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Observing the formation of TiO_2 mesocrystals from NH_4TiOF_3 microparticles using *in situ* thermo-WAXS measurements

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Experimental Details

Reagents were sourced from the suppliers indicated and were used as received. $(NH_4)_2TiF_6$ (Sigma-Aldrich UK) 0.1 mol L^{-1}, poly(ethylene glycol) PEG-2000 (Alfa Chemicals Ltd.) 0.05 mol L^{-1}, fluoride scavenger and gelation agent H_3BO_3 (Alfa Chemicals Ltd.) 0.2 mol L^{-1} were dissolved in distilled water (30 mL) under continuous stirring. After full dissolution of the reagents, the resultant solution was kept at 35 °C for 20 hours. The resultant precipitate was isolated by centrifugation/decantation and subsequently washed with water (3 × 20 mL) and acetone (3 × 20 mL). The obtained powder was dried in air at room temperature to a constant weight. Samples of NH_4TiOF_3 (ca. 0.5 g) were heated either in air or in an argon atmosphere at either 450 °C or 500 °C for 2, 4 or 8 hours. All TiO_2 mesocrystals were obtained from these NH_4TiOF_3 precursor mesocrystals in a thermally-mediated process. To enable the evaluation of time and temperature upon ordered arrays of TiO_2 nanocrystals formation, samples were either heated to 450 °C or 500 °C for 2, 4 or 8 hours. Heating was conducted in air and then in subsequent synthetic runs was conducted in an inert argon atmosphere.

The *in situ* variable-temperature synchrotron X-ray powder diffraction (SXRPD) data were collected at the Swiss-Norwegian beamlines BM01 at the European Synchrotron Radiation Facility (ESRF in Grenoble, France) using a PILATUS@SNBL diffractometer. The monochromatic beam (λ = 0.78487 Å) and 2-D detector parameters were calibrated on LaB_6 powder with PyFAI. The obtained calibrations were implemented to Bubble for further azimuthal

integration of 2D images. The sample was loaded into a 0.5 mm diameter glass capillary and heated by a hot air heat blower with ~3 °C/min heating rate from room temperature to 415 °C. The temperature of the sample was calibrated using the temperature dependence of the Ag unit cell parameter, which was measured prior to the NH_4TiOF_3 variable-temperature experiment. SEM was performed on a Carl Zeiss NVision 40 electron microscope, samples were not coated prior to imaging. TEM examination was carried out with a Libra 200 microscope (Carl Zeiss, Germany) controlled by the Aztec TEM (Oxford Inc., UK). Raman spectroscopy was conducted using a Renishaw inVia Reflex spectrometer with an illumination wavelength of 633 nm. TGA was carried out using a Perkin-Elmer thermogravimetric analyzer Pyris 1. Heating was conducted from room temperature to 600 °C with a heating rate increase of 5 °C min^{-1}.

