## **Electronic Supplementary Material**

# Yolk-shell $Fe_2O_3 \odot C$ composites anchored on MWNTs with enhanced lithium and sodium storage

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### **Experimental section**

#### 1.1 Synthesis of MWNTs@FeOOH composite

Pristine MWNTs (20-50 nm) were firstly refluxed with nitric acid (65 wt %) at 140 °C for 6 h, denoted as acid-MWNTs. 50 mg acid-MWNTs were then dispersed in 100 mL de-ionized H<sub>2</sub>O containing 2.16 g FeCl<sub>3</sub>. 6H<sub>2</sub>O by ultrasonication and stirred at 75 °C for 5h. Finally, the obtained composite was filtered, washed with water, and dried at 60 °C overnight.

#### 1.2 Synthesis of MWNTs@FeOOH@SiO2 composite

100 mg MWNTs@FeOOH was added into a mixture of 71.4 mL ethanol, 10 mL de-ionized water, and 3.14 mL NH<sub>3</sub>.H<sub>2</sub>O (25-28 wt%) and sonicated for 30 min. Then, a solution of 0.5 mL TEOS and 5 mL ethanol was dropped into the above solution and stirred for 3 h at room temperature. The product was washed with water and dried at 60  $^{\circ}$ C overnight.

#### 1.3 Synthesis of MWNTs@Fe<sub>2</sub>O<sub>3</sub> C composite

In a typical experiment, 180 mg MWNTs@FeOOH@SiO<sub>2</sub> composite was dispersed in 14 mL H<sub>2</sub>O by ultrasonication for 0.5 h, followed by addition of 0.05 mL NH<sub>3</sub>.H<sub>2</sub>O and 0.5 mL 0.01 M cetyltrimethylammonium bromide (CTAB) aqueous solution and stirred for 0.5 h. Then, 25 mg resorcinol and  $35\mu$ L formaldehyde (37% solution) were introduced and stirred for 16 h at room temperature. After carbonization at 700 °C for 2 h under Ar atmosphere with a heating rate of 10 °C min<sup>-1</sup>, the MWNTs@Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>@C composite was obtained. Finally, by etching the SiO<sub>2</sub> layer with 1 M NaOH solution at 50 °C for 12 h, the MWNTs@Fe<sub>2</sub>O<sub>3</sub>⊙C composite with yolk-shell Fe<sub>2</sub>O<sub>3</sub>OC composites anchored on MWNTs was achieved.

#### **Materials Characterization**

The morphology and structure properties of the samples were characterized by scanning electron microscopy (SEM, JSM-7600F), transmission electron microscope (TEM, JEM-2010F and FEI Tecani G2 F20), X-ray diffraction (Shimadzu, XRD-6000), and Brunauer–Emmett–Teller surface area analyzer (BET, Micromeritics ASAP2020). Thermogravimetry analyses (TGA, Q500) were carried out from 30 to 700  $^{\circ}$ C at a heating rate of 10 K min<sup>-1</sup> in air.

#### **Electrochemical Measurements**

The electrochemical measurements were carried out via CR2032 coin-type test cells assembled in an Ar-filled glove box. The working electrodes were consisted of 80 wt% active materials (MWNTs@Fe<sub>2</sub>O<sub>3</sub> $\odot$ C, or MWNTs@Fe<sub>3</sub>O<sub>4</sub>), 10 wt% conductivity agent (ketjen black, KB), and 10 wt% binder (carboxymethyl cellulose, Na-CMC), which were mixed with de-ionized water, pasted on Ni foam, and then dried at 80 °C for 12 h in a vacuum before use. For LIBs, lithium foil and celgard 2300 membrane were used as the counter electrode and separator, respectively. The electrolyte was 1M LiPF<sub>6</sub> in EC: EMC: DMC (1: 1: 1 in volume). For NIBs, Na foil was the counter electrode and glass fiber (EL-CELL) was the separator. The electrolyte was 1 M NaClO<sub>4</sub> in EC: DEC (1: 1 in volume) with 10 wt% fluoroethylene (FEC). Cells were galvanostatically discharged and charged on a Neware Battery tester with current densities from 160 to 3200 mA g<sup>-1</sup>. Cyclic voltammetry (CV) test was carried out on a PINE WaveDriver 20 bipotentiostat with a scan rate of 0.5 mV s<sup>-1</sup>.

