Electronic Supplementary Information (ESI)

Hierarchical Porous Hollow FeFe(CN)₆ Nanospheres Wrapped by I-Doped

Graphene as Anode Materials for Lithium-ion Batteries

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EXPERIMENTAL DETAILS

Synthesis of the FeFe(CN)₆ **nanocubes:** PVP (3.00 g) and K_3 [Fe(CN)₆] (138.2 mg) were added to a 0.05 M HCl solution (52.5 mL) under magnetic stirring. After 60 min of stirring, the pale yellow solution was obtained. Then, the pale yellow solution was then placed into water bath and heated at 80 °C for 24 h under magnetic stirring. The precipitates were collected by centrifugation and washed

several times in distilled water and ethanol. After drying at 60 $\,^\circ\!\!\mathbb{C}$ for 12 h,

FeFe(CN)₆ nanocubes were obtained. FeFe(CN)₆ spheres was prepared in the same way with 0.5-0.8 M HCl solution. When the concentration of hydrochloric acid is between 0.1-0.5 M, the morphology of FeFe(CN)₆ is between cubes and spheres.

Synthesis of the Prussian blue (Fe₄[Fe(CN)₆]₃): Fe₄[Fe(CN)₆]₃ was synthesized by a simple one-step co-precipitation method. Stoichiometric amounts of FeCl₃ (5 mmol) and K₄Fe(CN)₆ (3.75 mmol) were dissolved in 50 mL deionized water respectively. Then the K₄Fe(CN)₆ solution was slowly added to the FeCl₃ solution during continuous stirring. The resulting solution was stirred for another 2 h at

55 $^{\circ}$ C temperature. The dark blue solid product (Fe₄[Fe(CN)₆]₃) was collected by

centrifugation, washed several times with de-ionized water and ethanol, and dried

in vacuum at 60 $\,^\circ\!\mathrm{C}$ for overnight.



Fig. S1. Unit cell of FeFe(CN)₆.¹



Fig. S2. SEM images of the FeFe(CN)₆ cubes (0.05 M HCl) (a), the mixture of FeFe(CN)₆ cubes and spheres (0.2 M HCl) (b), FeFe(CN)₆ spheres (0.5 M HCl) (c).



Fig. S3. XRD pattern of FeFe(CN)₆-80, FeFe(CN)₆-100 and FeFe(CN)₆-120.



Fig. S4. Elemental mapping images of FeFe(CN)₆-100 nanospheres.



Fig. S5. (a) N_2 adsorption-desorption isotherm and (b) the corresponding pore size distribution of FeFe(CN)₆-80, FeFe(CN)₆-100 and FeFe(CN)₆-120, respectively.



Fig. S6. (a) Raman spectra of the IG and $FeFe(CN)_6$ -100@IG. (b) XPS spectra of the IG.



Fig. S7. Cycling performance of the I-doped graphene (IG) at a current density of 200 mA g^{-1} .



Fig. S8. CV curves of the FeFe(CN) $_6$ -100@IG nanocomposites for initial tow cycles at 0.001 V s⁻¹ scan rate.



Fig. S9. the voltage profile of FeFe(CN)₆-100@IG in the initial cycle at a current density of 100 mA g^{-1} .



Fig. S10. (a, b) SEM images of the $Fe_4[Fe(CN)_6]_3$ at different magnifications. (c, d) SEM images of hollow mesoporous $Fe_4[Fe(CN)_6]_3$.



Fig. S11. (a, b) TEM images of the $Fe_4[Fe(CN)_6]_3$ at different magnifications. (c, d) SEM images of hollow mesoporous $Fe_4[Fe(CN)_6]_3$.



Fig. S12. Cycling performance of the $Fe_4[Fe(CN)_6]_3$ @IG at a current density of 2000 mA g⁻¹.



Fig. S13. (a, b) SEM images of fresh electrode $FeFe(CN)_6$ -100@IG. SEM images of electrode after 100 cycles at a current density of 100 mA g^{-1} (c, d) and 1000 mA g^{-1} (e, f). (g, h) TEM images of the electrode after 10 cycles at a current density of 100 mA g^{-1} .



Fig. S14. XRD patterns of FeFe(CN)₆-100 electrodes collected from the batteries after their 1st discharge processes.

References

1 X. Wu, W. Deng, J. Qian, Y. Cao, X. Ai, and H. Yang, J. Mater. Chem. A, 2013, 1, 10130-10134.