

Electronic Supplementary Information for

**Self-assembled Fe_3O_4 nanoparticle-doped TiO_2 nanorod
superparticles with highly enhanced lithium storage properties**

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The calculation of ratio between Fe₃O₄ and TiO₂ for Fe₃O₄/(TiO₂)₇₀.

$$m(\text{TiO}_2) = c(\text{TiO}_2) \times V(\text{TiO}_2) = 40 \text{ mg/mL} \times 1.820 \text{ mL} = 72.8 \text{ mg}$$

$$m'(\text{single TiO}_2 \text{ NR}) = \rho(\text{TiO}_2) \times V(\text{single TiO}_2 \text{ NR})$$

$$= 3.9 \text{ g/cm}^3 \times \pi \times (5 \times 10^{-7} \text{ cm})^2 \times 5 \times 10^{-6} \text{ cm}$$

$$= 1.53 \times 10^{-17} \text{ g} = 1.53 \times 10^{-14} \text{ mg}$$

$$n(\text{TiO}_2) = m(\text{TiO}_2) / m'(\text{single TiO}_2 \text{ NR})$$

$$= 72.8 \text{ mg} / 1.53 \times 10^{-14} \text{ mg}$$

$$= 4.76 \times 10^{15}$$

$$m(\text{Fe}_3\text{O}_4) = c(\text{Fe}_3\text{O}_4) \times V(\text{Fe}_3\text{O}_4) = 40 \text{ mg/mL} \times 0.182 \text{ mL} = 7.28 \text{ mg}$$

$$m'(\text{single Fe}_3\text{O}_4 \text{ NP}) = \rho(\text{Fe}_3\text{O}_4) \times V(\text{single Fe}_3\text{O}_4 \text{ NP})$$

$$= 5.2 \text{ g/cm}^3 \times 4/3 \times \pi \times (1.7 \times 10^{-6} \text{ cm})^3$$

$$= 1.07 \times 10^{-16} \text{ g} = 1.07 \times 10^{-13} \text{ mg}$$

$$n(\text{Fe}_3\text{O}_4) = m(\text{Fe}_3\text{O}_4) / m'(\text{single Fe}_3\text{O}_4 \text{ NP})$$

$$= 7.28 \text{ mg} / 1.07 \times 10^{-13} \text{ mg}$$

$$= 6.80 \times 10^{13}$$

$$n(\text{TiO}_2) / n(\text{Fe}_3\text{O}_4) = 4.76 \times 10^{15} / 6.80 \times 10^{13} = 70/1$$

