

Electronic Supplementary Information (ESI) for

**Self-assembly of transition-metal-oxide nanoparticle
supraparticles with designed architectures and their enhanced
lithium storage properties**

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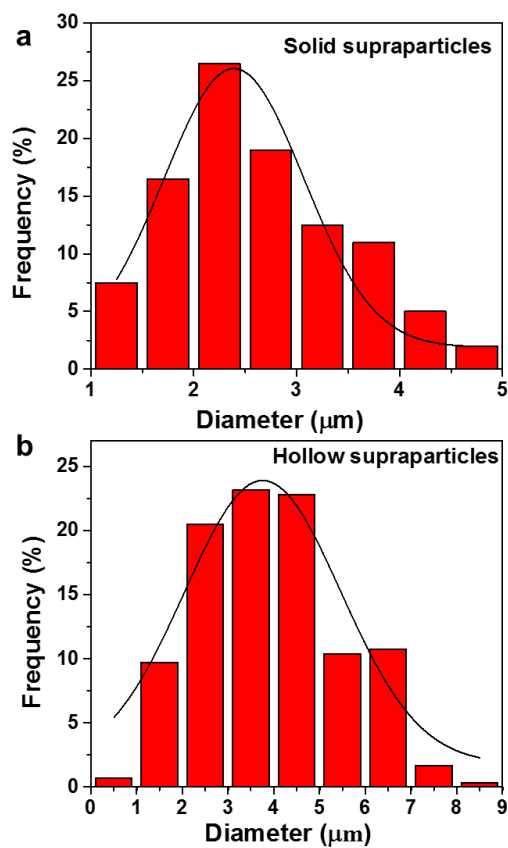


Figure S1. (a, b) Size distribution histograms of solid and hollow Fe_3O_4 NP supraparticles, respectively. The average diameter of solid and hollow Fe_3O_4 NP supraparticles was determined to be ~ 2.5 and $3.5 \mu\text{m}$, respectively.

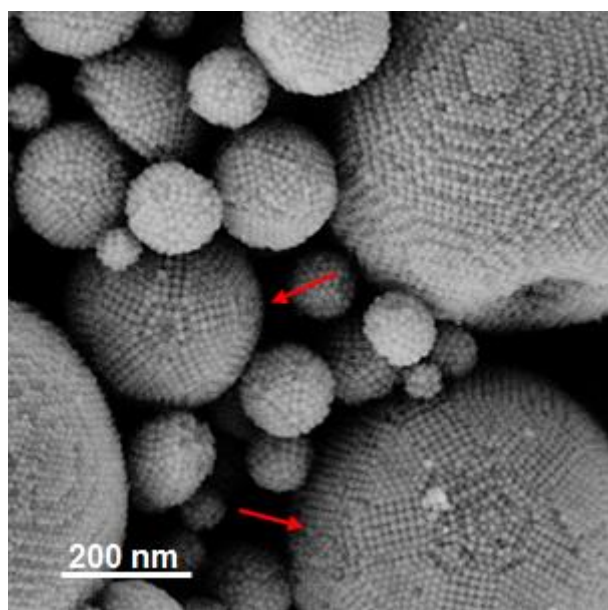


Figure S2. Representative HRSEM image of Fe₃O₄ NP supraparticles, showing the co-existence of icosahedral supraparticles (indicated by red arrows) with FCC supraparticles.

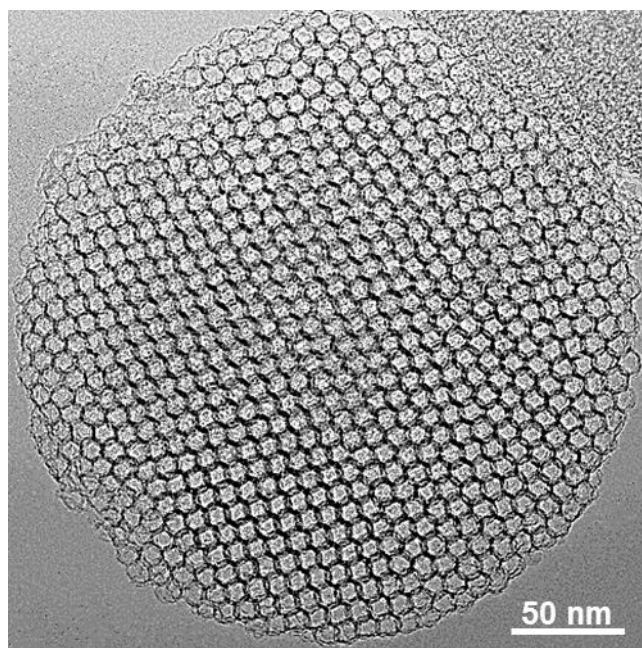


Figure S3. Typical TEM image of mesoporous carbon frameworks derived from the carbon-coated Fe_3O_4 NP supraparticles after acid etching. The 3D ordered carbon frameworks suggested the interconnection of carbon shells.

