

Solvent-free synthesis of crystalline mesoporous γ -Fe₂O₃ as an anode material in lithium-ion batteries

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Support Information

Experimental Section

Synthesis of mesoporous γ -Fe₂O₃: The solid raw materials of Fe(NO₃)₃•9H₂O and the triblock copolymer F127 (EO₁₀₆PO₇₀EO₁₀₆) was mixed together. Then the mixture was heated in an autoclave at 80 °C and 10 r/min for 6 h. The resulting melting liquid was transferred to a petri dish and heating again at 80 °C for 48 h. After that the melting liquid had solidified and the product was gradually heated to 200 °C (1 °C /min) and was maintained at 200 °C for 10 h (in the first 6 hours the product was in argon atmosphere and in the next 4 hours it was in vapor atmosphere). Finally the sample was further sintered at 300 °C (1 °C /min) for 4 h to remove the surfactant.

Characterization: Thermogravimetric (TG) was performed in NETZSCH STA 449C. The crystal structure was characterized by wide-angle X-ray powder diffraction (XRD) and the patterns were recorder on Philips X' Pro diffract meter using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. N₂ adsorption-desorption isotherms were examined at 77 K by an adsorption apparatus (Micromeritics Tristar 3020). The microstructures were identified by transmission electron microscope (TEM, JEOL-2011).

Electrochemical measurements: The electrochemical tests were carried out using CR2032 type coin cells. The working electrode was prepared by mixing the electroactive material (50 wt%), acetylene black (conducting additive, 40 wt%), and polyvinylidene fluoride (binder, 10 wt%) in N-methyl-2-pyrrolidone (NMP). Then the resulting slurry was uniformly spread onto a copper foil current collector. After the desiccation of 4 h in an oven (80 °C), the electrodes then pressed and dried under vacuum at 120 °C for 12 h. The pure lithium metal was used both the reference and

the counter electrode at room temperature with Celgard 2325 film as the separator, while a 1 M LiPF_6 in a mixture of ethylene carbonate (EC) / DMC / ethyl methyl carbonate (EMC) (1:1:1 in weight) was used as an electrolyte. The coin half cells were assembled in an Ar-filled glovebox in which both oxygen and moisture levels were strickly kept less than 1 ppm.

The obtained half cells were carried out Galvanostatical discharge-charge experiments at various current densities in a voltage range from 0.005 to 3.0 V (vs. Li^+/Li) by using a battery test system (LAND CT2001A model, Wuhan Jinnuo Electronics Co. Ltd.).

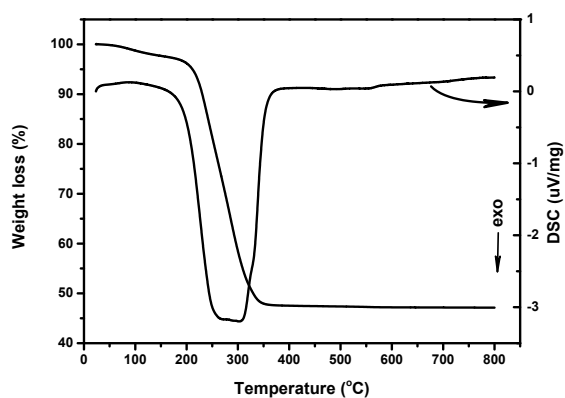


Fig. S1 TG-DSC curves of the Fe-based intermediate (prepared without the final calcination) in air at a heating rate of 5 °C/min.

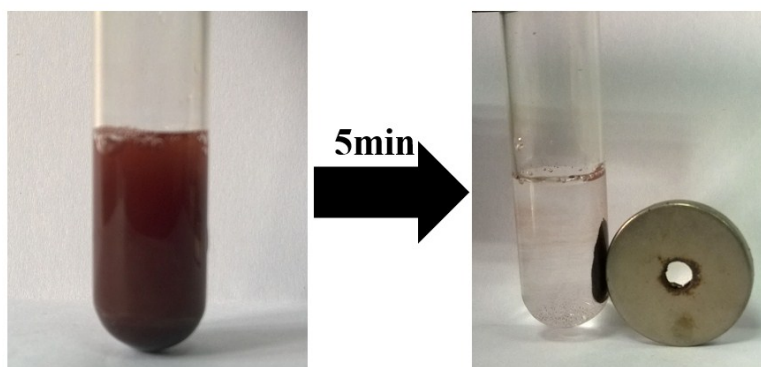


Fig. S2 Magnetic separation of the obtained crystalline mesoporous $\gamma\text{-Fe}_2\text{O}_3$.

