

## Continuous Hydrothermal Synthesis of Extensive 2D Sodium Titanate ( $\text{Na}_2\text{Ti}_3\text{O}_7$ ) Nano-sheets

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### Supplementary information for synthesis and analysis

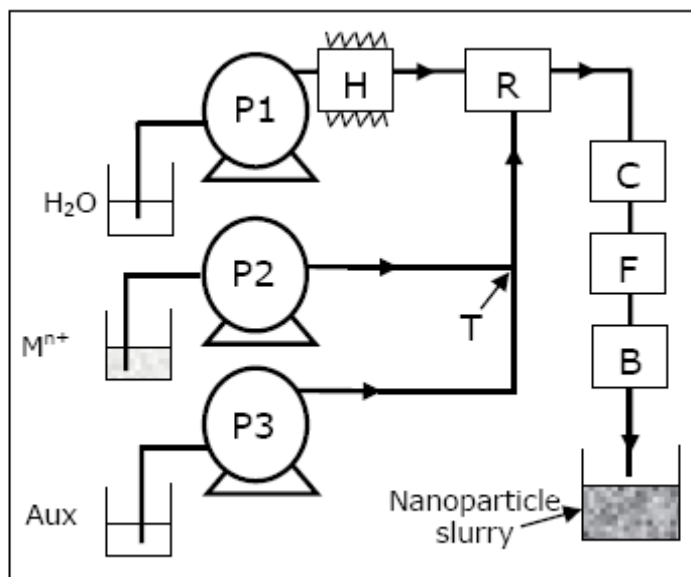
#### Experimental

##### Synthesis:

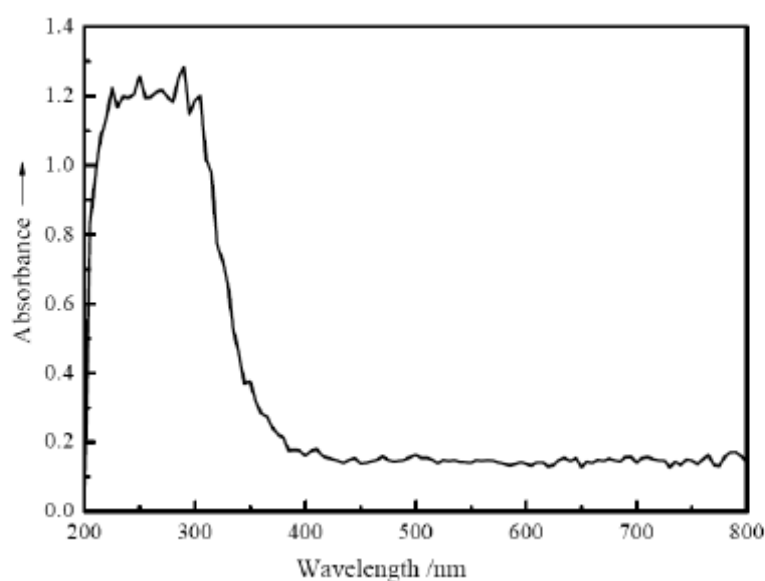
The as-prepared  $\text{Na}_2\text{Ti}_3\text{O}_7$  nano-powder was made using a CHFS reactor, the basic design of which has been reported elsewhere (Figure 1). The CHFS system incorporates three Gilson 305 HPLC pumps fitted with 25 mL pump-heads, 316SS Swagelok<sup>TM</sup> 1/8" stainless steel fittings and tubing (except for the counter-current mixing point) and a 2000 W electrically powered water preheater which were built from 1/4" fittings. For the synthesis of as-prepared  $\text{Na}_2\text{Ti}_3\text{O}_7$  nano-powder, an aqueous solution of 0.2 M titanium(IV) bis(ammonium lactato)dihydroxide (TiBALD) was pumped to meet a flow of NaOH (15 M) at room temperature at a Tee junction ('T' in Figure S1). This mixture then met a flow of superheated water at the mixing point (a counter-current mixer, 'R' in Figure 1), whereupon rapid precipitation occurred. The aqueous suspension was cooled via a water jacket cooler, passed through a 7  $\mu\text{m}$  in-line filter, and the white slurry was collected from the exit of the back-pressure regulator. HPLC pump rates of 20, 10 and 10 mL  $\text{min}^{-1}$  were used for superheated water (P1), TiBALD solution (P2) and the 15 M NaOH aqueous solution feed (P3), respectively. The supercritical water feed was at 450 °C and 24.1 MPa, whilst the other feeds were at room temperature initially. This slurry was centrifuged and the solids were washed with 2 x 40 mL aliquots of deionised (DI) water with thorough shaking to remove any residual NaOH (this was when the pH of the washing water also reached pH = 7). The wet solids were freeze-dried to yield a white powder in ca. 92 % yield (based on dry powder mass), hereafter referred to as as-prepared powder.

