**Supporting Information** 

## Core-Shell Anatase Anode Materials for Sodium-Ion Batteries: the Impact of

## **Oxygen Vacancies and Nitrogen-doped Carbon Coating**

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Fig. S1 SEM images of core-shell  $TiO_2$  (a, b) and (c, d)  $TiO_{2-x}$ .



Fig. S2 High-resolution Ti 2p and O 1s spectra of  $TiO_2$  and  $TiO_{2-x}$ 



Fig. S3 CV curves of  $TiO_2$  (a) and  $TiO_{2-x}$  (b) at a scan rate of 0.1 mV s<sup>-1</sup>.



**Fig. S4** (a) galvanostatic charge/discharge profiles at a current density of 0.1 A  $g^{-1}$  of (a) TiO<sub>2</sub> and (b) TiO<sub>2-x</sub>. The corresponding ICE are 39.1% and 50.1%, respectively.



**Fig. S5** Nyquist plots of the core-shell  $TiO_2$ ,  $TiO_{2-x}$ , and  $TiO_{2-x}$ @NC electrodes before cycling in the frequency range from 0.01 Hz to 100 kHz.



**Fig. S6** SEM images of the  $TiO_{2-x}$ @NC electrode after charge/discharge process at 0.1A g<sup>-1</sup> for 200 cycles.

Material	Current density (A g <sup>-1</sup> )	ICE	Capacity/cy cles Capacity retention (vs. the 2 <sup>nd</sup>	Rate capacity (mAh g <sup>-1</sup> )	Current density (A g <sup>-1</sup> )	Ref.
TiO <sub>2</sub> @NC	0.1	011170	213.3/200 96.5%	226.4, 206.3,	0.5, 1.0,	work
1102-10110				177.8, 155.6	2.0, 5.0	
yolk@shell	0.05	58.8%	230.7/200 <sup>th</sup>	221.6, 200.5,	0.05, 0.1,	Ref. 1
TiO <sub>2-x</sub>			120%	181.1, 147.1,	0.2, 0.5,	
				121.5, 95.8,	1, 2,	
				68.6	5	
TiO <sub>2</sub> (A/B)-MS	0.25		$\sim \! 175/1000^{th}$	215, 200,	0.025, 0.05,	Ref. 2
			100%	185, 180,	0.125, 0.25,	
				155, 140,	0.75, 1.25,	
				120, 90,	2.5, 5,	
				75, 45	7.5, 12.5	
TiO <sub>2</sub> ∩NCSN	0.167	36.7%	36/800 <sup>th</sup>	201, 171,	0.084, 0.167,	Ref. 3
flowers			100%	157, 149,	0.335, 0.67,	
				133, 119,	1.67, 3.35,	
				100	6.7	
TiO <sub>2</sub> @CMK-3	0.05	45.8%	186.3/100 <sup>th</sup>	220.7, 182.4,	0.05, 0.1,	Ref. 4
			124.5/500 <sup>th</sup>	157.4, 139.8,	0.2, 0.4,	
				128.8, 105.9	0.8, 1.6	
STiO <sub>2</sub> @SC	0.2	46%	212.9/200 <sup>th</sup>	230, 170, 140,	0.2, 0.4, 0.6,	Ref. 5
				130, 115	0.8, 1.0	
TiO2@RGO	0.05	60.7%	206.9/200 <sup>th</sup>	248.5, 204.2,	0.05, 0.1,	Ref. 6
- 🤍			74.0%	167.3, 151.3,	0.5, 1.0,	
				118.8	2.0	
R-TiO <sub>2-*</sub> -S	0.05	42.7%	254.2/100 <sup>th</sup>	264.8. 243 7	0.05, 0.1	Ref 7
	0.00	,,,	101.7%	222.5. 183.8	0.2, 0.5	
				162 9 138 3	1 2	

**Table S1** Comparison of the electrochemical performance of the Core-shell  $TiO_{2-}$ (aNC with  $TiO_{2}$ -based anode materials for SIBs reported previously.