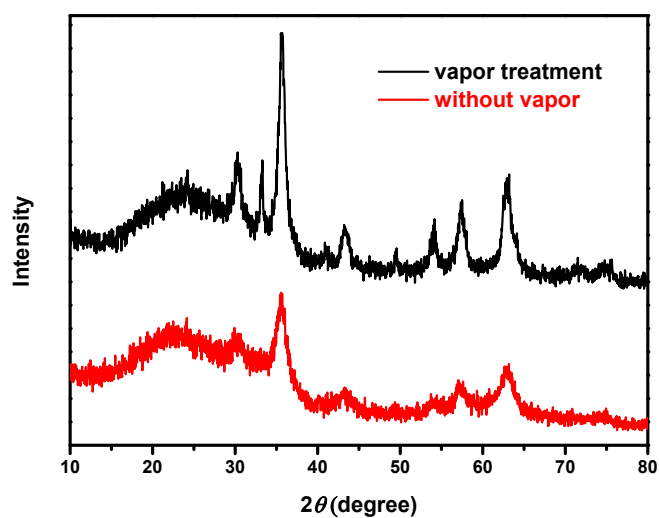


Fig. S3 XRD pattern of the product with vapor treatment (black) and the product without vapor treatment.

Table S1. The effect of the aron treatment on the specific surface area and pore diameter

Atmosphere of calcination	Specific Surface Area (m ² /g)	Pore Diameter (nm)
Aron + Vapor + Air	146	3.0
Vapor + Air	69	4.5, 17.0

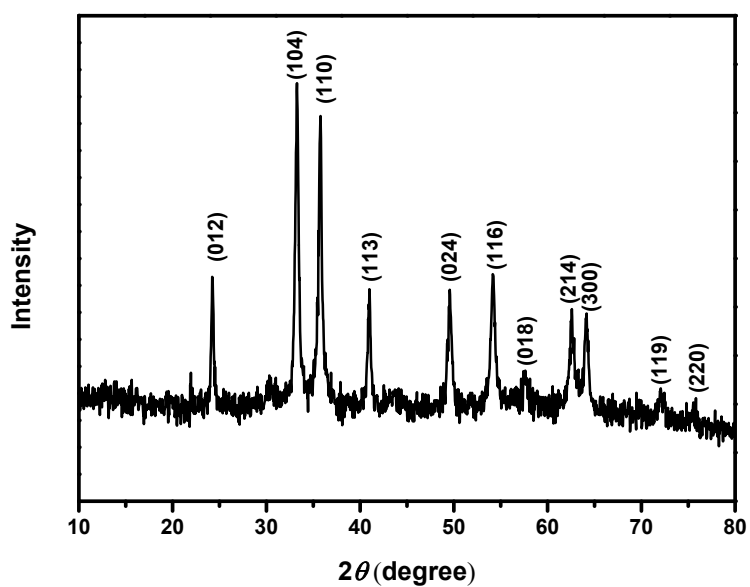


Fig. S4 XRD pattern of the product calcined at 400 °C (JCPDS no. 79-0007).

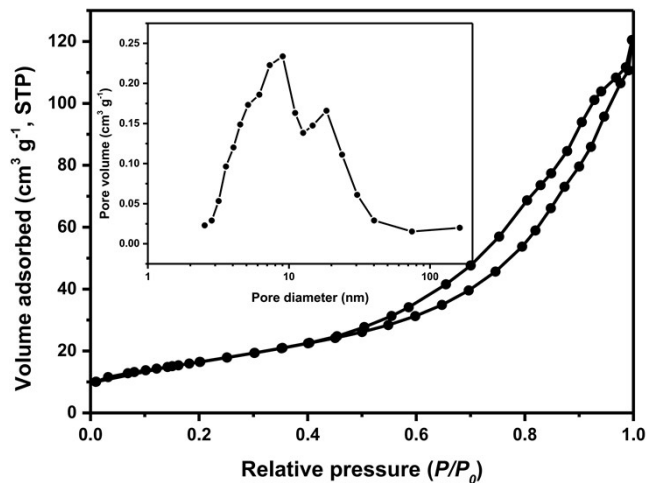


Fig. S5 N_2 adsorption-desorption isotherms and the pore size distribution of the product calcined at 400 °C.