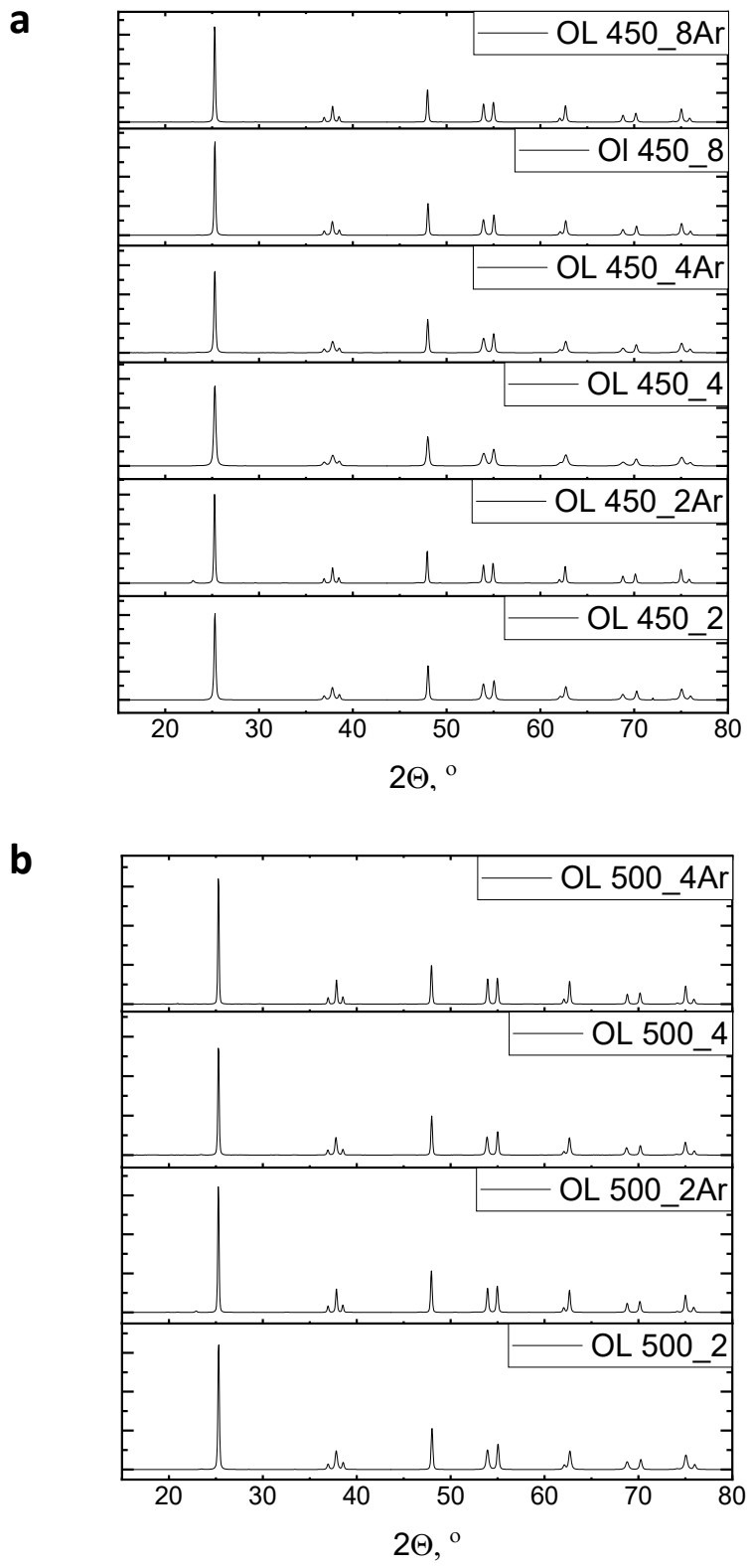

Figure S1 XRD patterns of TiO_2 mesocrystals generated by a) heating a sample of NH_4TiOF_3 at 450 °C in the atmosphere indicated for time periods of 2 and 4 hours; b) XRD patterns of TiO_2 mesocrystals generated by heating a sample of NH_4TiOF_3 at 450 °C in the atmosphere indicated for time periods of 2 and 4 hours.

