. Li, Y. Wang, J. Qiu, M. Ling, H. Wang, W. Martens and S. Zhang, *RSC Adv.*, 2014, **4**, 50148-50152.
- 11 H. Bian, X. Xiao, S. Zeng, M.-F. Yuen, Z. Li, W. Kang, D. Y. W. Yu, Z. Xu, J. Lu and Y. Y. Li, *J. Mater. Chem. A*, 2017, **5**, 2243-2250.