Supporting Information

Operando Transmission Electron Microscopy of Battery Cycling: Thickness-dependent Breaking of TiO_2 Coating on Si/SiO_2 Nanoparticles

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TiO_2 coating: The coating of Si/SiO_2 particles with average particle size of 100 nm was performed via Atomic Layer Deposition by the Delft IMP. ALD was conducted in fluidised bed reactor at 150°C and atmospheric pressure. To coat Si with TiO_2, titanium isopropoxide with water as a co-reactant were used. The carrier gas used to purge reactor chamber and remove by-products was nitrogen. The sequence of reaction was applied was 3-6-1-4 min for titanium isopropoxide-nitrogen-water-nitrogen, respectively which corresponds to 1 cycle. For the 5 nm and 10 nm of TiO_2 coating ~25 and ~125 cycles were used respectively.

In-situ TEM experiments: Half TEM copper grid with TiO_2 coated Si nanoparticles (NPs) and electro-polished tungsten needle with lithium/lithium oxide were mounted onto a Nanofactory TEM holder in an Ar glovebox and transferred to a FEI Titan G2 transmission electron microscope (TEM) operated at 300kV in an Ar-filled glove bag. In order to minimize the influence of the electron beam during the operando experiments, a low electron dose rate of below 10 e-/Å^2/s was used for recording image sequences using a Gatan K2 IS direct electron detection camera. A negative voltage with respect to Li was applied to the TiO_2 coated Si nanoparticles (NPs) to lithiate NPs electrochemically, while positive voltage with respect to Li was applied to de-lithiate NPs.

Electrode preparation for C-rate test: The electrodes were prepared by slurry casting method. All the components, active material (crystalline Si powder, mean particle size distribution of 100 nm, 99% purity, Alfa Aesar), conductive additive (Super P, TIMCAL) and binder (carboxymethyl cellulose, Mw = 90,000 g/mol, Sigma Aldrich) are mixed in an agate jars with 3 agate balls with weight ratio 0.6 : 0.2 : 0.2 at 250 rpm for 90 min. To mix the powders 2 ml of buffer solution (pH = 3, Fluka) was used. Mixed slurry was casted using doctor blade with wet thickness of ~100 μm on copper foil. Afterwards slurry was dried in air and under vacuum at 60°C for 12 h. Finally, electrodes were cut in circular shape with diameter 12.6 mm and cold-pressed under 2 t for 1 min. In order to avoid reactions with moisture and oxygen (< 2 ppm H_2O and < 0.1 ppm O_2), coin-cells were assembled in the glove box. A polymer separator (Celgard 2250) with 10 drops of electrolyte 1.0 M $LiPF_6$ in 1:1 v/v EC/DEC (<15 ppm H_2O, Sigma Aldrich) and Li metal as a counter electrode (Sigma-Aldrich), were used in cell assembly.

Electrochemical test: The C-rate test, was conducted using coin-cells within voltage 0.005 V to 1.5 V vs. Li/Li^+ for the first cycle and 0.01 to 1.2 V vs. Li/Li^+ for the next cycles. Cells were cycled in 0.1C, 0.2C, 0.5C, and again 0.1C for 5 cycles in each C-rate. Current was calculated based on the Si with the capacity of 1500 $mAhg^{-1}$.

X-ray diffraction

A PANalytical X'Pert Pro PW3040/60 diffractometer with Cu Kα radiation operating at 45 kV and 40 mA in an angular 2θ range of 10–100° was used for XRD measurements.

