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High Lithium Electroactivity of Boron-doped Hierarchical Rutile Submicrospheres TiO_2

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Supplementary Figure & Table:

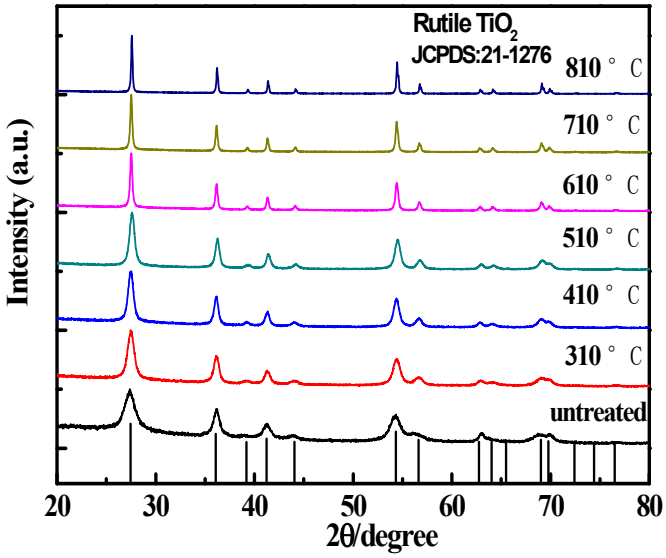

Figure S1. XRD patterns of the rutile samples prepared for different calcination temperature.

When the $TiCl_4$ was added dropwise into the deionized water continuously, the following reactions would occur:

$$TiCl_4 + H_2O \rightarrow TiOH^{3+} + H^+ + 4Cl^- \quad (1)$$

$$TiOH^{3+} \rightarrow TiO^{2+} + H^+ \quad (2)$$

$$TiO^{2+} + H_2O \rightarrow TiO_2 + 2H^+ \quad (3)$$

In addition,

$$B(OH)_3 + H_2O \rightarrow B(OH)_4 + H^+ \quad (4)$$

Obviously, the addition of boric acid increases the acidity of the reaction solution. Cheng et al. indicated that increasing the acidity in reaction medium favored of the formation for rutile type

TiO_2.[1] Chen et al. also found that The doping of boron could efficiently inhibit the grain growth and facilitate the anatase-to-rutile transformation prior to the formation of diboron trioxide phase. [2]Therefore, the samples prepared by the facial method could facilitate the formation of rutile type boron-doped TiO_2. This is in agreement with results of the XRD patterns.

Alternatively, during the aging of $TiCl_4$ aqueous sol, the complex of $[Ti(OH)_nCl_m]^{2-}$ (n+m=6) would form. [1]Yoon et al. also successfully synthesized hollow core□shell mesoporous TiO_2 spheres by a hydrothermal reaction without surfactant, followed by calcination at 500 °C. It was pointed out that, $TiCl_4$ formed a complex $[Ti(OH)_nCl_m]^{2-}$ (n+m=6) in the hydrothermal process, which on hydrolysis produced TiO_2 embryos that acted as seed for the growth of TiO_2. The linkage between the $[Ti(OH)_4Cl_2]^{2-}$ complex and TiO_2 embryos takes place by a dehydration reaction. As a result, the connection of TiO_2 nanoparticles and/or formation of mesopores occur in the TiO_2 samples.[3]

[1] Humin Cheng, Jiming Ma, Zhenguo Zhao, and Limin Qi. *Chem. Mater.* 1995, 7, 663-671
[2] Daimei Chen, Dong Yang, Qun Wang, and Zhongyi Jiang, *Ind. Eng. Chem. Res*. 2006, 45, 4110-4116
[3] Sukeun Yoon and Arumugam Manthiram. J. Phys. Chem. C 2011, 115, 9410–9416

Table S1 Crystallite and particle sizes obtained from XRD results for TiO_2 particles calcined at various temperatures

Calcinated temp., °C	Crystal phase	Crystallite size, nm
untreated	Rutile	8.7
310	Rutile	11.1
410	Rutile	14.5
510	Rutile	15.1
610	Rutile	36.8
710	Rutile	44.5
810	Rutile	86.8

Their average crystallite sizes were calculated from the broadening of the (110) XRD peak of the rutile phase, according to the Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where D is the crystal size, λ the X-ray wavelength (1.5418Å), β the full width at half maximum (FWHM) of the diffraction peak and θ is the diffraction angle. From the FigureS1 and Table S1, at higher calcination temperatures, the crystallites formed are larger in size, which can be attributed to the thermally promoted crystallite growth.