##### Characterisation

BET surface area measurements ( $\text{N}_2$  adsorption) were performed on a Micromeritics Gemini analyser. The powders were degassed at 150 °C for 2 h prior to BET analyses. X-ray powder diffraction (XRD) data were collected on a Siemens D5000 X-Ray diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 0.15418$  nm). Data were collected over the  $2\theta$  range 5- 80 ° with a step size of 0.02 ° and a count time of 2 s. Particle size and morphology of the as-prepared nanopowders were investigated using a HR-TEM model JEOL 4000EX high resolution transmission electron microscope (400 kV accelerating voltage). Samples were collected on carbon-coated copper grids (Holey Carbon Film, 300 meshes Cu, Agar Scientific, Essex, UK) after being briefly dispersed ultrasonically (Kerry<sup>TM</sup> Ultrasonic bath, Skipton, UK) in ethanol for 3 min. In addition, selected area diffraction patterns (SADP) were recorded in order to confirm the crystallinity of the powders. Raman spectra of the samples were recorded with a Renishaw InVia<sup>TM</sup> Raman microscope equipped with an 1800 line  $\text{mm}^{-1}$  grating and a LaserPhysics argon ion laser (514.5 nm). The spectral resolution of the instrument is 1  $\text{cm}^{-1}$ . Low temperature measurement was carried out with a Linkam THMS600 stage and temperature controller. Particle size analysis was performed using Digital Micrograph<sup>TM</sup> (Gatan) particle size analysis software. Heat-treatment of the as prepared sample was carried out at 700 °C for 5 h in a muffle furnace (Lenton UAF18/5, UK) in air (excluding heating and cooling rates of 10 and 20 °C  $\text{min}^{-1}$ , respectively). A UV-Vis absorption spectrum of the nano-sheets was recorded using a Perkin Elmer (Lambda 950) UV-Vis spectrophotometer. The UV-Vis data were recorded in the range 200 to 800 nm using Spectralon blank as reflecting standard and a D65 standard illuminant with a 10 ° viewing angle. SEM images were captured using a FEI Inspect-F (USA) scanning electron microscope; the SEM sample was mounted on an aluminium stub and evaporatively coated with carbon. Elemental analysis of the sample was conducted on the same SEM instrument using energy-dispersive spectroscopy (EDS) (Oxford Instruments INCA Energy 300), operating at 20 kV and 10 mm working distance. Average of 10 area scans (1 $\times$ 1  $\mu\text{m}$ ) were used to calculate average elemental compositions.



**Supplementary Figure S1** Scheme of the three-pump (P1, P2 and P3) hydrothermal flow system used for the synthesis of sodium titanate nano-sheets. Key: P = pump, C = cooling, F = filter, B = back-pressure regulator, R = counter-current reactor, H = heater, T = 'Tee' piece mixer. Mn<sup>+</sup> = metal salt (Ti<sup>4+</sup>) and Aux = auxiliary feed such as base solution.



**Supplementary Fig. S2** UV-Vis absorption spectrum of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> nanopowder made in the continuous hydrothermal flow synthesis system using a superheated water at 450 °C and 24 MPa.