Continuous Hydrothermal Synthesis of Extensive 2D Sodium Titanate (Na₂Ti₃O₇) Nano-sheets

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Supplementary information for synthesis and analysis

Experimental

Synthesis:
The as-prepared Na₂Ti₃O₇ 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™ 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 Na₂Ti₃O₇ 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 μm 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 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 ºC 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 (N₂ adsorption) were performed on a Micromeretics Gemini analyser. The powders were degassed at 150 ºC for 2 h prior to BET analyses. X-ray powder diffraction (XRD) data were collected on a Siemens D5000 X-Ray diffractometer using Cu-Kα radiation (λ = 0.15418 nm). Data were collected over the 2θ range 5- 80 º with a step size of 0.02 º 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™ 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™ Raman microscope equipped with an 1800 line mm⁻¹ grating and a LaserPhysics argon ion laser (514.5 nm). The spectral resolution of the instrument is 1 cm⁻¹. Low temperature measurement was carried out with a Linkam THMS600 stage and temperature controller. Particle size analysis was performed using Digital Micrograph™ (Gatan) particle size analysis software. Heat-treatment of the as prepared sample was carried out at 700 ºC for 5 h in a muffle furnace (Lenton UAF18/5, UK) in air (excluding heating and cooling rates of 10 and 20 ºC 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 (1×1 μm) 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⁺ = metal salt (Ti⁴⁺) and Aux = auxiliary feed such as base solution.

**Supplementary Fig. S2** UV-Vis absorption spectrum of Na₂Ti₃O₇ nanopowder made in the continuous hydrothermal flow synthesis system using a superheated water at 450 °C and 24 MPa.