Supporting Information

Hierarchical Nanosheet-constructed Yolk-shell TiO_2 Porous Microspheres for Lithium Batteries with High Capacity, Superior Rate and Long Cycle Capability

Jun Jin,[a] Shao-Zhuan Huang,[a] Yu Li,[a, *] He Tian,[b] Hong-En Wang,[a] Yong Yu,[a]

Li-Hua Chen,[a] Tawfique Hasan[c] and Bao-Lian Su[a, d, e, *]

[a]*Laboratory of Living Materials at the State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 122 Luoshi Road, 430070 Wuhan, Hubei, China; Email:* yu.li@whut.edu.cn *and* baoliansu@whut.edu.cn

[b]*Center of Electron Microscopy and State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, 310027 Hangzhou, Zhejiang, China.*

[c]*Cambridge Graphene Centre, University of Cambridge, Cambridge, CB3 0FA, United Kingdom.*

[d]*Laboratory of Inorganic Materials Chemistry (CMI), University of Namur, 61 rue de Bruxelles, B-5000 Namur, Belgium; E-mail:* bao-lian.su@unamur.be

[e]*Department of Chemistry and Clare Hall College, University of Cambridge, UK; E-mail:* bls26@cam.ac.uk

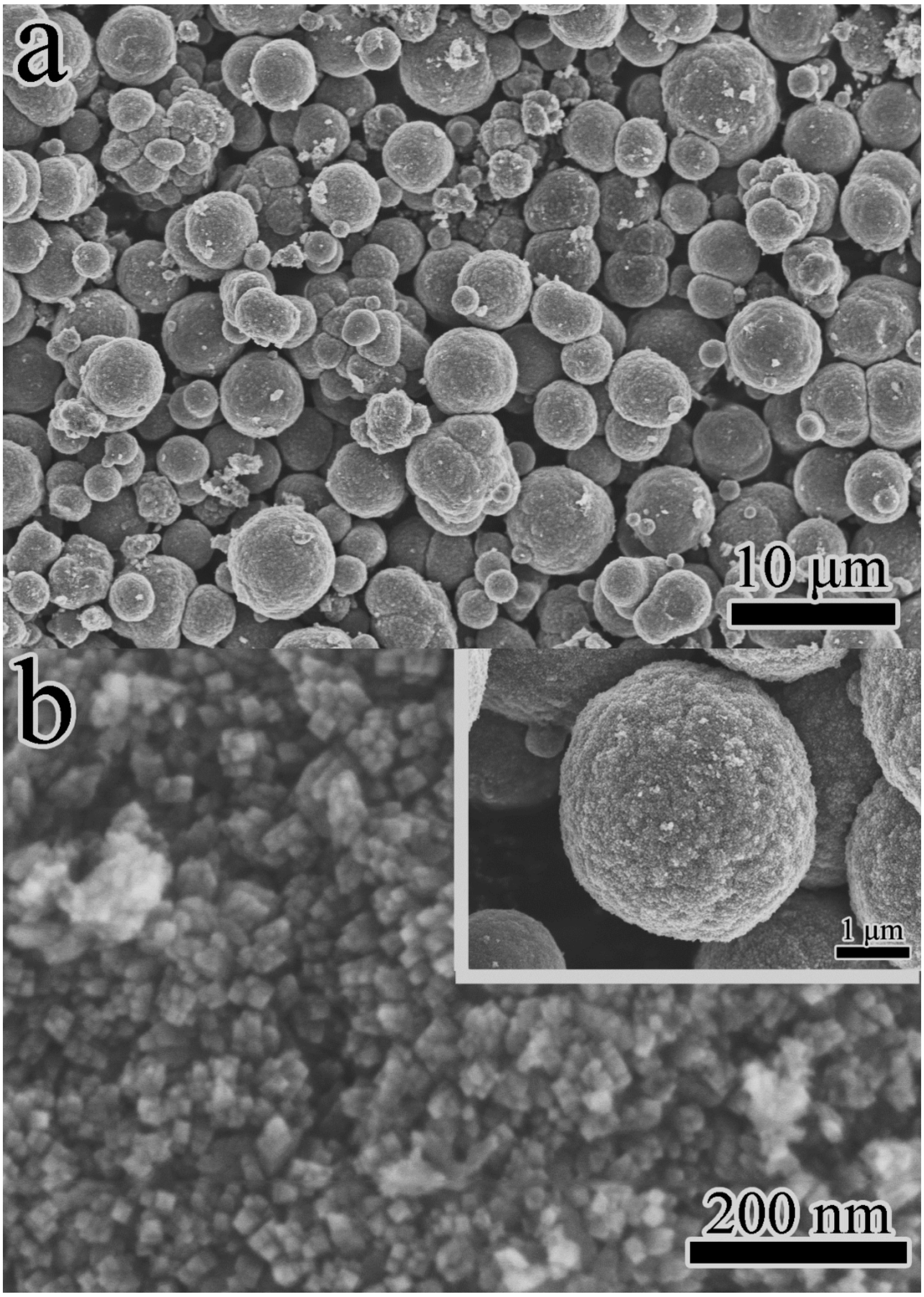

Fig. S1. (a) and (b) SEM images of TiO_2 samples without TEPA at 200 °C for 24 h. Inset of Fig. S1b is a higher magnification.

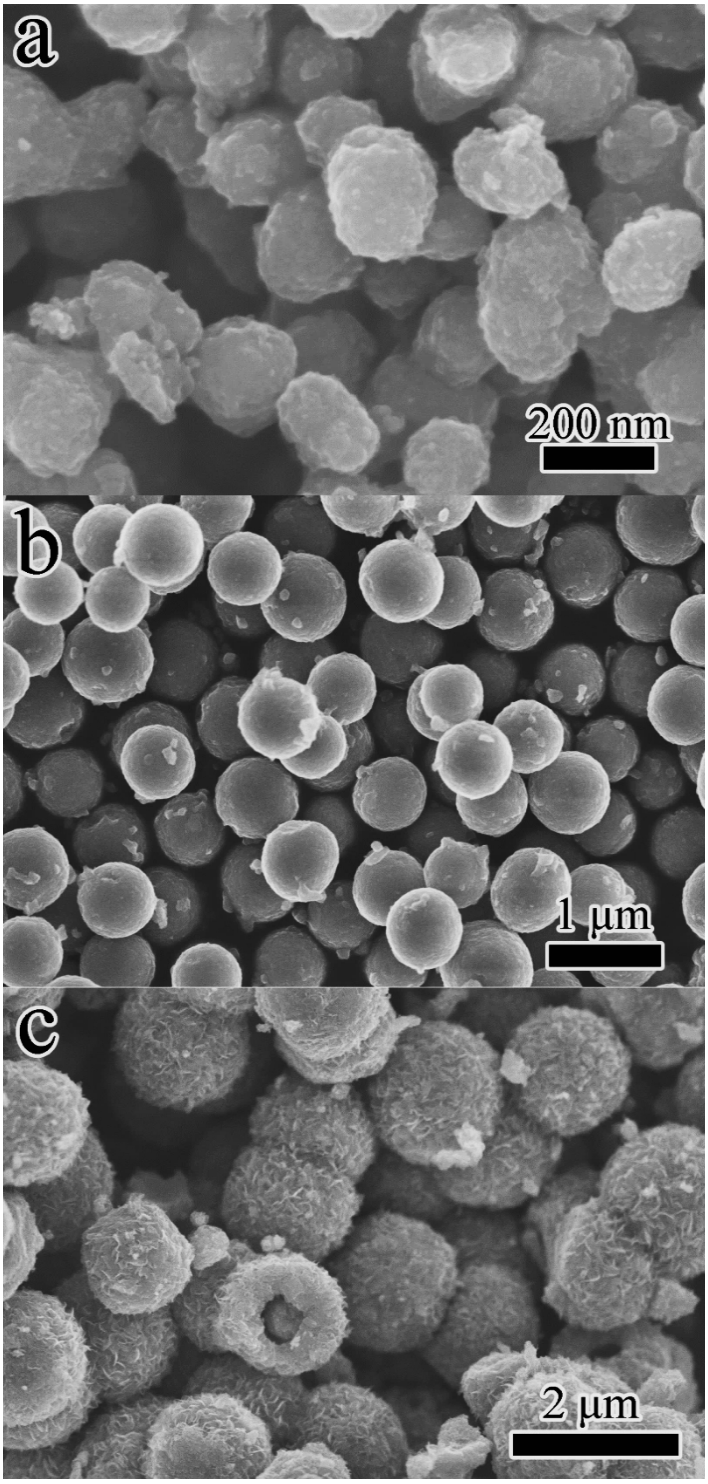

Fig. S2. SEM images of the products obtained at different reaction temperatures: (a) 160, (b) 180, (c) 200 °C for 24 h.

