## **Supplementary Information**

Hierarchical architecture of hybrid carbon-encapsulated hollow manganese oxide nanotube with porous-wall structure for high-performance electrochemical energy

storage

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## **Experimental Details**

**Materials.** Polyacrylonitrile (PAN,  $M_w$ = 150,000), *N*,*N*-Dimethylformamide (DMF, ≥99%), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, 95.0-98.0%), potassium permanganate (KMnO<sub>4</sub>,≥99.0%), glucose solution (~20% in H<sub>2</sub>O), n-methyl–2–pyrrolidinone (NMP, 99.5 %), poly(vinylidene fluoride) (PVDF,  $M_w$ = ~534,000), and manganese (III) oxide (Mn<sub>2</sub>O<sub>3</sub>, 99.99%) were purchased from Sigma–Aldrich. All the chemicals were used without any further purification. **Synthesis of carbon-encapsulated porous hollow Mn<sub>2</sub>O<sub>3</sub> nanotubes. Carbon-encapsulated porous hollow Mn<sub>2</sub>O<sub>3</sub> nanotubes (C-PHNT) were successfully synthesized using a simple microwave process followed by a hydrothermal method. First, carbon nanofibres (CNFs)** 

were fabricated as template materials using an electrospinning method. To synthesize the CNFs, 10 wt% PAN was dissolved in DMF. For the electrospinning process, the DC voltage and feeding rate were fixed at ~13 kV and 0.03 mL h<sup>-1</sup>, respectively. The distance between the aluminium foil collector and capillary tip was fixed at ~15 cm. The as-spun PAN nanofibres were stabilized at 280 °C for 2 h in ambient air and carbonized at 800 °C for 2 h in nitrogen atmosphere. After calcination, the CNFs were successfully formed. Second, to obtain the hollow MnO<sub>2</sub> nanotubes, 0.05 g CNFs were dissolved in deionized (DI) water and 2.0 M H<sub>2</sub>SO<sub>4</sub> with vigorous stirring at 80 °C for 0.5 h, and then 6 m mol KMnO<sub>4</sub> was added with vigorous stirring for 0.5 h. They were washed several times with DI water and dried using a convection oven at 80 °C. Then, to form porous hollow Mn<sub>2</sub>O<sub>3</sub> nanotubes, hollow MnO<sub>2</sub> nanotubes were sintered using microwave treatment with a wavelength of 2.45 GHz at 400, 500, 600, and 700 °C for 5 min at a heating rate of 20 °C/min in air. Finally, the porous hollow Mn<sub>2</sub>O<sub>3</sub> nanotubes were well encapsulated with carbon using a hydrothermal method. For this process, the porous hollow Mn<sub>2</sub>O<sub>3</sub> nanotubes dissolved in 30 mL of 0.1 M glucose aqueous solution were transferred into a 120-mL Teflon-sealed autoclave and then maintained at 180 °C for 3 h. The resultant samples after the encapsulation of carbon were calcined at 400 °C for 2 h under argon atmosphere to achieve improved crystallinity of the coated carbon. We obtained four different types of C-PHNTs microwave-treated at 400 °C, 500 °C, 600 °C, and 700 °C (herein called C-PHNT 400, C-PHNT 500, C-PHNT 600, and C-PHNT 700, respectively).

The structure, morphology, and chemical bonding states of the samples were investigated by field-emission scanning electron microscopy (FESEM; Hitachi S-4800) and transmission electron microscopy (MULTI/TEM; TecnaiG<sup>2</sup>, KBSI Gwangju Center). The crystal structures and chemical bonding states were examined using X-ray diffractometry (XRD, Rigaku D/MAX2500 V) in the range from 10° to 90° with a step size of 0.02° and X-

ray photoelectron spectroscopy (XPS, ESCALAB 250) with an Al  $K_{\alpha}$  X-ray source under a base pressure of 267 nPa.