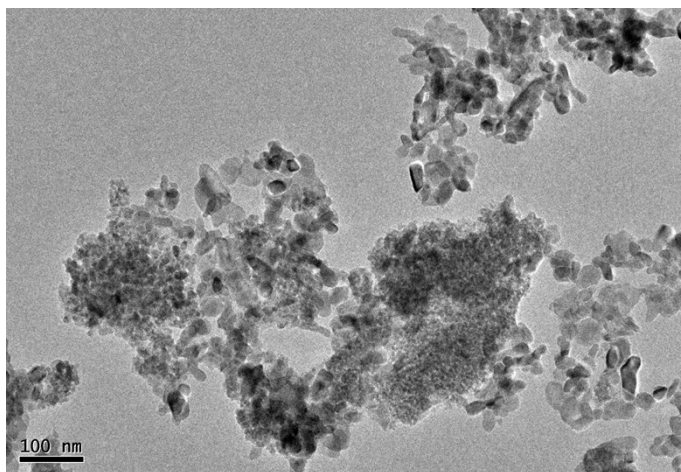


Fig. S6 TEM image of the product calcined at 400 °C

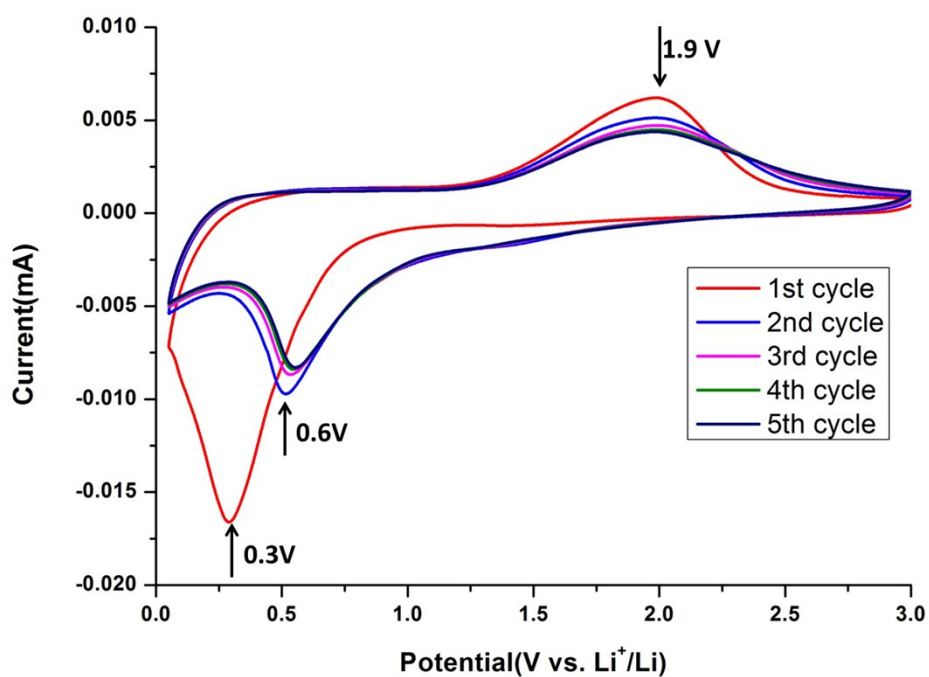


Fig. S7 Cycling voltammograms at a scan rate of 0.2 mV/s in the range of 0.005 ~ 3 V vs Li+/Li.

Table S2. LIBs performance of our obtained product and literature reported products

Fe ₂ O ₃ anode material	Active material : Carbon black : PVDF	Capacity retention (mAh/g) / cycle number (current density (mA/g))	Reference
Mesoporous nanostructure	5 : 4 : 1	1120 / 150 (200)	This work
Mesoporous nanostructure	5 : 4 : 1	1293 / 50 (200)	[1]
Tuneable porous hematites	5 : 4 : 1	1296 / 50 (50)	[2]

