Supporting Information

Metal-organic framework derived $ZnO/ZnFe_2O_4/C$ nanocages as stable cathode material for reversible lithium-oxygen batteries

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Preparation of α-MnO_2 nanowires

Nanocrystalline α-MnO_2 nanowires were synthesized by a modified hydrothermal method as reported elsewhere [1]. 0.1 mol l^{-1} $MnSO_4 \cdot H_2O$ was dissolved in 30 ml water and 0.1 mol l^{-1} $KMnO_4$ was added under stirring at room temperature. The solution was transferred to a Teflon-lined stainless-steel autoclave, sealed and maintained at 140 °C for 12 h. After cooling to room temperature, the resulting mixture was collected by centrifugation, and washed with de-ionized water and ethanol for several times, and then dried at 80 °C for 12 h to obtain the α-MnO_2 nanowires.

Preparation of Co_3O_4 nanoflakes

CoOOH with a thickness of 8 nm was synthesized by using an air oxidation method[2] . 100 ml dilute aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.02 mol) was slowly added to 100 ml 5 mol l^{-1} NaOH aqueous solution. The resulting pink $Co(OH)_2$ suspension was poured into 1800 ml water, and then the mixture was stirred in air overnight, affording a brown CoOOH precipitate. The precipitate was centrifuged and washed with water twice, and then dried at 80 °C in vacuum for 12 h to give nanoplatelet CoOOH. Then the as-prepared CoOOH was sintered at 400 °C for 3 h in air atmosphere to obtain the Co_3O_4 nanoflakes.

Preparation of Fe_2O_3 nanoflakes

Fe_2O_3 nanoflakes were synthesized via a hydrothermal method as reported elsewhere [3]. In a typical synthesis procedure, 0.2 g $FeCl_3 \cdot 6H_2O$ was dissolved in 40 ml mixed solvent containing glycerol (6 ml) and de-ionized water (34 ml). The mixture was stirred for 30 min and then transferred into a 60 ml Teflon-lined stainless steel autoclave, heated to 160 °C in an oven for 10 h. After cooling to room temperature, the red product was collected by centrifugation, and washed with de-ionized water and ethanol for several times, and then dried at 80 °C for 12 h to get the Fe_2O_3 nanoflakes.

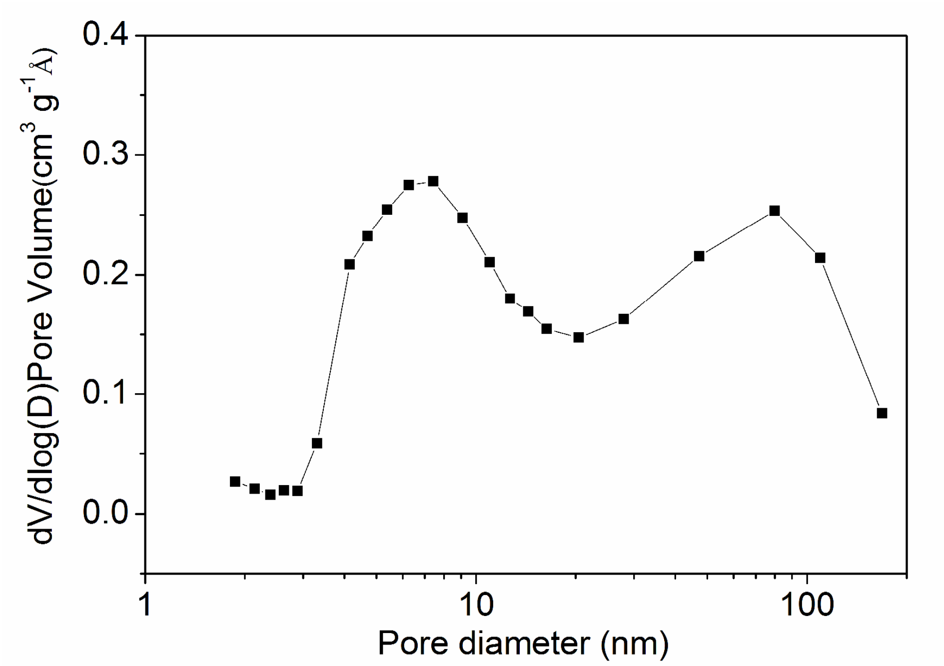

Figure S1. Pore-size distribution of the as-prepared ZZFC obtained in N_2 atmosphere at 500 °C.

