

Supplementary information

An Effective Template-Free Synthesis Strategy for Hierarchical Titanium Oxide Hybrids: Tailoring Solvent Environment

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Experimental Details

Materials synthesis

Chemicals used in the material syntheses are reagent grade without any further purification, including titanium butoxide (97%, Sigma Aldrich), acetonitrile (Ajex Fine Chemical), butan-1-ol (Ajex Fine Chemical), ethanol (Ajex Fine Chemical) and ammonia hydroxide solution (28% NH₃ in H₂O, Ajex Fine Chemical). The synthesis of spherical hybrid precursors were based on the approach demonstrated in our previous report [13]. Titanium butoxide (7.16 mL) was added dropwise to 200 mL of an acetonitrile and butan-1-ol (1:1) solvent mixture under moderate stirring. A second solution was formed by adding distilled water of 3.6 mL and ammonia of 2.7 mL the same amount of acetonitrile and butanol solvent mixture. Then it was quickly mixed with the first solution under stirring. While stirring speed was maintained, white spherical precipitates were formed within a few seconds in the solution mixture. After aging for 2 hours under constant stirring, the white precipitates were collected and then washed with ethanol. These white precursor spheres were then dispersed in a solvent mixture of 30 mL containing different volume ratios of absolute ethanol, distilled water and/or ammonia. Following subsequent solvothermal treatment at 150 °C

for 15 hours in a Teflon-lined autoclave, the final products were then washed with ethanol, acetone and dried at room temperature.

Characterizations

Morphologies of the products were investigated using a Hitachi S-900 high-resolution field emission scanning electron microscope (SEM) and a FEI Tecnai G2 20 transmission electron microscope (TEM). Crystal phases of the products were verified on a PANalytical Xpert Multipurpose X-ray Diffraction System (MPD) with Cu K α radiation under 40 kV working voltage. Nitrogen adsorption – desorption isotherms were measured on a Micromeritics Tristar 3000 system. Samples were degassed at 100 °C on a vacuum line overnight. Specific surface areas were calculated by means of a standard Brunauer-Emmett-Teller (BET) analysis with the Barrett – Joyner – Halenda (BJH) method. Adsorption of the isotherms was used to provide pore size distribution. Temperature programmed reduction of deposited Pt was carried out on a Micromeritics Autochem II 2920 with hydrogen.

Heavy metal removal

In a typical adsorption test, a sample of 60 mg was dispersed into a lead nitrate solution of 40 mL with an initial concentration of 16.1 mg/L. Solution samples were taken out at different adsorption intervals (10, 30, 60 and 120 min, and 16 hours). Adsorbents were removed by centrifugation. Lead concentrations were analysed using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES, Perkin Elmer OPTIMA 7300).

Photocatalytic formic acid degradation

A photocatalyst solution of 50 mL with solid loading of 1 g/L or 0.6 g/L was adjusted to pH=3.0 with perchloric acid pre-illuminated for 30 min in a spiral reactor using an 18 W UVA lamp. Following the injection of 60 μ L formic acid (20000 ppm carbon) into the solution, a conductivity meter was used to monitor the photooxidation (degradation) process under illumination.

Deposition of Pt

Sample powder of 1 g was dispersed in distilled water of 100 mL and then a 50 mL solution containing H_2PtCl_6 (Pt : Ti molar ratio of 1 at% or 5at%) was added dropwisely into the suspension using a syringe pump under moderate stirring. An oil bath of 80 °C was used to evaporate the solvent before the solid product was further dried at 100 °C in an oven overnight for hydrogen TPR.