Electrochemical characterization. Electrochemical measurements were performed using coin cells (CR2032, Hohsen Corporation) composed of C-PHNTs as the anode, Li metal foil (Honjo Chemical, 99.8%) as the cathode, a 1.0 M LiPF<sub>6</sub> solution in a mixture of ethylene carbonate-dimethyl carbonate (1:1) as the electrolyte, and a porous polypropylene membrane (Celgard 2400) as the separator. The C-PHNT electrodes were prepared on a Cu foil substrate (Nippon Foil, 18 µm) as the current collector by coating an NMP based slurry with a mixture of 80 wt% of active materials, 10 wt% Ketjen black as the conducting material, and 10 wt% PVDF as the binder. The electrode slurry was coated on a Cu foil substrate about 20 µm in thickness. The resultant electrodes were dried in an oven at 100 °C for 12 h. The mass loading of C-PHNT was optimized and fixed with 11.3±0.5 mg cm<sup>-2</sup>. All the coin cells were assembled in an argon-filled glove box with H<sub>2</sub>O and O<sub>2</sub> contents of less than 5 ppm. Cyclic voltammetry (CV) measurements were performed at a scan rate of 0.1 mV s<sup>-1</sup> in the voltage range of 0-3 V (versus Li/Li<sup>+</sup>) using a potentiostat/galvanostat (Eco chemie Autolab, PGSTAT302N). The charge-discharge performance was investigated using a battery cycler system (Won-A Tech, WMPG 3000) in the potential range of 0–3 V (versus Li/Li<sup>+</sup>). The rate performance was measured using the same instrument at current densities of 100, 300, 500, 700, and 100 mA g<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of  $10^5$  to  $10^{-2}$  Hz by applying an AC signal of 5 mV.



Fig. S1 XRD patterns of pure Mn<sub>2</sub>O<sub>3</sub>, C-PHNT 400, C-PHNT 500, and C-PHNT 600.

The hollow MnO<sub>2</sub> nanotubes exhibited unclear reflections in the XRD pattern because of the amorphous structure. The main characteristic diffraction peaks of C-PHNTs were observed at 23.1°, 32.9°, 38.2°, and 55.1°, which correspond to the (211), (222), (400), and (440) planes of Mn<sub>2</sub>O<sub>3</sub>, respectively (space group Ia<sup>3</sup>[206]; JCPDS card No. 71-0636). These XRD results are in good agreement with the TEM and XPS results (Figs. 2d and 2e).



**Fig. S2** FESEM images of four different types of PHNFs microwave-treated at (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C before carbonation.



**Fig. S3.** TGA curves of C-PHNT 600 from 150 to 700 °C at a heating rate of 10 °C min<sup>-1</sup> under air environment.



Fig. S4 CV curves of the (a) commercial  $Mn_2O_3$ , (b) C-PHNT 400, (c) C-PHNT 500, and (d) C-PHNT 600 at a scan rate of 0.1 mV s<sup>-1</sup> in the voltage range of 0–3 V (versus Li/Li<sup>+</sup>).



Fig. S5 Comparison of high-rate performance with previously reported studies of  $Mn_2O_3$ -based anode materials in LIBs.



Fig. S6 FESEM images of C-PHNT 600 after 100 cycles at a current density of 100 mA g<sup>-1</sup>.



**Fig. S7** Cycling performance of the charge–discharge capacities of C-PHNT 600 at current density of 700 mA g<sup>-1</sup> up to 100 cycles.



**Fig. S8** Cycling performance of the charge–discharge capacities of PHNT without carbon encapsulation layers and C-PHNT 600 at current density of 100 mA g<sup>-1</sup> up to 100 cycles.



Fig. S9 Nyquist plots of the PHNT without carbon encapsulation layers and C-PHNT 600 in the frequency range of  $10^5$  to  $10^{-2}$  Hz before the charge–discharge tests.

Material	Capacity (mA h g <sup>-1</sup> )	Current density (mA g <sup>-1</sup> )	Ref.
C-PHNT based manganese oxide	875, 100cycle	100	This work
Porous Mn <sub>2</sub> O <sub>3</sub> nanoplates	813, 50cycle	100	26
Porous Mn <sub>2</sub> O <sub>3</sub> microspheres	796, 50cycle	100	25
Porous Mn <sub>2</sub> O <sub>3</sub> hierarchical microspheres	748, 45cycle	50	29
Mn <sub>2</sub> O <sub>3</sub> microspheres	524 200cycle	200	28
Porous Mn <sub>2</sub> O <sub>3</sub>	521, 100cycle	300	27
Mn <sub>2</sub> O <sub>3</sub> nanofibers	404 30cycle	100	31
Hollow Mn <sub>2</sub> O <sub>3</sub> nanocones	280, 200cycle	200	30
Spherical Mn <sub>2</sub> O <sub>3</sub>	265, 15cycle	200	32

**Table S1** Cycling stability comparison of previously reported  $Mn_2O_3$ -based anode materialswith various geometries in LIBs.

## **Graphic abstract**



Uniquely designed hierarchical architecture of hybrid carbon-encapsulated porous hollow nanotube with favorable routes and sites for Li ion insertion/extraction, resulting in the improved high-rate performance and cycling stability.