

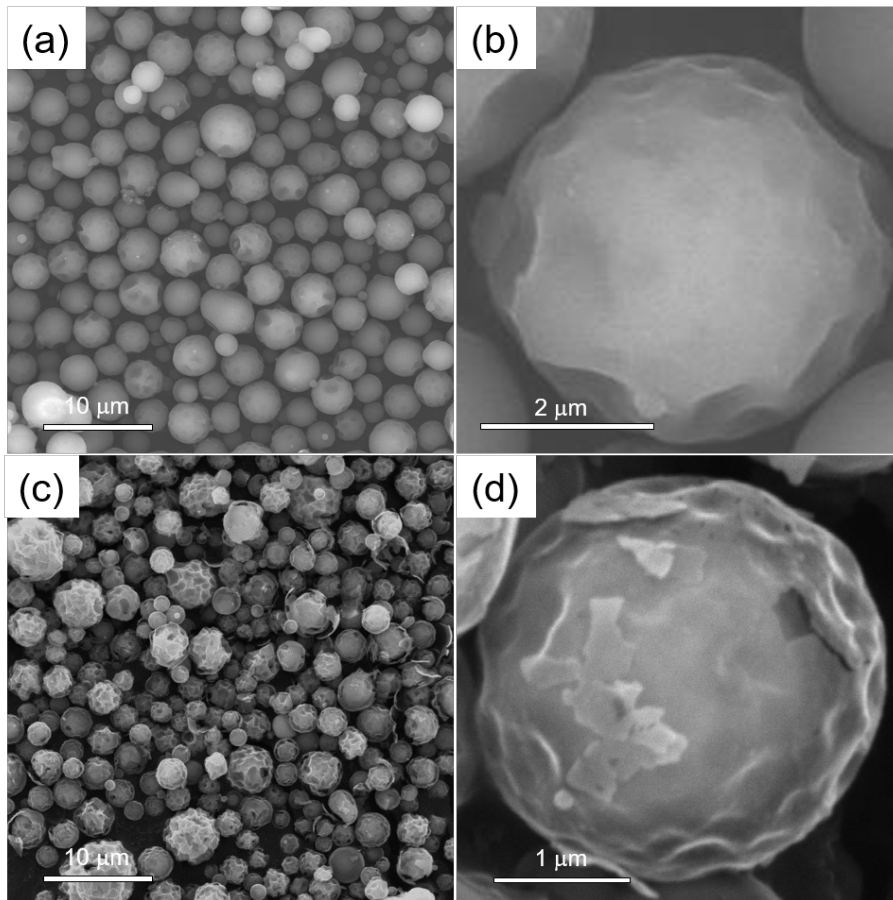
## SUPPLEMENTARY INFORMATION

### **Unique structured microspheres with multishells comprising graphitic carbon-coated Fe<sub>3</sub>O<sub>4</sub> hollow nanopowders as anode materials for high-performance Li-ion batteries**

