

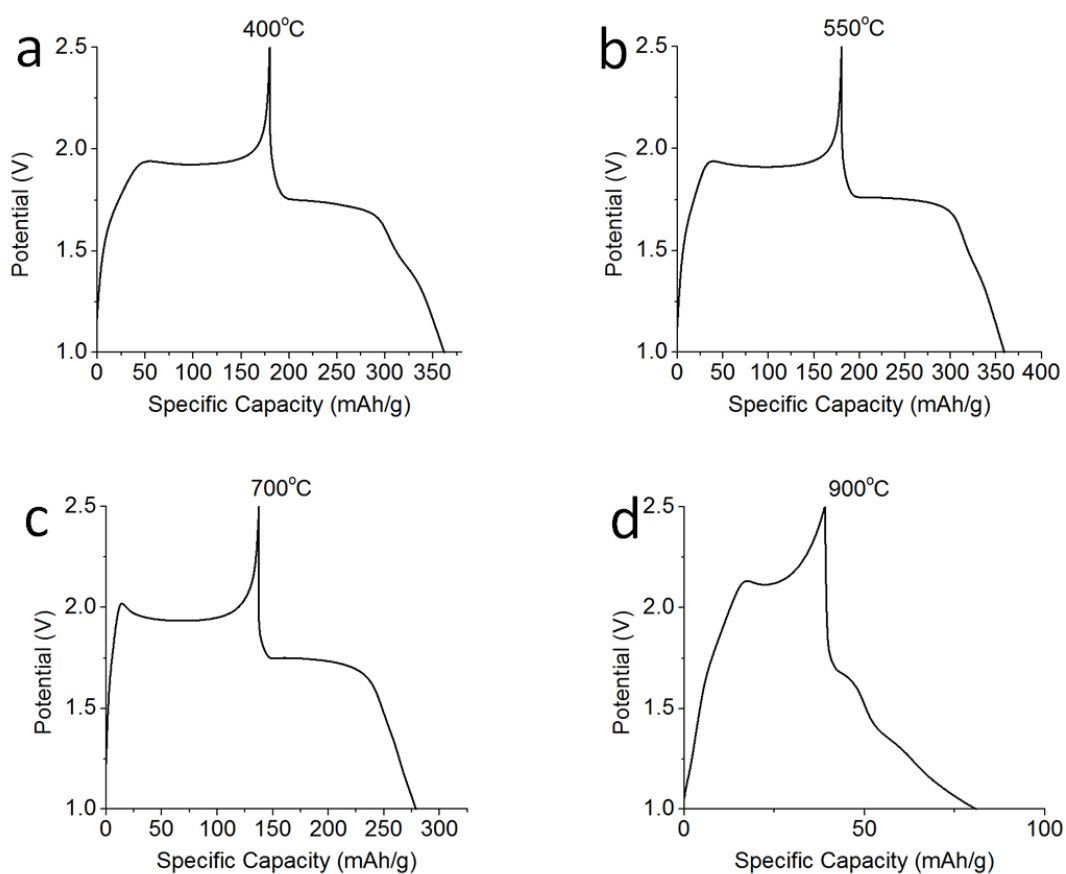
## Gram-Scale Synthesis of High-Temperature (900°C) Stable Anatase TiO<sub>2</sub> Nanostructures

### Assembled by Tunable Building Subunits for Safer Lithium Ion Batteries

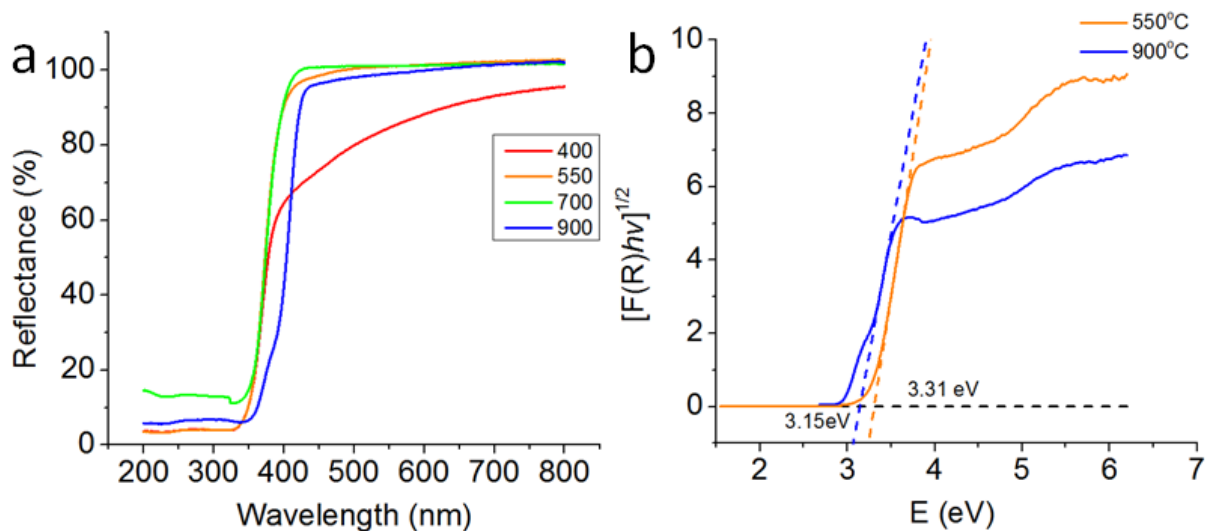
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**S.1.** Charge (delithiation)-discharge (lithiation) profiles of the anatase TiO<sub>2</sub> nanoparticle formed by aggregation of subunits with different unit sizes obtained by calcination at (a) 400, (b) 550, (c) 700 and (d) 900 °C.