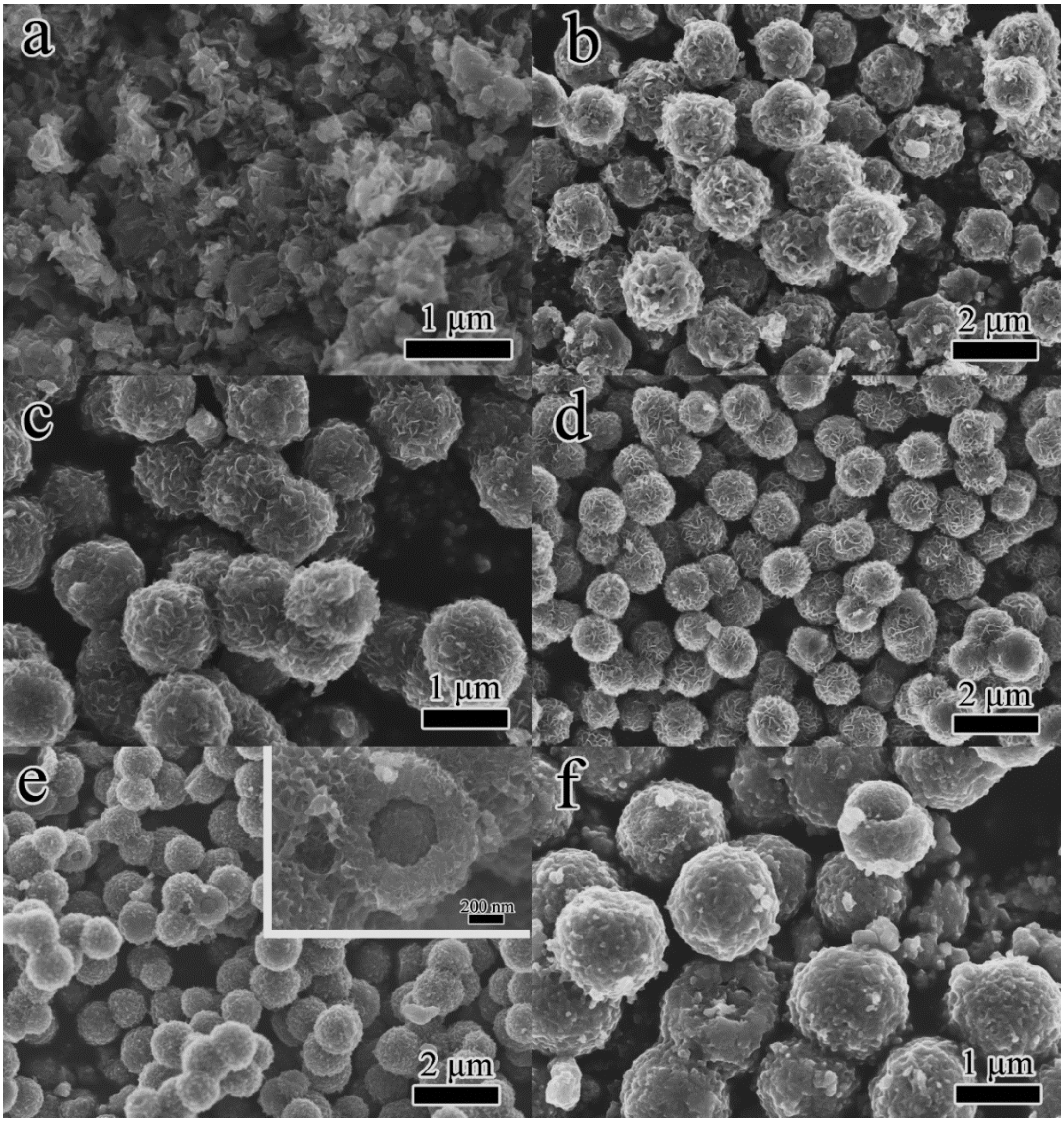

Fig. S3. SEM images of the products with various content of TEPA: (a) 0.01, (b) 0.03, (c) 0.06, (d) 0.09, (e) 0.12 and (f) 0.15 mL. Figure S3a shows that only a very small amount of nanosheet fragments is obtained at 0.01 mL TEPA. Figure S3b displays that plenty of nanosheets are assembled into spherical morphology and there are still some nanosheet fragments existing in the product. With the increase of TEPA, the product tends to