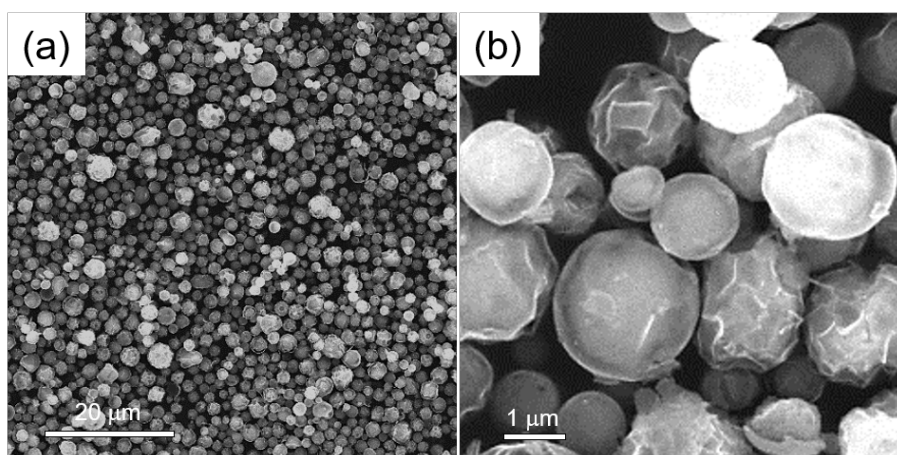
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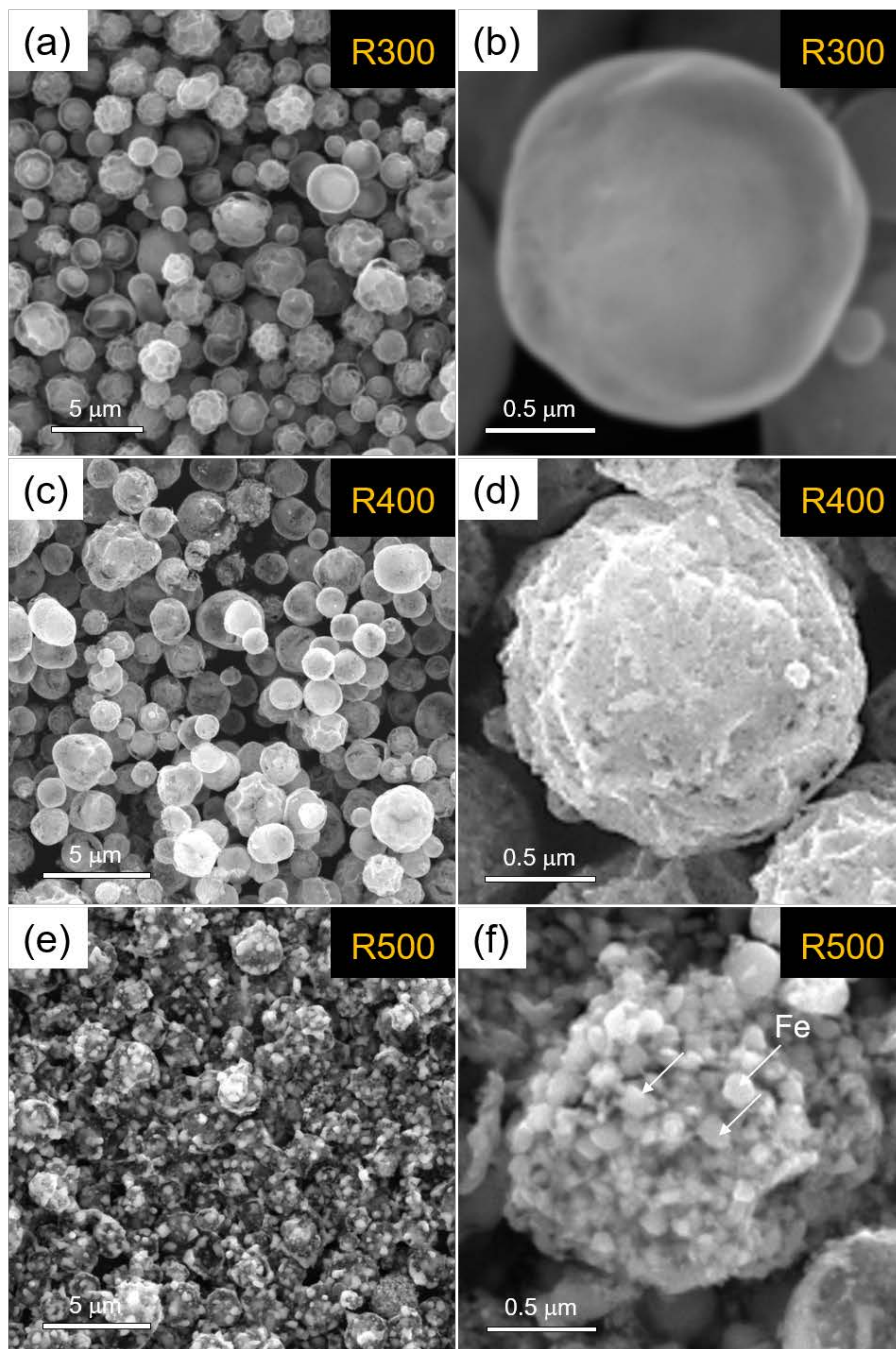
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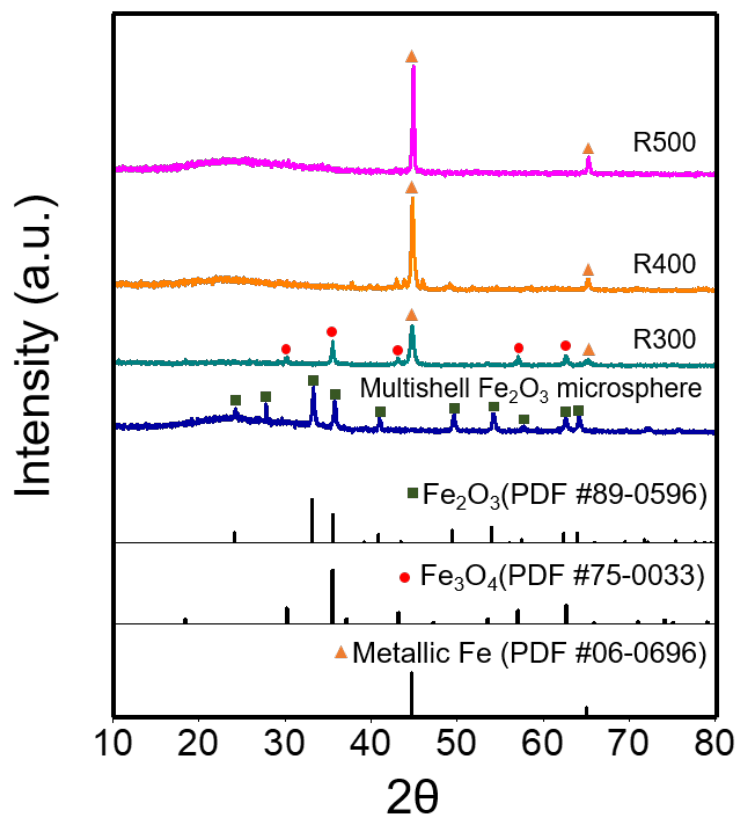
**Fig. S1** Morphologies of microspheres synthesized by spray drying process before and after post-treatment process. (a,b) as-prepared and (c,d) post-treated microspheres.