**S2.** (a) UV-Vis reflectance spectra of anatase  $\text{TiO}_2$  nanoparticle formed by nanoparticle aggregates with different unit size obtained from the same precursor but at different calcination temperature of 400, 550, 700 and 900 °C for 2h in air. (b) Band gap measurement for two representative samples obtained by calcination at 550 and 900 °C.

Diffuse reflectance spectra of the anatase  $\text{TiO}_2$  with building subunits at different size are shown in Fig. 5a. The dramatic decreases in reflectance at around 400 nm were observed for all the pure anatase  $\text{TiO}_2$  samples obtained by calcination at 550, 700 and 900 °C. Specifically, the absorption edges appear at 400, 410, 425 nm, respectively. The gradual red shift of the absorption edge suggests that along with the increase in size of nanocrystalline subunits, quantization effect and defect induced energy traps associated with the nanoparticles play crucial roles in tuning optical properties of  $\text{TiO}_2$ .<sup>1</sup> Given that the absorption edge of  $\text{TiO}_2$  around 400 nm is attributed to the band transition from  $\text{O}2p$  to  $\text{Ti}3d$ ,<sup>2</sup> the size of nanocrystalline units can affect this band transition. The sample obtained at 400 °C, which is impurity doped as TGA analysis suggests, demonstrates different optical properties. A distinguishable new absorption shoulder in the visible light region is observed, although the absorption edge in the UV range is still at about 400 nm. It is believed that the impurity doping, most likely carbon released from oxalate ions, can decrease the band gap and absorbs visible light. This phenomenon is also

observed in N-doped TiO<sub>2</sub> spheres.<sup>2</sup> Kubelka-Munk function, F(R) (equivalent to the absorption coefficient), was obtained based on the Kubelka-Munk relation of  $F(R) = (1 - R)^2/2R$ , where R is the reflectance. The Tauc plot was obtained based on the following equation:  $(F(R)h\nu)^n = A(h\nu - E_g)$ , where  $h$  = Planck's constant,  $\nu$  = light frequency,  $E_g$  = band gap,  $A$  = proportional constant,  $n = 1/2, 3/2, 2$  or  $3$  depending on the transition nature. Anatase TiO<sub>2</sub>, with indirect allowed transition, has exponent  $n = 2$ . The Tauc plot shown in Fig. 5b clearly shows the different band gaps of 3.31 and 3.15 eV between two typical TiO<sub>2</sub> nanoparticles with crystalline size at 17 and 33 nm obtained by calcination at 550 and 900°C respectively. The band gap of 3.24 eV was similarly estimated for TiO<sub>2</sub> with crystalline size at 24 nm obtained by calcination at 700 °C. The decrease of band gap with the increase of nanocrystalline size could be attributed to the bulk defects induced delocalization of molecular orbitals in the conduction band edge.<sup>1</sup> When the crystalline size decreased below the band gap minimum, e.g., 16.8 nm obtained at 400 °C, the band gap trend reversed (Table 1). This could be attributed to the shift in shallow/deep traps in electronic energy.<sup>1</sup> Effectiveness in tuning the optical properties of anatase TiO<sub>2</sub> high-order aggregates by temperature was successfully demonstrated.

- (1) Lin, H.; Huang, C. P.; Li, W.; Ni, C.; Shah, S. I.; Tseng, Y. H. *Appl Catal B-Environ* **2006**, *68*, 1.
- (2) Cho, H.-J.; Hwang, P.-G.; Jung, D. *Journal of Physics and Chemistry of Solids* **2011**, *72*, 1462.