Supporting Information for

Ready Fabrication of Thin-Film Electrodes from Building Nanocrystals for Micro-Supercapacitors

Zheng Chen,^a Ding Weng,^a Xiaolei Wang,^a Yanhua Cheng,^a Ge Wang^b* and Yunfeng Lu^a*

^aDepartment of Chemical and Biomolecular Engineering, University of California, Los Angeles, CA 90095,USA.E-mail: luucla@ucla.edu; Fax: 310-206-410;Tel: 310-794-7238;^bSchool of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, 100083, China.

Email: gewang@mater.ustb.edu.cn

Experimental

Synthesis of TiO_2 NCs: The TiO_2 NCs were synthesized using a two-phase hydrothermal reaction.[1] In a typical synthesis, 0.4 mL of *tert*-butylamine was dissolved in 40 mL of de-ionized water and the solution was transferred into a 100 mL Teflon-line stainless-steel autoclave. Subsequently, 0.6 g of titanium (IV) n-propoxide (2 mmol) and 4.0 mL of oleic acid were dissolved in 40 mL of toluene in air and the solution was transferred into the autoclave without any stirring. The autoclave was sealed and maintained at 180 °C for 8 h and cooled to room temperature with tap water. The crude solution of TiO_2 NCs was precipitated with methanol and further isolated by centrifugation and decantation. The purified TiO_2 NCs were re-dispersed in toluene to form a NCs ink with desired concentration.

*Fabrication of TiO*₂ *NCs thin-films*: To make NC thin-films, different amounts of above NC solution were directly coated on clean indium tin oxide (ITO) substrates. After solvent evaporation at room temperature, the films were sintered at 450 °C for 1 hr at a ramp rate of 2 °C min⁻¹. The NC loading can be varied from μ g to mg by controlling coating solution, though typical thin-films reported here have an active mass loading of 0.1-0.2 mg cm⁻².

*Fabrication of P25 TiO*₂*-based thin-films*: To make P25-based films, powder sample was dispersed in ethanol under sonication and stirring. The formed solution was directly coated on ITO substrates and thermal treated at 250 $^{\circ}$ C to removal solvent.

Material and Electrode Characterization: The X-ray diffraction measurements were taken on Panalytical X'Pert Pro X-ray powder diffractometer using the copper K α radiation (λ =1.54 Å). Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 analyzer. The samples were degassed in vacuum at 200 °C for three hours. The specific surface areas (S_{BET}) were calculated by the Brunauer-Emmett-Teller (BET) method using adsorption branch in a relative pressure range from 0.04 to 0.25. The pore size distributions were derived from the adsorption branches of isotherms using the Barrett-Joyner-Halenda (BJH) model. Scanning electron microscopy (SEM) experiments were conducted on a JEOL JSM-6700 FE-SEM. Transmission electron microscopy (TEM) experiments were conducted on a Philips CM120 operated at 120 kV.

To test thin-film electrodes, CV and galvanostatic charge/discharge measurements were carried out in three-electrode flood cells in an argon-filled glove box. The measurements were carried out on a Solartron 1860/1287 electrochemical interface. The electrolyte solution was a 1 M LiClO₄ in propylene carbonate (PC) solution and lithium foils were used as both the counter and reference electrodes.



Figure S1. X-ray powder diffraction patterns of TiO_2 NCs before and after sintering treatment to remove the capping ligands (oleic acid). The diffraction pattern of as-synthesized TiO_2 NCs matches well to that of tetragonal anatase TiO_2 (according to JCPDS reference card no. 21-1272) with no indication for either rutile or brookite phases. The broadening of peaks is originated from the small crystal size, which is calculated to be 5.3 nm from Scherrer equation and is close to the average size observed from TEM. Sintering treatment at 450 °C effectively removed the ligands (**Fig. S2**) leading to slight increase of grain size (~ 8.2 nm), which is favorable for fast ion-storage kinetics



Figure S2. TGA plot of OA-capped TiO₂ NCs.



Figure S3. A representative galvanostatic charge/discharge plots of TiO₂ thin-film electrode at a rate of 0.5C. The plots show two regions, plateau region which is mainly associated with bulk diffusion process (A) and sloping region which is more likely related to interfacial charge storage (B),[2] which corresponds to different phase compositions and agrees well with CV measurement.

From CV and galvanostatic charge/discharge at a rate of 0.5C, we note a maximum specific capacity of ~ 200 mAh g⁻¹ (x=0.59 in Li_xTiO₂) was achieved for the NC thin-film electrodes, close to most of anatase TiO₂ (150-230 mAh g⁻¹)[3] but lower than the theoretical maximum capacity based on x=1 (~330 mAh g⁻¹) and some other high-surface-area nanoporous anatase electrodes.[2, 4] In order to understand and explain the different charge storage behavior, we compared various anatase TiO₂ electrodes and found the following possible reasons leading to relatively lower capacity of the NC thin-film electrodes:

Relatively small surface area. For nanostructured anatase TiO₂ electrodes, various studies have revealed that the overall charge storage is contributed from two different storage modes: a) bulk diffusion-controlled insertion which relates to a charge/discharge plateau at ~1.75 V (vs. Li/Li⁺), and b) interfacial storage which corresponds to a linear charge/discharge region below 1.75 V (Fig S2).[2-4] Typically, the higher surface area enables shorter diffusion length and more surface active sites, which lead to larger overall capacity. For example, we note capacities of >300 mAh

 g^{-1} (close to theoretical capacity) for TiO₂ with surface area of over 200 m² g⁻¹.[2,4] For other nanostructured TiO₂ with moderate surface areas, the capacities range from 150-230 mAh g⁻¹.[3] Our NC TiO₂ has a surface area of ~140 m² g⁻¹, which provides a moderate capacity of ~200 mAh g⁻¹.