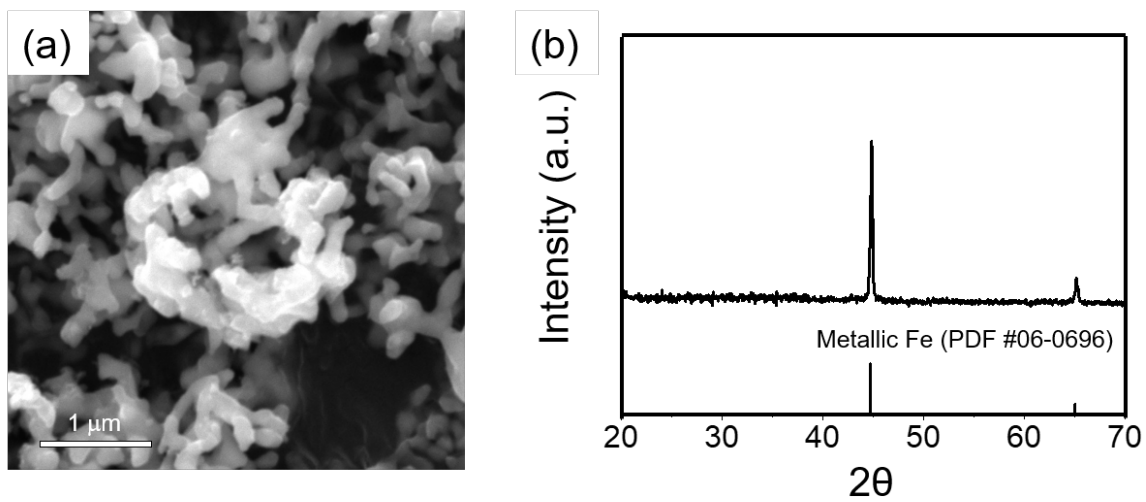
**Fig. S2** Morphologies of pitch infiltrated  $\text{Fe}_2\text{O}_3$  yolk-shell microspheres.



