Supporting information

on

Black Anatase Titania Enabling Ultra High-Rate Cycling for Rechargeable Lithium Batteries

by

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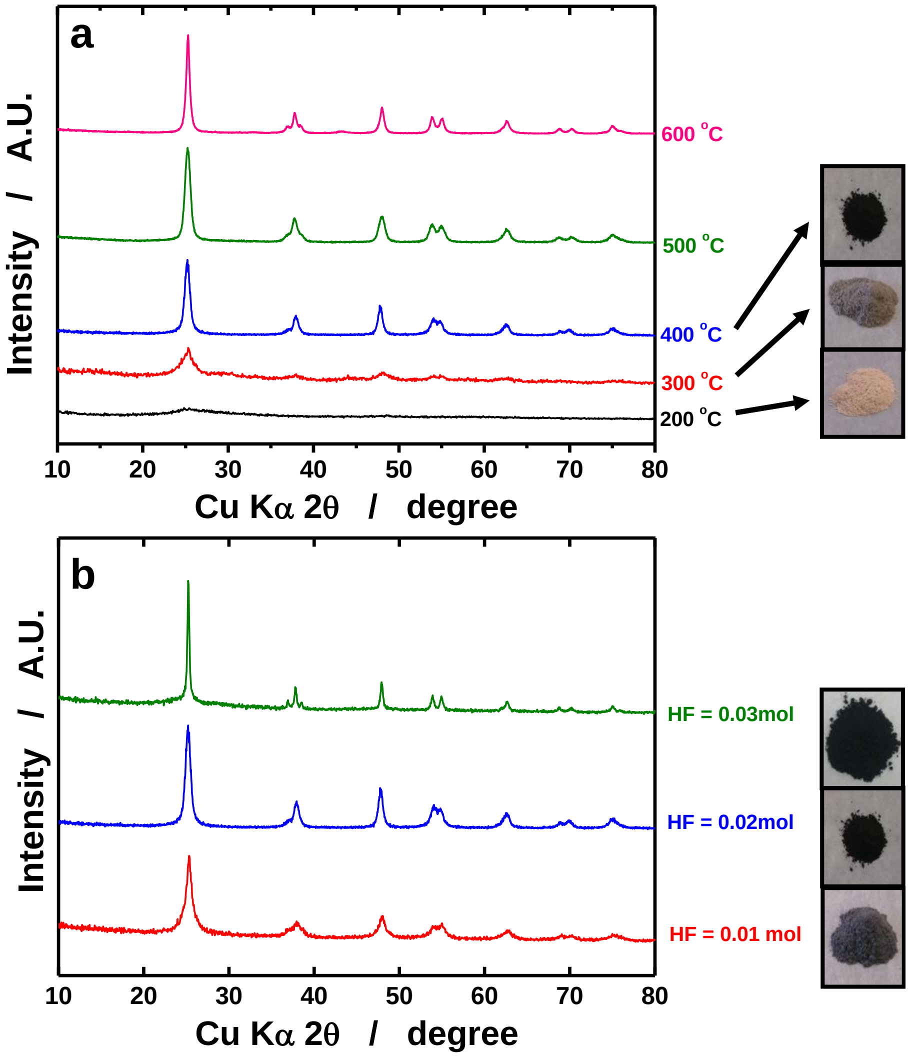
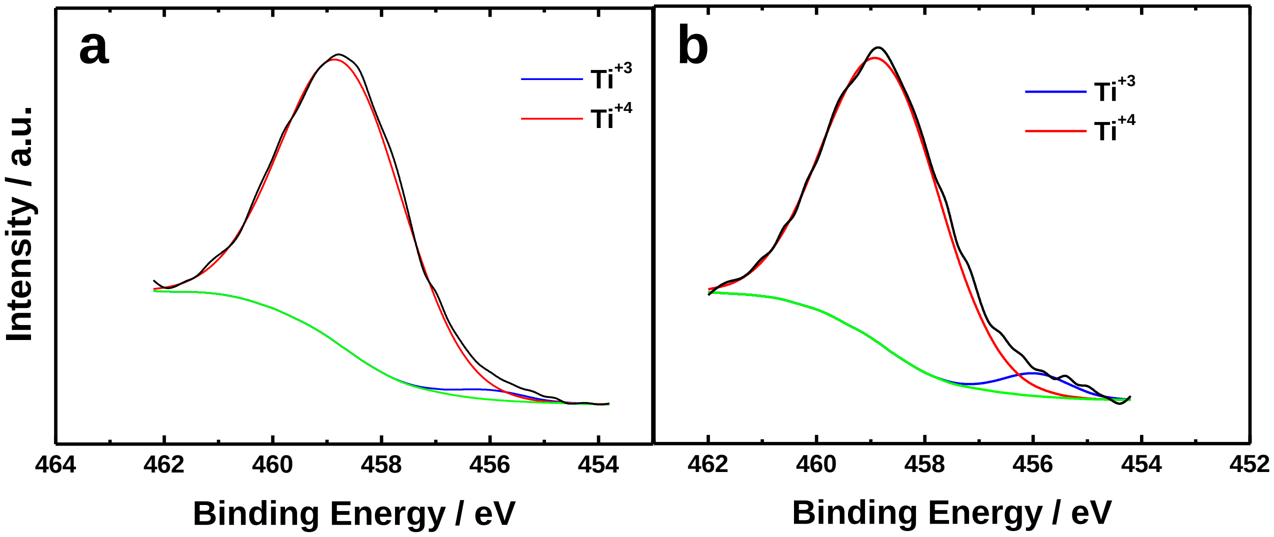