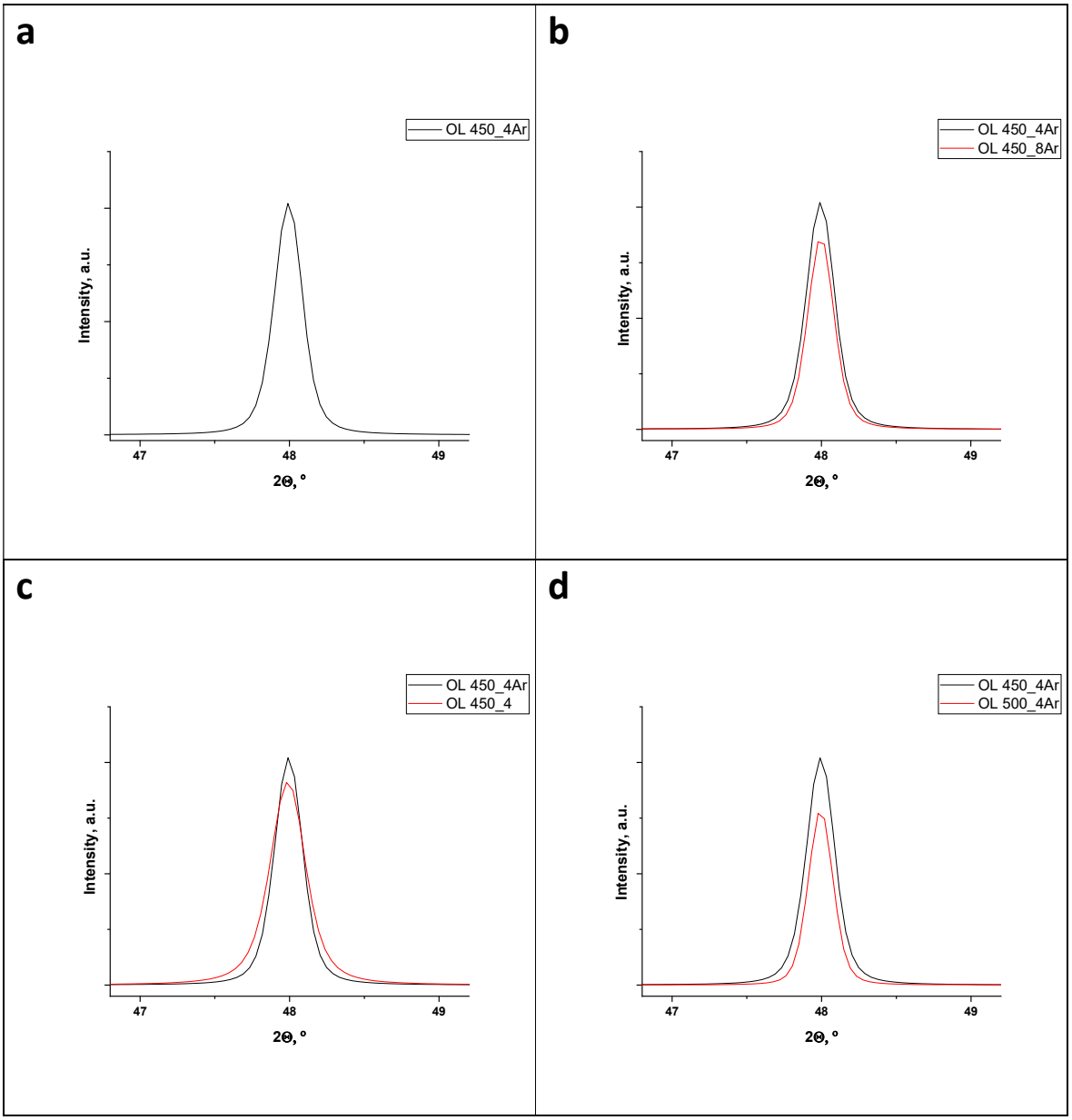

Figure S2 Expansion of the XRD region showing the (200) reflexes for TiO_2 mesocrystal samples generated from a sample of NH_4TiOF_3 by a) heating under argon at 450 °C for 4 hours; b) heating under argon at 450 °C for four hours (black trace) and for eight hours (red trace); c) heating under argon at 450 °C for four hours (black trace) and heating in air at 450 °C for four hours (red trace); and d) heating under argon at 450 °C for four hours (black trace) and at 500 °C for 4 hours (red trace).