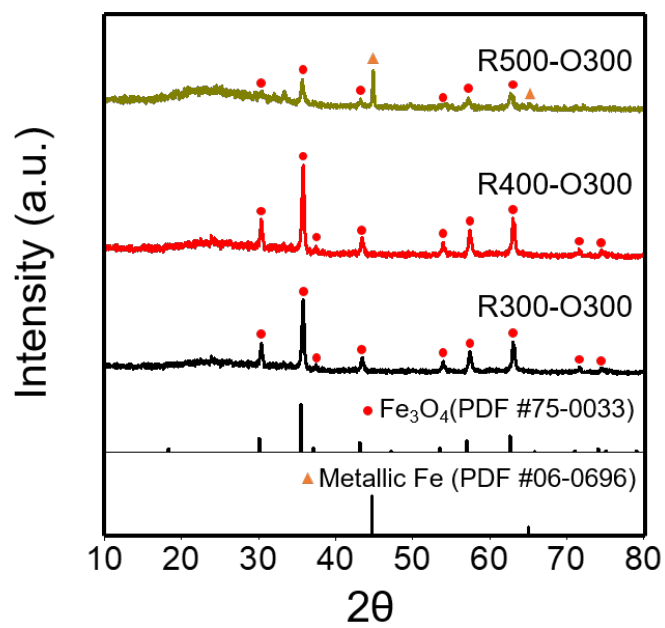
**Fig. S3** Morphologies of microspheres formed after reduction process of pitch-infiltrated  $\text{Fe}_2\text{O}_3$  yolk-shell microspheres at (a,b) 300 °C, (c,d) 400 °C, and (e,f) 500 °C.



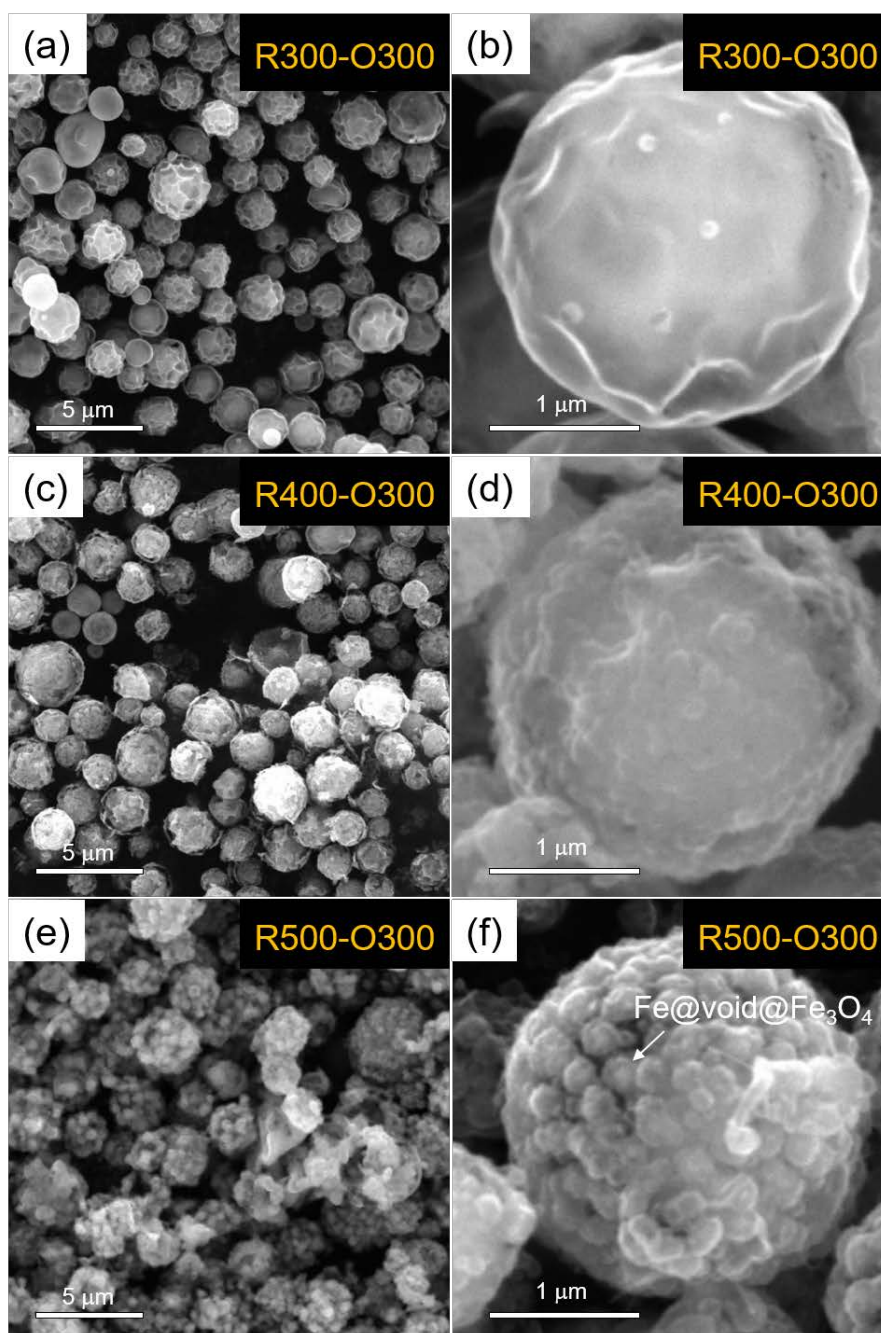
**Fig. S4** XRD patterns of microspheres obtained before and after reduction process at 300 (R300), 400 (R400) and 500 °C (R500).



