

Supporting Information

Three-dimensional Porous Microspheres Comprising Hollow Fe₂O₃ Nanorods/CNT Building Blocks with Superior Electrochemical Performance for Lithium Ion Batteries

Seung-Keun Park, Gi Dae Park, and Yun Chan Kang*

Department of Materials Science and Engineering, Korea University, Anam-Dong,
Seongbuk-Gu, Seoul 136-713, Republic of Korea

*Corresponding authors.

E-mail: yckang@korea.ac.kr. Tel.: +82-2-928-3584. Fax: +82-2-3290-3268.
(Yun Chan Kang)

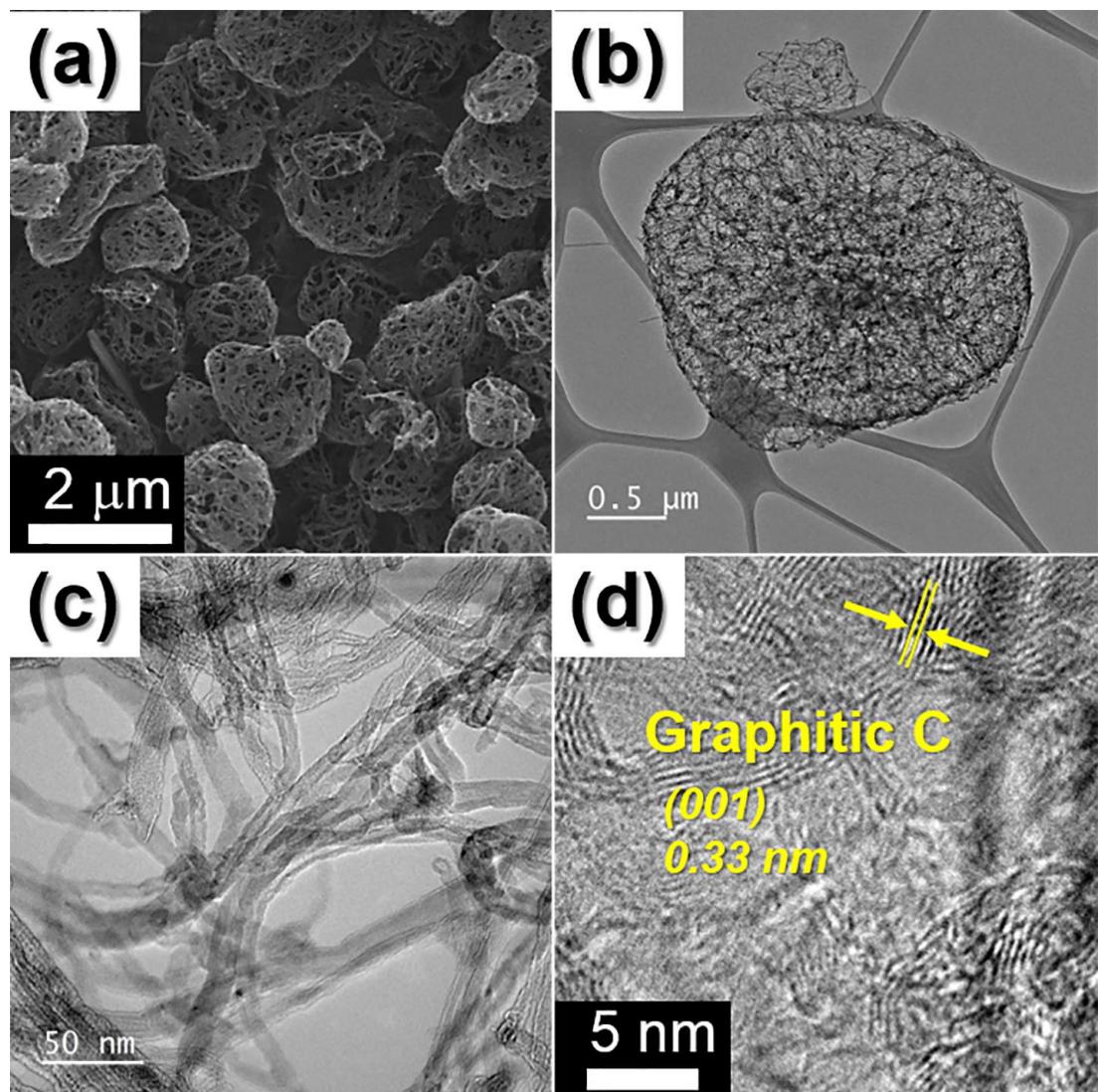


Fig. S1 (a) SEM, (b,c) TEM and (d) HR-TEM images of CNT porous microspheres.