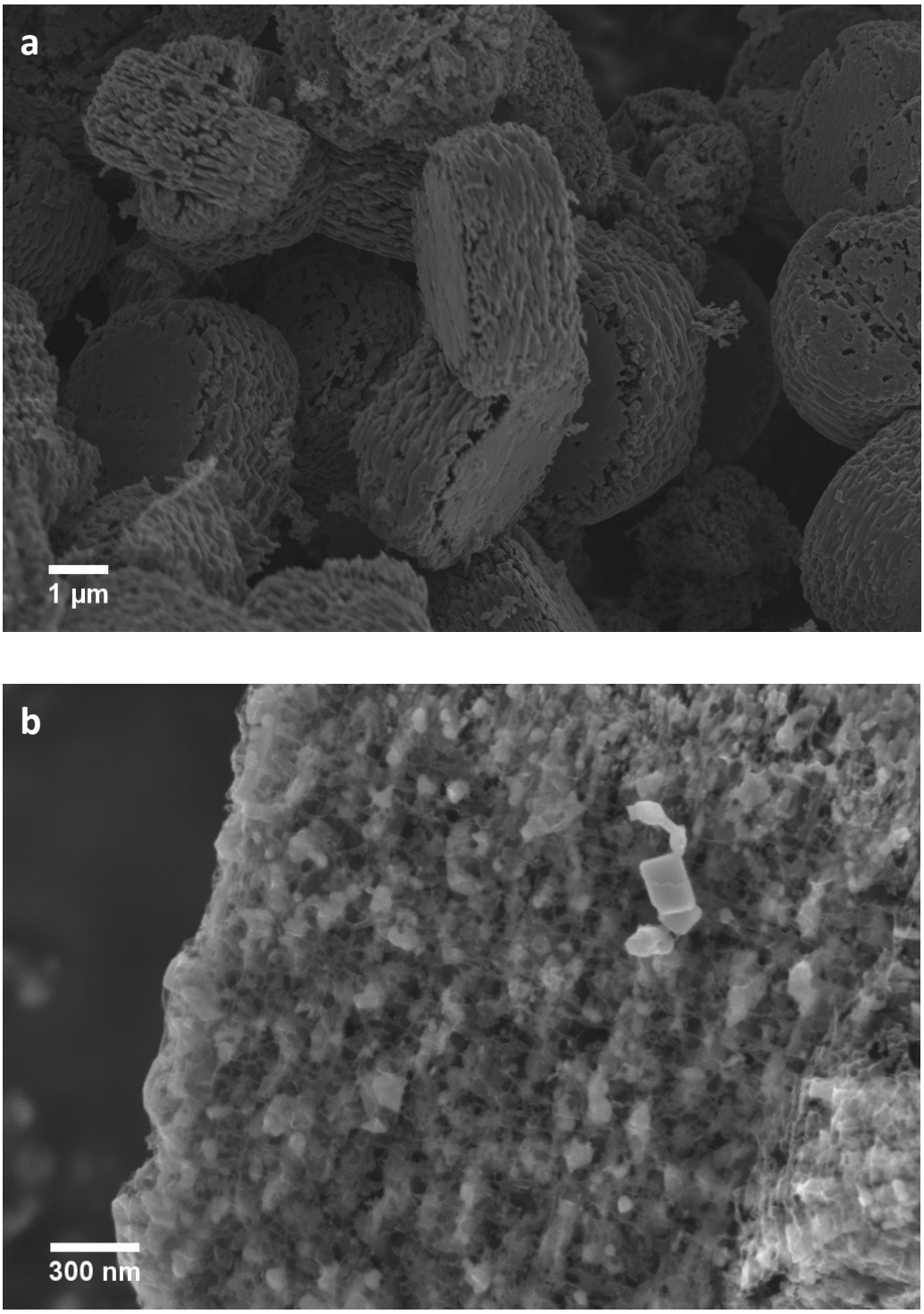

Figure S3 Scanning electron micrographs of a sample of TiO_2 mesocrystals generated from a sample of NH_4TiOF_3 by heating under argon at 500 °C for 2 hours; a) showing porous layered structure of a collection of mesocrystals (white scale bar = 1 µm) and b) an expanded s of a single TiO_2 mesocrystal showing individual component nanoparticle building blocks comprising the mesocrystal (white scale bar = 300 nm).