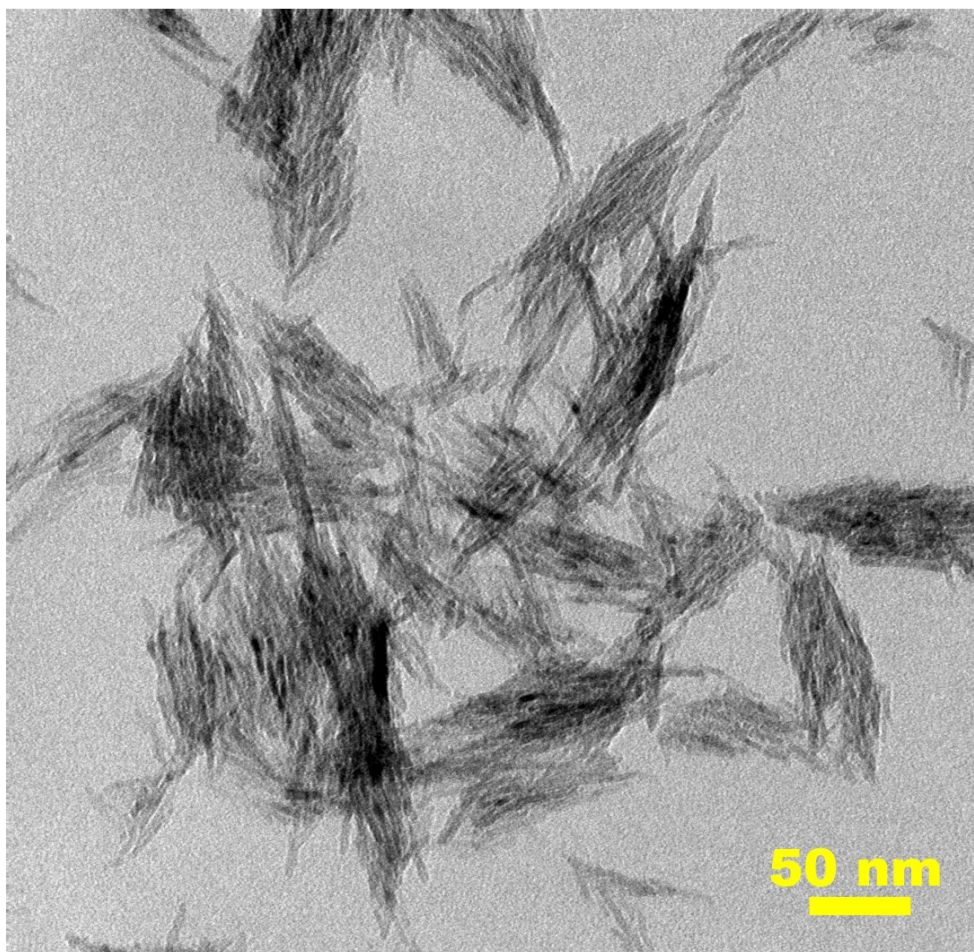


Fig. S1 High-magnification TEM image of TiO_2 NRs.