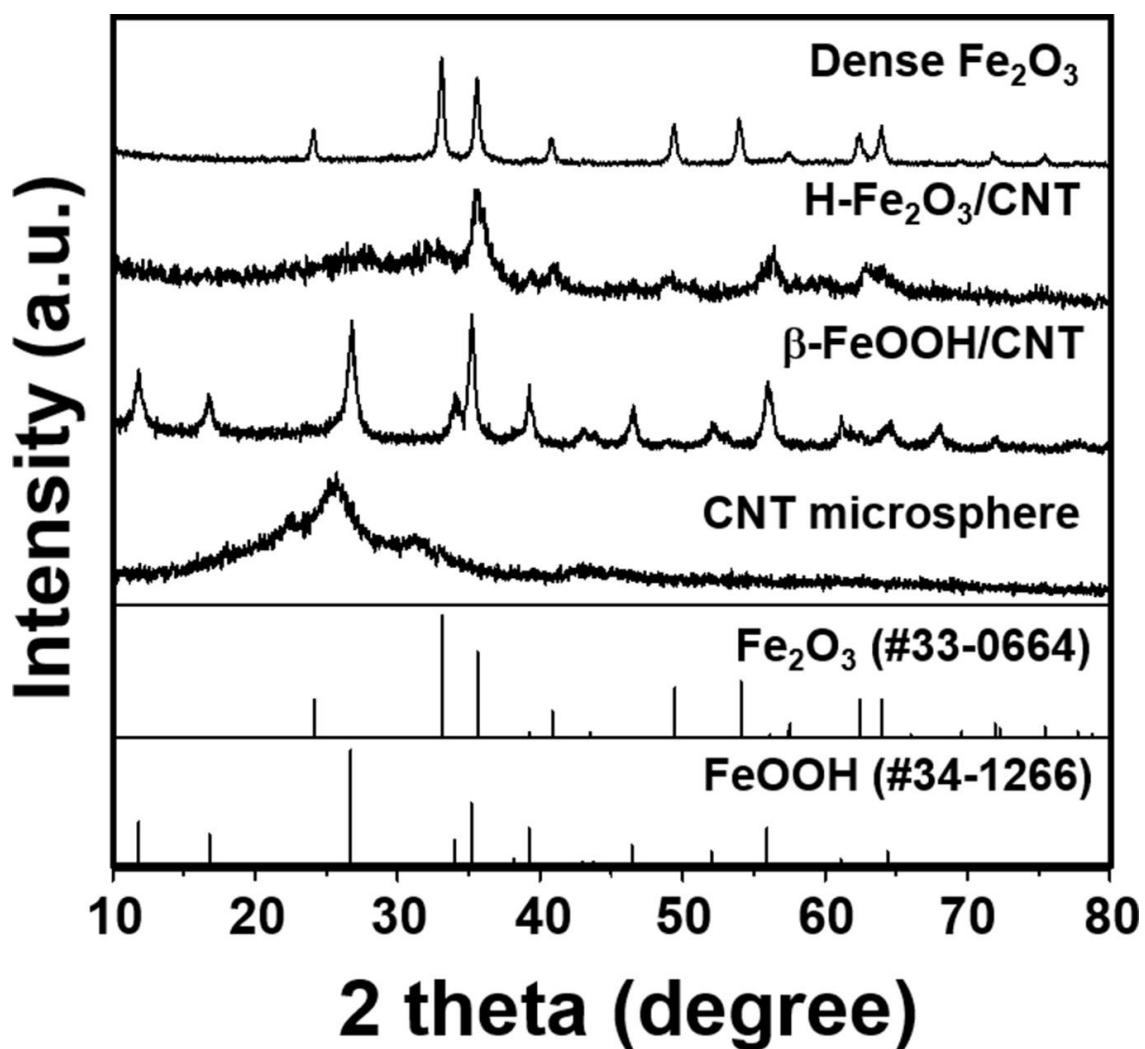


Fig. S2 XRD patterns of β - FeOOH/CNT microspheres, H- $\text{Fe}_2\text{O}_3/\text{CNT}$ microspheres, dense Fe_2O_3 nanorods and CNT porous microspheres.