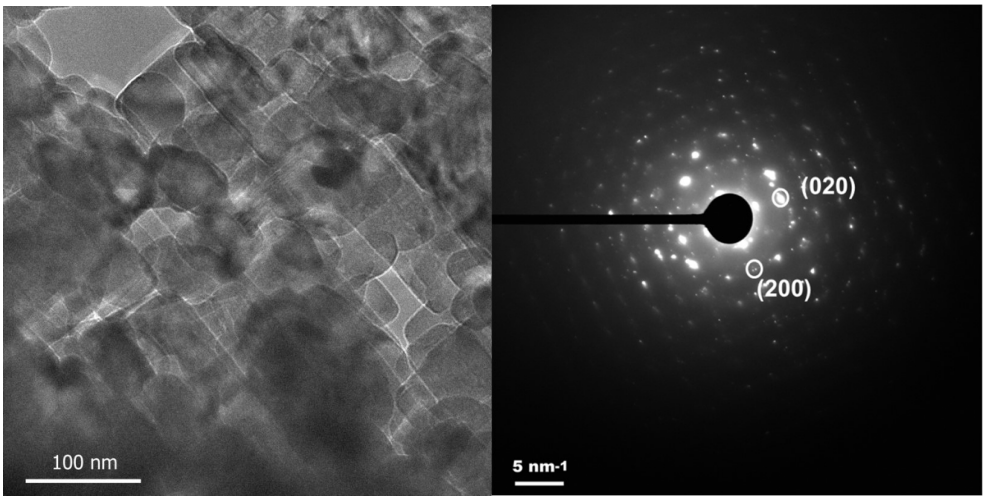

Figure S4 Transmitting electron micrograph (TEM) and Selected Area Electron Diffraction (SAED) pattern from a TiO_2 mesocrystal, generated from a sample of NH_4TiOF_3 by heating at 450 °C for 2 hours, providing evidence of mesocrystallinity.

