## **Supporting Information**

## Metal-Organic-Framework Approach to Engineer Hollow Bimetal Oxide Microspheres towards Enhanced Electrochemical Performances of Lithium Storage

Weiwei Sun<sup>†</sup>, Si Chen<sup>†</sup>, Yong Wang\*

Department of Chemical Engineering, School of Environmental and Chemical Engineering, Shanghai University, 99 Shangda Road, Shanghai, P. R. China, 200444 Corresponding authors: Tel: +86-21-66137723; Fax: +86-21-66137725; Email address: yongwang@shu.edu.cn (Y. Wang)



**Fig. S1** XRD patterns of the benchmarked products: (a)  $Fe_2O_3/C$  and (b)  $MnFe_2O_4$ . The characteristic peaks in the XRD patterns of  $Fe_2O_3/C$  and  $MnFe_2O_4$  are in good accordance with the standard  $Fe_2O_3$  (PDF Card No.39-1346) and  $MnFe_2O_4$  (PDF Card No.10-0319).



**Fig. S2** N<sub>2</sub> adsorption/desorption isothermal curves and the pore distribution (the insert) of Fe<sub>2</sub>O<sub>3</sub>/C composite. The specific surface area of ~55.4 m<sup>2</sup> g<sup>-1</sup> can be detected with the existence of mesopores (pore size centered at ~12-27 nm) and micropores (pore size centered at ~0.4-1.0 nm).



**Fig. S3** TGA curve of Fe-Mn-O/C in air atmosphere. The weight loss of 12.7 % between 200-700  $^{\circ}$ C should be assigned to the oxidation of carbon, indicating 12.7 % carbon in the Fe-Mn-O/C composite.



**Fig. S4** EDS spectrum of Fe-Mn-O/C. Four elements of Fe, Mn, O, and C can be detected with the molar ratios being 9:1:15:10. The content of C in the Fe-Mn-O/C composite can also be detected to be 12.6 %.



**Fig. S5** (a) CV curves of the as-synthesized  $Fe_2O_3/C$  electrode with different scan rates of 0.2, 0.4, 0.6, and 0.8 mV s<sup>-1</sup>. The linear fit of (b) peak currents vs. scan rate and (c) peak currents vs. square root of scan rate for the as-synthesized  $Fe_2O_3/C$  electrode. (d) Contribution ratio of capacitive and diffusion-controlled behaviors at different scan rates of as-prepared  $Fe_2O_3/C$  electrode. (e) CV curves of the cycled  $Fe_2O_3/C$  electrode after 200 cycles with different scan rates of 0.2, 0.4, 0.6, and 0.8 mV s<sup>-1</sup>. The linear fit of (f) peak currents vs. scan rate and (g) peak currents vs. square root of scan rate for the cycled  $Fe_2O_3/C$  electrode after 200 cycles  $Fe_2O_3/C$  electrode after 200 cycles. (h) Contribution ratio of capacitive and diffusion-controlled behaviors at different scan rates of cycled  $Fe_2O_3/C$  electrode after 200 cycles. (h) Contribution ratio of capacitive and diffusion-controlled behaviors at different scan rates of cycled  $Fe_2O_3/C$  electrode after 200 cycles. (h) Contribution ratio of capacitive and diffusion-controlled behaviors at different scan rates of cycled  $Fe_2O_3/C$  electrode after 200 cycles. (h) Contribution ratio of capacitive and diffusion-controlled behaviors at different scan rates of cycled  $Fe_2O_3/C$  electrode after 200 cycles.



**Fig. S6** TEM image of the Fe-Mn-O/C electrode after 200 cycles. The sustainably retained hollow nanosphere morphology of the Fe-Mn-O/C electrode can be detected after cycling.

