Electronic Supplementary Information

Integrating three-dimensional graphene/Fe₃O₄@C composite and mesoporous Co(OH)₂ nanosheets arrays/graphene foam into a superior asymmetric electrochemical capacitor

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Figure S1 Nitrogen adsorption-desorption isotherms (A) and pore size distributions (B) for graphene/Fe₃O₄@C composite.



Figure S2 FESEM and TEM images of graphene/Fe₃O₄@C composites after cycling.



Figure S3 Electrochemical properties of pure graphene. (A) CV curves at different scan rates.
(B) galvanostatic charge–discharge curves at 2 A g⁻¹.

FeO _x electrode	Electrolyte	Potential range (V vs. SCE)	Specific capacitance (F g ⁻¹)	Rate capability	Ref
graphitic nanoflake/Fe ₃ O ₄	2M KOH	-1.2 to -0.6 V	299 at 0.5 A $\rm g^{-1}$	131 at 0.5 A g^{-1}	S1
Fe ₃ O ₄ film	1M Na ₂ SO ₄	-0.55 to 0.05 V	105 at 20 $\rm mV~s^{-1}$	Not reported	S2
Fe ₃ O ₄ powders	0.1M K ₂ SO ₄	–0.8 to 0.25 V	75 at 10 mV $\rm s^{-1}$	Not reported	S3
C-dots/Fe ₃ O ₄	1M Na ₂ SO ₃	-1 to 0 V	208 at 1 $\mathrm{A}\mathrm{g}^{-1}$	80 at 20 $A g^{-1}$	S 4
Fe ₂ O ₃ nanotube	1M Li ₂ SO ₄	-0.8 to 0 V	138 at 1.3 A g^{-1}	91 at 12.8 A g^{-1}	S 5
FeOOH rods	1M Li ₂ SO ₄	-0.85 to -0.1 V	116 at 0.5 $\rm A~g^{-1}$	93 at 1.5 A g^{-1}	S6
Octadecahedron Fe ₃ O ₄	1M Na ₂ SO ₃	-1 to 0.1 V	118 at 2 A g ⁻¹	50 at 3.3 A g^{-1}	S 7
Fe ₃ O ₄ nanoparticles	1M Na ₂ SO ₃	-0.9 to 0.1 V	207.7 at 0.4 A $\rm g^{-1}$	90.4 at 10 A $\rm g^{-1}$	S8
Fe ₃ O ₄ /CNF composite	1M Na ₂ SO ₃	-0.9 to 0.1 $\rm V$	127 at 10 mV $\rm s^{-1}$	53 at 10 mV $\rm s^{-1}$	S9
Fe ₃ O ₄ /CNT composite	6M KOH	-1 to 0 V	129 at 2.5 mA cm^{-1}	103 at 40 mA cm^{-1}	S10
Fe ₃ O ₄ /carbon nanosheets	1M Na ₂ SO ₃	-0.8 to -0.2 V	163.4 at 1 A g ⁻¹	113 at 10 A g ⁻¹	S11
Fe ₃ O ₄ /carbon black	1M Na ₂ SO ₃	-0.75 to 0.5 V	510 at 15 mA g^{-1}	Not reported	S12
Fe ₂ O ₃ nanotubes/rGO	1M Na ₂ SO ₄	-1 to 0 V	215 at 2.5 mV $\rm s^{-1}$	88 at 100 $\rm mV~s^{-1}$	S13
FeO _x /carbon foams	$2.5M \text{ Li}_2 \text{SO}_4$	-0.8 to 0.2 V	343 at 5 mV s ⁻¹	Not reported	S14
Fe ₃ O ₄ particles-graphene	1M KOH	-1 to 0.1 V	220.1 at 0.5 A g^{-1}	134.6 at 5 A g^{-1}	S15
FeOOH/graphene	1M LiOH	-1.15 to 0.1 V	326 at 0.5 A g^{-1}	293 at 10 A g^{-1}	S16
Au-Fe ₃ O ₄ nanoparticles	6M KOH	-1 to 0.4 V	464 at 1 A g ⁻¹	120 at 10 A g ⁻¹	S17
Fe ₃ O ₄ -f-HEG	1M Na ₂ SO ₄	-0.5 to -0.5 V	180 at 10 mV s ⁻¹	160 at 100 mV s ⁻¹	S18

Table S1. Specific capacitances of recently published state-of-the-art FeO_x -based materials,tested in three-electrode configuration.