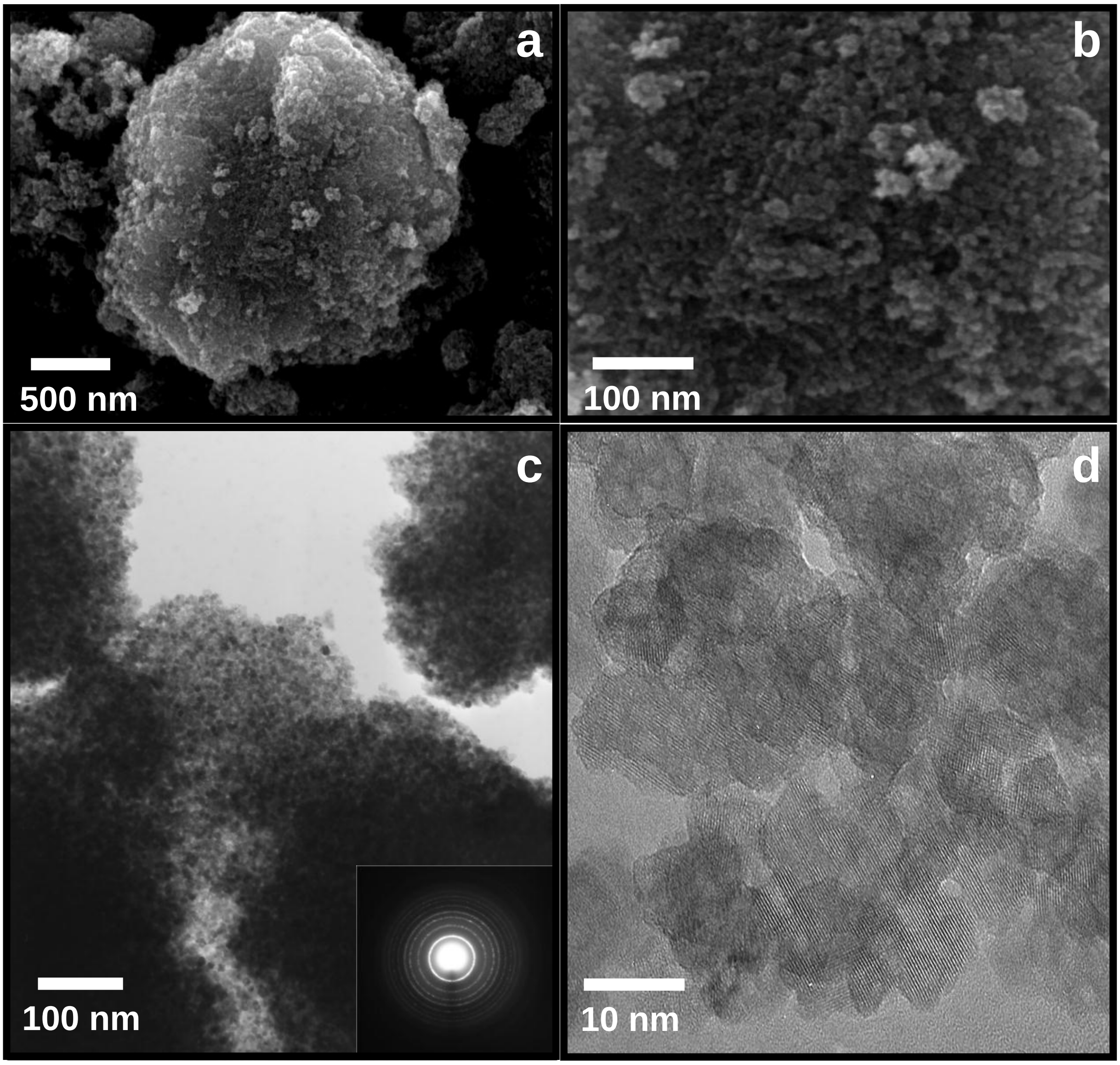
S-Figure 1. (a) XRD patterns of light yellow gel heated at various temperatures for 5 h in Ar atmosphere; (b) light yellow gel varying HF concentration heated at 400 °C for 5 h in Ar atmosphere.