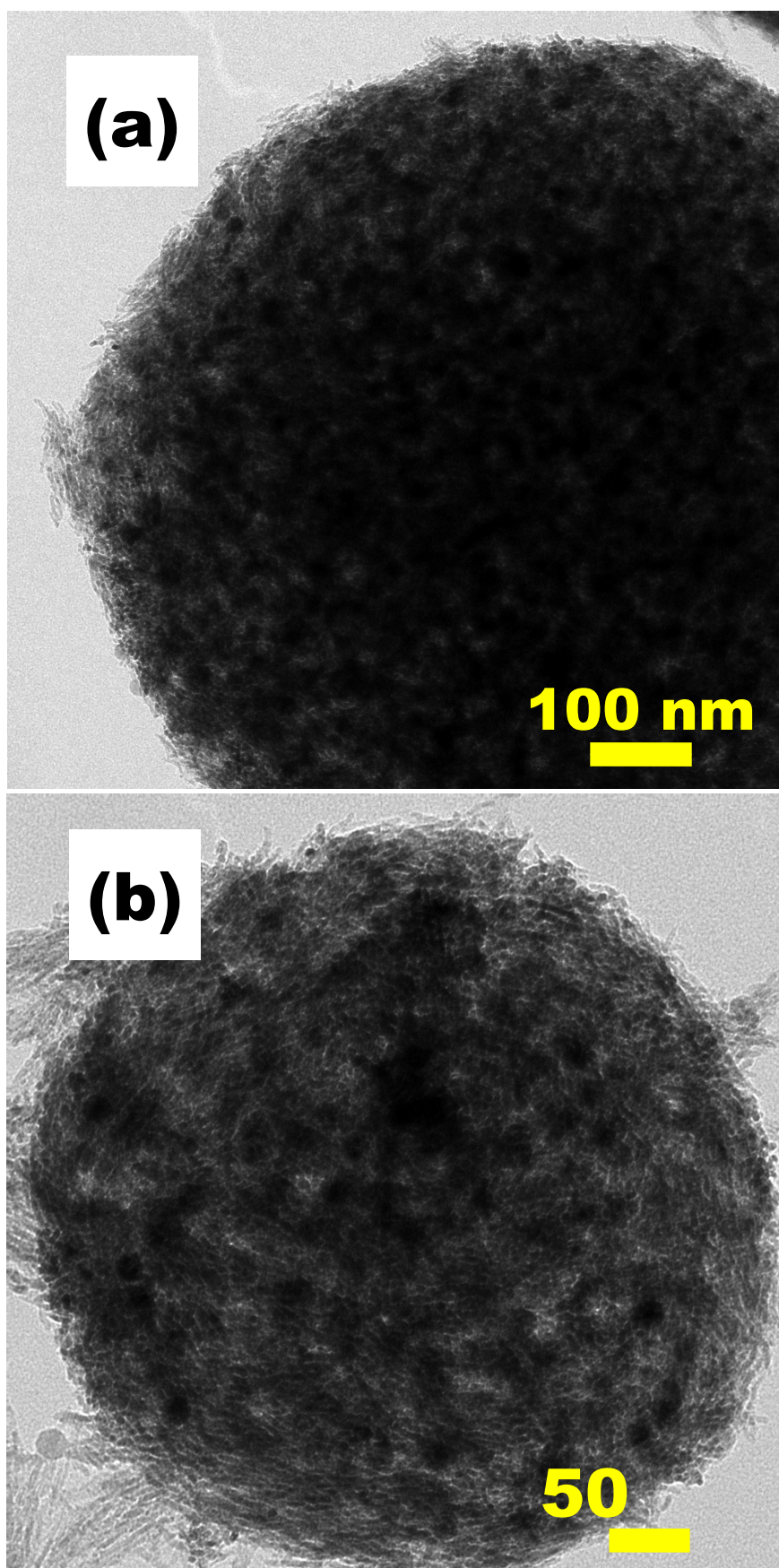


Fig. S2 TEM image of (a) enlarged Fig. 3e and (b) a smaller $\text{Fe}_3\text{O}_4/(\text{TiO}_2)_{70}$ SPs.