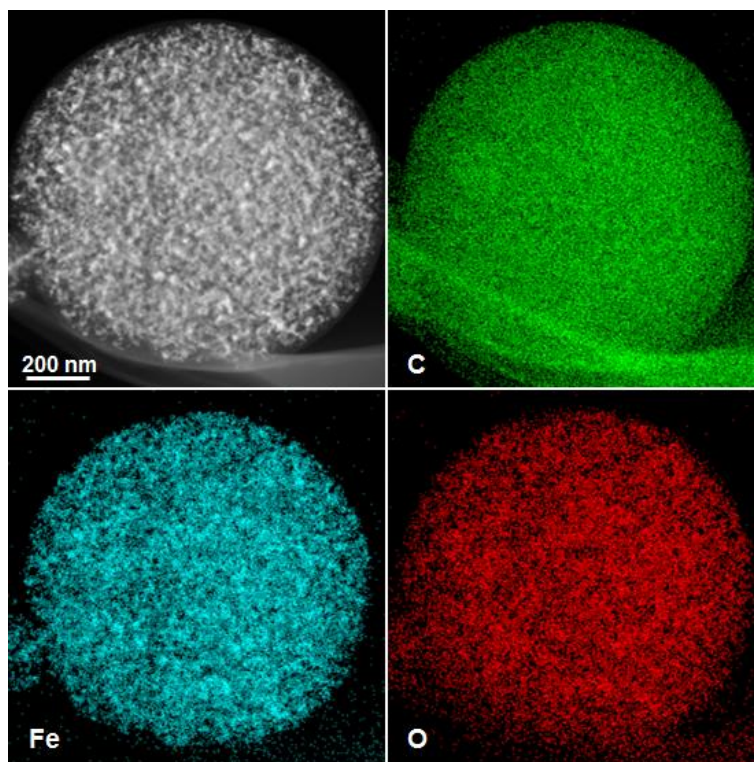


Figure S4. STEM image and the corresponding elemental mapping of a single Fe_3O_4 NP supraparticles after ligand carbonization. The homogeneous distribution of carbon suggested the formation of a 3D continuous carbon network after *in situ* ligand carbonization.

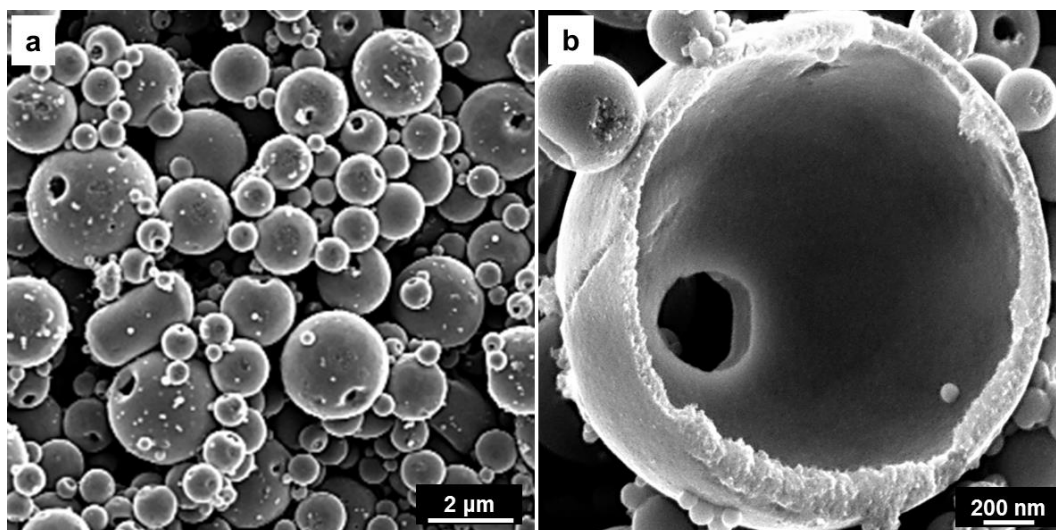


Figure S5. (a, b) SEM images of hollow supraparticles self-assembled from 6 nm NiFe_2O_4 NPs.

Table S1. Electrochemical performance of representative Fe₃O₄-based anodes reported previously.