be more spherical and uniform (Figure S3c and S3d). When the content of TEPA is increased to 0.12 mL, the morphology of the product becomes more spherical than any other content of TEPA (Figure S3e). Inset of Fig S3e is a higher magnification picture. When the TEPA is 0.15 mL, the nanosheet shell structure disappears (Figure S3f). Instead, the shell structure is replaced by many nanoparticles.

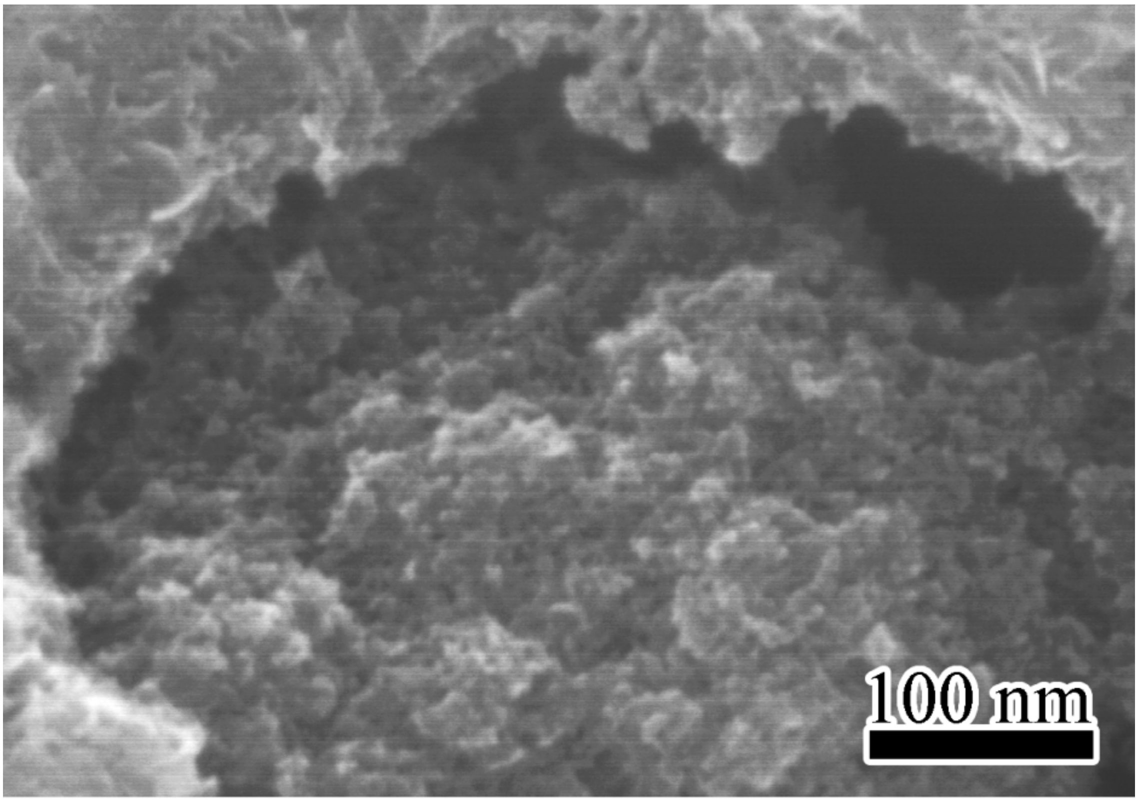

Fig. S4. Enlarged SEM image of Fig.1d.