**Table S1** Electrochemical properties of Fe-Mn-O/C of this work and previous related work derived from MOFs. (IRC: initial reversible capacity, mA h g<sup>-1</sup>; RRC: retained reversible capacity, mA h g<sup>-1</sup>; CN: cycle number; CD: current density, A g<sup>-1</sup>; V: voltage, V)

Composite	Morphology	IRC	RRC/CN	CD	V	References
Fe <sub>2</sub> O <sub>3</sub> -Mn <sub>3</sub> O <sub>4</sub> -C	Hollow nanosphere	837	1294/200	0.1	0.005-3.0	This work
Fe <sub>2</sub> O <sub>3</sub>	Nanocube	~850	~800/50	0.2	0.05-3.0	1
Fe <sub>2</sub> O <sub>3</sub>	Microbox	917	~630/30	0.2	0.05-3.0	2
Fe <sub>2</sub> O <sub>3</sub>	Nanospindle	~1024	~920/40	0.1	0.005-3.0	3
Fe <sub>2</sub> O <sub>3</sub>	Hierarchical microbox	~945	~920/30	0.2	0.01-3.0	4
Fe <sub>2</sub> O <sub>3</sub>	Nanospindle	940	911/50	0.2	0.01-3.0	5
Fe <sub>2</sub> O <sub>3</sub>	Yolk-shell octahedron	1060	1176/200	0.1	0.005-3.0	6
Fe <sub>2</sub> O <sub>3</sub>	Microcube	~1420	~608/50	0.1	0.05-3.0	7
Fe <sub>2</sub> O <sub>3</sub> @N-doped C	Hollow nanosphere	1368	1573/50	0.1	0.01-3.0	8
Fe <sub>2</sub> O <sub>3</sub> /graphene	Nanoparticle in	~1174	1129/130	0.2	0.01-3.0	9
	graphene aerogel					
Fe <sub>2</sub> O <sub>3</sub> @graphene	Hollow nanosphere	~950	~833/100	1	0.01-3.0	10
Mn <sub>3</sub> O <sub>4</sub> /C	Sponge network	722	770/100	0.2	0.005-2.5	11
Mn <sub>3</sub> O <sub>4</sub> /C	Microsphere	1205	1032/500	0.2	0.01-3.0	12

## **References:**

- 1 L. Zhang, H. B. Wu, R. Xu, and X. W. Lou, CrystEngComm, 2013, 15, 9332-9335..
- 2 L. Zhang, H. B. Wu, and X. W. Lou, J. Am. Chem. Soc., 2013, 135, 10664-10672.
- 3 A. Banerjee, V. Aravindan, S. Bhatnagar, D. Mhamane, S. Madhavi and S. Ogale, *Nano Energy*, 2013, **2**, 890-896.
- 4 L. Zhang, H. B. Wu, S. Madhavi, H. H. Hng, and X. W. Lou, J. Am. Chem. Soc., 2012, 134, 17388-17391.
- 5 X. Xu, R. Cao, S. Jeong, and J. Cho, Nano Lett, 2012, 12, 4988-4991..
- 6 W. X. Guo, W. W. Sun, L. P. Lv, S. F. Kong, and Y. Wang, ACS Nano, 2017, 11, 4198-4205.
- 7 M. Li, W. Wang, M. Yang, F. Lv, L. Cao, Y. Tang, R. Sun, and Z. Lu, *RSC Adv.*, 2015, 5,7356-7362.
- 8 F. Zheng, M. He, Y. Yang, and Q. Chen, Nanoscale, 2015, 7, 3410-3417.
- 9 T. Jiang, F. Bu, X. Feng, I. Shakir, G. Hao, and Y. Xu, ACS Nano, 2017, 11, 5140-5147.
- 10 J. Hu, J. Zheng, L. Tian, Y. Duan, L. Lin, S. Cui, H. Peng, T. Liu, H. Guo, X. Wang, and F. Pan, *Chem. Commun.*, 2015, **51**, 7855-7858.
- 11 B. Sambandam, V. Soundharrajan, J. J. Song, S. Kim, J. Jo, D. P. Tung, S. Kim, V. Mathew, and J. Kim, *Inorg. Chem. Front.*, 2016, **3**, 1609-1615.
- 12 H. J. Peng, G. X. Hao, Z. H. Chu, J. Lin, X. M. Lin, and Y. P. Cai, *Cryst. Growth Des.*, 2017, 17, 5881-5886.