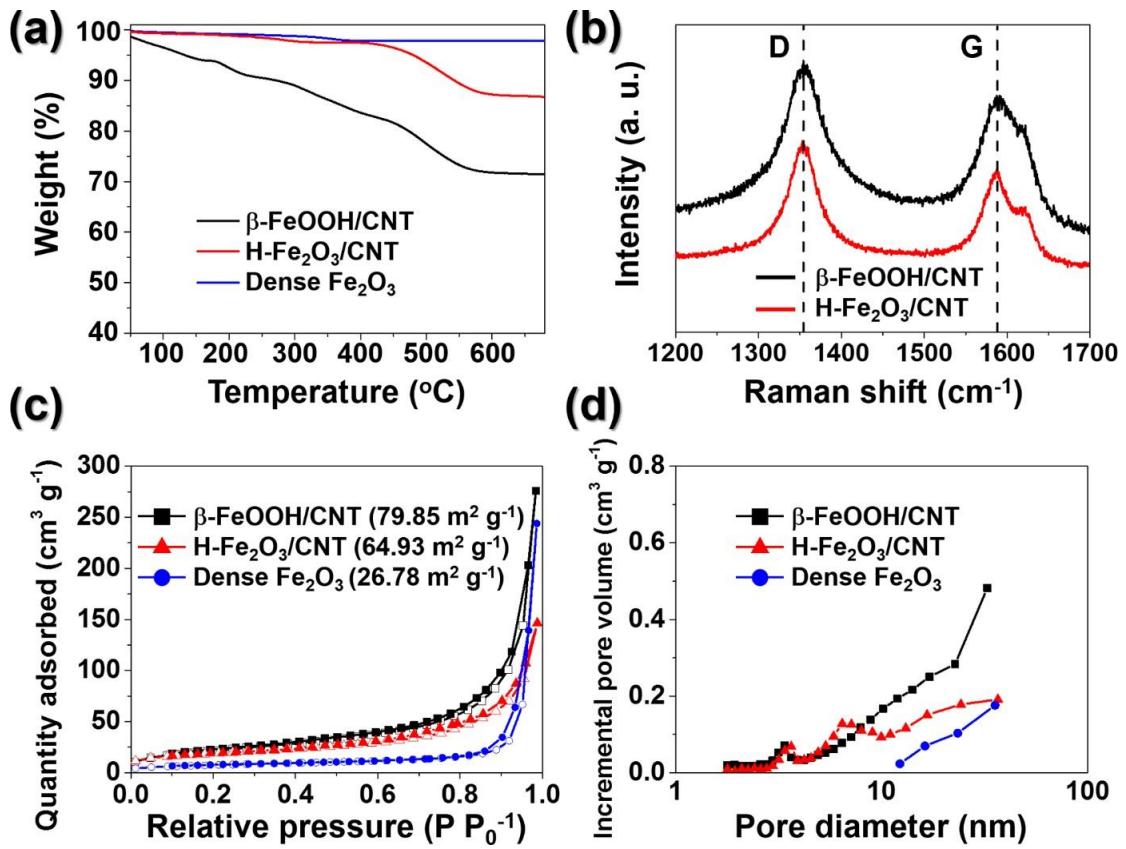


Fig. S3 (a) TGA curves, (b) Raman spectra, (c) N_2 adsorption and desorption isotherms and (d) BJH pore size distributions of $\beta\text{-FeOOH/CNT}$ microspheres, $\text{H-Fe}_2\text{O}_3/\text{CNT}$ microspheres and dense Fe_2O_3 nanorods.