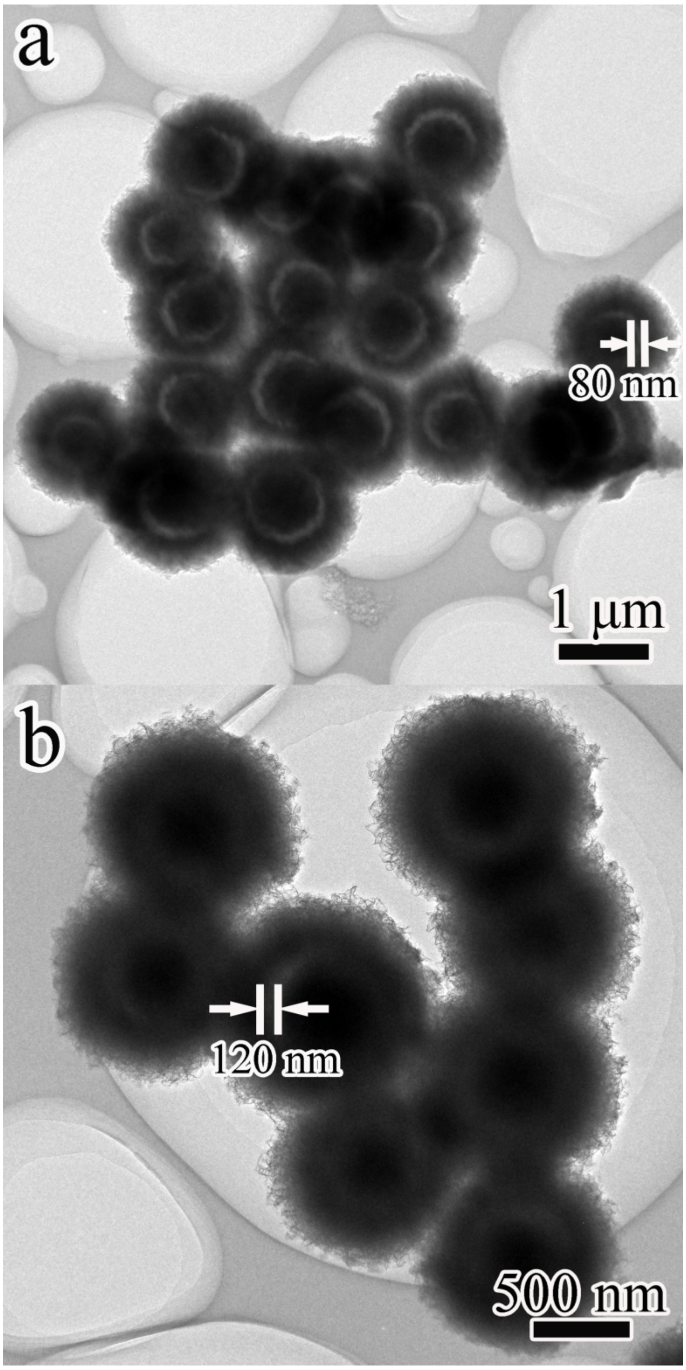

Fig. S5. (a) the enlarged TEM image of Fig. 1e and (b) enlarged TEM image of Fig. 3d, clearly displaying the enlarged voids between the shell and the core after calcination at 400 °C.

