Supporting Information

Self-formed Channel Boosts Ultra-fast Lithium Ion Storage in Fe₃O₄@Nitrogen-doped Carbon Nanocapsule

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Pure Fe₂O₃ particles and Fe₂O₃ electrode:

In this work, the pure Fe_2O_3 material, an annealed product of precursor FeOOH at air atmosphere under the same temperature, can be used as a comparison to compare with $Fe_3O_4@NC$ because they possess similar morphology, reaction mechanism and approximate theoretical capacity. ¹⁻³

We also note that the capacity of Fe_2O_3 electrode is higher than that of Fe_3O_4 @NC at initial stage, because it has a higher theoretical capacity (~1007 mAh g⁻¹). This behavior also existed in rate test, at small current densities during first 30 cycles.



Figure S1. XRD profile of pure Fe₂O₃.



Figure S2. FT-IR spectra of precursor FeOOH, intermediate FeOOH@PDA and $Fe_3O_4@NC$.

There existed a series of peaks at 639, 704, 863, 1087, between 3359 and 3490 cm⁻¹ for precursor FeOOH. Among them, the peaks of 639, 863 and 3359 – 3490 cm⁻¹ reflected the signal of Fe-O, α -FeOOH and -OH group, respectively. ⁴⁻⁵ And the peaks at 704 and 1087 cm⁻¹ could be assigned to in-plane and out-of-plane Fe-O-H bending modes (Figure S2). ⁶ We also observed that the absorption peak signals of intermediate FeOOH@PDA were similar with those of precursor except for intensity difference due to PDA coating.



Figure S3. TG analysis of Fe₃O₄@NC.

The carbon content of Fe₃O₄@NC composite was accurately determined by thermogravimetric (TG) analysis carried out in air atmosphere with a heating rate of 10 °C min⁻¹. In Figure S3, we observed three steps during heating process. The first 2.94% weight loss below 150 °C was due to a physical process, *i.e.*, the volatilization of absorbed water. Similar to literature, an oxidation reaction of Fe₃O₄ \rightarrow Fe₂O₃ could cause a slightly increased weight between 200 °C and 300 °C. ⁷ Soon afterwards, the carbon component was completely combusted above 400 °C, resulting in a fast weight loss. Thus the carbon content of 23.36% could be calculated according to above results.



Figure S4. (a) XPS spectrum and (b) Fe 2p XPS analysis of Fe_3O_4 @NC.



Figure S5. Nitrogen adsorption/desorption isothermal curves of pure Fe₂O₃.



Figure S6. SEM images of (a, b) precursor FeOOH, (d, e) intermediate FeOOH@PDA and (g, h) $Fe_3O_4@NC$; TEM images of (c) precursor FeOOH, (f) intermediate FeOOH@PDA and (i) $Fe_3O_4@NC$.



Figure S7. SEM image of pure Fe₂O₃.

Figure S7 showed the morphology of pure Fe_2O_3 material, with a block structure and mesoporous nature. It is due to a serious aggregation occurring in phase conversion from precursor FeOOH to Fe_2O_3 under annealing process, in the absence of PDA coating layer.



Figure S8. Cyclic voltammetry curves of Fe_2O_3 electrode with first three cycles at a scan rate of 0.5 mV s⁻¹.



Figure S9. Nyquist plots of Fe_3O_4 @NC and Fe_2O_3 electrodes (Inset: equivalent circuit diagram; R_s represents electrolyte resistance, R_{sei} represents SEI resistance, R_{ct} represents charge transfer resistance, Z represents Warburg impedance, CPE1/CPE2: surface films capacitance/double-layer capacitance).

Table S1. The specific simulated values of Fe_3O_4 @NC and Fe_2O_3 electrodes according to equivalent circuit diagram above.

Electrode	R _s (ohm)	R _{sei} (ohm)	R _{ct} (ohm)	
Fe ₃ O ₄ @NC	6.12	11.26	39.08	
Fe ₂ O ₃	5.05	18.90	96.34	



Figure S10. The EIS simulated values of Fe_3O_4 @NC electrode at different states of charge (SOCs).