Dissolution of Ti^{IV} ($TiCl_4$ (IV)) readily produces the Ti^{3+} ion in acidic media below pH 2 (here, HF was used) [21]. In course of the synthesis, urea ($(NH_2)_2CO$) was added to delay hydrolysis of Ti^{4+} to $Ti(OH)_4$ in the present work. Transparent light yellow gel is received after evaporation of the solution at 80 °C, and consequent heating of the resultant at 200 °C leads to dark yellow powders with low crystallinity (5h in Ar, S-Fig. 1a). Further heat treatments at elevated temperatures, surprisingly, alter the colors of the products, gray at 300 °C and black at 400 – 600 °C, and the resulting crystallinity for X-ray diffraction (XRD) patterns is progressively developed with temperatures. Also, the crystallinity and colors of the powders are dependent on the added amount of HF in the starting solution (S-Fig. 1b). For comparison, the calcination was also performed in air atmosphere (400 °C for 5 h). Products produced in air and Ar exhibit a typical anatase type TiO_2 as confirmed in X-ray diffraction (XRD) patterns (Fig. 1a and S-Fig. 1). Besides, the powders obtained in air shows the same white color as ordinary anatase TiO_2.



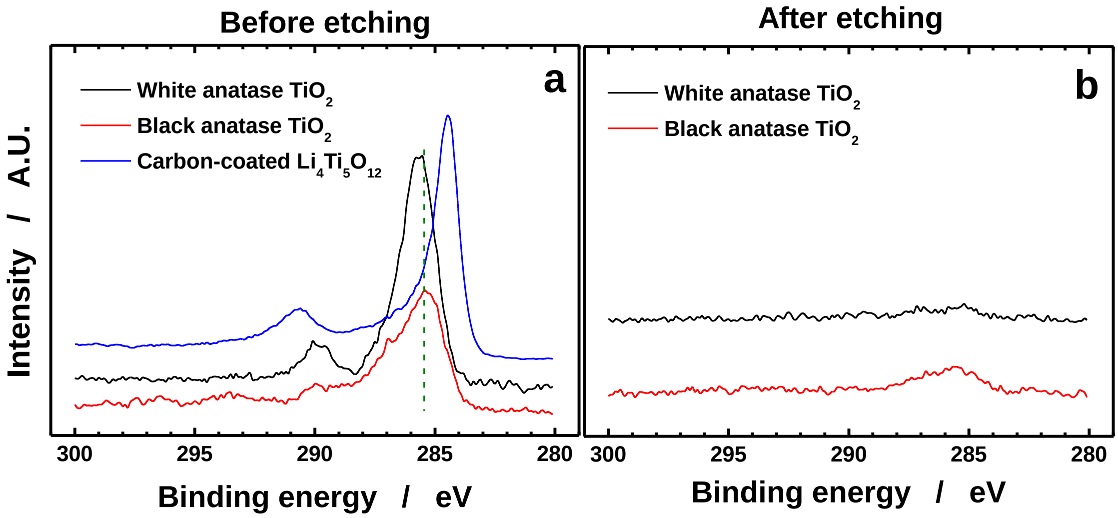
S-Figure 2. XPS spectrum of the black anatase TiO_2 heated at 400 °C for 5 h in Ar: HF concentration was (a) 0.1 mol and (b) 0.3 mol for the starting solution.)