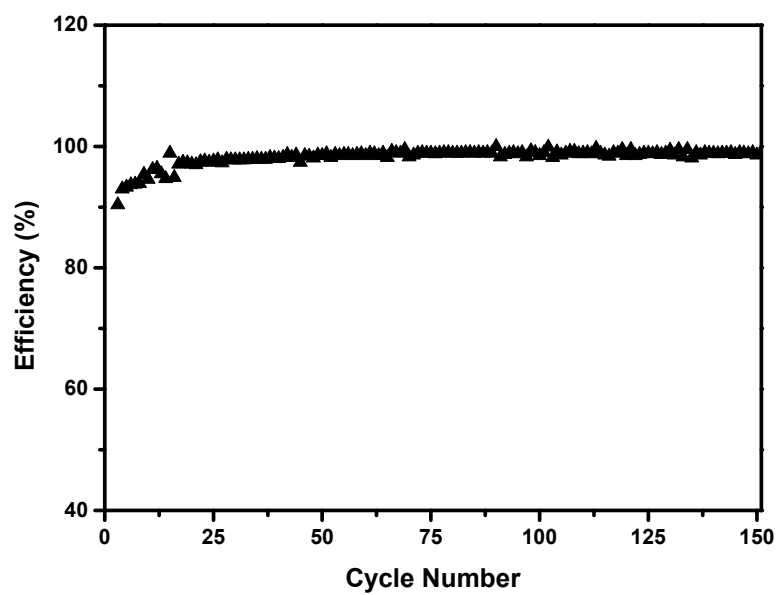


Fig. S8 Coulombic efficiency of the obtained crystalline mesoporous $\gamma\text{-Fe}_2\text{O}_3$.

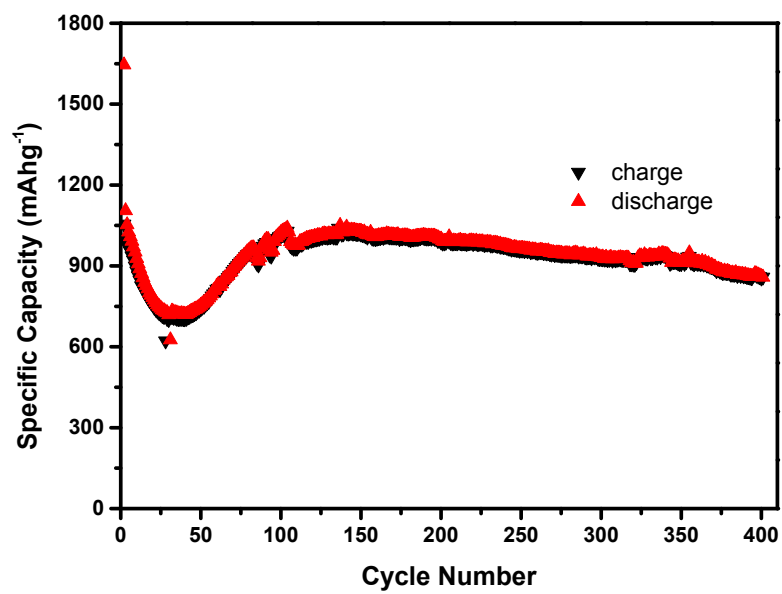


Fig. S9 Cycling performance of the obtained crystalline mesoporous $\gamma\text{-Fe}_2\text{O}_3$ at 2000 mA g^{-1} .

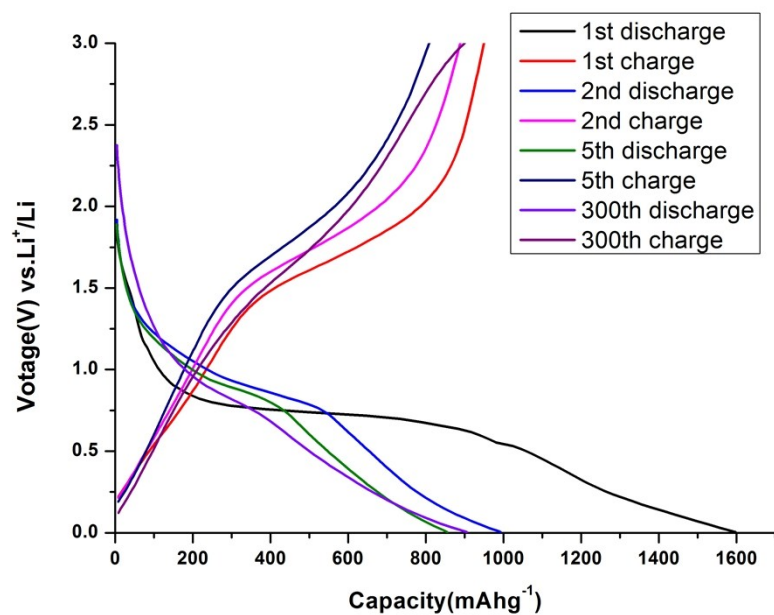


Fig. S10 discharge-charge curves of the obtained crystalline mesoporous $\gamma\text{-Fe}_2\text{O}_3$ at 2000 mA g^{-1} .

References:

- 1 B. Sun, J. Horvat, H. S. Kim, W-S. Kim and J. Ahn, G. Wang, *J. Phys. Chem. C*, 2010, **114**, 18753.
- 2 D. Su, H-S. Kim, W-S. Kim and G. Wang, *Microporous Mesoporous Mater.*, 2012, **149**, 36.