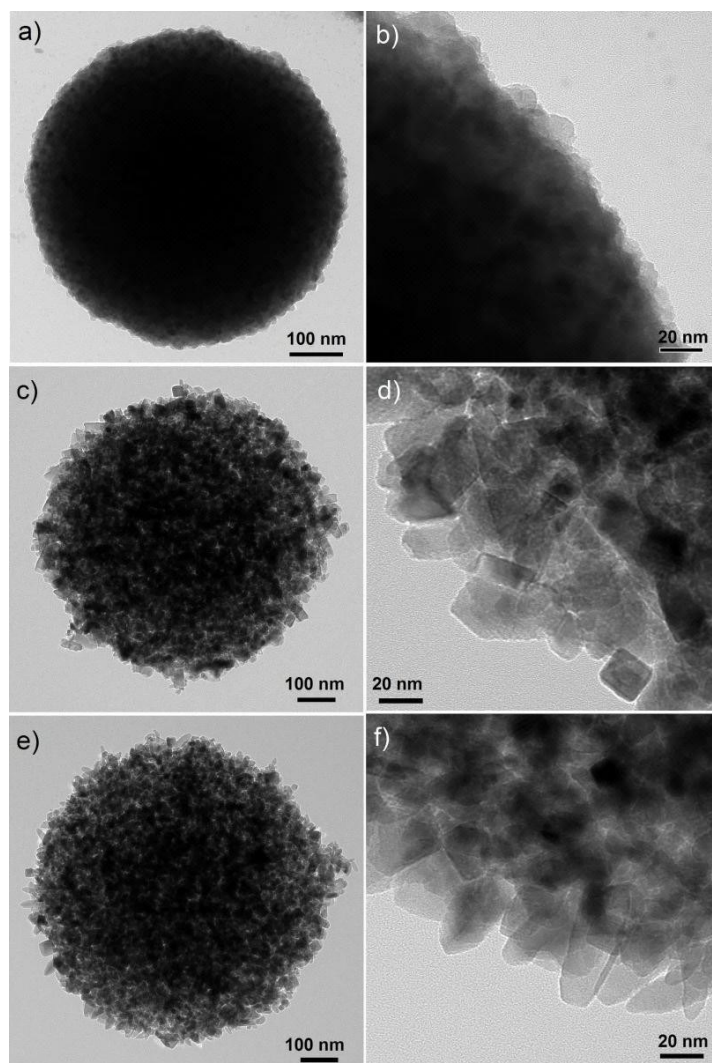


Figure S1. TEM images of mesoporous TiO₂ nanoparticle aggregates prepared using different amounts of water: a) and b) 0 mL; c) and d) 1 mL; e) and f) 2 mL.

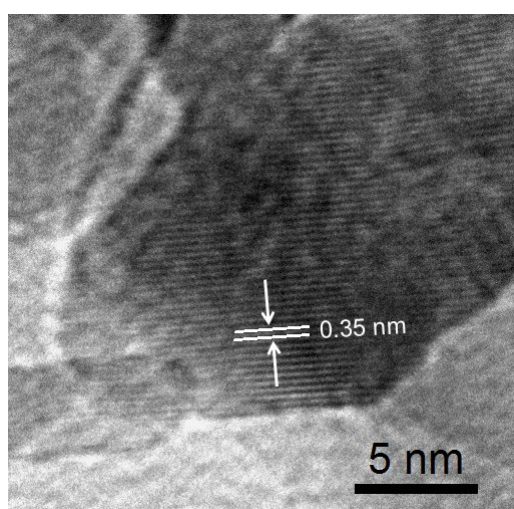


Figure S2. High-resolution TEM image of the exposed {101} facets of nanorods from **Sample T-A0.5**.