TiO <sub>2</sub> @NFG hybrid nanosheets	0.167	49%	185/800 <sup>th</sup>	205, 190, 170, 157, 140, 129, 120, 116, 110	0.084, 0.167, 0.335, 0.670, 1.675, 3.35, 6.70, 10.05, 13.4	Ref. 8
TiO <sub>2</sub> /SA	0.0335	62%	205/100 <sup>th</sup> 82%	230, 200, 190, 175, 155, 130, 110, 82	0.0335, 0.0670, 0.167, 0.335, 0.670, 1.67, 3.35, 6.70	Ref. 9
TiO <sub>2-x</sub> /NCFs	0.1	~38.9 %	210/100 <sup>th</sup> ~87.5%	230, 200, 176, 145, 120	0.05, 0.1, 0.2, 0.5, 1	Ref. 10
N-doped C- coated TiO <sub>2-x</sub>	0.084	52.7%	272/200 <sup>th</sup> ~91.5%	338, 301, 280, 258, 226, 197, 170, 150	33.6, 84, 168, 336, 840, 1680, 3360, 5040	Ref. 11
a-TiO <sub>2-x</sub> /r- TiO <sub>2-x</sub>	0.067	40%	210/300 <sup>th</sup> 76.3%	330, 255, 228, 199, 158, 130, 103	0.067, 0.167, 0.335, 0.67, 1.67, 3.35, 6.70	Ref. 12
TiO2@CNT@ C Nanorods	0.5		183/350 <sup>th</sup> 98%	230, 200, 159.6, 141.6, 115.5, 85, 71	0.05, 0.2, 1, 2, 4, 8, 12	Ref. 13
NC TiO <sub>2</sub> -Y	0.167	58.3%	243.2/200 <sup>th</sup> 116%	253.3, 211.5, 179.1, 162.1, 140.9, 122.2, 115.9	0.167, 0.335, 0.670, 1.67, 3.35, 5.03, 6.70	Ref. 14
defect-rich TiO <sub>2-d</sub> /C (D- MTO-700)	0.2	57.3%	238.5/600 <sup>th</sup> 91.3%	330.2, 280.5, 249.4, 217.2, 172.2, 128.3, 98.1, 88.6	0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10	Ref. 15
S-TiO <sub>2</sub> nanotube array	0.0335	52%		322, 271, 242, 216, 197, 167	0.0335, 0.167, 0.335, 0.670, 1.67, 3.35	Ref. 16
(TiO <sub>2</sub> @rGO	0.066		124/300 <sup>th</sup> 87%	170, 151, 128, 108, 90, 70, 55	0.033, 0.066, 0.165, 0.33, 0.66, 0.165, 3.3	Ref. 17

TiO <sub>2</sub> @C-600	0.0167 8	56.4%	190/100 <sup>th</sup> 95%	181, 167, 95, 65	0.01678, 0.03356, 0.3356, 3.356	Ref. 18
TiO <sub>2</sub> microspheres	0.0168	44.1	121.3/200 <sup>th</sup> 83.1%	135.3, 105.2, 72.3, 48.8, 17.7	0.084, 0.168, 0.336, 0.84, 1.68	Ref. 19
TiO <sub>2</sub> hollow spheres	0.02		212/200 <sup>th</sup>	266, 245, 226, 192, 139	0.04, 0.08, 0.16, 0.32, 0.64	Ref. 20
Ni-TiO <sub>2</sub> Nanoarrays	0.05		200/100 <sup>th</sup>	220, 192, 157, 132, 110, 95	0.1, 0.2, 0.5, 1, 2, 5	Ref. 21
TiO <sub>2</sub> -F/CNTs	0.025	36.3%	234/100 <sup>th</sup> 97%	210, 118	2.5, 25	Ref. 22