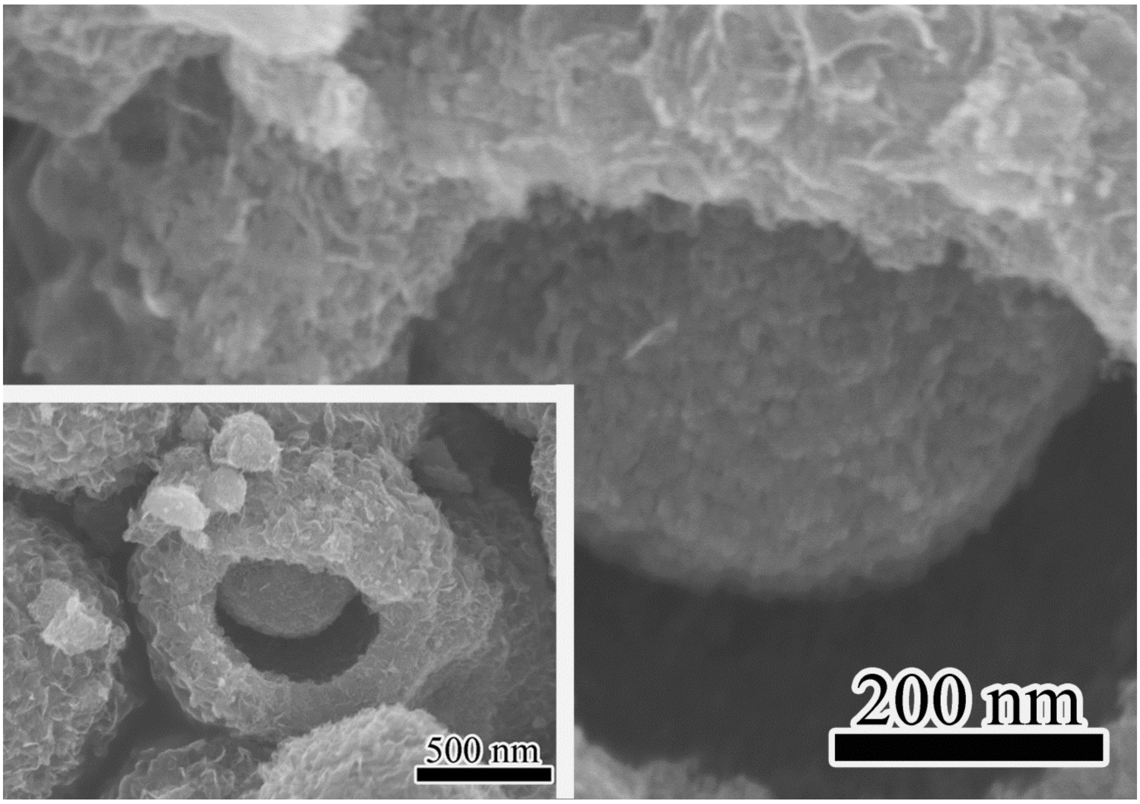

Fig. S6. The enlarged SEM image of Fig. 3c. Inset is a low magnification picture showing a broken yolk-shell organization of TiO_2.