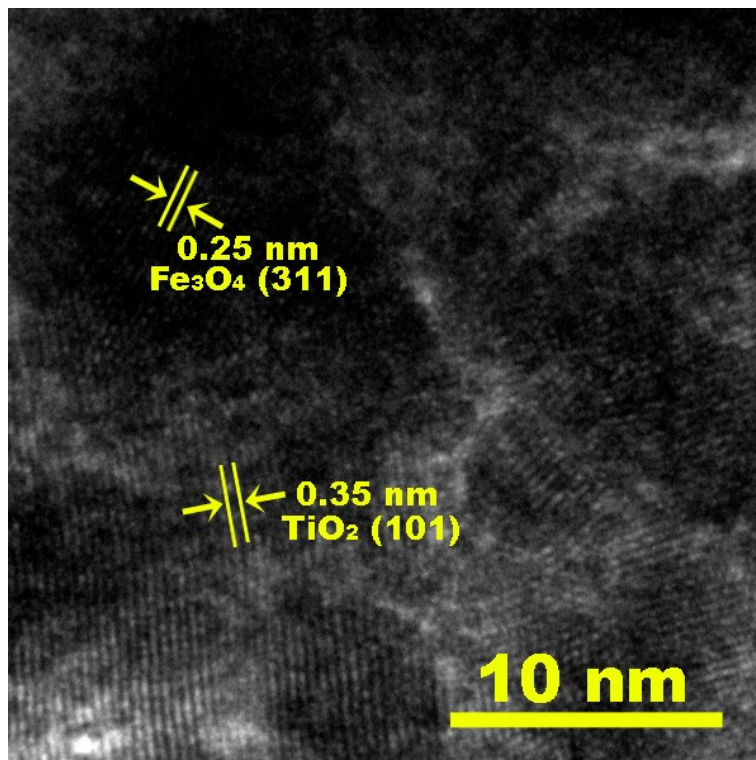


Fig. S3 HRTEM image of $\text{Fe}_3\text{O}_4/(\text{TiO}_2)_{70}$ SPs

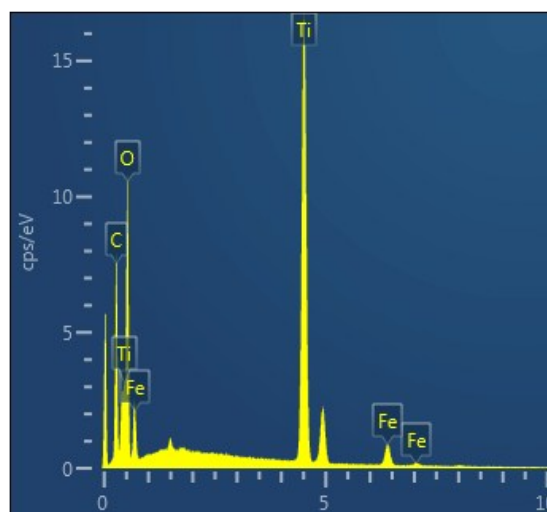


Fig. S4 EDS analysis on the cross-section of the $\text{Fe}_3\text{O}_4/(\text{TiO}_2)_{70}$ SPs after ion-beam cutting.

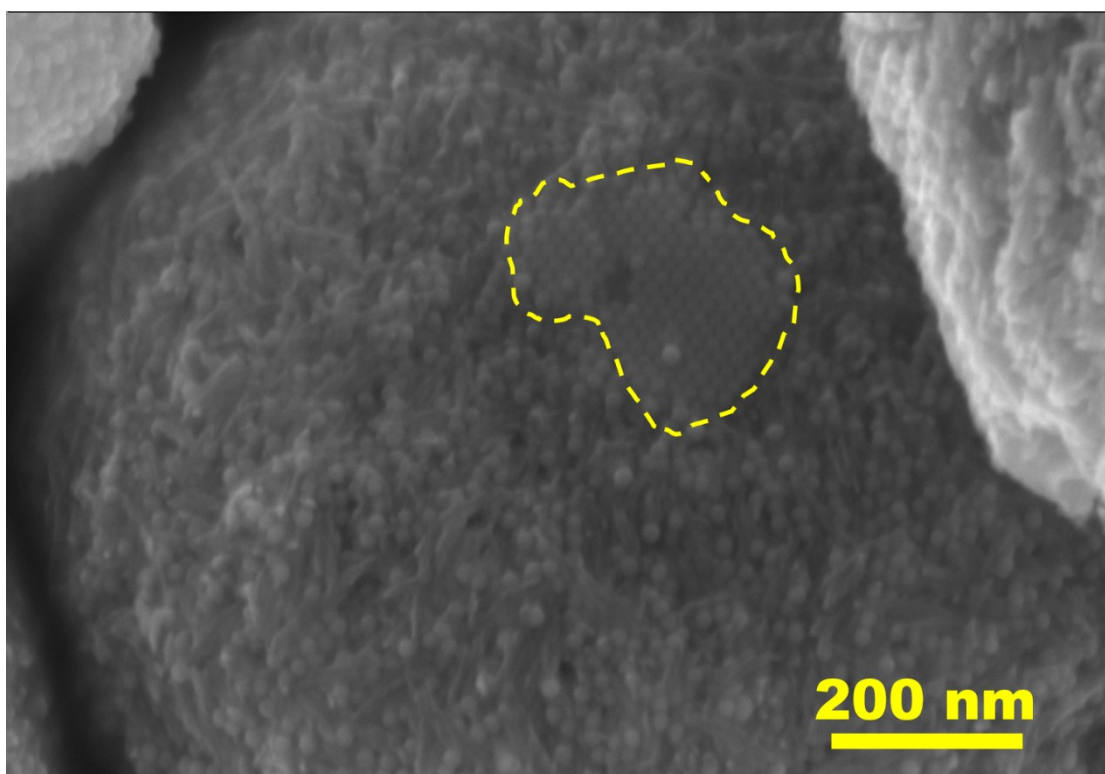


Fig. S5 FESEM image of phase separation in the Fe₃O₄/(TiO₂)₇ SPs.