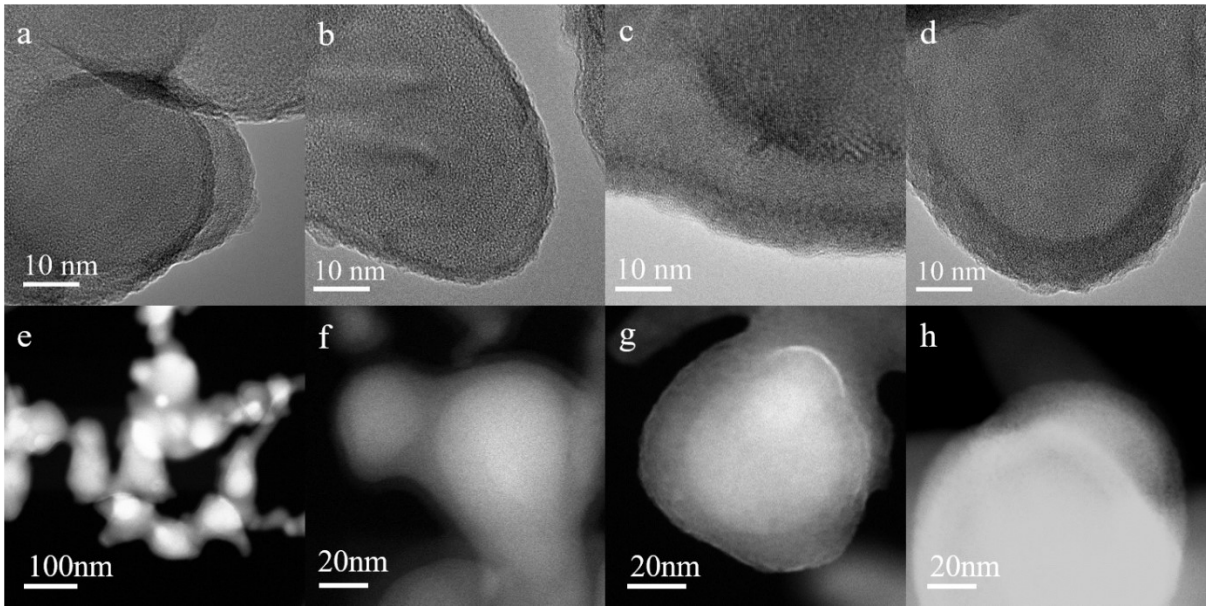

Figure S1. Si/SiO_2 particles with/without TiO_2 coating. (a-b) TEM images of the 5nm TiO_2 coated particles, (c-d) TEM images of the 10nm TiO_2 coated particles, (e-f) STEM images of the Si/SiO_2 particles without coating, (g) STEM images of the 5nm TiO_2 coated particles, and (h) STEM images of the 10nm TiO_2 coated particles.

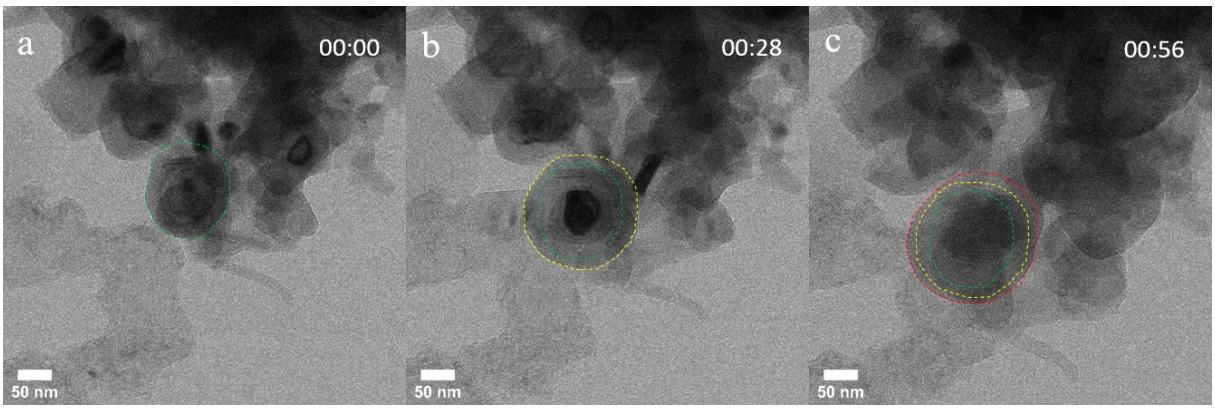

Figure S2. The gradual swelling of the 5nm TiO_2 coated Si/SiO_2 particle during first lithiation is highlighted using green, yellow and red dotted lines. For particle size estimation frames were first chosen from the corresponding dataset, then particle shapes were carefully inspected and traced using the 'polygon selection' tool of ImageJ.

