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Synthesis and characterisation of potassium polytitanate for photocatalytic degradation of crystal violet

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ABSTRACT

Potassium titanate nanostructures were synthesised by hydrothermal treatment of TiO_2 (P25) in KOH and H_2O_2. As-produced powders were characterised by scanning electron microscopy, energy-dispersive X-ray spectroscopy, transmission electron microscopy, X-ray diffraction, and nitrogen adsorption–desorption methods. Longitudinally-oriented-wire-like structures with a length up to several micrometres and diameters ranging from 10 to 30 nm were obtained. Larger size fibrous nanowires resulting from the hydrothermal treatment showed high affinity in adsorbing crystal violet (CV), which was mainly due to their high surface area. The photocatalytic bleaching of CV solution revealed that the wires are photoactive under ultraviolet light irradiation. Macroporous nanowires are considered as effective adsorbents of CV, capable of photocatalytic degradation, and they can be easily separated from the solution by settling.

Introduction

Nanostructured titanates produced by hydrothermal treatment of titanium dioxide (TiO_2) with strong alkaline solutions have generated much interest due to their unique combination of physico-chemical (Bavykin et al., 2006; Chen and Mao, 2007; Morgan et al., 2008) and structural (Chen and Peng, 2007; Yang et al., 2003) properties. Titanates, typically potassium titanate, exhibit attractive physico-chemical properties owing to their distinct crystal structures, which show great potential for cation exchange, catalysis (Izawa et al., 1982; Lee et al., 2000; Um et al., 2001) and photocatalysis (Dmitry et al., 2008; Ishihara et al., 2002; Zhuang et al., 2007).

Numerous potassium titanates, each with unique crystal structures containing layered and tunnel structures, have been synthesised (Berry et al., 1960; Masaki et al., 2000). Potassium titanates can be fabricated in the form of whiskers and fibres and have found applications as photocatalysts for water cleavage (Inoue et al., 1991; Janes and Knightley, 2004). Masaki et al. (2000) adopted a hydrothermal oxidation of titanium metal powder in concentrated potassium hydroxide solutions above 150°C to obtain potassium titanates ($K_2Ti_2O_5$, $K_4Ti_3O_8$ and $KTiO_2(OH)$) as a single phase and fibrous amorphous product that was transformed into $K_2Ti_4O_9$, $K_2Ti_6O_{13}$ or $K_2Ti_2O_5$ by calcination. Hydrothermal reaction of TiO_2 nanoparticles and KOH solution resulted in titanate ($K_2Ti_6O_{13}$) nanowires with diameters of ~10 nm and length ranges

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from 500 nm to 2 μm (Du et al., 2003a). Fine nanowires of $K_2Ti_8O_{17}$ with diameters of 5–10 nm and a surface area >300 m^2/g have been synthesised by a hydrothermal treatment of titania particles with KOH solution (Yuan et al., 2004). Due to their large surface areas, titanate nanowires have potential applications in environmental purification with enhanced photocatalytic activity (Du et al., 2003b; Fujishima and Honda, 1972).

In the past decades, there have been several reports on the synthesis and characterisation of potassium titanate nanostructures by high temperature hydrothermal treatment of powdered TiO_2 in a strong aqueous alkaline solution. Potentially, nanostructured titanates can be utilised in applications including catalysis, photocatalysis, lithium batteries and solar cells. However, rapid preparation route combining the use of low temperature, atmospheric pressure and simple apparatus in the preparation of higher-order assemblies of titanate has not been well investigated. Therefore, in this work, attempts have been made to achieve a faster rate of nanofibre formation by carrying out reflux synthesis in a mixture of aqueous KOH and H_2O_2 at relatively low temperature. We report here on the synthesis of potassium titanate nanostructures utilising a redox strategy combined with a hydrothermal reaction involving TiO_2 powder, a basic KOH solution and an oxidising H_2O_2 solution. The adoption of the environmentally friendly H_2O_2-assisted hydrothermal route has been employed to synthesise other inorganic materials under hydrothermal conditions (Li et al., 2006; Piquemal et al., 2013). The nanostructures were characterised and tested for adsorption and photocatalytic activity using crystal violet (CV) as a model pollutant.