From the XPS specturum, compared with the simulated Ti^{3+} ($Ti^{III}N$, blue line) and Ti^{4+} ($Ti^{III}O_2$, red line) spectrua, the calculated content of the trivalent Ti is found to be 2.1 % (for the 0.1 mol HF starting solution) and 7.2 % (for the 0.3 mol HF starting solution) present in the surface region, implying that much acidic environment from solution gives rise to the further formation of the trivalent Ti.



S-Figure 3. SEM images of black anatase TiO_2 heated at 400 ^{o}C for 5 h in Ar: (a) low and (b) high magnification; TEM bright-field images: (c) low (inset: SAD pattern) and (d) high magnification.

SEM images display that the synthesized TiO_2 powders are agglomerates and they are nanoparticles. TEM images also reveals that the particles are high agglomerated showing polycrystalline diffraction pattern.



S-Figure 4. Comparison of Cls XPS spectra of white anatase TiO_2, black anatase TiO_2, and carbon-coated spinel $Li_4Ti_5O_{12}$: (a) before Ar^+ etching and (b) after Ar^+ etching for 10 min (corresponding to 2.7 nm in depth for the standard SiO_2 powders) in N_2 atmosphere.

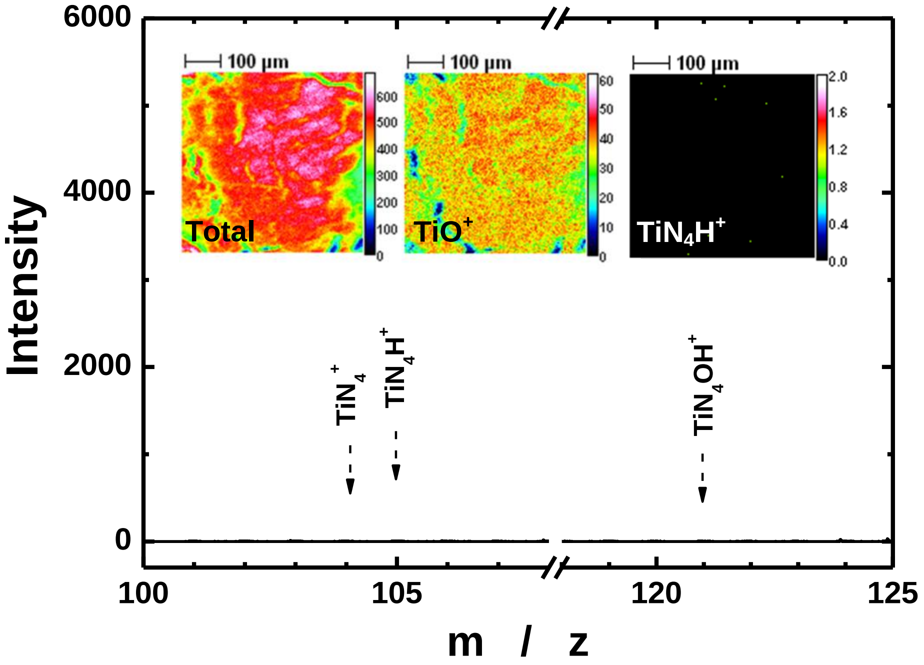
The above data represent XPS C1s spectra for both white and black anatase TiO_2. Carbon-coated $Li_4Ti_5O_{12}$ was also added to compare the presence of carbon on the surface. Air-formed carbon layers (C with N, S, and O) are mainly observed in range of 284 – 288 eV for both black and white anatase TiO_2 before Ar^+ etching. Another peak observed at 288 – 291 eV would be ascribed to the carbonate layer formed in air. In comparison with the carbon-coated $Li_4Ti_5O_{12}$ (carbonized from pitch showing high intensity of G-band in Raman spectroscopy), carbon-derived peak is evident at 284.5 eV. Furthermore, carbide-related trace is not found in range of 280.5 – 283 eV both black and white anatase TiO_2 before and after Ar^+ etching for 10 min corresponding 2.7 nm in depth. The above results indicate that carbon is not doped in the black anatase TiO_2 nor not coated on the surface of black anatase TiO_2.

