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Supporting Information

Hierarchically porous anatase TiO_2 microspheres composed of tiny octahedra with enhanced electrochemical properties in lithium-ion batteries \dagger

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Fig. S1 Anatase TiO₂ obtained at 120 °C for different times: (a) XRD patterns, and SEM images of (b) 1, (c) 1.5 and (d) 6 h.



Fig. S2 N_2 adsorption-desorption isotherms of anatase TiO₂ obtained at 120 °C for 12 h.



Fig. S3 SEM images of hierarchical TiO₂ microspheres (a) before discharge-charge and (b) after 200 discharge-charge at 10 C.

s In order to further understand the enhanced electrochemaical properties of hierarchical TiO_2 microspheres, the morphology of hierarchical TiO_2 microspheres after 200 cycles charge/discharge was investigated. As showed in Fig. S3, the microspherical structures mainly can be retained.

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Hierarchical TiO ₂	Discharge capacity (mA h g ⁻¹)	Current density (mA g ⁻¹)	Reference
Hierarchical TiO ₂ composed of tiny octahedra	142.3 (after 200 cycles)	1680	Present work
Hierarchical TiO ₂ composed of nanosheets	136 (after 100 cycles)	850	S1
TiO ₂ composed of nano-grains	135 (after 5 cycles) 108 (after 500 cycles)	1675	S2
Spherical TiO ₂ composed of nanowires	102 (after 50 cycles)	1000	S 3
Hierarchical TiO ₂ composed of nanorods	129.1 (after 100 cycles)	850	S4
Hierarchical TiO ₂ with high surface area of 221.9 $m^2 g^{-1}$ **	229 (after 100 cycles)	1685	S5

Table 1 Summary of discharge capacity for various hierarchical TiO₂ as an anode for LIBs.

** the sample contains brookite TiO₂.

⁵ [S1] J. S. Chen, Y. L. Tan, C. M. Li, Y. L. Cheah, D. Luan, S. Madhavi, F. Y. C. Boey, L. A. Archer and X. W. Lou, *J. Am. Chem. Soc.*, 2010, **132**, 6124.

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[S4] L. Gao, X. Li, H. Hu, G. Li, H. Liu and Y. Yu, *Electrochi. Acta*, 2014, **120**, 231.

¹⁰ [S5] J. Y. Shin, D. Samuelis and J. Maier, *Adv. Funct. Mater.*, 2011, **21**, 3464.

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