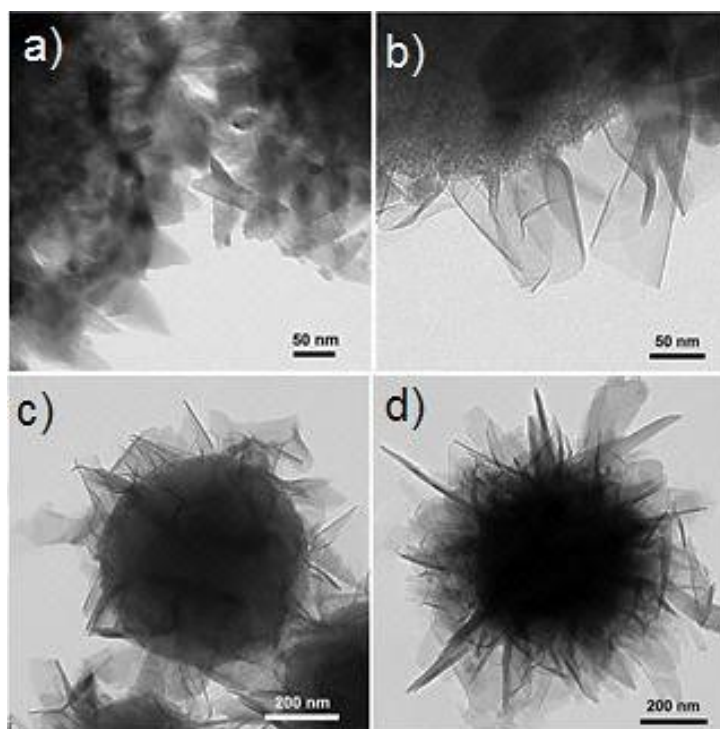


Figure S3. TEM images of structural evolution as a function of ammonia content: a) 1 mL; b) 5 mL; c) 10 mL; and d) 20 mL.

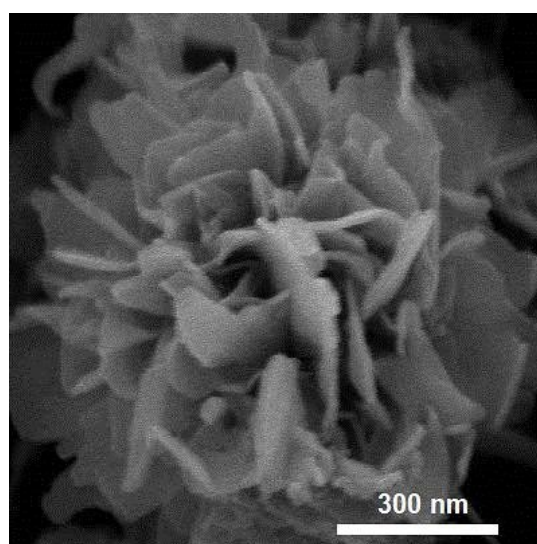


Figure S4. SEM images of ammonia titanate synthesized using 25 mL ammonia (28%).