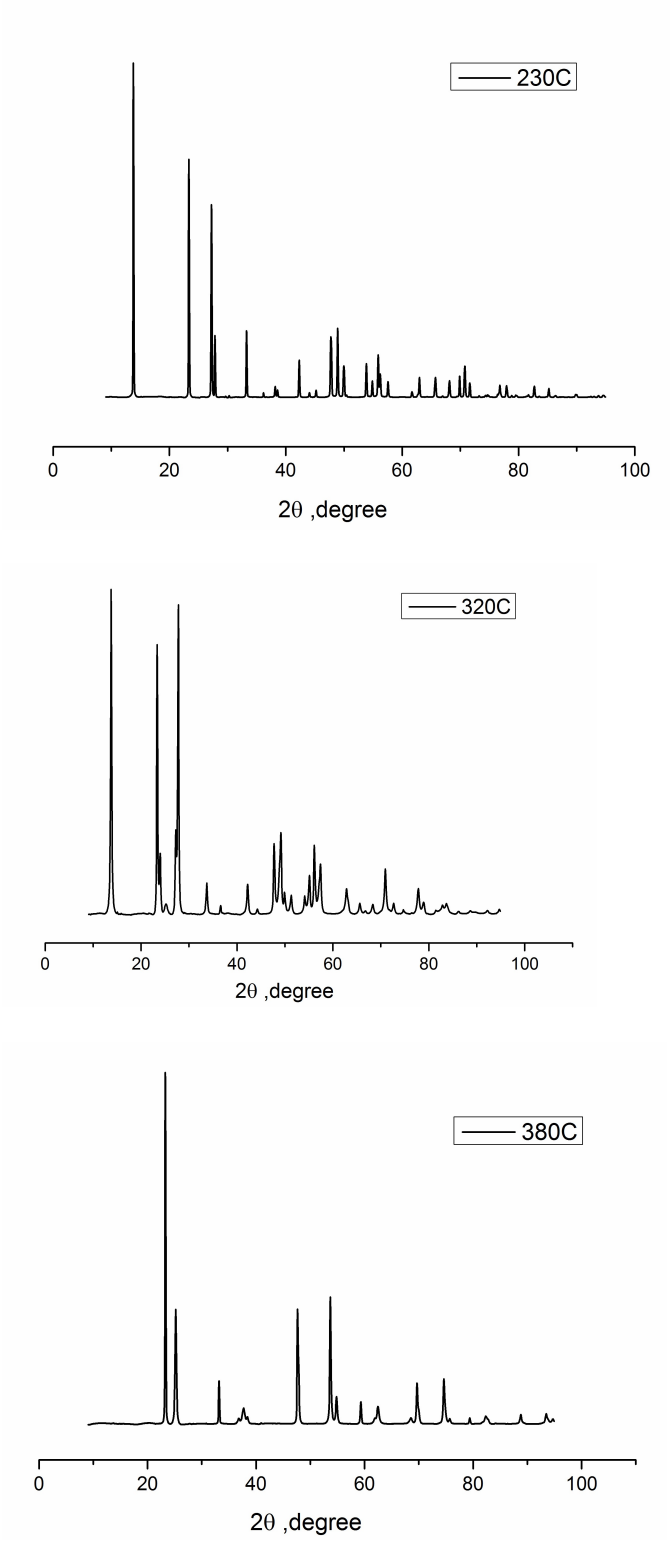

Figure S5 Three single *in situ* XRD patterns, generated from a sample of NH_4TiOF_3 mesocrystals heated at 225 to 385 °C in air (230, 320 and 380°C)

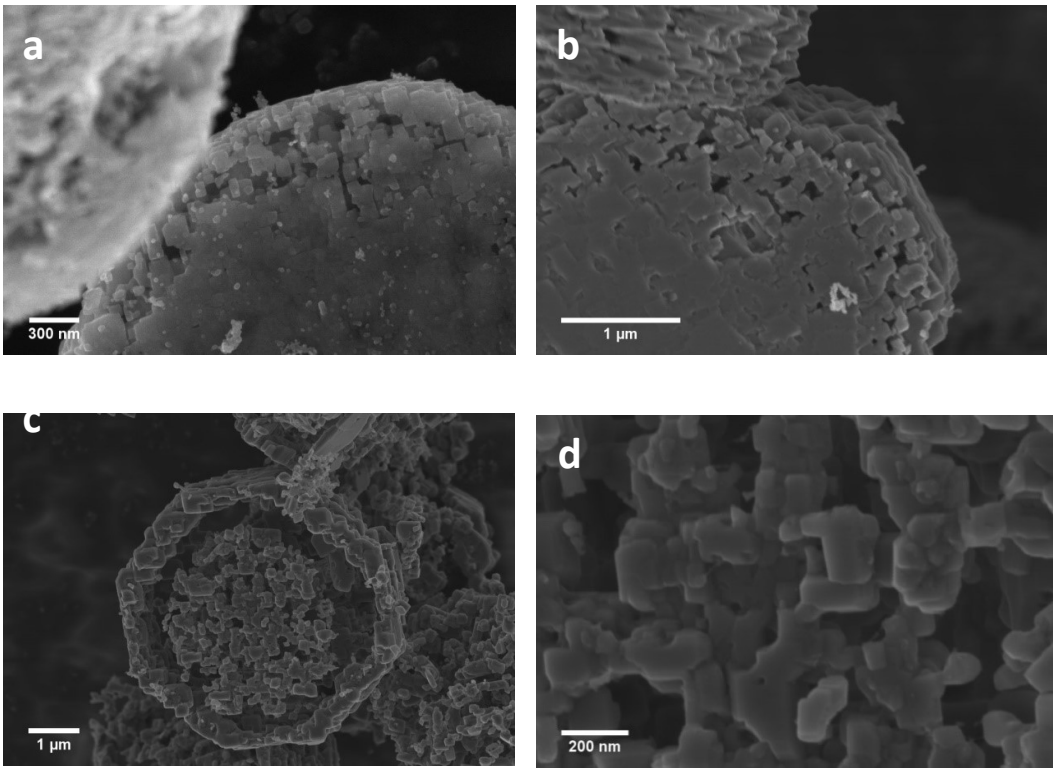

Figure S6 Scanning electron micrographs of TiO_2 mesocrystals generated from a sample of NH_4TiOF_3 by heating a) in air at 450 °C for 4 hours (white scale bar = 300 nm); b) under argon at 450 °C for 4 hours (white scale bar = 1 µm); c) under argon at 500 °C for 4 hours (white scale bar = 1 µm); and d) under argon at 500 °C for 4 hours (white scale bar = 200 nm)