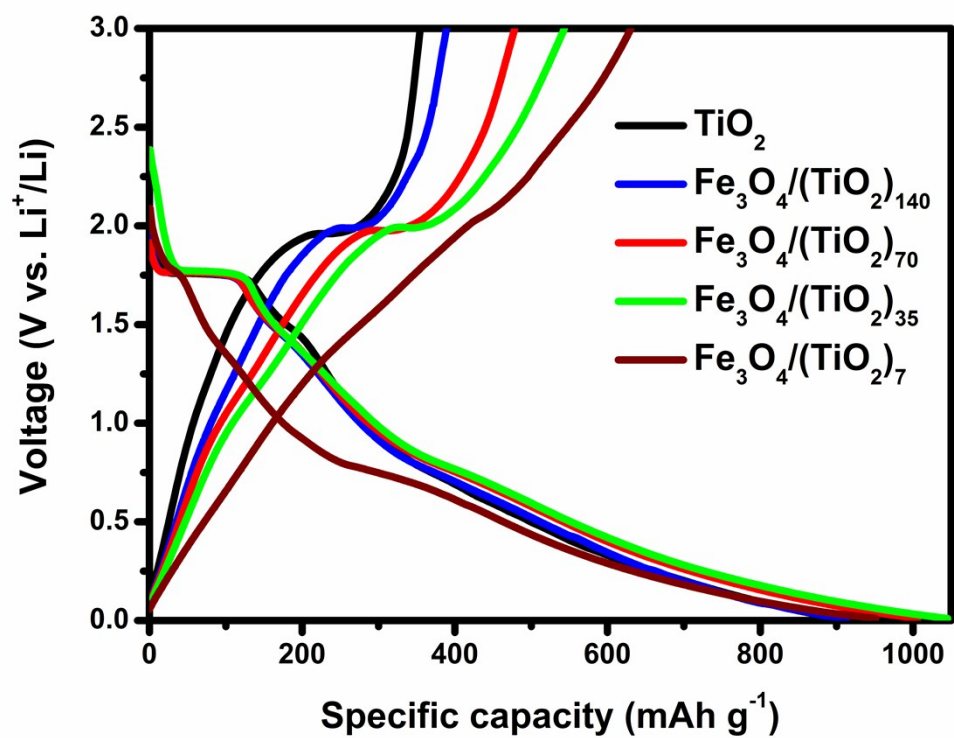


Fig. S6 First galvanostatic charge/discharge curves of the TiO_2 NRs and Fe_3O_4 NP doped- TiO_2 NR SPs at 100 mA g^{-1} .