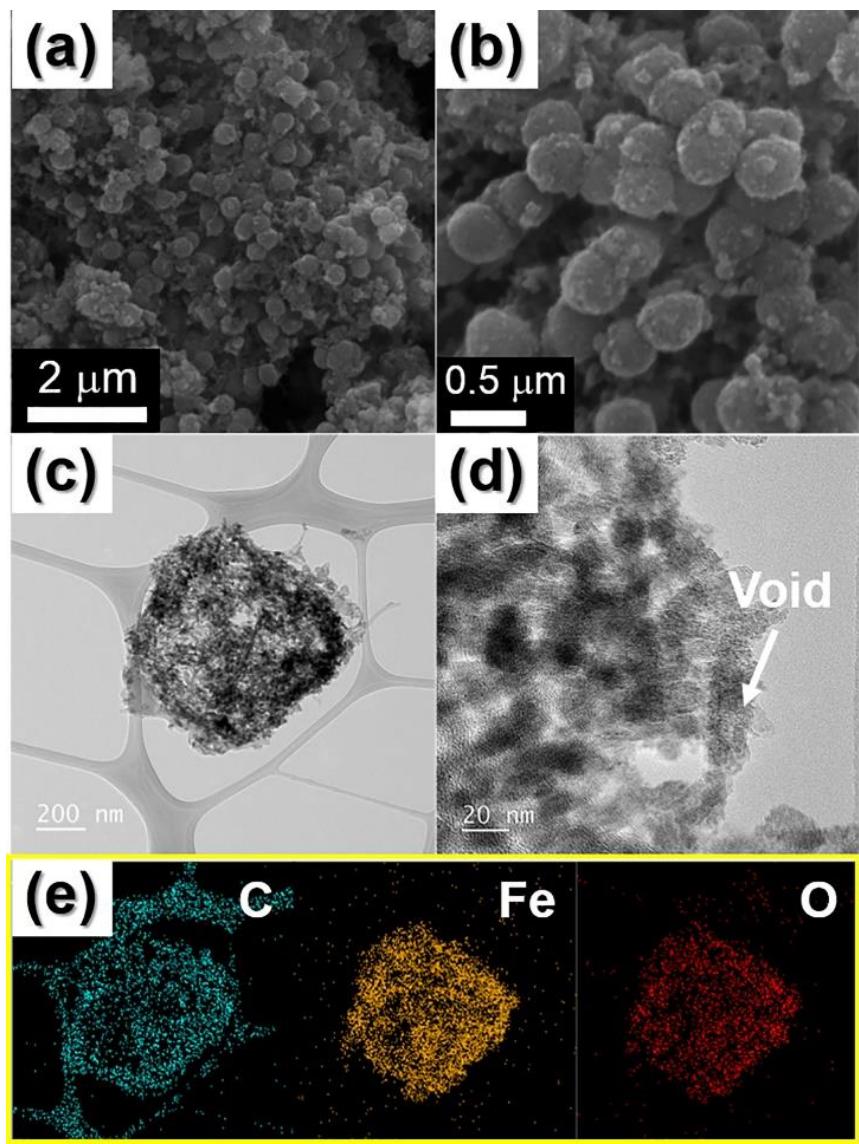


Fig. S4 (a and b) SEM, (c and d) TEM and (e) EDX mapping images of H- Fe_2O_3 /CNT microspheres after 200 cycles.

