Supplementary Information

Structural Evolution in Ordered Mesoporous TiO₂ Anatase Electrode

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Experimental Section

Synthesis of characterization of nanoporous 3DOm TiO₂

34 nm colloidal silica spheres for use as low-temperature templated synthesis of TiO₂ were prepared following previously reported seeded growth techniques [Fan *et al.*, *Nat. Mater.*, 2008, **23**, 9924]. Sols of seed silica nanoparticles of molar composition $x \operatorname{SiO}_2/y$ L-lysine/ 9500 Water / 4x Ethanol (x=61.5, y=1.23) were synthesized by hydrolysis of tetraethylorthosilicate (TEOS, 98%, Sigma-Aldrich) in aqueous solutions of L-lysine (Sigma-Aldrich) at 90°C for 24 hr under 500 rpm stirring. Three additional aliquots of TEOS were added every 12 hrs to the seed solution under the same temperature and stirring conditions, yielding a final molar composition of x=492. The resulting sols of 34 nm silica particles were filtered (200 nm disc filter) and dried into colloidal crystals at 70°C followed by 600°C calcination (ramp 5°C/min, 8 hr soak).

TiO₂ replication of the colloidal crystal silica was carried out within a Teflon-lined stainless steel autoclave by first soaking the silica powder in TiOSO₄ (15wt% in dilute sulfuric acid) for 10 min, adding tert-butanol (tBA) to a molar ratio of 1 TiOSO₄/ 7 SiO₂/ 103.6 tBA, and heating at 115°C for 48 hrs. The resulting solids were separated from the supernatant, washed with ethanol, and dried at ambient conditions before carrying out one additional replication with TiOSO₄ per the conditions described above. The resulting solids were collected and washed with ethanol and water at room temperature. 2M NaOH was used to selectively etch the silica template under stirring (750 rpm) at room temperature, with five exchanges of the NaOH solution for fresh solution every 6-8 hrs. The etched sample (3DOm TiO2-AP) was washed with copious amounts of DI water and dried at room temperature. The 3DOm TiO2-450 sample was prepared in the same fashion, but with the additional calcination of the silica-TiO₂ composite at 450°C (ramp1°C/min, 5 hr soak) prior to etching.

The as prepared (3DOm TiO2-AP) and 450°C TiO₂ (3DOm TiO2-450) samples were structurally characterized using powder X-ray diffraction (PANalytical X'Pert, CuK α radiation), scanning electron microscopy (JEOL JSM-7400F SEM at 3 kV, sample Au/Pd coated), transmission electron microscopy (JEOL JEM-2010F field-emission microscope at 200kV) and gas adsorption using N₂ at 77 K (ASAP 2020, Micromeritics). Samples were degassed at 200°C for 10h before analysis. BET surface areas were calculated, and pore size was estimated based on the BJH model.

Electrochemical Characterization

The 3DOm TiO₂, polyvidineylflouride (PVDF) and SuperP were mixed in N-methyldipyrildone (NMP) with a 70:15:15 weight ratio. After stirring overnight the slurry was cast using the doctor blade method onto Cu foil and dried first at room temperature then at 100^oC in air. The films were punched into disks with a typical loading of 2-4mg TiO₂. Inside an Ar glovebox (H₂O & O₂ <0.5ppm) 2025 coin cells were assembled with a Whatman GF/D separator and 1M LiPF₆ DEC/DMC/EC 1/1/1 by volume electrolyte, and a lithium foil anode. Galvanostatic charge-discharge tests were performed on a Maccor 4200 between 2.6-1 V. The ex-situ PXRD samples were made in 316 stainless steel Swagelok® cells with a 70/30 TiO₂/SuperP ratio.

Ex-Situ Characterization

Swagelok cells were opened inside an Ar glovebox and the powder was rinsed with DMC before drying under vacuum. For PXRD the dried powder was placed on a 2.5μ mylar film. Then a glass sample holder with double sided scotch tape surrounding the intended sample area was pressed onto the mylar film to seal the sample from air during measurement. For TEM the powder was removed from the glovebox, dispersed in ethanol and then loaded onto the grid. Coin cells cycled at 600mA/g for SEM were dismantled in the glovebox, rinsed with DMC and dried before analysis.





Figure S2: Powder x-ray diffraction (PXRD) confirmed that the materials are phase pure anatase. Further analysis of the PXRD spectra show that the ratio between the (004)/(101) peak heights change from 0.35 for TiO₂-AP to 0.3 for TiO₂-450, suggesting that coarsening of the crystallites towards the thermodynamically preferred (101) crystal face occurs during calcination. Despite the coarsening, the Scherer equation estimates for crystallite size using the (101) plane have minimal change from 13.4nm for TiO2-AP to 14.54nm for TiO2-450.



Figure S3: High resolution TEM of (a,c) TiO_2 -AP and (b, d) TiO_2 -450 taken near the particle edges show wall thicknesses around 10nm, agreeing with the crystallite size estimates, and the successful inverse templating of the 34nm SiO₂ colloidal spheres is easily observed



Figure S4: Pore size distribution calculated using the BJH method on the adsorption isotherm results in a peak at 33.2 nm for TiO_2 -AP and 39.4 nm for TiO_2 -450, proving we successfully nanocast our 3DOm materials around the silica colloids (SI Fig4). In addition, the apparent BET surface area of 147 m²/g for TiO₂-AP and 105m²/g for TiO₂-450 is consistent with most hard cast mesoporous materials, demonstrating that the template has been successfully removed from the interior of the anatase particles.



Figure S5: (a-c) Electrochemical cycling of TiO₂-AP (black) and TiO₂-450 (red). (a) 100 mA/g, (b) various rates as listed, (c) 600 mA/g. (c) were the coin cells used for ex-situ SEM analysis. (d) TiO₂-450 discharge capacities for selected cycles at a variety of current densities.



Figure S6: PXRD of TiO₂-450 at various positions during first and second cycle. LiTiO₂, $Li_{0.5}TiO_2$, and TiO₂ are simulated patterns of the 3 possible crystal phases. Scans start at 30 because mylar has a large peak that interferes with the (101) peak.