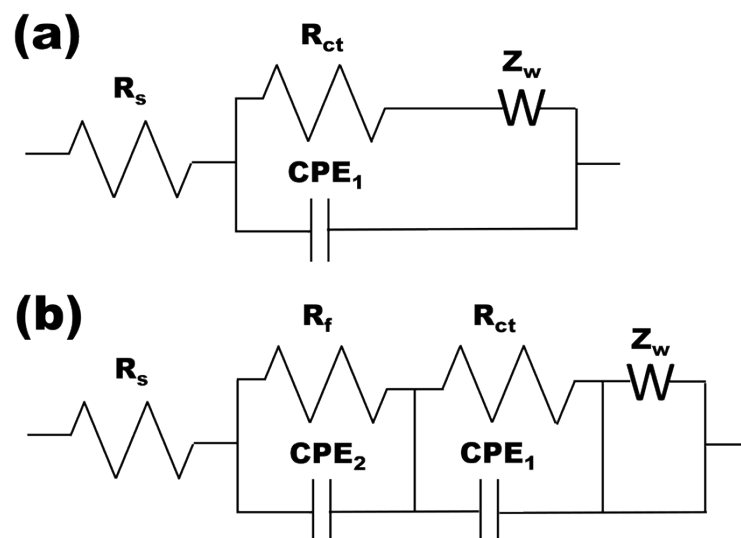


Fig. S7 The equivalent circuit modes for fitting the EIS in (a) Fig. 6e and (b) Fig. 6f. (R_s , ohmic resistance; R_{ct} , charge transfer resistance; CPE_1 , interfacial capacitance at the electrode/electrolyte interface; Z_w , Warburg resistance; R_f , surface layer resistance; CPE_2 , surface layer capacitance.)

Table S1 Impedance parameters of the fitting equivalent circuit.

Samples		$R_s (\Omega)$	$R_f (\Omega)$	$R_{ct} (\Omega)$
Before cycling	TiO ₂ SPs	5.52	-	531
	Fe ₃ O ₄ /(TiO ₂) ₇₀	1.18	-	112
After cycling	TiO ₂ SPs	1.41	41.3	127
	Fe ₃ O ₄ /(TiO ₂) ₇₀	0.869	5.89	32.3

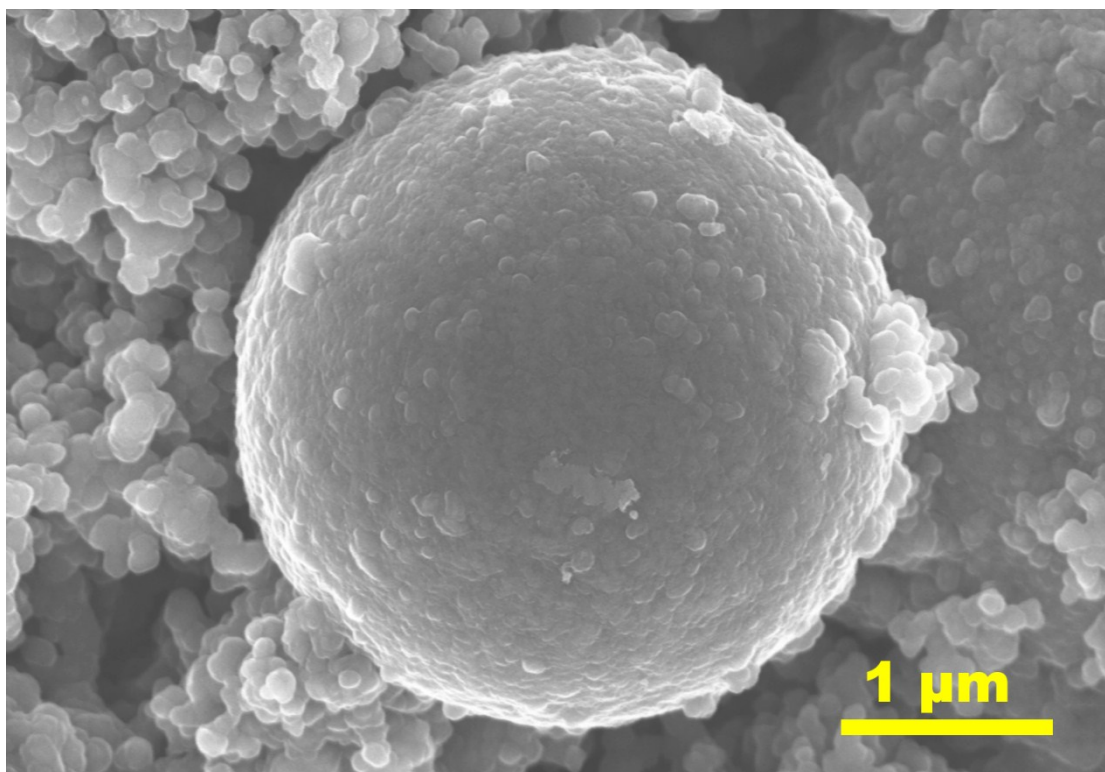


Fig. S8 Enlarged *ex-situ* FESEM image of the $\text{Fe}_3\text{O}_4/(\text{TiO}_2)_{70}$ SPs after cycling.