**Fig. S5** (a) Morphology and (b) XRD pattern of metallic Fe powders formed after reduction of  $\text{Fe}_2\text{O}_3$  yolk-shell microspheres at 400 °C.

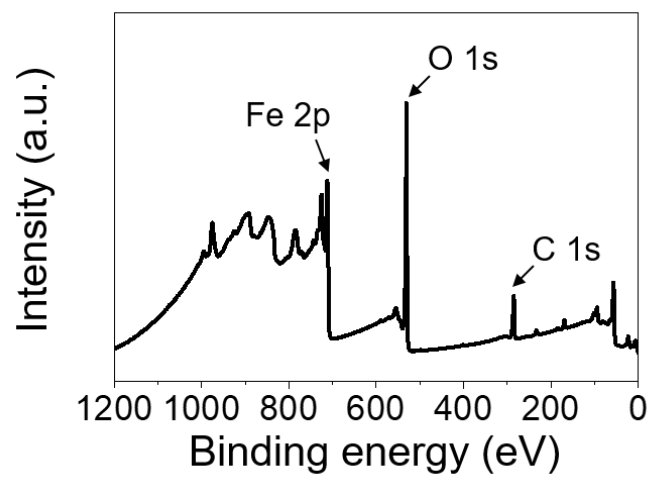


**Fig. S6** XRD patterns of R300-O300, R400-O300, and R500-O300 microspheres.

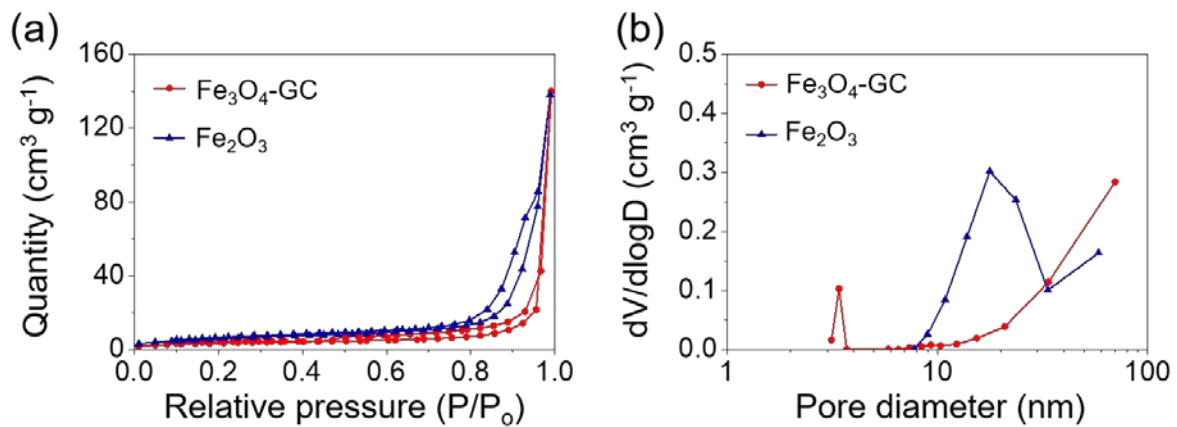


**Fig. S7** Morphologies of (a,b) R300-O300, (c,d) R400-O300, and (e,f) R500-O300 microspheres.

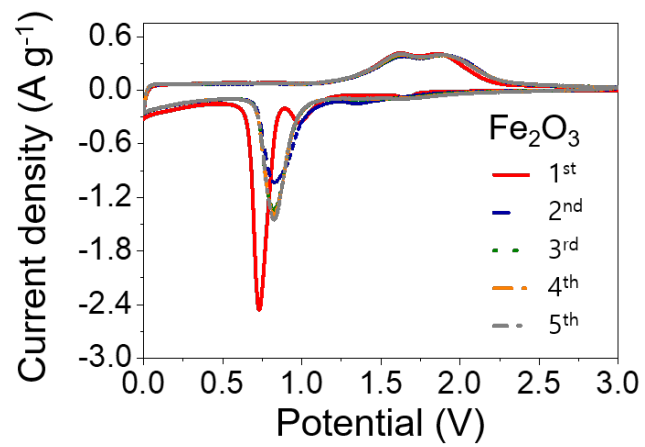




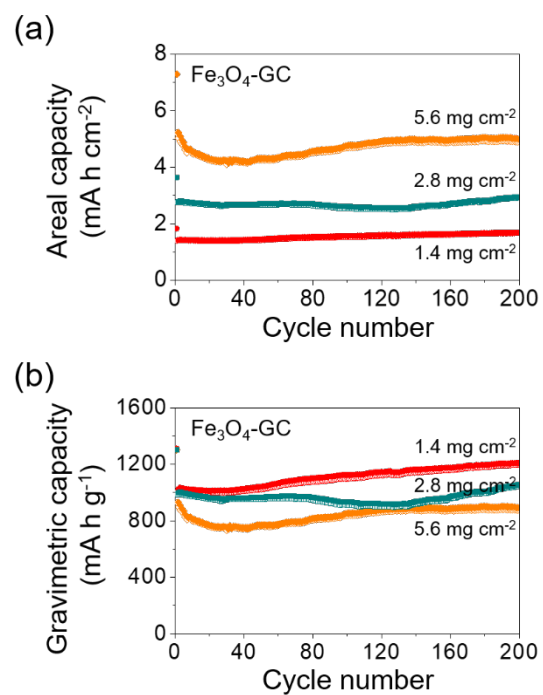
**Fig. S8** XPS survey scan of  $\text{Fe}_3\text{O}_4$ -GC (R400-O300) microspheres.



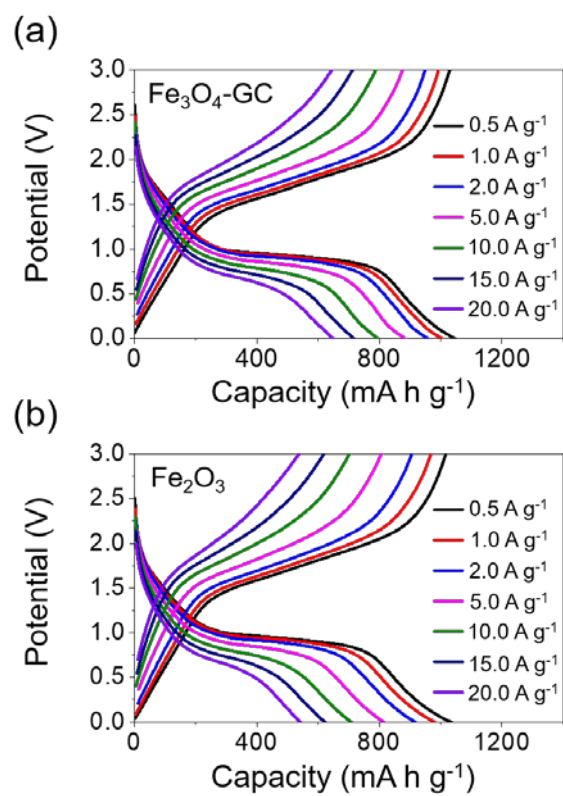
**Fig. S9** (a) N<sub>2</sub> gas adsorption and desorption isotherm and (b) BJH pore-size distribution of Fe<sub>3</sub>O<sub>4</sub>-GC (R400-O300) and bare Fe<sub>2</sub>O<sub>3</sub> microspheres.