Figure S4 FESEM images (A, B) and TEM images (C) and the SAED pattern (D) of graphene

foam.



Figure S5 The TEM image of the Co(OH)₂ nanosheet on the GFs.



Figure S6 FT-IR spectrum of Co(OH)₂ NAs/GF.



Figure S7 Nyquist plots for the Co(OH)₂ NAs/GF//graphene/Fe₃O₄@C ASC. The frequency range is from 10^{-1} to 10^{5} at the bias potential of 1.4 V. The lower right inset presents high-frequency region of the plot.



Figure S8 the FESEM image (A) and the photograph (B) of the graphene.



Figure S9 Electrochemical properties of the Co(OH)₂ NAs/GF//graphene ASC devise in 1 M KOH electrolyte. (A) CV curves at various scan rates. (B, C) GCD curves at various current densities. (D) Specific capacitances at various current densities. (E) Ragone plot.

The specific capacitances, energy densities, and power densities can be calculated by the following equations on the basis of galvanostatic charge–discharge curves:

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

$$E = \frac{1}{2 \times 3.6} C V^2 \tag{2}$$

$$P = \frac{E \times 3600}{\Delta t}$$
(3)

Where C (F g⁻¹) is the specific capacitance, E (Wh kg⁻¹) is the energy density, P (W kg⁻¹) is the power density, I(A) is the discharge current, Δt (s) is the discharge time, m (g) is the sum mass of the active material and ΔV (V) is the potential drop during the discharge process.

- [S1] M. Wang, W. Wang, W. Wang, X. Guo, RSC Adv., 4 (2014) 39625–39633.
- [S2] K. W. Chung, K. B. Kim, S. H. Han, H. Lee, Electrochem. Solid-State Lett. 8 (2005) A259–A262.
- [S3] T. Brousse, D. Bélanger, Electrochem. Solid-State Lett. 6 (2003) A244–A248.
- [S4] P. DEB, K. Bhattacharya, Dalton Trans., 44 (2015) 9221–9229.
- [S5] K. Xie, J. Li, Y. Lai, W. Lu, Z. Zhang, Y. Liu, L. Zhou, H. Huang, Electrochem. Commun. 13 (2011) 657–660.
- [S6] W. H. Jin, G. T. Cao, J. Y. Sun, J. Power Sources 175 (2008) 686-691.
- [S7] J. Chen, K. Huang, S. Liu, Electrochim. Acta 55 (2009) 1–5.
- [S8] L. Wang, H. Ji, S. Wang, L. Kong, X. Jiang, G. Yang, Nanoscale 5 (2013) 3793–3799.[S9] J. Mu, B. Chen, Z. Guo, M. Zhang, Z. Zhang, P. Zhang, C. Shao, Y. Liu, Nanoscale 3
- (2011) 5034–5040.
- [S10] D. Guan, Z. Gao, W. Yang, J. Wang, Y. Yuan, B. Wang, M. Zhang, L. Liu, Materials Science and Engineering B 178 (2013) 736–743.
- [S11] D. Liu, X. Wang, X. Wang, W. Tian, J. Liu, C. Zhi, D. He, Y. Bandoa, D. Golberg, J.Mater. Chem. A, 1 (2013) 1952–1955.
- [S12] N. L. Wu, S. Y. Wang, C. Y. Han, D. S. Wu, L. S. Shiue, J. Power Sources 113 (2003) 173–178.
- [S13] K. K. Lee, S. Deng, H. M. Fan, S. Mhaisalkar, H. R. Tan, E. S. Tok, K. P. Loh, W. S.
- Chin, C. H. Sow, Nanoscale 4 (2012) 2958–2961.
- [S14] M. B. Sassin, A. N. Mansour, K. A. Pettigrew, D. R. Rolison, J. W. Long, ACS Nano 4 (2010) 4505–4514.
- [S15] Q. Wang, L. Jiao, H. Du, Y. Wang, H. Yuan, J. Power Sources 245 (2014) 101–106.
- [S16] Q. Qu, S. Yang, X. Feng, Adv. Mater. 23 (2011) 5574–5580.
- [S17] S. Liu, S. Guo, S. Sun, X. Z. You, Nanoscale, 7 (2015) 4890-4893.
- [S18] A. K. Mishra, S, Ramaprabhu, J. Phys. Chem. C 115 (2011) 14006–14013.