For LIBs, the specific capacities were calculated based on the total mass of the MWNTs@Fe<sub>2</sub>O<sub>3</sub> $\odot$ C or MWNTs@Fe<sub>3</sub>O<sub>4</sub> composite. For NIBs, the specific capacities were calculated based on the mass of Fe<sub>2</sub>O<sub>3</sub>, which was consistent with the calculation method used in NIBs literatures.



Fig. S1 (a) High resolution TEM image and (b) XRD pattern of MWNTs@FeOOH composite. The HRTEM in (a) showed the lattice fringes of the FeOOH nanorods. The XRD pattern in (b) displayed the diffraction peaks of FeOOH, which were well indexed to the tetragonal structure of  $\beta$ -FeOOH (JCPDS No. 75-1594).



**Fig. S2** (a-b) SEM and (c-d) TEM images of the MWNTs@FeOOH@SiO<sub>2</sub> composite, revealing the uniform SiO<sub>2</sub> coating on MWNTs@FeOOH.



Fig. S3 Scanning transmission electron microscopy (STEM) images of (a) MWNTs@FeOOH, (b) MWNTs@FeOOH@SiO<sub>2</sub>, and (c) MWNTs@Fe<sub>2</sub>O<sub>3</sub> $\odot$ C composites as well as their corresponding element mapping images for carbon, iron, oxygen, and silicon.



**Fig. S4** XRD pattern of the MWNTs@Fe<sub>3</sub>O<sub>4</sub> by directly annealing MWNTs@FeOOH composite at 700 °C for 2h under Ar. The XRD peaks in (c) were well indexed to face-centered-cubic Fe<sub>3</sub>O<sub>4</sub> (JCPDS Card No. 19-0629). The small diffraction peaks around  $26^{0}$  were resulted from MWNTs. The diffraction peaks were sharper than the MWNTs@Fe<sub>2</sub>O<sub>3</sub> $\odot$ C, indicating the large particle size of Fe<sub>3</sub>O<sub>4</sub> in this composite.



Fig. S5 (a-b) SEM images of the MWNTs@ $Fe_3O_4$  composite. As can be seen, without the protection of SiO<sub>2</sub> and carbon layer, the Fe<sub>3</sub>O<sub>4</sub> particles were aggregated with particle size up to several hundred nanometers.



**Fig. S6** (a) Nitrogen adsorption—desorption isotherms, and (b) pore size distribution of MWNTs@Fe<sub>3</sub>O<sub>4</sub> composite, which only possessed a low surface area of 26 m<sup>2</sup> g<sup>-1</sup> and a small pore volume of 0.08 cm<sup>3</sup> g<sup>-1</sup>.



**Fig. S7** Typical discharge and charge profiles of MWNTs@Fe<sub>2</sub>O<sub>3</sub> $\odot$ C electrode under various current densities from 200 to 3200 mA g<sup>-1</sup> for LIBs, which remained the similar electrochemical reaction plateaus and delivered high capacities even at current densities.



**Fig. S8** Lithium storage performance of MWNTs@Fe<sub>3</sub>O<sub>4</sub> anode. (a) First discharge and charge profiles at 200 mA g<sup>-1</sup>. (b) Cycling performance at 2000 mA g<sup>-1</sup> after being activated at 200 mA g<sup>-1</sup> in the initial two cycles. As can be seen, the MWNTs@Fe<sub>3</sub>O<sub>4</sub> anode delivered low discharge and charge capacities of 1047 and 690 mAh g<sup>-1</sup> in the first cycle at 200 mA g<sup>-1</sup>, probably due to the large particle size of Fe<sub>3</sub>O<sub>4</sub>, which can be not fully utilized during Li insertion and extraction process. Meanwhile, without the void space and carbon layer protection in this composite, a gradual capacity fading was observed with a low capacity of 180 mAh g<sup>-1</sup> remained after 400 cycles at 200 mA g<sup>-1</sup>.