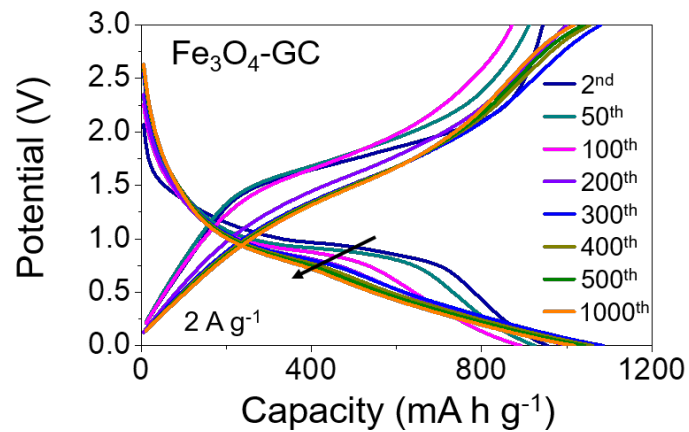
**Fig. S10** CV curves of yolk-shell structured Fe<sub>2</sub>O<sub>3</sub> microspheres.



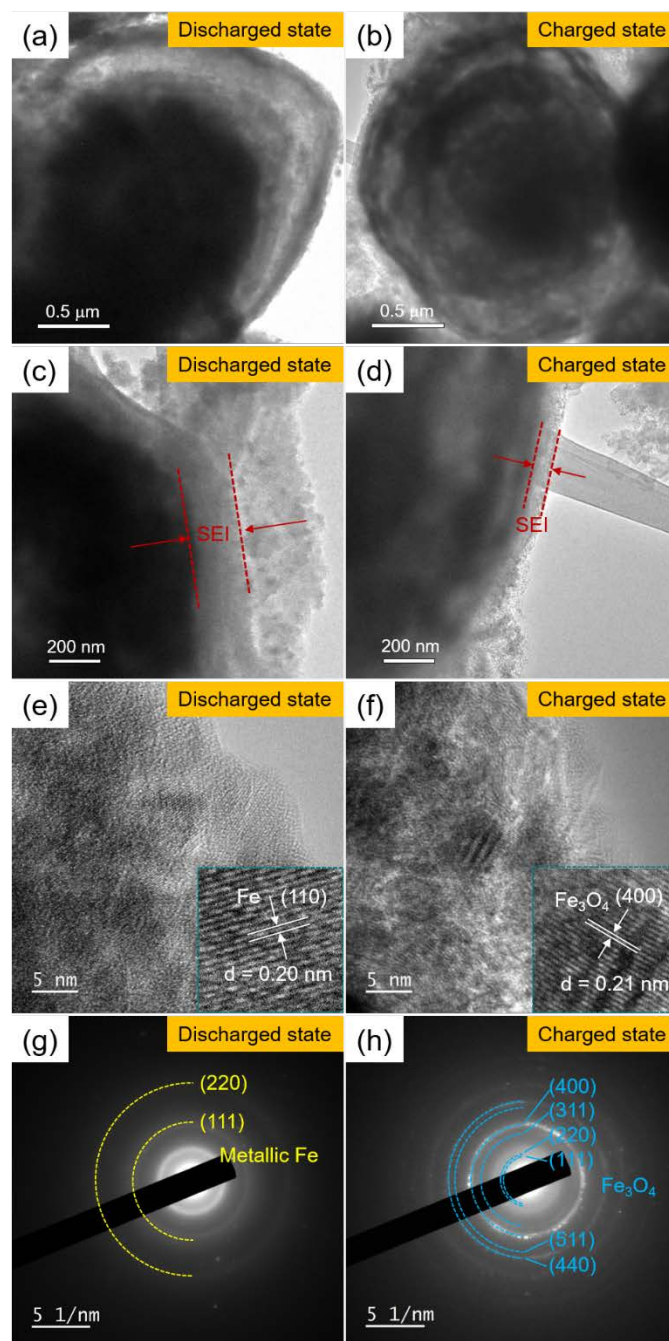
**Fig. S11.** (a) Areal and (b) gravimetric capacities of yolk-shell structured Fe<sub>3</sub>O<sub>4</sub>-GC composite microspheres at the different active materials mass loadings on the electrode.