Figure S11. Galvanostatic current intermittent titration (GITT) curves of Fe_2O_3 electrode (Inset: partial enlarged detail).



Figure S12. The specific internal resistances of (a) Fe_3O_4 @NC electrode and (b) Fe_2O_3 electrode obtained by GITT tests.



Figure S13. Cycling performance and corresponding Coulombic efficiency of Fe_2O_3 electrode at a high rate of 5 A g⁻¹.

Table S2. The structure, synthetic method and electrochemical performances of Fe_3O_4 -based composites reported in literatures.

Structure	Synthetic method	Mass loading (mg cm ⁻²)	Current density (mA g ⁻¹)	Cycle number	Capacity (mAh g ⁻¹)	Ref.
Double-shelled constructed Fe ₃ O ₄ yolk-shell magnetite nanoboxes	precipitation approach	~1	500 3000	200 600	870 670	8
1D sandwich-like C@Fe ₃ O ₄ @C coaxial nanotubes	bottom-up method		100	150	1087	9
3D sandwich-like C@Fe ₃ O ₄ @C coaxial nanocables	bottom-up approach		92	100	1357	10
C/Fe ₃ O ₄ sea-sponge-like structure	ultrasonic spray pyrolysis/therm al decomposition		1500	1000	460	11
Pomegranate-like, carbon-coated Fe ₃ O ₄ nanoparticle	bottom-up assembly/top-d own etching	~1.2	5000	1000	520	12
Fe ₃ O ₄ @C-N yolk-shell nanocapsules	hydrothermal method/calcinat ion	~2	500	150	832	13
Honeycomb-like carbon network-encapsula ted Fe/Fe ₃ C/Fe ₃ O ₄ composites	in situ synthesis method		200 5000	120 500	1295 345	14
Porous Fe ₃ O ₄ /carbon microspheres	electrostatic spraying/heat treatment.	0.32	100 1000 5000	130 300 300	1317 746 525	15
Fe ₃ O ₄ @nitrogen- doped carbon nanocapsule	Hydrothermal -coating-annea ling route	~1	500 5000 10000 20000	200 500 500 1000	1028 873 612 480	This work



Figure S14. Long-term cycling performances and corresponding Coulombic efficiencies of (a) $Fe_3O_4@NC-S1$ electrode, $Fe_3O_4@NC-S2$ electrode and (b) solid $Fe_3O_4@NC$ electrode at a high rate of 20 A g⁻¹.



Figure S15. TEM images of (a) Fe₃O₄@NC-S1 and (b) Fe₃O₄@NC-S2.



Figure S16. TEM image of solid Fe₃O₄@NC sample.



Figure S17. The shape of atrovirens area represents capacitive contribution at different sweep rates of (a) 0.1 mV s^{-1} , (b) 0.3 mV s^{-1} , (c) 1.0 mV s^{-1} and (d) 1.5 mV s^{-1} , respectively.



Figure S18. (a) The potential-time profile of Fe₃O₄@NC electrode for a single current pulse; (b) The linear relation of E vs $\tau^{1/2}$.

We calculated the apparent diffusion coefficient of lithium ion through GITT tests for Fe₃O₄@NC and Fe₂O₃ electrodes, respectively. Figure S18a showed the potential-time curve of a single current pulse for Fe₃O₄@NC electrode with prominent signs of different parameters. We further determined the perfect linear relation between E and $\tau^{1/2}$ existed for above titration (Figure S18b). Hence, we could directly apply Equation S1 to confirm apparent Li⁺ diffusion coefficient (D_{app, Li+}). ¹⁶⁻¹⁷

$$D_{Li^+} = \frac{4}{\pi \tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau} \right)^2 \qquad \left(\tau \ll L^2 / D_{Li^+} \right) \qquad (\text{Equation S1})$$

The means of every parameter was defined as follows.

 τ : The time of galvanostatic current.

 m_B : The molar mass of electrode material.

- M_B : The molecular weight of electrode material.
- V_M : The molar volume of electrode material.
- S: The contact surface area of electrode and electrolyte.
- ΔE_S : The quasi-equilibrium voltage after relaxation period of 2h.

 ΔE_{τ} : The voltage change during current pulse.

L: The thickness of electrode.

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