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Pilot plant scale continuous hydrothermal synthesis of nano-titania; effect of size on photocatalytic activity

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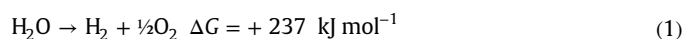
ABSTRACT

A pilot plant scale continuous hydrothermal flow synthesis (CHFS) process was used to control the crystallite size (and surface area) for nano-TiO₂ in the range ca. 5–18 nm. In CHFS, a room temperature solution of titanium oxysulfate (and boric acid) was mixed in flow with a feed of potassium hydroxide solution (at 24.1 MPa), and then this combined stream was mixed with a flow of superheated water (at 400 °C and 24.1 MPa) in a confined jet mixer. Nano-TiO₂ particles were formed instantly and then cooled inline before being collected as a slurry from the exit of the process. It was observed that the boric acid concentration in the precursor feed affected reaction pH, which in turn, determined the average crystallite size of the nano-TiO₂; as the pH increased, larger crystallites were obtained. The nanomaterials were evaluated in a sacrificial photocatalytic water splitting system (hydrogen evolution), and it was found that TiO₂ prepared under mildly acidic conditions, yielded the highest photoactivity.

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1. Introduction

The need for a clean, safe, and abundant energy source as an alternative to fossil fuels, is one of the major challenges facing the current generation. Solar energy is widely accepted as one of the most attractive future energy contributors towards the ever-increasing global demand for energy. However, solar energy is diurnal, intermittent and can vary in intensity from day-to-day. Furthermore, electrical energy is not, at present, stored widely in domestic homes in large amounts. This highlights the need for a technology that harnesses the abundance of sunlight to produce a fuel (energy source) that can be stored and is available when it is required most, potentially locally. One solution is the use of hydrogen as a fuel for energy production, which is sustainable as its combustion yields only water. The majority of hydrogen is currently produced by steam reforming, which is both costly and environmentally harmful, with CO₂ being produced as a by-product. An alternative strategy for the production of hydrogen, is to use a photocatalytic water splitting process that converts solar to chemical energy, by separating hydrogen (and oxygen) from water:



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One of the most popular photocatalysts for solar hydrogen production is titanium dioxide, which is highly stable, non-toxic and cheap to produce. These properties have made it one of the most widely studied photocatalytic materials for a range of applications, such as air and water purification [1], self-cleaning glass [2] and photodegradation of organic pollutants [3]. Titanium dioxide in its anatase polymorph, has a band-gap of approximately 3.2 eV, allowing it to absorb photons with wavelengths < 400 nm, corresponding to the ultraviolet (UV) portion of light and photons with higher energies. This is a drawback, since the solar radiation that reaches the Earth's atmosphere consists of ca. 4% UV and 46% visible light (with the remainder largely consisting of infrared radiation), leading to very low maximum photocatalytic efficiencies for UV absorbing photocatalysts. A common strategy to achieve photocatalysis under visible light, is to attempt band engineering of wide band gap semiconductors (such as TiO₂) through the introduction of dopant (metal or non-metal) ions into the semiconductor lattice. Non-metal ion dopants can create an upward shift of the valence band edge, narrowing the band gap and shifting the light absorption into the visible region [4]. TiO₂ doped with anions such as nitrogen [5–8], sulfur [9–11], and boron [12–16] have shown enhancement in photocatalytic activity under UV and/or visible light, however, the long term stability of these dopants is often in question.

In addition to metal or non-metal doping, the crystallite size, morphology, phase composition and the presence of exposed facets, can significantly affect overall photocatalytic efficiency and

activity [17]. Therefore, the relationship between nanoparticle synthesis conditions for semiconductors and their effect on particle properties, and consequently photoactivity, are of utmost importance. In some common synthesis routes, it is often difficult to demonstrate a high degree of particle size control, since reactions may be slow or require high temperatures, which can give poorly defined products. Additionally, in some synthesis processes, there may be a need to post-treat materials, which can result in uncontrolled particle growth or agglomeration and a loss of surface area. Therefore, methods that can directly offer well-defined nanoparticles are of interest to be able to better understand structure–composition–property relationships.

Continuous hydrothermal flow synthesis (CHFS) offers a rapid way of preparing nanoceramics in a single-step process, with well-defined properties. The process also offers potential as a high-throughput [18–20] method, in which many unique samples can be rapidly generated in a short time [21,22]. Furthermore, by virtue of being a continuous process, it is also very scalable as has been shown in recent publications by the authors [23,24]. The CHFS process as developed by the authors, mixes aqueous metal salts (mixed with other reagents such as pH modifiers in flow) with a stream of supercritical water in an engineered confined jet mixer, the design of which is described elsewhere [23,24]. Upon mixing with the superheated water, the metal salt(s) in the reagents, experience a sudden change in conditions, resulting in rapid hydrolysis and dehydration and crystallisation of nanomaterials, typically as oxides. The nanoparticle slurry is then cooled to room temperature in flow before being collected at the exit of the process (i.e. after a backpressure regulator, BPR, which maintains pressure in the system). By altering synthesis conditions in the confined jet mixer, it is possible to achieve some control over particle properties e.g. crystallite size, morphology, surface area, faceted growth etc. Nano-TiO₂ has previously been synthesised by continuous hydrothermal methods [25–30], and these materials have been investigated for the photocatalytic degradation of organic species (such as model dyes). However, the authors are not aware of any studies concerning photocatalytic sacrificial water splitting for such materials made via CHFS.