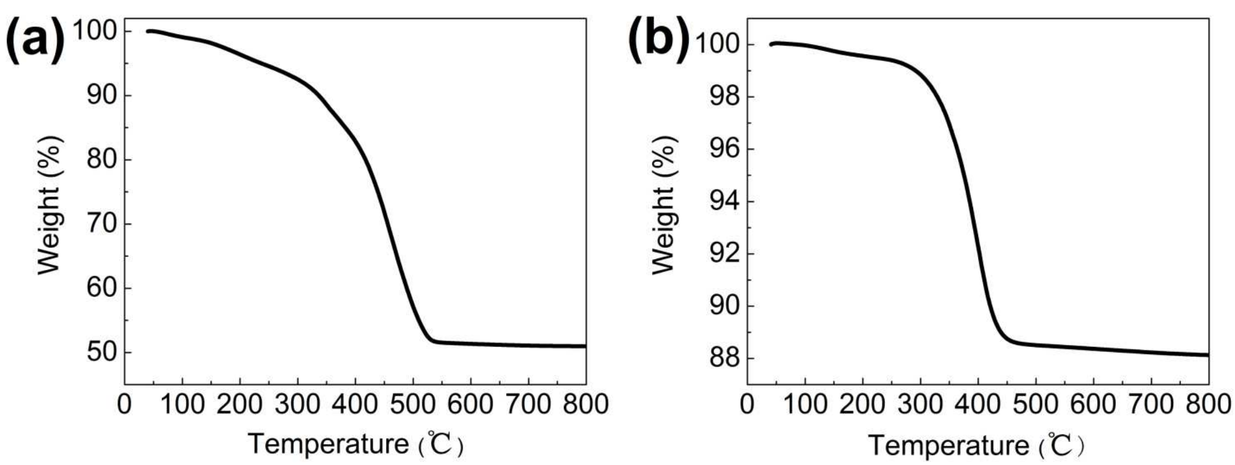

Figure S2. Thermogravimetric (TG) curves at a heating rate of 10 °C min^{-1} for (a) Fe(III)-modified MOF-5 obtained in the nitrogen flow, and (b) ZZFC obtained in air flow.

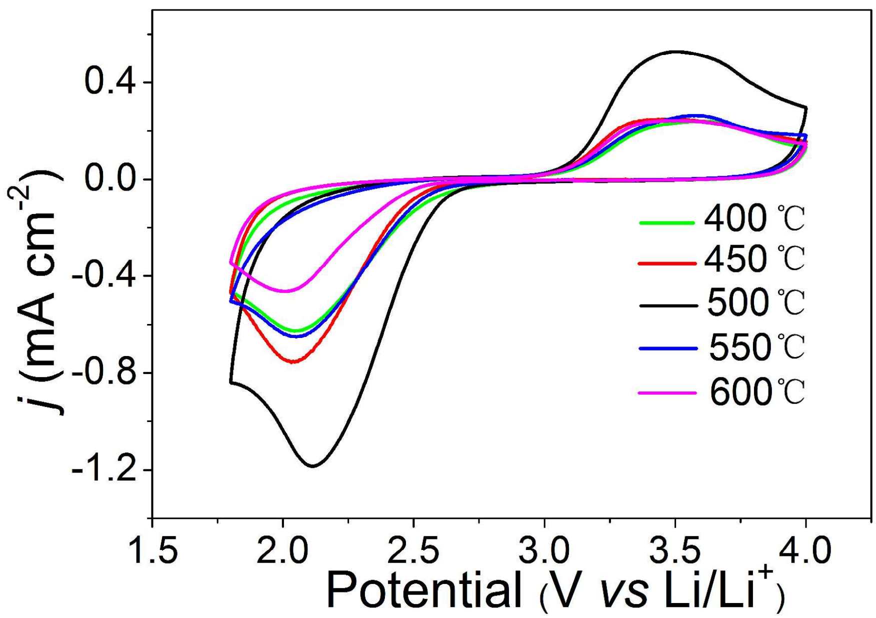

Figure S3. CVs of the samples after sintering Fe(Ⅲ)-MOF-5 in N_2 at various temperatures: 400 °C (green line), 450 °C (red line), 500 °C (black line), 550 °C (blue line), 600 °C (magenta line). CVs were obtained on 80% as-prepared sample+10% super P+10% PVDF electrode in electrolyte of 1.0 M LiTFSI in TEGDME at O_2-staurated atmosphere. The scan rate was set at 0.1 V s^{-1}.