S-Table I. Rietveld refinement results of XRD pattern for TiO_2 calcined at 400 ^{o}C for 5 h in Air (white).

Formula			TiO_2			
Crystal system			Tetragonal			
Space group			$I4_1/amd$			
Atom	Site	*X*	*Y*	*Z*	*g*	B / Å^2
Ti	4*b*	0	0.25	0.375	1	0.8
O	8*e*	0	0.25	0.165(3)	1	0.8
a-axis / Å			3.7887(2)			
c-axis / Å			9.4894(7)			
Ti-O1 / Å			1.9327(7)			
Ti-O2 / Å			1.9956(16)			
R_{wp} / %			11.1			
R_p / %			8.90			

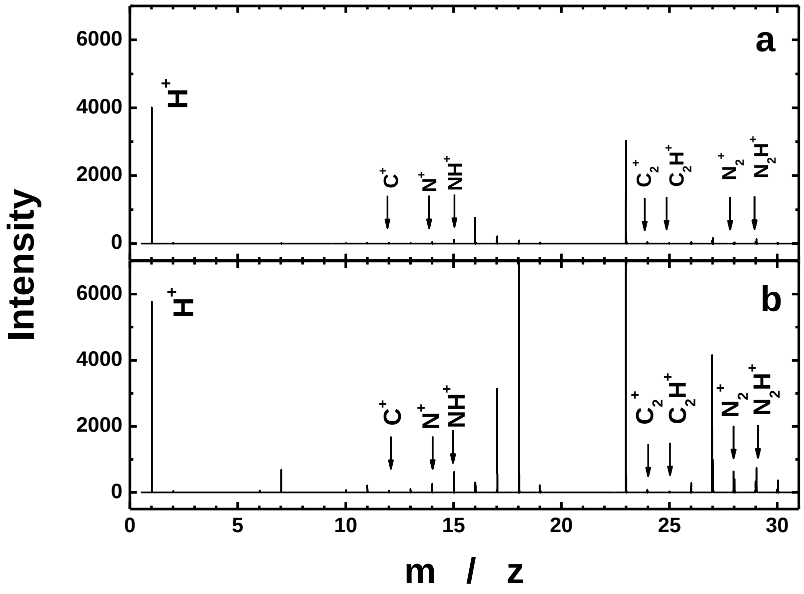
S-Table II. Rietveld refinement results of XRD pattern for TiO_2 calcined at 400 ^{o}C for 5 h in Ar (black).

Formula			TiO_2			
Crystal system			Tetragonal			
Space group			$I4_1/amd$			
Atom	Site	*X*	*Y*	*Z*	*g*	B / Å^2
Ti	4*b*	0	0.25	0.375	1	0.8
O	8*e*	0	0.25	0.164(4)	1	0.8
a-axis / Å			3.8038(3)			
c-axis / Å			9.5148(7)			
Ti-O1 / Å			1.9382(7)			
Ti-O2 / Å			1.9991(16)			
R_{wp} / %			12.9			
R_p / %			9.29			