Material	Current density (mA g ⁻¹)	Coulombic efficiency (1 st cycle)	Capacity (mAh g ⁻¹)	Ref.
Porous Fe ₃ O ₄ /VO _x / graphene nanowires	100		1164	S1
	2000		808	
Fe ₃ O ₄ @Fe ₃ C-C yolk/shell nanospindles	500	68.30%	1120 after 100 cycles	S2
	2000		604.8	
CNT@Fe ₃ O ₄ @C coaxial nanocables	200	65.50%	1290 after 80 cycles	S3
	2000		690 after 200 cycles	
Graphene-wrapped Fe ₃ O ₄ graphene nanoribbons	400		708 after 300 cycles	S4
	200		390 after 50 cycles	
Fe ₃ O ₄ /Fe nanocomposites	2000		260	S5
Hollow and yolk-shell Fe ₃ O ₄ nanostructures	1000		585 after 100 cycles	S6
Fe ₃ O ₄ /carbon composite microspheres	2000	72%	1022 for 150 cycles	S7
	5000		733	
Fe ₃ O ₄ /SnO ₂ coaxial nanofibers	100	74%	850 after 50 cycles	S8
	200			
Foam-like Fe ₃ O ₄ /C composite	5000		1008 after 400 cycles	S9
			580	
Novel Fe ₃ O ₄ -CNTs nanocomposite	92.8		850 after 100 cycles	S10
Carbon-coated Fe ₃ O ₄ nanosheets	200		1232 after 120 cycles	S11
	1000		853	
Sandwich-structured Fe ₃ O ₄ @carbon	~ 100		860 after 100 cycles	S12
C@Fe ₃ O ₄ @C coaxial nanotubes	100	68%	1134 after 150 cycles	S13
Fe ₃ O ₄ nanoparticles on graphene foam	924	68%	1200 after 500 cycles	S14
Fe ₃ O ₄ nanoparticles on porous carbon	100	61%	1462 after 100 cycles	S15
	1000		676 after 500 cycles	
Hollow Fe₃O₄ NP supraparticles	1600	70.8%	1152 after 300 cycles	This work

References

S1. Q. An, F. Lv, Q. Liu, C. Han, K. Zhao, J. Sheng, Q. Wei, M. Yan and L. Mai, *Nano Lett.*, 2014, **14**, 6250-6256.

- S2. J. Zhang, K. Wang, Q. Xu, Y. Zhou, F. Cheng and S. Guo, *ACS Nano*, 2015, **9**, 3369-3376.
- S3. J. Cheng, B. Wang, C. Park, Y. Wu, H. Huang and F. Nie, *Chem - Eur. J.*, 2013, **19**, 9866-9874.
- S4. L. Li, A. Kovalchuk, H. Fei, Z. Peng, Y. Li, N. D. Kim, C. Xiang, Y. Yang, G. Ruan and J. M. Tour, *Adv. Energy Mater.*, 2015, **5**, 1500171.
- S5. M. Lübke, N. M. Makwana, R. Gruar, C. Tighe, D. Brett, P. Shearing, Z. Liu and J. A. Darr, *J. Power Sources*, 2015, **291**, 102-107.
- S6. Z. Sun, K. Xie, Z. A. Li, I. Sinev, P. Ebbinghaus, A. Erbe, M. Farle, W. Schuhmann, M. Muhler and E. Ventosa, *Chem - Eur. J.*, 2014, **20**, 2022-2030.
- S7. S. H. Choi, Y. N. Ko, K. Y. Jung and Y. C. Kang, *Chem - Eur. J.* 2014, **20**, 11078-11083.
- S8. W. Xie, S. Li, S. Wang, S. Xue, Z. Liu, X. Jiang and D. He, *ACS Appl. Mater. Interfaces*, 2014, **6**, 20334-20339.
- S9. F. Wu, R. Huang, D. Mu, B. Wu and S. Chen, *Appl. Mater. Interfaces*, 2014, **6**, 19254-19264.
- S10. L. Yang, J. Hu, A. Dong and D. Yang, *Electrochim. Acta*, 2014, **144**, 235-242.
- S11. G. Gao, S. Lu, B. Dong, Z. Zhang, Y. Zheng and S. Ding, *J. Mater. Chem. A*, 2015, **3**, 4716-4721.
- S12. L. Zhao, M. Gao, W. Yue, Y. Jiang, Y. Wang, Y. Ren and F. Hu, *Appl. Mater. Interfaces*, 2015, **7**, 9709-9715.
- S13. Q. Qu, J. Chen, X. Li, T. Gao, J. Shao and H. Zheng, *Nano Lett.*, 2015, **3**, 18289-18295.
- S14. X. Hu, M. Ma, M. Zeng, Y. Sun, L. Chen, Y. Xue, T. Zhang, X. Ai, R. G. Mendes, M. H. Rummeli and L. Fu, *Appl. Mater. Interfaces*, 2014, **6**, 22527-22533.
- S15. L. Wang, L. Zhuo, C. Zhang and F. Zhao, *Chem - Eur. J.*, 2014, **20**, 4308-4315.