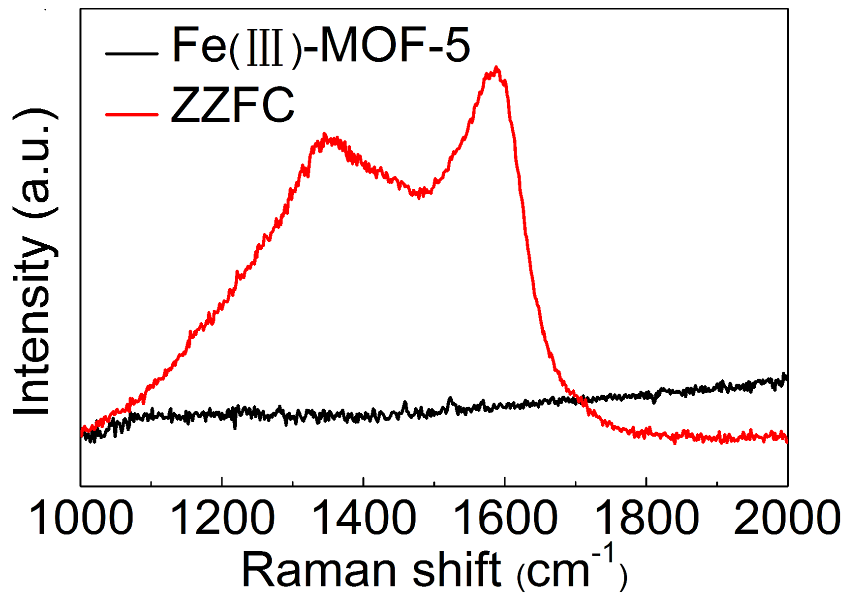

Figure S4. Raman spectrum of Fe(III)-MOF-5 and ZZFC.

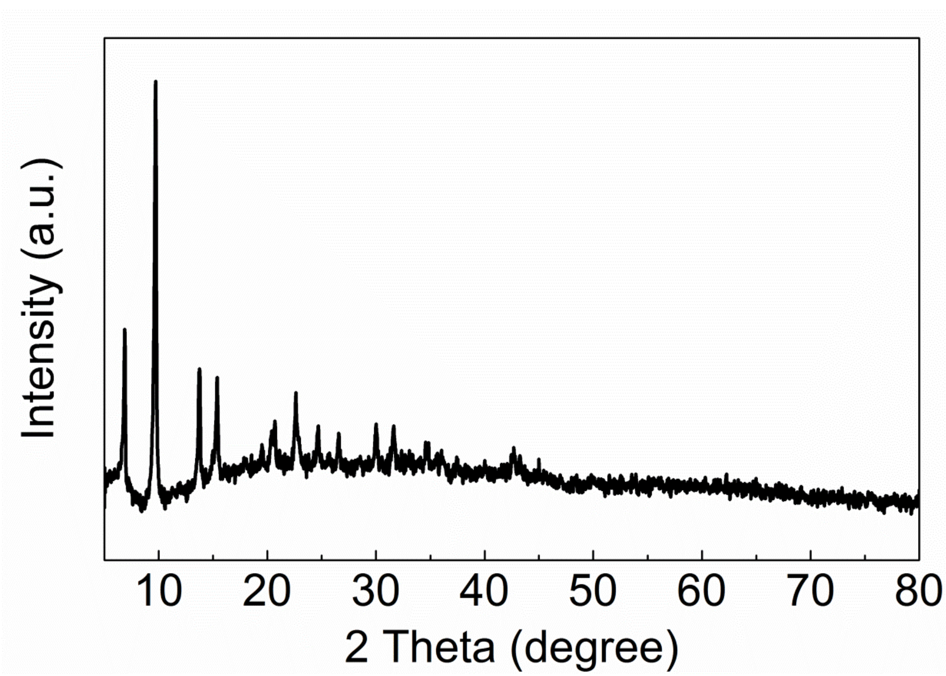

Figure S5. XRD patterns of the Fe(III)- MOF-5.