- 2) High charge voltage. <u>The overall storage capacity strongly depends on the cut-off charge voltage (1.2V)</u>. The maximum TiO₂ capacity has been reported based on charging down to 1 V.[2,4] In such cases, much more interfacial storage was realized at the low voltage window. Our electrodes were charged to 1.2V, which further resulted in a lower capacity. It is worthwhile to mention that we emphasized the supercapacitor application, where the easy formation of solid-electrolyte-interface at ~1 V should be avoided. Therefore, we chose 1.2V as the cut-off voltage.
- 3) Rapid charge/discharge rate. <u>The overall storage capacity also strongly depends on the charge/discharge rate.</u> The largest TiO₂ capacity was achieved by charging/discharge for a few hours,[2,4] which allowed full Li-insertion in the anatase framework, leading to high capacity. With regard to supercapacitor application in our case, much higher rates were used (charging/discharge in mins), which sacrificed some capacity simply due to less time for Li⁺ to diffuse into the titania framework.

In addition, as far as the theoretical capacity concern, a lithium concentration of x=1 in Li_xTiO₂ will result in a maximum capacity of 336 mAh g⁻¹ at cut-off charging voltage at 1.0 V. However, at x>0.5, the Li-rich titinia no longer reversibly dissolve Li and the diffusion kinetics is slow.[2] Although high capacity can be achieved at the first charge cycle, the capacity might decrease appreciably at the second cycle due to the irreversible reactions.[2,4] Similarly, for NC-based thin films, we noted a first-cycle charge capacity of ~220 mAh g⁻¹ which decreased to ~200 mAh g⁻¹ in the second cycle (Fig S4) due to the similar reason.



Figure S4. Example of plotting the total voltammetric charge q_T of TiO₂ NC thin-film electrode against the reciprocal of the square root of the potential sweep rate (*v*) and extrapolating *v* to ∞ .



Figure S5. Nyquist representation of impedance spectra for the TiO_2 NC thin-film electrode (0.2 mg/cm²) at four different potentials, before any lithiation at open-circuit (2.2 V) and after lithiating to 2.0, 1.8 and 1.7 V. Inset shows enlarged Nyquist plots. The electrode showed a typical capacitive

feature as indicated by the close-to-vertical line at low-frequency region. The small semicircle at high-frequency region showed the charge-transfer resistance from electrode reaction. After slightly lithiating (at 1.8 V), the electrode showed a small Warburg region, which was associated with lithium diffusion in the titania framework. The electrode at 1.7 V showed a typical Warburg tail, indicating the electrode kinetics was then limited by diffusion after substantial lithiating.



Figure S6. Cycling performance of a representative TiO_2 NC thin-film electrode with a mass loading of 0.16 mg.





Figure S7. Cyclic voltammograms of TiO₂ NC thin-film electrodes at mass loading of 0.12 mg/cm² (A) and 0.32 mg/cm² (B); Capacity and rate dependence on the thickness of the NC thin-film electrodes (The electrodes with NC loading of 0.12, 0.20, and 0.32 mg/cm² showed thickness of 0.78, 1.3 and 2.1 μ m, respectively).

Reference:

- [1] D. Pan, N. Zhao, Q. Wang, S. Jiang, X. Ji and L. An, Adv. Mater., 2005, 17, 1991.
- [2] J.-Y. Shin, D. Samuelis and J. Maier, Adv. Funct. Mater., 2011, 21, 3464.
- [3] a) I. Moriguchi, R. Hidaka, H. Yamada, T. Kudo, H. Murakami and N. Nakashima, *Adv. Mater.*, 2006, 18, 69; b) Y.-G. Guo, Y.-S. Hu, W. Sigle and J. Maier, *Adv. Mater.*, 2007; 19, 2084;
 c) C. Jiang, M. Wei, Z. Qi, T. Kudo, I. Honma and H. Zhou, *J. Power Sources*, 2007, 166, 239; d)
 T. Brezesinski, J. Wang, J. Polleux, B. Dunn and S. H. Tolbert, *J. Am. Chem. Soc.*, 2009, 131, 8.;
- e) D. Wang, D. Choi, J. Li, Z. Yang, Z. Nie, R. Kou, D. Hu, C. Wang, L. V. Saraf, J. Zhang, I. A.
- Aksay and J. Liu, ACS Nano, 2009, 3, 907.
- [4] Y. Ren, L. J. Hardwick and P. G. Bruce, Angew. Chem. Int. Ed., 2010, 49, 2570.