Hydrothermal synthesis of mixed phase blue titanium dioxide from oxalate stabilised sols

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Abstract: Blue coloured titanium dioxide nanoparticles were synthesised by the hydrothermal treatment of oxalic acid stabilised titania sols in the presence of NH4F as a modifying agent. The NH4F concentration determined the phase of titania produced and influenced the shape of the rutile crystallites produced. The blue colour originated from the F-stabilised Ti3+ centres formed under the reaction conditions. Organic residues in the sol decomposed to generate a hydrogen-rich atmosphere. Photocatalytic activity studies revealed the rutile phase titania produced was extremely active for a given surface area when compared to P-25.

Keywords: titanium dioxide; blue; self-doped; Ti3+; NH4F; sols; hydrothermal; photocatalytic.


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Her research expertise is on sol-gel synthesis of fluorine-modified titanium dioxide as an active photocatalyst in degradation of dye (focusing on Reactive Dye, C.I: RB19). Her research focus has been on synthesizing a shape and size controlled titanium dioxide as well as researching the effect of gold-doping towards boosting visible-light photoactivity of titanium dioxide.

Vladimir Golovko graduated with a BSc from the Kyiv-Mohyla Academy and a degree of Specialist in Chemistry from the National Taras Shevchenko University of Kyiv in 1996. He completed a PhD in Organometallic Chemistry at the Department of Chemistry, University of Cambridge, UK. After earning a PhD in Cluster Chemistry at the University of Cambridge in 2003, he continued as a post-doc in the group of Professor Brian F.G. Johnson, FRS focusing on applications of clusters and metal nanoparticles in controlled nanofabrication and catalysis, contributing to multi-national grants such as the European Community FP5 and FP6 programs. He joined the Department of Chemistry, University of Canterbury, Christchurch, New Zealand as a Lecturer in 2007 (promoted to a Senior Lecturer in 2010 and Senior Lecturer above the bar in 2015). His research interests have strong emphasis on precise fabrication and detailed structural characterisation of nanomaterials (metal colloids, gold and gold-containing atomically precise clusters, metal oxide nanostructures etc.), their applications in heterogeneous (electro/photo) catalysis and catalytic nanofabrication, sensors and bio-nanotechnology. Since 2002, he has published 44 papers in prestigious international journals (Nature, Angewandte Chemie International Edition, Chemical Communications with his most recent paper in the ACS Catalysis highlighted on the front cover in January 2015) that have attracted over 1100 citations.

Tim Kemmitt is based at Callaghan Innovation, a New Zealand Research Institute set up to accelerate innovation. He completed his PhD in Inorganic Chemistry in Southampton, UK in 1989. His research expertise is in inorganic materials synthesis, largely focused on oxide materials applied to the formation of functional thin film coatings. His focus has been on the application of photocatalytic materials and understanding how the nano-surface properties influence the material properties and functionality. The formation of ZnO-based transparent conductive thin films has led to an interest in the control of nanocrystal growth.

1 Introduction

Over the past 40 years the use of anatase as a photocatalyst has attracted immense attention [1]. It can be used in the degradation of waste, used to produce self-cleaning materials and photocatalytic water splitting [1–3]. Many studies have been carried out to maximise its photocatalytic activity by modifying crystal phase [4], morphology [5] and crystal size [1]. Other phases of titania include rutile and brookite which exhibit lower photocatalytic activity [4].

Crystallite shape, and hence the specific exposed facets also affects the photoactivity. In anatase phase titania it is commonly believed that the 001 facet is the most photoactive. Maximising the presence of the 001 facets using a hydrothermal synthesis in the presence of HF have been effective [6]. However, the use of HF considered by some to be dangerous and environmentally unfriendly [7]. Less is known about the activity of different facets of rutile [8]. A further consideration is crystallite size and overall catalyst
surface area. Reducing the size of nano particulate titania can increase the photoactivity, however as crystallites become smaller and smaller their crystallinity decreases. Poorly crystalline titania shows low photoactivity owing to impaired electron and hole movement [1].

Anatase and rutile have bandgaps of 3.2 eV and 3.0 eV respectively [1], confining their photocatalytic utility to the ultra violet (UV) portion of the solar spectrum. The band structure of titania can be altered by using dopants such as nitrogen or transition metals to extend the activity into the visible light region [9]. More recently, an oxygen deficient titania has been reported demonstrating visible light activity [10]. The missing oxygen results in Ti$^{3+}$ defects that altered the band structure and allow visible light absorption [11]. This change in bandgap and visible light absorption results in light blue to black titania [12]. These are often synthesised by growing titania crystallites in reducing conditions such as in a flame or under high temperature in the presence of H$_2$ [10,11].