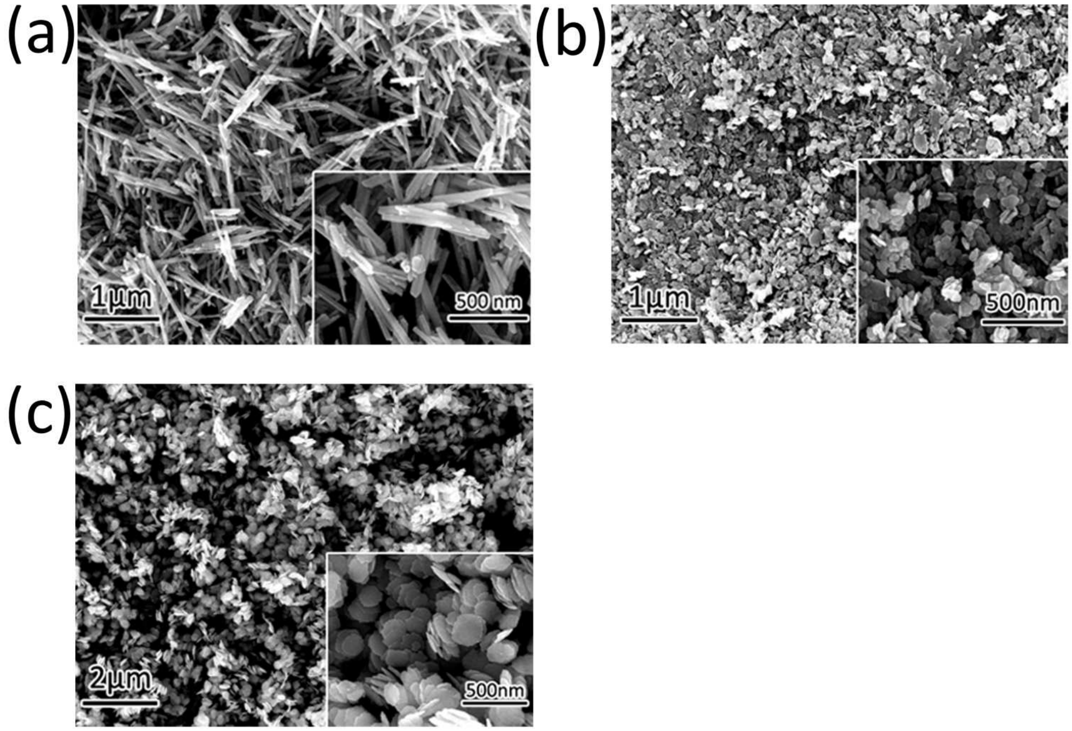

Figure S6. SEM images of (a) α-MnO_2 nanowires, (b) Co_3O_4 nanoflakes, (c) Fe_2O_3 nanoflakes.

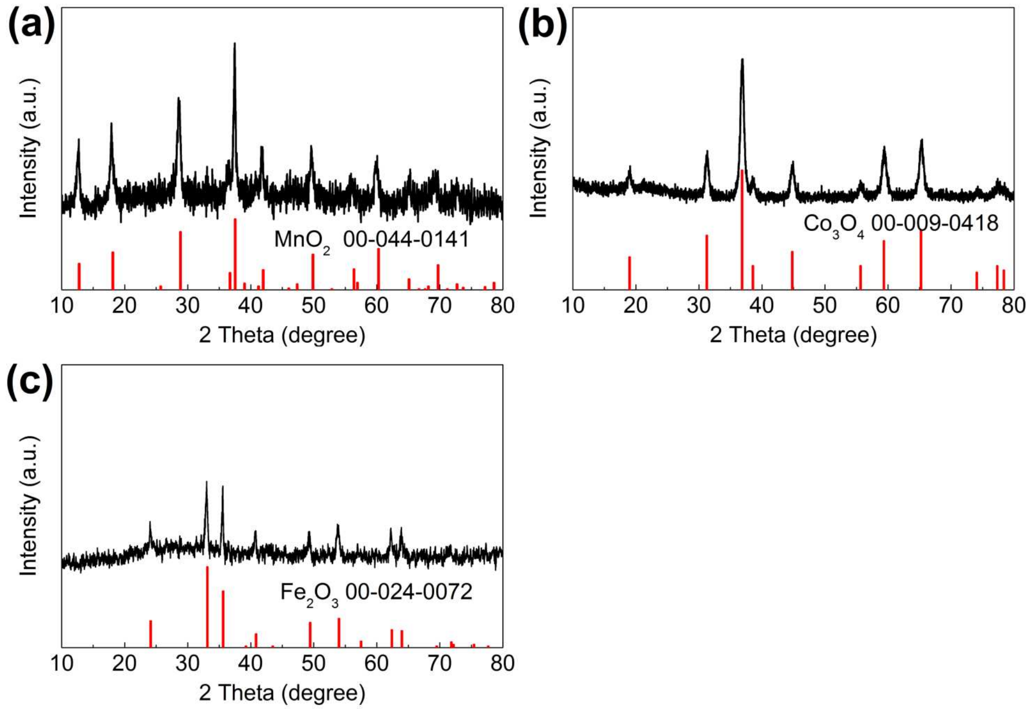

Figure S7. XRD patterns of (a) α-MnO_2 nanowires, (b) Co_3O_4 nanoflakes, (c) Fe_2O_3 nanoflakes.