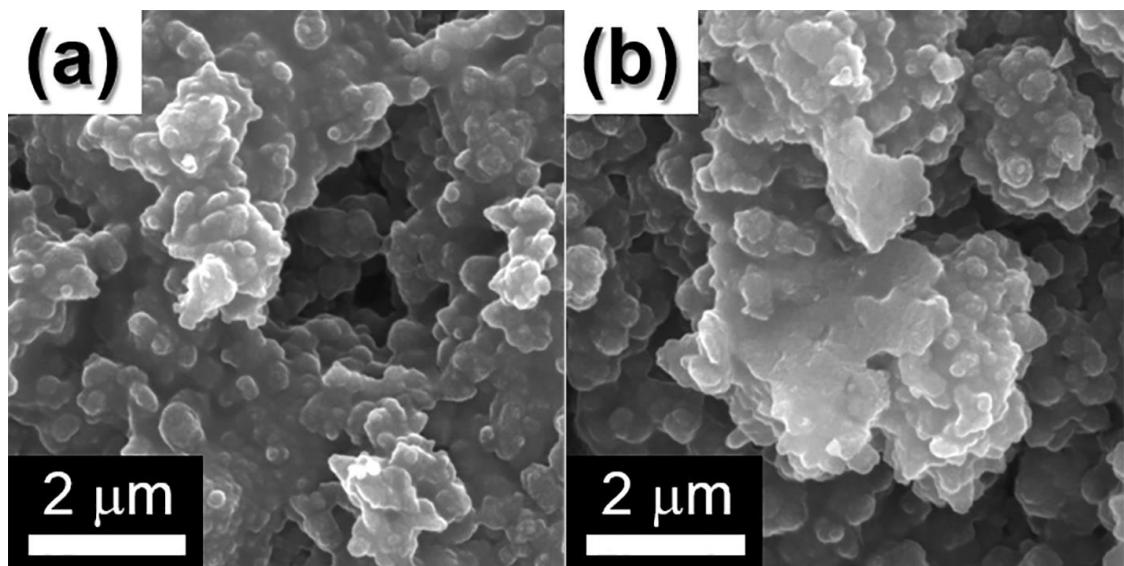


Fig. S5 (a and b) SEM images of dense Fe₂O₃ nanorods obtained after 200 cycles.