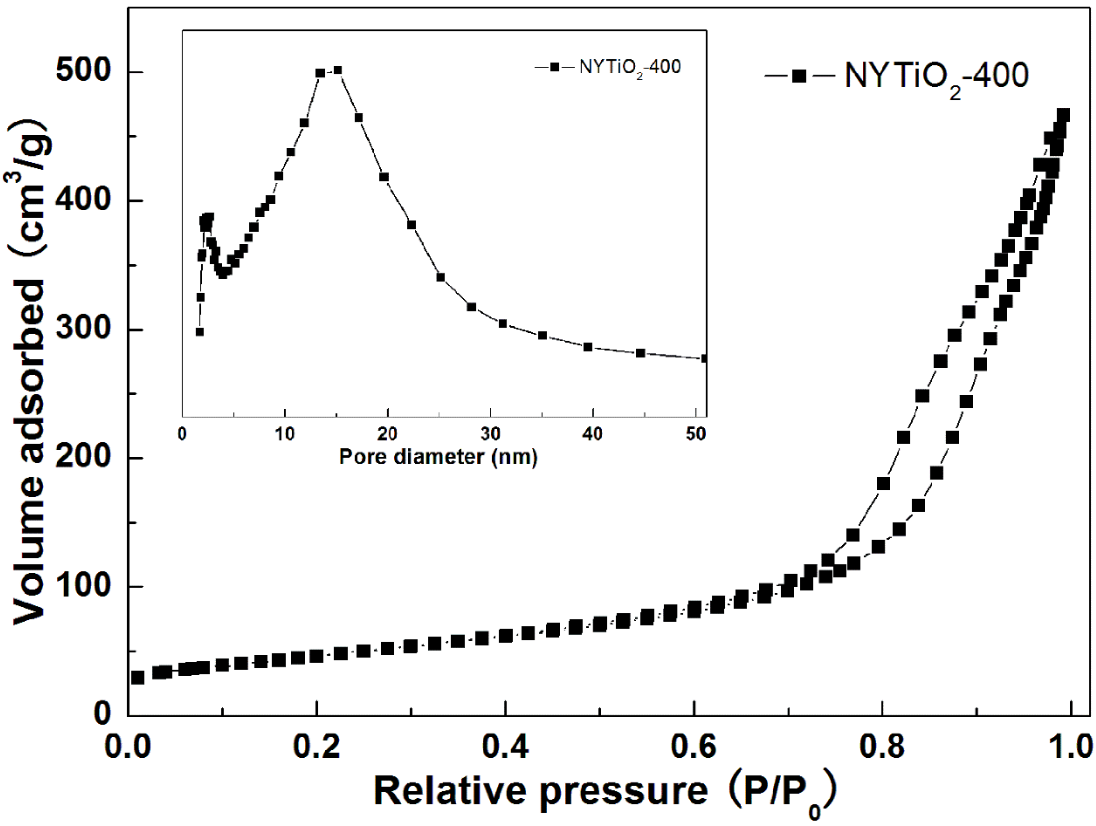

Fig. S7. Nitrogen adsorption-desorption isotherms and BJH pore size distribution plots (inset) of the $NYTiO_2$-400, clearly displaying dual pore sizes of 15 nm and 3 nm.