Fig. S9 Electrochemical impedance spectroscopy (EIS) profiles of the MWNTs@Fe<sub>2</sub>O<sub>3</sub> C and MWNTs@Fe<sub>3</sub>O<sub>4</sub> electrodes after (a) lithium and (b) sodium storage cycles. As can be seen, the diameters of the semicircles for MWNTs@Fe<sub>2</sub>O<sub>3</sub>  $\odot$  C electrodes in the high-medium frequency region was smaller than the MWNTs@Fe<sub>3</sub>O<sub>4</sub> electrode, indicating the lower contact and charge-transfer impedances of MWNTs@Fe<sub>2</sub>O<sub>3</sub> $\odot$ C electrode, benefitting from the highly conductive carbon layer and MWNTs networks.



Fig. S10 TEM images of the MWNTs@ $Fe_2O_3$  C composite after (a) lithium and (b) sodium storage cycles, demonstrating the good structure stability of the yolk-shell structure  $Fe_2O_3@C$  after cycles.



**Fig. S11** Cycling performance of MWNTs@Fe<sub>3</sub>O<sub>4</sub> anode for NIBs at 160 mA  $g^{-1}$ , which only delivered low capacities of ~30 mAh  $g^{-1}$ .



**Fig. S12** Cycling performance of MWNTs@ $Fe_2O_3 \odot C$  anode for NIBs at 500 mA g<sup>-1</sup> being activated at 160 mA g<sup>-1</sup> in the initial five cycles. As can be seen, this electrode also delivered good cycling stability during sodium storage at 500 mA g<sup>-1</sup>, which still remained discharge capacities of 200 and 168 mAh g<sup>-1</sup> after 300 and 600 cycles, respectively.

Materials	Current density (mAg <sup>-1</sup> )	Cycle Number	Capacity (mAh g <sup>-1</sup> )	Rate ( mA g <sup>-1</sup> ) /Capacity ( mAh g <sup>-1</sup> )	Ref
Fe <sub>3</sub> O <sub>4</sub> @C	55	10	238	-	[1]
Nano-Fe <sub>2</sub> O <sub>3</sub>	130	60	250	-	[2]
Graphene/Fe <sub>2</sub> O <sub>3</sub>	100	200	410	1000/190	[3]
C/Fe <sub>3</sub> O <sub>4</sub> /CNT	50	50	298	2400/196	[4]
Nano-Fe <sub>3</sub> O <sub>4</sub>	83	50	248	1668/~60	[5]
Fe <sub>2</sub> O <sub>3</sub> @C	200	200	740	8000/317	[6]
Fe <sub>2</sub> O <sub>3</sub> film	100	200	385	5000/233	[7]
MWNTs@Fe2O3 C	160	100	272	1000/251	This
	500	600	168		work

Table. S1 Sodium storage performance of the reported iron oxides anode for NIBs.

- [1] S. Hariharan, K. Saravanan, V. Ramar and P. Balaya, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2945.
- [2] M. Valvo, F. Lindgren, U. Lafont, F. Bjorefors and K. Edstrom, J. Power Sources, 2014, 245, 967.
- [3] Z. L. Jian, B. Zhao, P. Liu, F. J. Li, M. B. Zheng, M. W. Chen, Y. Shi and H. S. Zhou, *Chem. Commun.*, 2014, **50**, 1215.
- [4] D. Y. Park and S. T. Myung, *Acs Appl. Mater. Inter*, 2014, **6**, 11749.
- [5] P. R. Kumar, Y. H. Jung, K. K. Bharathi, C. H. Lim and D. K. Kim, *Electrochim Acta*, 2014, **146**, 503.
- [6] N. Zhang, X. Han, Y. Liu, X. Hu, Q. Zhao and J. Chen, *Adv. Energy Mater.*, 2014, **4**, 1401123.
- [7] Y. Z. Jiang, M. J. Hu, D. Zhang, T. Z. Yuan, W. P. Sun, B. Xu and M. Yan, *Nano Energy*, 2014, 5, 60.