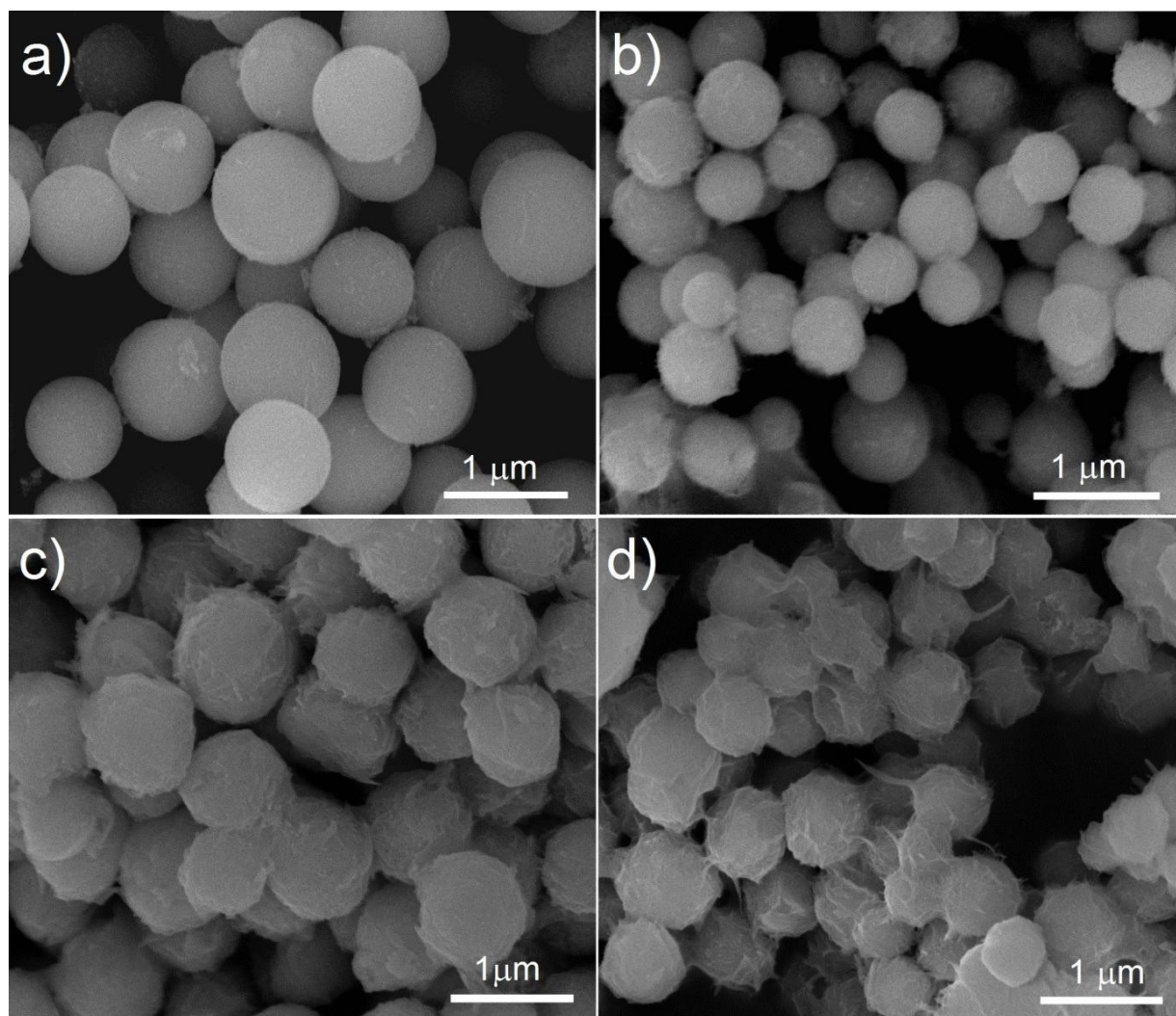


Figure S5. SEM images of structural evolution as a function of NaOH content for an equivalent concentration to ammonia (28%): a) and b) 1mL; c) and d) 5mL; e) and f) 10 mL; g) and h) 20 mL.

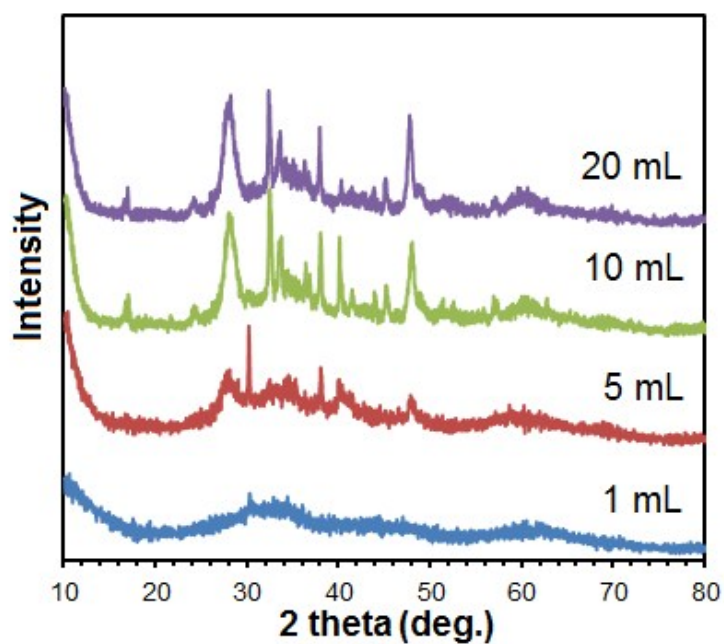


Figure S6. XRD of samples from the structural evolution as a function of NaOH content for an equivalent concentration to ammonia (28%): a) and b) 1mL; c) and d) 5mL; e) and f) 10 mL; g) and h) 20 mL. XRD analyses suggest the transformation from amorphous to sodium titanate following the increase of NaOH concentration in the solvothermal mixture.