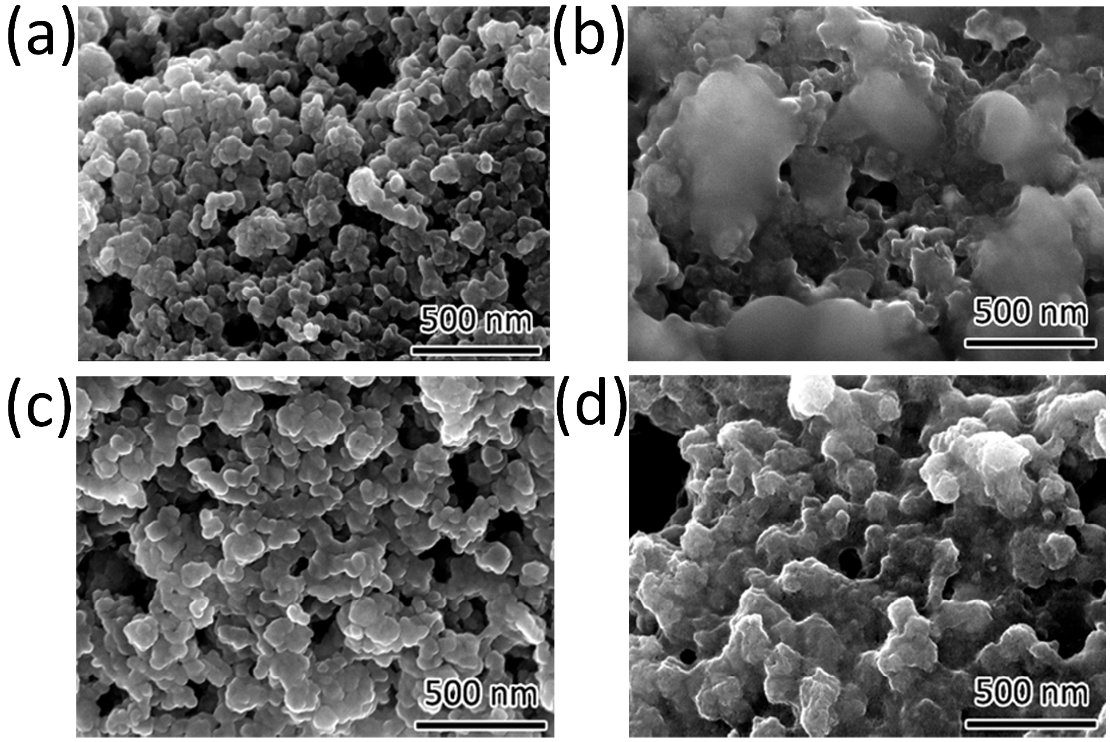

Figure S8. SEM images for the as-prepared ZZFC cathodes: (a) before cycling, (b) full discharge, (c) after charge, and (d) after 10 cycles.

References

(1) Song, K.; Jung, J.; Heo, Y. U.; Lee, Y. C.; Cho, K.; Kang, Y. M. Alpha-MnO_2 Nanowire Catalysts with Ultra-High Capacity and Extremely Low Overpotential in Lithium-Air Batteries Through Tailored Surface Arrangement. *Phys. Chem. Chem. Phys.* **2013**, *15*, 20075-20079.

(2) Okubo, M.; Hosono, E.; Kim, J.; Enomoto, M.; Kojima, N.; Kudo, T.; Zhou, H.; Honma, I. Nanosize Effect on High-Rate Li-Ion Intercalation in $LiCoO_2$ Electrode. *J. Am. Chem. Soc.* **2007**, *129*, 7444-7452.

(3) Zhang, Z.; Zhou, G.; Chen, W.; Lai, Y.; Li, J. Facile Synthesis of Fe_2O_3 Nanoflakes and Their Electrochemical Properties for Li-Air Batteries. *ECS Electrochem. Lett.* **2013**, *3*, A8-A10.