## Reference

- Z. Chen, L. Xu, Q. Chen, P. Hu, Z. Liu, Q. Yu, T. Zhu, H. Liu, G. Hu, Z. Zhu,
  L. Zhou and L. Mai, *J. Mater. Chem. A*, 2019, 7, 6740-6746.
- J. Y. Hwang, H. L. Du, B. N. Yun, M. G. Jeong, J. S. Kim, H. Kim, H. G. Jung and Y. K. Sun, ACS Energy Lett., 2019, 4, 494-501.
- B. Li, B. Xi, F. Wu, H. Mao, J. Liu, J. Feng and S. Xiong, *Adv. Energy Mater.*, 2019, 9, 1803070.
- 4 D. Zhang, L. Liu, Y. Zhang, H. Wu, Y. Zheng, G. Gao and S. Ding, Nanotechnology, 2019, **30**, 235401.
- 5 H. Xu, Q. Chen, M. Ren, W. Liu, M. Li and G. Li, *J. Electrochem. Soc.*, 2019, 166, A1096-A1102.
- 6 Y. Liu, J. Liu, D. Bin, M. Hou, A. G. Tamirat, Y. Wang and Y. Xia, ACS Appl. Mater. Interfaces, 2018, 10, 14818-14826.
- H. He, D. Huang, W. Pang, D. Sun, Q. Wang, Y. Tang, X. Ji, Z. Guo and H.
  Wang, *Adv. Mater.*, 2018, **30**, e1801013.
- B. Li, B. Xi, Z. Feng, Y. Lin, J. Liu, J. Feng, Y. Qian and S. Xiong, Adv.
  Mater., 2018, 30, 1705788.
- L. Ling, Y. Bai, Z. Wang, Q. Ni, G. Chen, Z. Zhou and C. Wu, ACS Appl.
  Mater. Interfaces, 2018, 10, 5560-5568.
- Q. Zhao, R. Bi, J. Cui, X. Yang and L. Zhang, ACS Appl. Energy Mater., 2018, 1, 4459-4466.
- 11 Q. Gan, H. He, K. Zhao, Z. He, S. Liu and S. Yang, ACS Appl. Mater.

Interfaces, 2018, 10, 7031-7042.

- 12 Y. Wu, Y. Jiang, J. Shi, L. Gu and Y. Yu, *Small*, 2017, **13**, 1700129.
- 13 Y.-E. Zhu, L. Yang, J. Sheng, Y. Chen, H. Gu, J. Wei and Z. Zhou, *Adv. Energy Mater.*, 2017, 7, 1701222.
- Y. Zhang, C. Wang, H. Hou, G. Zou and X. Ji, *Adv. Energy Mater.*, 2017, 7, 1600173.
- H. He, Q. Zhang, H. Wang, H. Zhang, J. Li, Z. Peng, Y. Tang and M. Shao, J. Power Sources, 2017, 354, 179-188.
- J. Ni, S. Fu, C. Wu, J. Maier, Y. Yu and L. Li, *Adv. Mater.*, 2016, 28, 2259-2265.
- 17 X. Zhu, Q. Li, Y. Fang, X. Liu, L. Xiao, X. Ai, H. Yang and Y. Cao, Part. Part. Syst. Charact., 2016, 33, 545-552.
- A. Henry, N. Louvain, O. Fontaine, L. Stievano, L. Monconduit and B. Boury, *ChemSusChem*, 2016, 9, 264-273.
- Y. Zhang, X. Pu, Y. Yang, Y. Zhu, H. Hou, M. Jing, X. Yang, J. Chen and X.
  Ji, *Phys. Chem. Chem. Phys.*, 2015, **17**, 15764-15770.
- 20 D. Su, S. Dou and G. Wang, Chem. Mater., 2015, 27, 6022-6029.
- 21 Y. Xu, M. Zhou, L. Wen, C. Wang, H. Zhao, Y. Mi, L. Liang, Q. Fu, M. Wu and Y. Lei, *Chem. Mater.*, 2015, **27**, 4274-4280.
- J. Y. Hwang, S. T. Myung, J. H. Lee, A. Abouimrane, I. Belharouak and Y. K.
  Sun, *Nano Energy*, 2015, 16, 218-226.