## Electronic supplementary information

## Production of hollow and porous Fe<sub>2</sub>O<sub>3</sub> from industrial mill scale and its potential for large-scale electrochemical energy storage applications

Chaopeng Fu, \* Amoghavarsha Mahadevegowda, Patrick S. Grant

Department of Materials, University of Oxford, Oxford, United Kingdom, OX1 3PH

\* E-mail: <a href="mailto:chaopeng.fu@materials.ox.ac.uk">chaopeng.fu@materials.ox.ac.uk</a>



Figure S1: XRD pattern of the as-supplied mill scale



Figure S2: XRD pattern of the product after reaction of the mill scale with oxalic acid.



Figure S3: SEM images of the products after reaction of mill scale with (a) oxalic acid and (b) HCl.



Figure S4: XRD pattern of the product obtained after calcination at 400 °C for 2 hrs.



Figure S5: SEM image of the product obtained after calcination at 800 °C for 2 hrs.



Figure S6:  $N_2$  adsorption-desorption isotherms of the feedstock mill scale powder after 4 hr ball milling (B) and then the hollow and porous  $Fe_2O_3$  powder after chemical and heat treatment (A).



Figure S7: (a) Charge/discharge curves at 0.1 C of the ball milled mill scale powder and (b) specific capacity as a function of cycle number.



Figure S8: Photograph of a 15 cm x 15 cm sprayed electrode on a Cu foil current

collector

Electrodes	Electrolyte	Specific capacitance F/g	Current density or scan rate	Reference	
Fe <sub>2</sub> O <sub>3</sub> nanostructure	Na <sub>2</sub> SO <sub>4</sub>	90	10 mV/s	1	
Fe <sub>2</sub> O <sub>3</sub> porous fiber	LiOH	256	1 mV/s	2	
Fe <sub>2</sub> O <sub>3</sub> nanograin	LiOH	102	1 mV/s	2	
Porous Fe <sub>2</sub> O <sub>3</sub> nanostructures	$Na_2SO_3$	127	1 A/g	3	
Fe <sub>2</sub> O <sub>3</sub> sheets	Li <sub>2</sub> SO <sub>4</sub>	147	0.36 A/g	4	
Porous Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> SO <sub>3</sub>	193	1 A/g	5	
Fe <sub>3</sub> O <sub>4</sub> nanowires	Na <sub>2</sub> SO <sub>3</sub>	70	1 A/g	6	
Fe <sub>3</sub> O <sub>4</sub> nanorods	Na <sub>2</sub> SO <sub>3</sub>	40	1 A/g	6	
Fe <sub>3</sub> O <sub>4</sub> nanosheets	Na <sub>2</sub> SO <sub>3</sub>	83	0.42 A/g	7	
Fe <sub>3</sub> O <sub>4</sub> /FeOOH nanowire	Na <sub>2</sub> SO <sub>3</sub>	300	2 mV/s	8	
Fe3O4 thin film	Na <sub>2</sub> SO <sub>3</sub>	118	2 A/g	9	
Hollow and porous		346	2 mV/s	This work	
Fe <sub>2</sub> O <sub>3</sub>	INd2303	213	2 A/g		

Table S1: Specific capacitances of iron oxides reported in the recent literature.

Table S2. Specific capacity and cycle life of  $Fe_2O_3$  anodes reported in the recent literature

Electrodes	Stable capacity (mAh/g)	C-rate (A/g)	Cycle life Retained (mAh/g)	First efficiency	Reference
3D network Fe <sub>2</sub> O <sub>3</sub>	852	0.2	1105@100 cycles	75%	10
	520	5			
Nano-Fe <sub>2</sub> O <sub>3</sub>	926	0.1	982@50	75%	11
			cycles		
porous Fe <sub>2</sub> O <sub>3</sub> nanotubes	881	0.2	750@100	74%	12
	358	1	cycles		
Fe <sub>2</sub> O <sub>3</sub> rod	700	0.15	415@30	70%	13
			cycles		
Mesoporous Fe <sub>2</sub> O <sub>3</sub>	900	0.1	900@100	75%	14
	450	1	cycles		
Fe <sub>2</sub> O <sub>3</sub> /rGO	600	0.1C	300@100	70%	15
	250	5C	cycles		
Graphene	851	0.1 C	700 @ 50 cycles	79%	16
wrapped Fe2O3	295	5C			
Hollow and porous $Fe_2O_3$	953	0.1	933@100	71%	This work
	673	5	cycles		

## Reference

- 1. M. S. Wu, R. H. Lee, J. J. Jow, W. D. Yang, C. Y. Hsieh and B. J. Weng, *Electrochemical and Solid State Letters*, 2009, **12**, A1-A4.
- G. Binitha, M. S. Soumya, A. A. Madhavan, P. Praveen, A. Balakrishnan, K. R. V. Subramanian, M. V. Reddy, S. V. Nair, A. S. Nair and N. Sivakumar, *J. Mater. Chem. A*, 2013, 1, 11698-11704.
- S. Shivakumara, T. R. Penki and N. Munichandraiah, *Ecs Electrochemistry Letters*, 2013, 2, A60-A62.
- J. C. Huang, S. N. Yang, Y. Xu, X. B. Zhou, X. Jiang, N. N. Shi, D. X. Cao, J. L. Yin and G. L.
  Wang, J. Electroanal. Chem., 2014, **713**, 98-102.
- S. Shivakumara, T. Penki and N. Munichandraiah, J. Solid State Electrochem., 2014, 18, 1057-1066.
- X. Zhao, C. Johnston, A. Crossley and P. S. Grant, *J. Mater. Chem.*, 2010, **20**, 7637-7644.
- J. B. Mu, B. Chen, Z. C. Guo, M. Y. Zhang, Z. Y. Zhang, P. Zhang, C. L. Shao and Y. C. Liu, Nanoscale, 2011, 3, 5034-5040.
- 8. L. O'Neill, C. Johnston and P. S. Grant, *J. Power Sources*, 2015, **274**, 907-915.
- 9. J. Chen, K. L. Huang and S. Q. Liu, *Electrochim. Acta*, 2009, **55**, 1-5.
- 10. X. Li, L. Qiao, D. Li, X. Wang, W. Xie and D. He, J. Mater. Chem. A, 2013, 1, 6400-6406.
- 11. H. Wang, S. Liu, X. Yang, R. Yuan and Y. Chai, *J. Power Sources*, 2015, **276**, 170-175.
- 12. H.-g. Wang, Y. Zhou, Y. Shen, Y. Li, Q. Zuo and Q. Duan, *Electrochim. Acta*, 2015, **158**, 105-112.
- 13. L. Huang, Z. Min and Q. Zhang, *Mater. Res. Bull.*, 2015, 66, 39-44.

- 14. J. Zhang, T. Huang, Z. Liu and A. Yu, *Electrochem. Commun.*, 2013, **29**, 17-20.
- L. Xiao, M. Schroeder, S. Kluge, A. Balducci, U. Hagemann, C. Schulz and H. Wiggers, J. Mater. Chem. A, 2015, 3, 11566-11574.
- 16. Y. Wang, L. Yang, R. Hu, W. Sun, J. Liu, L. Ouyang, B. Yuan, H. Wang and M. Zhu, *J. Power Sources*, 2015, **288**, 314-319.