1. Experimental

1.1. Materials

Titanium dioxide (Degussa P25, Evonik Degussa, Parsippany, NJ) was used for the synthesis of potassium titanate. P25 is a mixed phase nanopowder with 70% anatase and 30% rutile with a surface area of 57.14 m^2/g and a mean primary particle size of about 30 nm. Hydrogen peroxide (50%, W/W) was obtained from Australian Scientific Pty Ltd. (Australia), hydrochloric acid (37%, V/V) from Scharlau Chemie S.A. (Spain), and potassium hydroxide (85%, W/W) and crystal violet (86%, W/W) from ChemSupply (Australia). Milli-Q water (Merck, Millipore) was used to prepare solutions and to wash powder samples.

1.2. Synthesis

A modified peroxotitanate method was adopted, which involved mixing 2 g of P25 powder with 1% (designated as method A), 3% (designated as method B) and 5% (designated as method C) of H_2O_2 (50%, W/W) in 10 M of KOH. For example, to prepare the samples through method A, 2 g P25 powder was added to a solution containing 1 mL H_2O_2 and 99 mL KOH. The mixtures were homogenised using a magnetic stirrer and placed separately into Teflon-coated containers, which were sealed and heated at 100°C in an oven for 24 hr. After the hydrothermal treatment, the autoclave was naturally cooled to room temperature. The solid specimens were recovered by centrifugation (Centurion Sci., 2040, United Kingdom) at 3000 r/min for 5 min, washed with 1 mol/L HCl solution and Milli-Q water until pH 7, and then dried in oven at 100°C for 12 hr. The obtained powder samples, designated as A, B, and C from their respective synthesis methods, were also calcined in a furnace (CE-MLS, Labec, Australia) at 600°C for 4 hr and these samples are designated as AC, BC and CC, respectively.

1.3. Characterisation

Morphology and elemental composition analyses were carried out using a scanning electron microscope (SEM, S-4700, Hitachi, Japan) equipped with an energy dispersive X-ray detector (EDX-250 supplied by Horiba, Japan) operating at 15 kV. A Philips CM200 (Philips, the Netherlands) transmission electron microscope (TEM) operating at 200 kV was employed to obtain micrographs of the specimens. X-ray diffraction (XRD) patterns were generated on a MDI Jade 5.0 (X-ray diffractometer, Materials Data Inc., USA) X-ray diffractometer with Cu Kα radiation source. The data were measured within the range of scattering angle 2θ of 5°–90°. Powders of specimens were used without further treatment. Brunauer, Emmet and Teller (BET) surface area analyses were performed on an automated surface area analyser (BET Analyser, Micromeritics Gemini 2360, USA) by means of nitrogen adsorption–desorption. The BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.18. The mean pore diameter and the total pore volume of samples were determined from the desorption isotherm *via* Barret–Joyner–Halender (BJH) model.

1.4. Adsorption and photocatalysis

CV powder was dissolved in pure water to prepare a stock solution of 10 mg/L concentration and the pH of the solution was adjusted to 7 using 0.1 mol/L NaOH. Dye adsorption experiments were carried out in an orbital shaking incubator (Model TU-400, Thermoline Sci., Australia) operating at 150 r/min and 25°C for 30 min to reach adsorption equilibrium. Samples were collected and filtered through 0.45 μm (PTFE) syringe filters before analyses.

The photocatalytic activity of potassium titanates was assessed by batch experiments using a 2 L volume of stock CV solution. After the addition of 0.05 g/L photocatalyst, the slurry was mixed with a magnetic stirrer at 400 r/min for 30 min for dark adsorption. The cylindrical reactor (40 cm × 10 cm) vessel had three (15 W each) immersed UVC lamps (Perkin Elmer, USA), a temperature controlling device and an air sparger (0.6 L/min) to provide dissolved oxygen. Photocatalysis was carried out for 120 min at a stable temperature of 26°C. Slurry samples were collected at 15 min intervals and analysed for CV decomposition

Table 1 – Textural parameter of nanomaterial synthesis in this study.

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Mean pore diameter (Å)
P25	57.14	0.4277	80.72
A	330.10	1.271	96.11
AC	116.30	0.6063	150.70
B	263.68	1.1644	95.16
BC	105.09	1.482	129.52
C	235.81	1.103	104.26
CC	84.92	0.8928	208.96