**Fig. S12.** Charge-discharge curves at different rates (0.5, 1, 2, 5, 10, 15, and 20  $\text{A g}^{-1}$ ) of yolk-shell structured  $\text{Fe}_3\text{O}_4\text{-GC}$  composite and  $\text{Fe}_2\text{O}_3$  microspheres.



**Fig. S13.** The 2<sup>nd</sup>, 50<sup>th</sup>, 100<sup>th</sup>, 200<sup>th</sup>, 300<sup>th</sup>, 400<sup>th</sup>, 500<sup>th</sup>, and 1000<sup>th</sup> charge-discharge curves obtained during the long-term cycling test of yolk-shell structured Fe<sub>3</sub>O<sub>4</sub>-GC composite microspheres.



**Fig. S14.** TEM images and SAED patterns of yolk-shell structured  $\text{Fe}_3\text{O}_4$ -GC composite at fully (a,c,e,g) discharged and (b,d,f,h) charged states after 100 cycles : (a-d) TEM images, (e,f) HR-TEM images, (g,h) SAED pattern.

**Table S1.** Electrochemical properties of various Fe<sub>3</sub>O<sub>4</sub> materials applied as lithium-ion batteries reported in the previous literatures.

Materials	Current rate	Discharge capacity [mA h g <sup>-1</sup> ] and (cycle number)	Rate capacity [mA h g <sup>-1</sup> ] (current rate)	Ref
Graphene-wrapped Fe <sub>3</sub> O <sub>4</sub>	0.7 A g <sup>-1</sup>	~600 (100)	~600 (1.75 A g <sup>-1</sup> )	[S1]
Carbon coated Fe <sub>3</sub> O <sub>4</sub> nanospindles	0.4 A g <sup>-1</sup>	530 (80)	190 (4.0 A g <sup>-1</sup> )	[S2]
Carbon-encapsulated Fe <sub>3</sub> O <sub>4</sub> nanoparticles	5.0 A g <sup>-1</sup>	836 (350)	297 (20.0 A g <sup>-1</sup> )	[S3]
Dual layers N-doped carbon@mesoporous carbon@Fe <sub>3</sub> O <sub>4</sub> nanoparticle	2.0 A g <sup>-1</sup>	576 (500)	322 (5.0 A g <sup>-1</sup> )	[S4]
Fe <sub>3</sub> O <sub>4</sub> -embedded and N-doped hierarchically porous carbon nanospheres	1.0 A g <sup>-1</sup>	581 (400)	290 (10.0 A g <sup>-1</sup> )	[S5]
N-doped dual carbon-confined 3D architecture rGO/Fe <sub>3</sub> O <sub>4</sub> /AC	5.0 A g <sup>-1</sup>	~500 (500)	437 (10.0 A g <sup>-1</sup> )	[S6]
Porous Fe <sub>3</sub> O <sub>4</sub> /carbon microspheres	1.0 A g <sup>-1</sup>	746 (300)	410 (5.0 A g <sup>-1</sup> )	[S7]
Pomegranate-like, carbon-coated Fe <sub>3</sub> O <sub>4</sub>	5.0 A g <sup>-1</sup>	520 (1000)	416 (10.0 A g <sup>-1</sup> )	[S8]
Neuron-inspired Fe <sub>3</sub> O <sub>4</sub> -conductive carbon	1.0 A g <sup>-1</sup>	971 (1000)	206 (8.0 A g <sup>-1</sup> )	[S9]
Macroporous Fe <sub>3</sub> O <sub>4</sub> @C	2.0 A g <sup>-1</sup>	645 (1000)	300 (10.0 A g <sup>-1</sup> )	[S10]
<b>Yolk-shell-structured microsphere with multishells of hollow Fe<sub>3</sub>O<sub>4</sub> nanopowders covered with GC</b>	<b>2.0 A g<sup>-1</sup></b>	<b>1018 (1000)</b>	<b>649 (20.0 A g<sup>-1</sup>)</b>	<b>Our work</b>

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