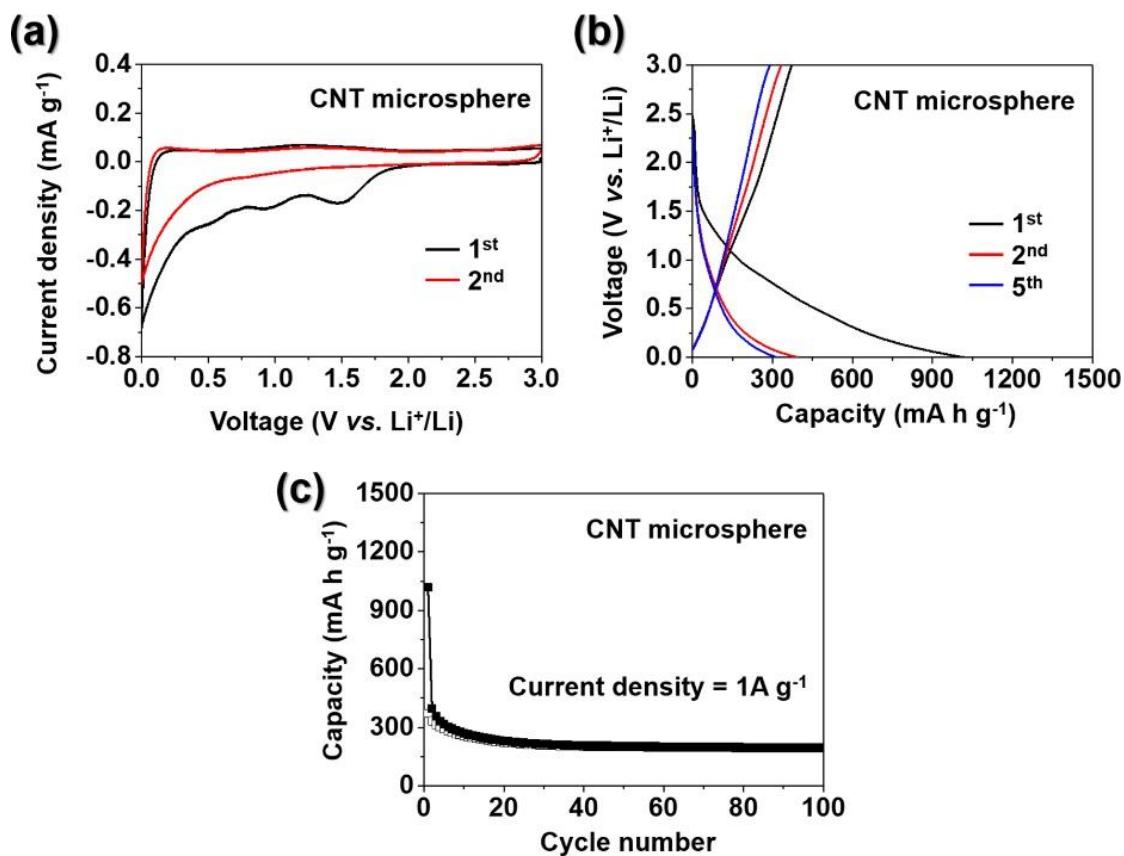


Fig. S6 (a) CV curves, (b) charge-discharge profiles and (c) cycling performance of CNT microspheres.

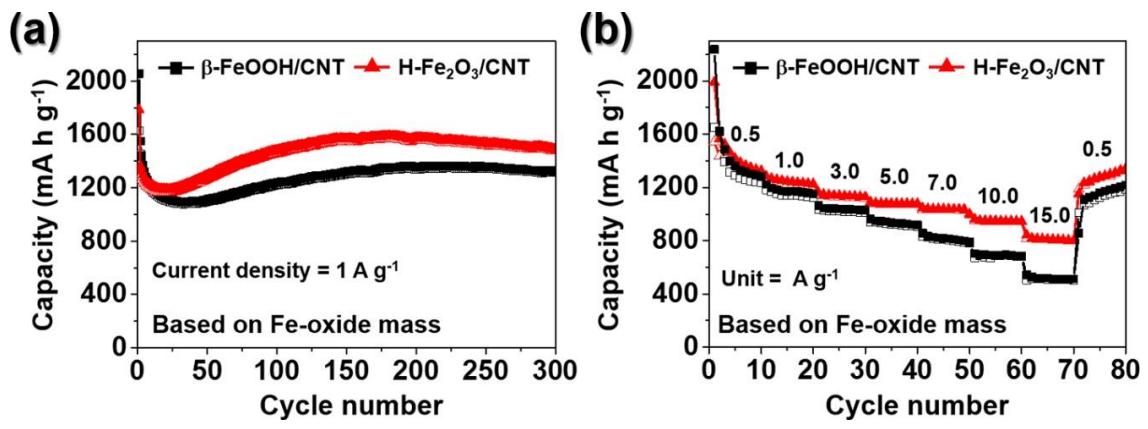
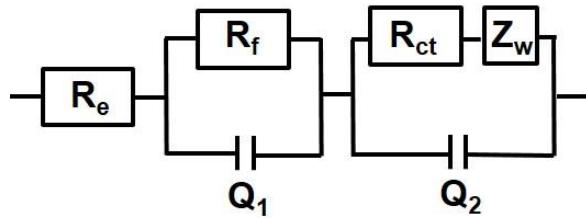


Fig. S7 (a) cycling and (b) rate performances of $\beta\text{-FeOOH/CNT}$ and $\text{H-Fe}_2\text{O}_3/\text{CNT}$ microspheres based on Fe-oxide mass.

Equivalent circuit model



R_e : the electrolyte resistance, corresponding to the intercept of high frequency semicircle at Z' axis

R_f : the SEI layer resistance corresponding to the high-frequency semicircle

Q_1 : the dielectric relaxation capacitance corresponding to the high-frequency semicircle

R_{ct} : the denote the charger transfer resistance related to the middle-frequency semicircle

Q_2 : the associated double-layer capacitance related to the middle-frequency semicircle

Z_w : the Li-ion diffusion resistance

Fig. S8 Randle-type equivalent circuit model used for AC impedance fitting.

Table S1. Electrochemical properties of the Fe₂O₃ materials with various structures as anode materials for LIBs.