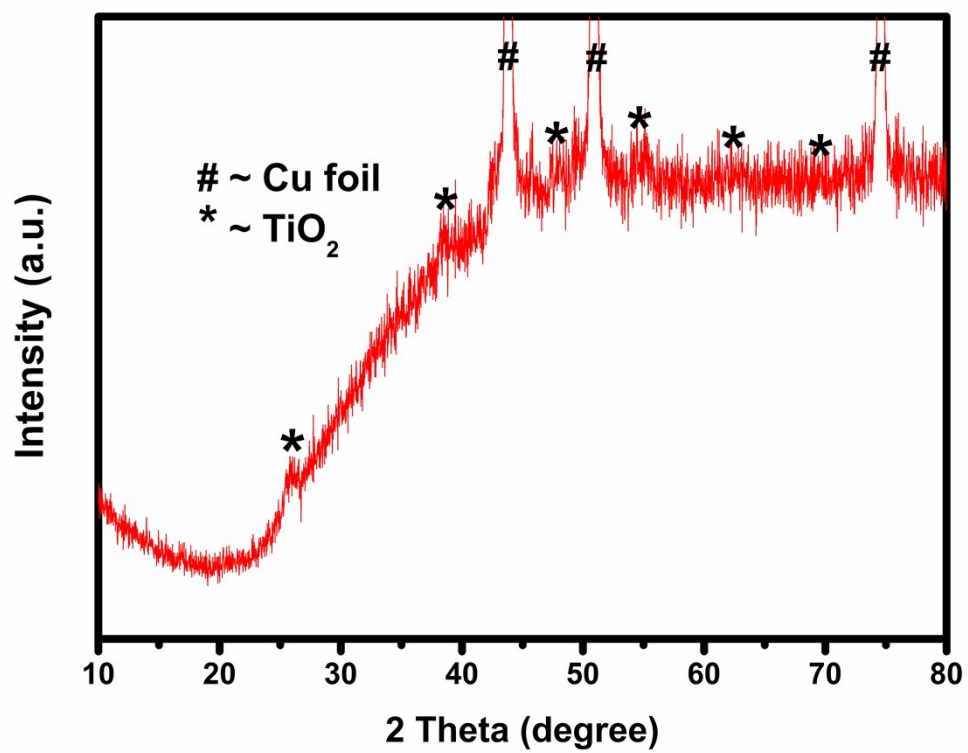


Fig. S9 *Ex-situ* XRD pattern of the Fe₃O₄/(TiO₂)₇₀ SPs after cycling.

Table S2 Lithium storage performance comparison between $\text{Fe}_3\text{O}_4/(\text{TiO}_2)_{70}$ SPs and representative TiO_2 -based composite anode materials.