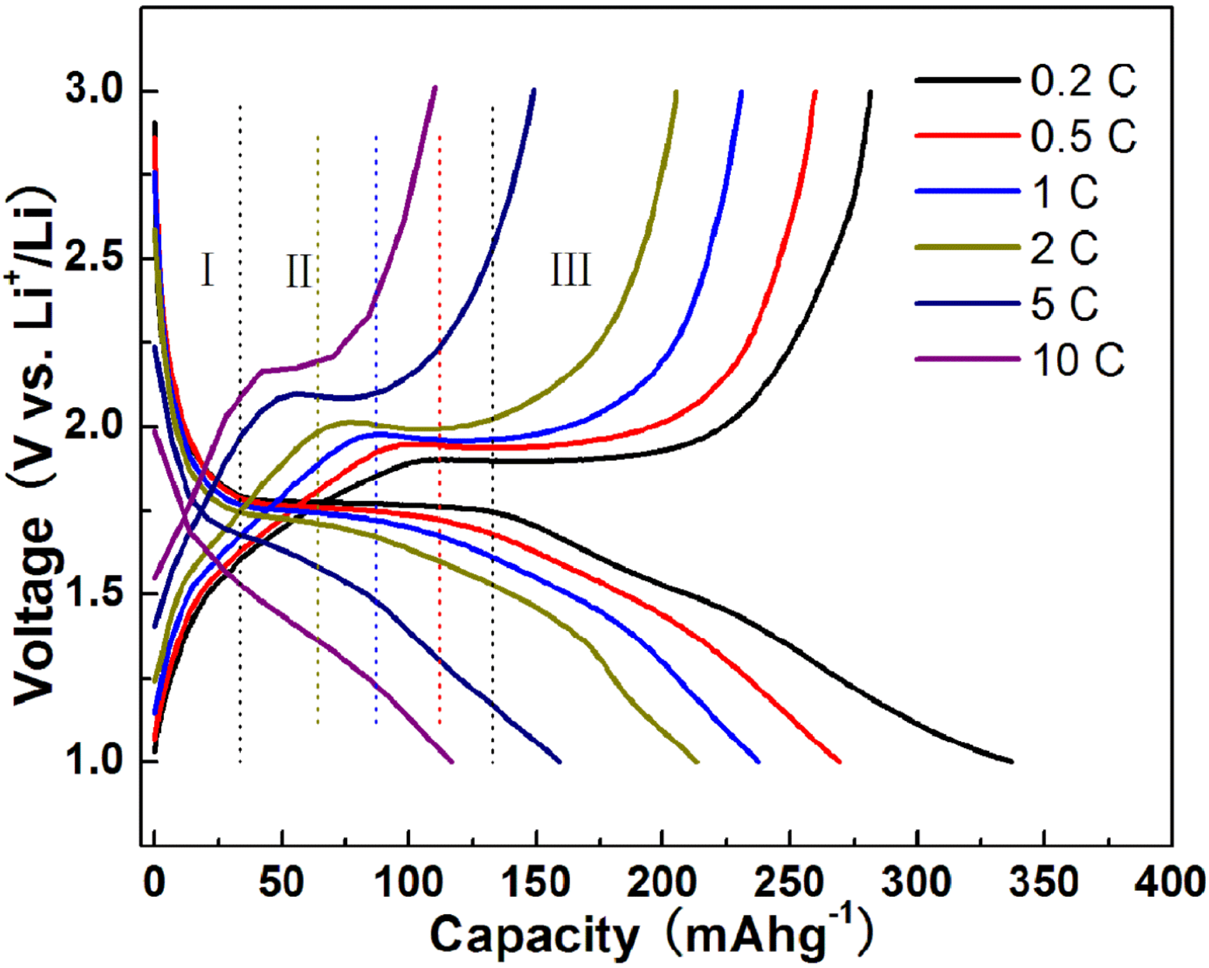

Fig. S8. The discharge-charge profiles at various discharge-charge rates shown in Fig. 4c. The dash lines indicate the different stages for the discharging process.

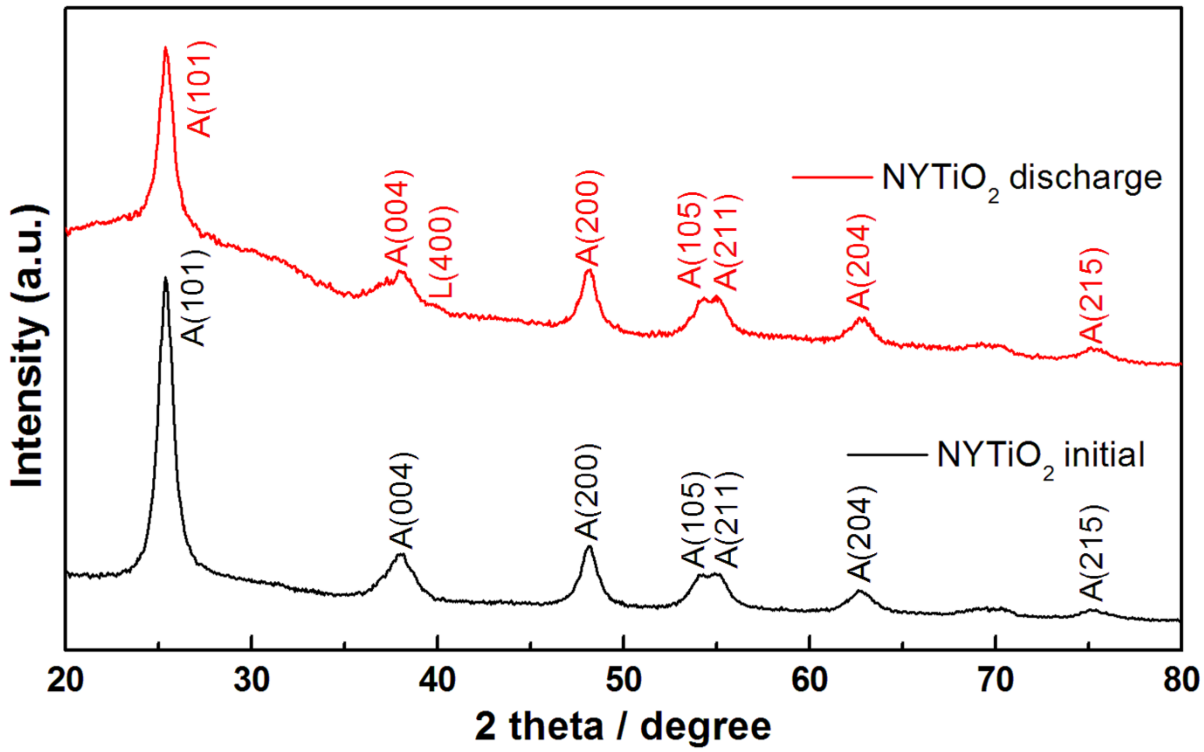

Fig. S9. XRD patterns of the as-prepared $NYTiO_2$-400 and *ex-situ* XRD patterns of the lithiated $NYTiO_2$-400 anode material. A and L represent the anatase and $L_2Ti_2O_4$ phases, respectively.