Materials	Voltage range [V]	Current rate [A g ⁻¹]	Discharge capacity after cycling [mA h g ⁻¹]	Rate capability [mA h g ⁻¹] /[A g ⁻¹]	Ref
<i>H-Fe₂O₃/CNT microspheres</i>	0.001 – 3.0	1.0	1307 (300 th)	703 (15.0 A g ⁻¹)	<i>Our work</i>
Hollow Fe ₂ O ₃ spheres	0.05-3.0	0.2	710 (100 th)	-	[1]
Hierarchical hollow spheres composed of Fe ₂ O ₃ nanosheets	0.01-3.0	0.5	815 (200 th)	330 (5.0 A g ⁻¹)	[2]
Hierarchical Fe ₂ O ₃ microboxe	0.005-3.0	0.2	945 (30 th)	-	[3]
Hollow Fe ₂ O ₃ nanospheres	0.01-3.0	0.25	490 (50 th)	-	[4]
Hollow Fe ₂ O ₃ nanobarrels	0.01-3.0	0.5	916 (100 th)	403 (10.0 A g ⁻¹)	[5]
Multi-shelled hollow Fe ₂ O ₃ spheres	0.05-3.0	0.4	861 (50 th)	294 (4.0 A g ⁻¹)	[6]
Graphene-constructed hollow Fe ₂ O ₃ spheres	0.01-3.0	0.1	950 (50 th)	640 (1.0 A g ⁻¹)	[7]
Carbon coated hollow Fe ₂ O ₃ sphere	0.01-3.0	0.3	950 (100 th)	-	[8]
Fe ₂ O ₃ nanorods	0.005-3.0	0.5	970 (100 th)	300 (5.0 A g ⁻¹)	[9]
Spindle-like Fe ₂ O ₃	0.01-3.0	0.2	911 (50 th)	424 (10.0 A g ⁻¹)	[10]
Fe ₂ O ₃ nanoparticle-loaded carbon nanofibers	0.05-2.8	0.05	488 (75 th)	288 (0.5 A g ⁻¹)	[11]
Fe ₂ O ₃ nano-assembled spindle	0.005-3.0	0.1	~900 (40 th)	430 (1.0 A g ⁻¹)	[12]

References

1. B. Wang, J. S. Chen, H. B. Wu, Z. Y. Wang and X. W. Lou, *J. Am. Chem. Soc.*, 2011, **133**, 17146-17148.
2. J. X. Zhu, Z. Y. Yin, D. Yang, T. Sun, H. Yu, H. E. Hoster, H. H. Hng, H. Zhang and Q. Y. Yan, *Energy Environ. Sci.*, 2013, **6**, 987-993.
3. L. Zhang, H. B. Wu, S. Madhavi, H. H. Hng and X. W. Lou, *J. Am. Chem. Soc.*, 2012, **134**, 17388-17391.

4. M. Sasidharan, N. Gunawardhana, M. Yoshio and K. Nakashima, *Ionics*, 2013, **19**, 25-31.
5. K. S. Lee, S. Park, W. Lee and Y. S. Yoon, *ACS Appl. Mater. Interfaces*, 2016, **8**, 2027-2034.
6. Z. Padashbarmchi, A. H. Hamidian, H. W. Zhang, L. Zhou, N. Khorasani, M. Kazemzad and C. Z. Yu, *RSC Adv.*, 2015, **5**, 10304-10309.
7. Y. W. Chen, J. Z. Wang, J. Z. Jiang, M. A. Zhou, J. Zhu and S. Han, *RSC Adv.*, 2015, **5**, 21740-21744.
8. Z. J. Du, S. C. Zhang, J. F. Zhao, X. M. Wu and R. X. Lin, *J. Nanosci. Nanotechno.*, 2013, **13**, 3602-3605.
9. Y. M. Lin, P. R. Abel, A. Heller and C. B. Mullins, *J. Phys. Chem. Lett.*, 2011, **2**, 2885-2891.
10. X. Xu, R. Cao, S. Jeong and J. Cho, *Nano Lett.*, 2012, **12**, 4988-4991.
11. L. W. Ji, O. Toprakci, M. Alcoutlabi, Y. F. Yao, Y. Li, S. Zhang, B. K. Guo, Z. Lin and X. W. Zhang, *ACS Appl. Mater. Interfaces*, 2012, **4**, 2672-2679.
12. A. Banerjee, V. Aravindan, S. Bhatnagar, D. Mhamane, S. Madhavi and S. Ogale, *Nano Energy*, 2013, **2**, 890-896.