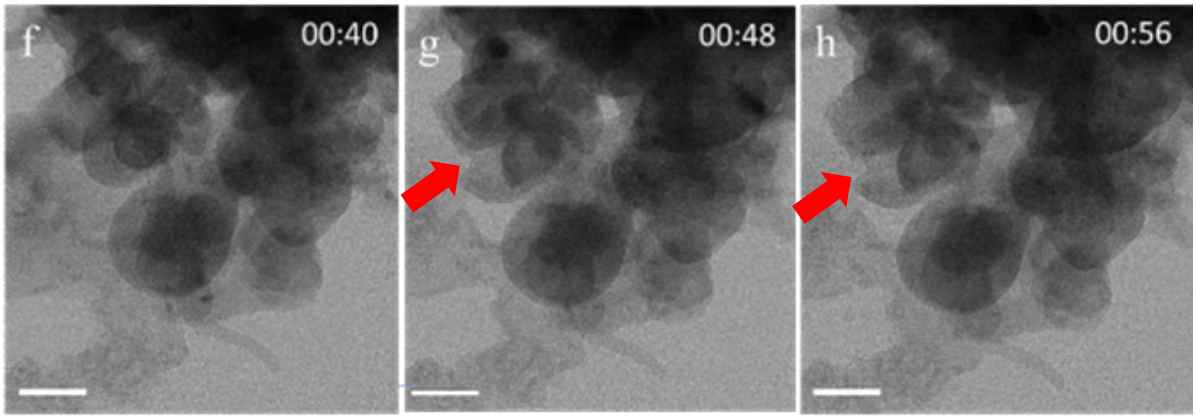

Figure S3. Arrow highlights the rare occurrence of particle breakage for 5nm TiO_2 coated Si/SiO_2 particles (The images are from same dataset as in Figure 3 of the manuscript).

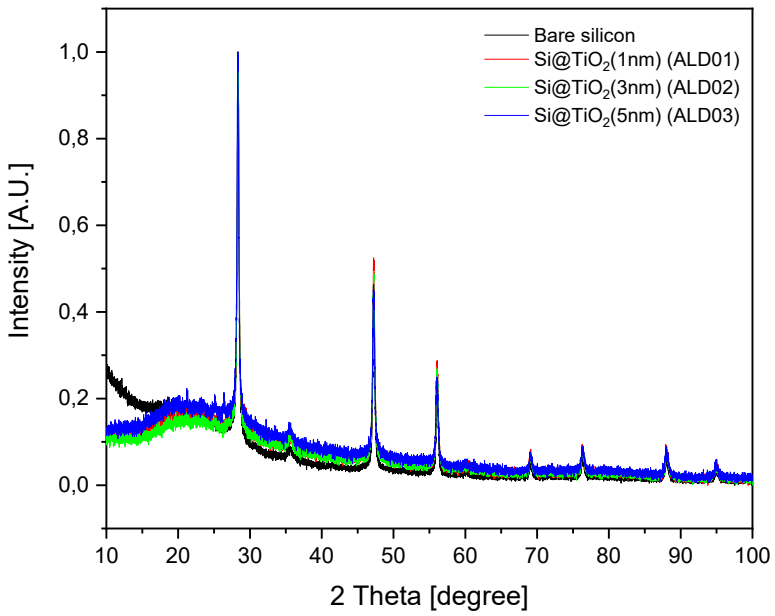

Figure S4. X-ray diffraction patterns of TiO_2 coated Si/SiO_2 nanoparticles. No visible changes of diffraction peaks upon TiO_2 coating refers to the amorphous nature of the TiO_2 coatings.

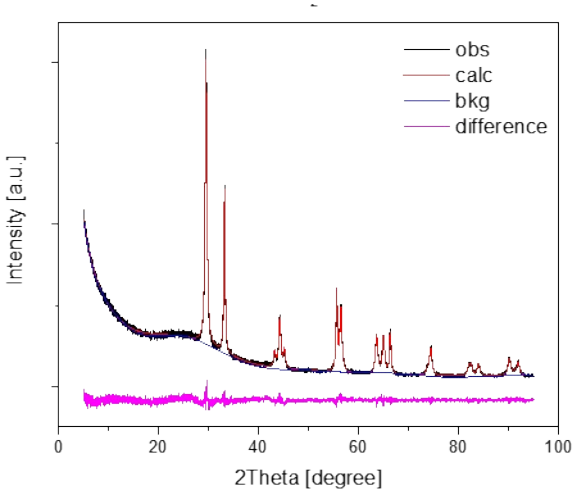

Figure S5. X-ray diffraction pattern shows sintering at 450°C for 5 hours in argon atmosphere transform the ALD deposited amorphous 10 nm TiO_2 coating to crystalline.

Movie S1: Shows lithiation-delithiation cycles of 5nm TiO_2 coated Si nanoparticles. The video plays at 24x speed.

Movie S2: Shows lithiation-delithiation cycles of 5nm TiO_2 coated another Si nanoparticles cluster. The video plays at 24x speed.

Movie S3: Shows lithiation-delithiation cycles of 10nm TiO_2 coated Si nanoparticles. The video plays at 24x speed.

Movie S4: Shows lithiation-delithiation cycles of 10nm TiO_2 coated another Si nanoparticles cluster. The video plays at 24x speed.