Materials	Weight ratio (%)	Capacity (mAh g^{-1})	Cycles	Current density (mA g^{-1})	References
Hierarchical nanofibrous Fe_3O_4 - TiO_2 -carbons composite	32.5 of Fe_3O_4 content	525	100	100	S1
Carbon-coated $\text{TiO}_2(\text{B})$ nanosheets decorated with Fe_3O_4 nanoparticles	$\text{TiO}_2:\text{Fe}_3\text{O}_4:\text{C}$ 72.31:19.23:7.99	763	200	500	S2
Fe_3O_4 -nanoparticle-decorated TiO_2 nanofiber hierarchical heterostructures	18.2 of iron content	454.5	200	100	S3
		187.8	400	1000	
Nanoporous $\text{TiO}_2/\text{Co}_3\text{O}_4$ composite	$\text{TiO}_2:\text{Co}_3\text{O}_4$ 70.5:29.5	290	500	100	S4
ZnO decorated TiO_2 nanosheet composites	$\text{TiO}_2:\text{ZnO}$ 66.2:33.8	340.2	100	200	S5
Hierarchal mesoporous $\text{SnO}_2@\text{C}@\text{TiO}_2$ nanochains	73.7 of TiO_2 content	369	100	100	S6
Porous ternary $\text{TiO}_2/\text{MnTiO}_3@\text{C}$ hybrid microspheres	$\text{TiO}_2:\text{MnTiO}_3:\text{C}$ 75.09:20.18:4.73	402.6	300	100	S7
Lattice-mismatched core-shell $\text{TiO}_2@\text{MoS}_2$	$\text{TiO}_2:\text{MoS}_2$ 25.9:74.1	632	100	100	S8
$\text{Fe}_3\text{O}_4/(\text{TiO}_2)_{70}$ SPs	$\text{TiO}_2:\text{Fe}_3\text{O}_4:\text{C}$ 82:7.7:10.3	526	100	100	This work
		550	400	1000	

References

- (S1) Li, S.; Wang, M.; Luo, Y.; Huang, J. Bio-Inspired Hierarchical Nanofibrous Fe₃O₄-TiO₂-Carbon Composite as a High-Performance Anode Material for Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 17343-17351.
- (S2) Xu, H.; Zhu, X. D.; Sun, K. N.; Liu, Y. T.; Xie, X. M. Elaborately Designed Hierarchical Heterostructures Consisting of Carbon-Coated TiO₂(B) Nanosheets Decorated with Fe₃O₄ Nanoparticles for Remarkable Synergy in High-Rate Lithium Storage. *Adv. Mater. Interfaces* **2015**, *2*, 1500239.
- (S3) Wang, H.; Wang, G.; Yuan, S.; Ma, D.; Li, Y.; Zhang, Y. Fe₃O₄-Nanoparticle-Decorated TiO₂ Nanofiber Hierarchical Heterostructures with Improved Lithium-Ion Battery Performance over Wide Temperature Range. *Nano Res.* **2015**, *8*, 1659-1668.
- (S4) Zhao, D.; Hao, Q.; Xu, C. Nanoporous TiO₂/Co₃O₄ Composite as an Anode Material for Lithium-Ion Batteries. *Electrochim. Acta* **2016**, *211*, 83-91.
- (S5) Gao, L.; Li, S.; Huang, D.; Shen, Y.; Wang, M. ZnO Decorated TiO₂ Nanosheet Composites for Lithium Ion Battery. *Electrochim. Acta* **2015**, *182*, 529-536.
- (S6) Luo, G.; Liu, W.; Zeng, S.; Zhang, C.; Yu, X.; Fang, Y.; Sun, L. Hierarchal Mesoporous SnO₂@C@TiO₂ Nanochains for Anode Material of Lithium-Ion Batteries with Excellent Cycling Stability. *Electrochim. Acta* **2015**, *184*, 219-225.
- (S7) Guo, S.; Liu, J.; Qiu, S.; Liu, W.; Wang, Y.; Wu, N.; Guo, J.; Guo, Z. Porous Ternary TiO₂/MnTiO₃@C Hybrid Microspheres as Anode Materials with Enhanced Electrochemical Performances. *J. Mater. Chem. A* **2015**, *3*, 23895-23904.
- (S8) Dai, R.; Zhang, A.; Pan, Z.; Al-Enizi, A. M.; Elzatahry, A. A. Hu, L.; Zheng, G. Epitaxial

Growth of Lattice-Mismatched Core-Shell $\text{TiO}_2@\text{MoS}_2$ for Enhanced Lithium-Ion Storage. *Small*

2016, *12*, 2792-2799.