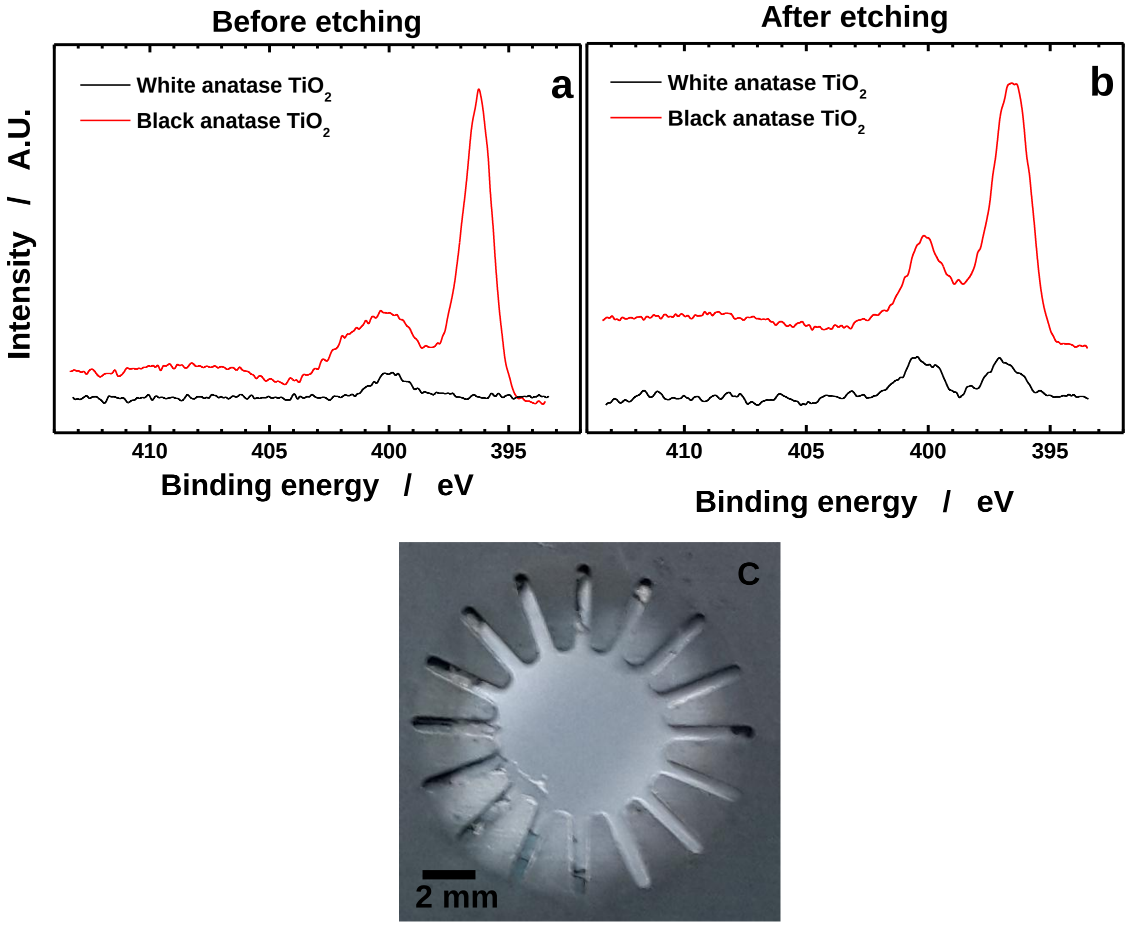
S-Figure 5. ToF-SIMS spectrum for the white anatase TiO_2 heated at 400 ^{o}C for 5 h in air.

It is evident that the white anatase TiO_2 does not show any fragment related with the Ti-N-O-H bond, which is identified as TiN_4^+ (m = 104), TiN_4H^+ (m = 105), and TiN_4OH^+ (m = 121) in the black anatase TiO_2.



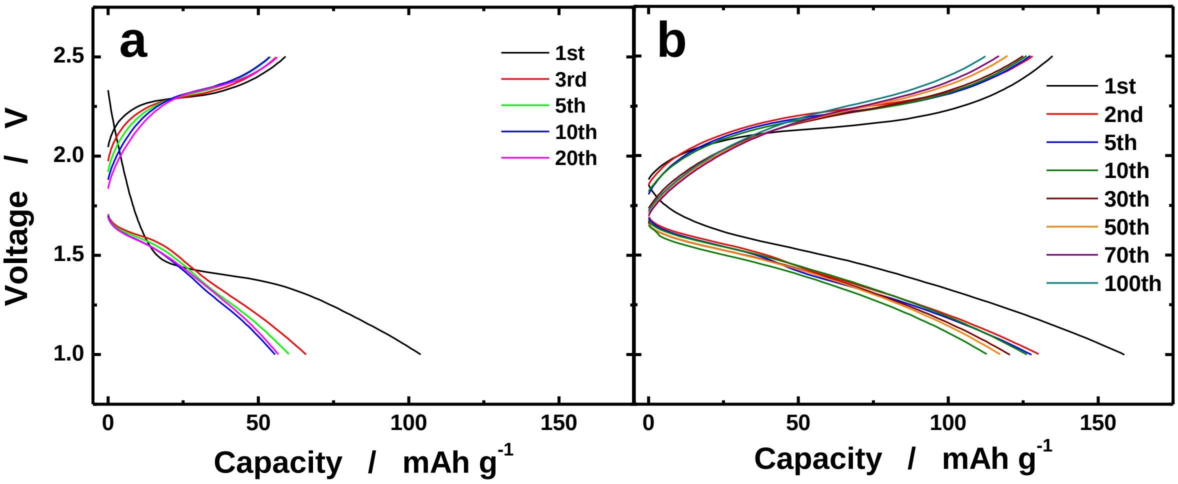
S-Figure 6. ToF-SIMS spectra of (a) white anatase TiO_2 heated at 400 ^{o}C for 5 h in air and (b) black anatase TiO_2 heated at 400 ^{o}C for 5 h in Ar.