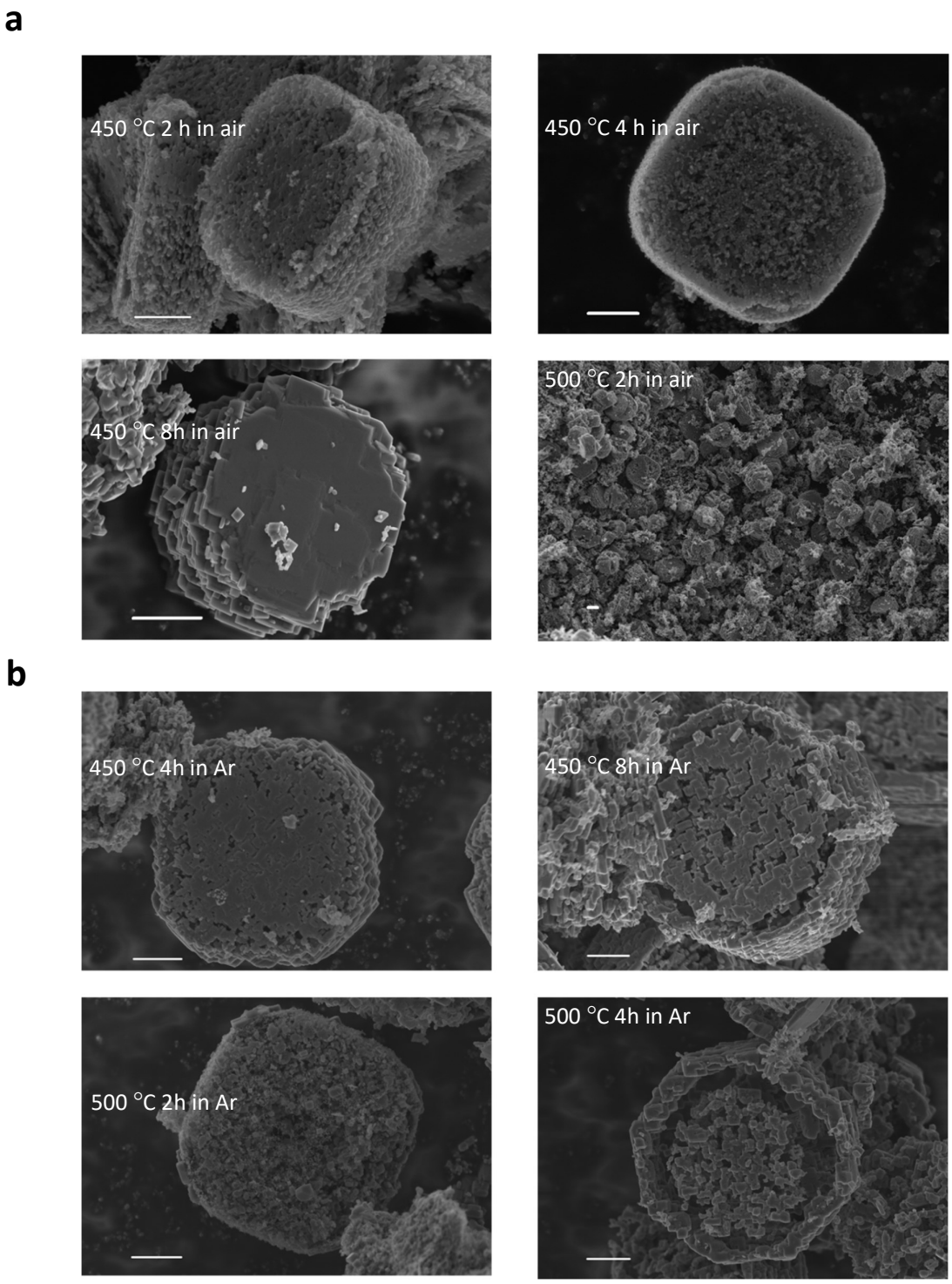

Figure S7 Scanning electron micrographs of samples of TiO_2 mesocrystals generated from a sample of NH_4TiOF_3 a) by heating in air at the temperatures and for the time period indicated; and b) by heating under argon at the temperature and for the time period indicated. The white scale bars in the bottom left of each micrograph = 1 μm.