Herein, CHFS was employed for the synthesis of nano-TiO₂ particles. The addition of varying amounts of boric acid in the reagent feed was investigated to determine, (a) whether boron doping can be induced by CHFS, and/or, (b) the effects of addition of boric acid on the reaction pH, and therefore on the crystallite size (and surface area). The as-synthesised nano-TiO₂ samples, were characterised by a number of techniques and assessed for their ability to photocatalytically split water (in a sacrificial system) for hydrogen evolution.

2. Experimental methods

2.1. Chemicals and materials

Titanium(IV) oxysulfate [TiOSO₄ · xH₂O; ≥ 29% Ti (as TiO₂); ≤ 17% free acid (as H₂SO₄)] and potassium hydroxide pellets (KOH; ≥ 85%) were supplied by Sigma-Aldrich (Dorset, UK). Boric acid (H₃BO₃) was supplied by Fluka Analytical. Ethanol (absolute) and HCl (~36%) (Fisher Scientific, Leicestershire, UK) were used in the preparation of sacrificial solutions. Compressed air, nitrogen (oxygen free) and high-purity hydrogen gases [BOC, Surrey, UK] were used in the operation of the gas chromatograph. All chemicals and gases were used as received. Deionised (DI) water (10 MΩ) was used throughout.

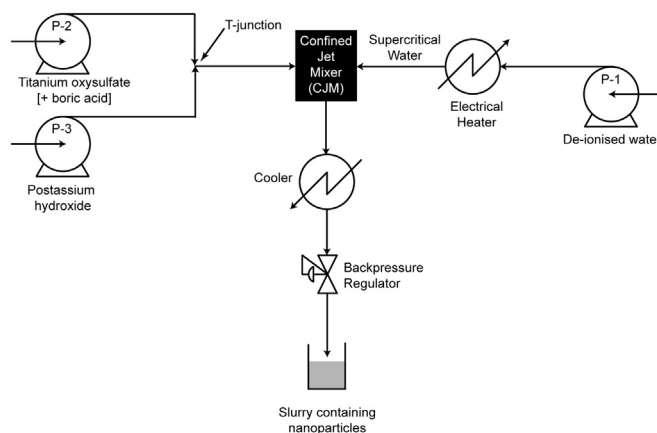


Fig. 1. Simplified schematic diagram of the continuous hydrothermal flow synthesis (CHFS) pilot plant.

Table 1

Details of experimental conditions and products obtained from continuous hydrothermal flow synthesis reactions^a.

[H ₃ BO ₃] (mol %)	0	0.5	1	1.5	2	2.5	3	5	7	10
Cs (nm)	5.0	7.8	12.9	17.2	10.3	14.1	9.7	6.5	5.4	5.0
SA(m ² g ⁻¹)	245	182	129	112	150	123	167	235	270	233
ESD (nm)	6.3	8.5	12.0	13.8	10.3	12.6	9.3	6.6	5.7	6.6

Key: Cs=crystallite size, SA=BET surface area, ESD=equivalent sphere diameter.

^a Note: the flow rates were fixed for all syntheses at 400 mL min⁻¹ (P-1), 200 mL min⁻¹ (P-2) and 200 mL min⁻¹ (P-3), generating a reaction point temperature of 305 °C. The total metal salt concentration was fixed at 0.5 M and KOH was used at 0.7 M throughout.

2.2. Continuous hydrothermal synthesis of nano-TiO₂

All samples were prepared using a continuous hydrothermal flow synthesis (CHFS) pilot plant reactor (Fig. 1), the design of which is described elsewhere [23,24]. A T-piece junction was used to premix the aqueous solution of titanium oxysulfate containing a specific amount of dissolved boric acid (total metal salt concentration of 0.5 M; details provided in Table 1) with a second solution of potassium hydroxide (0.7 M), before the combined flow met a flow of supercritical water (at 400 °C and 24.1 MPa) in a confined jet mixer (patent GB1008721), whereupon rapid crystallisation of the nanoparticles occurred. The products of each reaction were cooled in flow via a water jacket cooler and collected at the exit of the process, where the pH was also measured. The slurries were dialysed in de-ionised water (to remove residual ions), centrifuged (4500 rpm for 5 min) and washed twice before being freeze-dried overnight for ca. 22 h at 1.3 × 10⁻⁷ MPa (Virtis Genesis 35XL freeze dryer). The samples were collected as off-white powders and labelled according to the nominal concentration of boric acid used in the reagents (in mol%), as shown in Table 1.

2.3. Materials characterisation

Powder X-ray diffraction (XRD) patterns were obtained on a Bruker D4 diffractometer using Cu-Kα radiation (λ=1.54 Å) over the 2θ range 10–80° with a step size of 0.05° and a count time of 2 s. The crystallite size of each sample was estimated using the full width at half maximum (FWHM) of the anatase (101) peak by application of the Scherrer equation:

$$d = \frac{K \times \lambda}{\beta \times \cos \theta} \quad (2)$$

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