It is further demonstrated by ToF-SIMS data that the present black anatase is carbon-free product, because carbon-related fragments such as C^+ (m = 12), C_2^+ (m = 24), and C_2H^+ (m = 25) (See Fig. b), are not detected in the spectra (see Figure S-6b). Provided that they present, the resulting spectra should be notable like N-related fragments, N^+ (m = 14), NH^+ (m = 15), N_2^+ (m = 28), N_2H^+ (m = 28) (see Figure S-5b). On the contrary, these fragments are not perceived for the white anatase TiO_2(see Figure S-6a).



S-Figure 7. Comparison of Nls XPS spectra of white anatase TiO_2 and black anatase TiO_2, and carbon-coated spinel $Li_4Ti_5O_{12}$: (a) before Ar^+ etching, (b) after Ar^+ etching for 10 min (corresponding to 2.7 nm in depth for the standard SiO_2 powders) in N_2 atmosphere, and (c) digital camera image of white anatase TiO_2 after Ar^+ etching for 10 min in N_2 atmosphere.

It is evident for the white anatase TiO_2 that only contaminates layer, probably NO_x formed in air, is found in range of 399 – 401 eV. Meanwhile, nitride-related layer (395 – 398 eV) and contaminates layer (399 – 401 eV) with ammonium salt (NH_4^+, 401 – 404 eV) are found for the black anatase TiO_2 in S-Fig. 7a, confirming the presence of TiN_4H^+ fragment in ToF-SIMS data (shown in Fig. 2a). Therefore, the absence of TiN_4H^+ fragment in ToF-SIMS data (S-Figs. 5 and 6) is proved in the XPS spectrum for the white anatase TiO_2 that does not show the binding energy of ammonium salt (NH_4^+, 401 – 404 eV) in S-Fig. 7b.
Since Ar^+ etching was carried out in N_2 atmosphere, adhesion or incorporation N element is possible so that the white surface was changed to black as shown in S-Fig. 7c. For the reason, nitride-related peak is observed for the white anatase TiO_2. Also, one can able to understand the ready formation of the trivalent Ti after the Ar^+ etching in N_2 atmosphere (see S-Fig. 7b). Again, the above XPS data clarify the presence of Ti-N-H bond in the black anatase TiO_2.



S-Figure 8. Continuous charge and discharge curves of black anatase TiO_2 heated at 400 ^{o}C for 5 h in Ar: (a) starting HF concentration: 0.1 mol and (b) 0.3 mol.

Electronic conductivity is also dependent on the starting HF content, since the acidity of the starting solution affect the formation of trivalent Ti: the lower solution pH, the higher trivalent Ti concentration in the black anatase TiO_2, as is found in the XPS data (see S-Fig. 2). As a result, the electronic conductivity is improved from 1.5 x 10^{-3} S cm^{-1} for the gray anatase TiO_2 (for the 0.1 mol HF starting solution) to 8.9 x 10^{-2} S cm^{-1} for the black anatase TiO_2 (for the 0.3 mol HF starting solution)).Since the formation of the trivalent Ti is favored in much acidic environment, here 0.3 mol HF added (S-Fig. 5b), the black anatase TiO_2, which exhibits black color in S-Fig. 1b, delivers high capacity and superior retention at 100 C-rates (20 A g^{-1}) charge and discharge test.