In a previous paper we explored the synthesis of oxalic acid passivated titania sols, McNicoll et al. [13] noting the conditions controlling nanocrystal size, morphology, and crystal phase. In an extension to this work, we now report how the addition of varying amounts of NH$_4$F influences the nanocrystal properties and discuss the chemistry dominating the transformations during the hydrothermal synthesis. The unique conditions involved in this synthesis route explain the contrasting results obtained from alternative syntheses using NH$_4$F, e.g., Ye et al. [14]. In particular the high temperatures of hydrothermal treatment and decomposing oxalic acid make for a unique reducing environment not seen in Ye et al. [14] resulting in the formation of dark blue titanias.

2 Experimental

The synthesis of the titania explored in this paper was done in two stages. In the first stage an oxalic acid passivated sols was synthesised as previously reported in our paper [13]. The sols were then hydrothermally treated in a similar fashion as reported in McNicoll et al. [13] however NH$_4$F added as a modifying agent.

All reagents were used as received. Reagents: titanium (IV) isopropoxide (TIPP) Aldrich reagent grade 97%, oxalic acid Schrallau reagent grade, ammonium fluoride anhydrous Aldrich reagent grade, ethanol anhydrous solvent grade and water distilled. Hydrothermal temperatures are reported ±2°C.

Briefly, in a 250 ml beaker 1.58 g (0.0125 mol) oxalic acid was dissolved in 28 g (0.6087 mol) ethanol, agitation was necessary to fully dissolve the oxalic acid. To the fully dissolved oxalic acid solution 14.2 g (0.05 mol) TIPP was added dropwise. The resulting solution was agitated to homogeneously disperse the TTIP. Distilled water (180 ml) was added to the ethanol solution forming a milky white solution. The solution was placed in a water bath (70–80°C) and vigorously stirred with an overhead stirrer for approximately 60 min or until a transparent solution was achieved. The resulting sol was filtered through a Büchner filter and then diluted with water to a final volume of 180 ml.

Hydrothermal treatment of the oxalic acid sols was performed in the following manner. First the modifying solutions containing 0 to 1 equivalents NH$_4$F were prepared by dissolving (0 g, 0.046 g, 0.093 g, 0.116 g, 0.139 g, 0.185 g, 0.231 g, 0.278 g, 0.324 g, 0.370 g, 0.417 g, 0.463 g) NH$_4$F in 5 mL distilled water. 45 mL of the oxalic acid sol was transferred into a 75 mL Teflon lined autoclave. 5 mL of the modifying solution was added to the 45 mL of sol. The autoclave was then sealed and placed in a preheated oven.
at 275°C. The autoclave remained in the oven for 24 hours before being removed and allowed to cool to room temperature. Once cooled the titanium dioxide was separated by centrifugation and washed twice with 50 mL distilled water. Samples were named with respect to the number of equivalents of NH$_4$F to TiO$_2$, i.e., 0.25 equivalents NH$_4$F was named 0.25 F.

The as-synthesised titania was characterised using the following methods. Powder X-ray diffraction (PXRD) was performed on a Philips PW3700 series diffractometer using Co-K$_\alpha$ radiation ($\lambda = 1.7889$ Å). Scans were recorded from 4° to 80° with a 0.01 step size and count time of one second. Size and phase of titania was determined by fitting the PXRD data with the Bruker software package EVA. Scanning electron microscopy (SEM) was performed JEOL JSM 7000F instrument. Samples were prepared by dispersing titania in a small amount of methanol and depositing particles on a silicon wafer. Nitrogen absorption isotherms were measured on a Micrometics ASAP2010. Approximately 100 mg of sample was degassed at 250°C for three hours at 3 µmHg. Surface area was calculated using Brunauer-Emmett-Teller (BET) theory. Ultraviolet visible light diffuse reflectance spectroscopy (UV-Vis-DRS) and UV-Vis spectra were recorded on a Cary 100 Bio UV-Vis spectrophotometer.

To analyse the gases released from the hydrothermal synthesis a syringe was used to sample the gases released from the autoclave. The contents of the syringe were analysed using an Ametek dymaxion mass spectrometer. Masses were measured from 0 to 50 atomic mass units, count time per atomic mass unit was 500 ms and each point was averaged 12 times.

Photoactivity measurement was performed using RB19 reactive blue dye as described by Abu Bakar et al. [15]. Briefly, in a quartz 170 mL vessel, 30 mg of synthesised titania powder was ultrasonically dispersed into a 100 mL of RB19 stock solution (0.000127 mol/L). 0.00001 mols of hydrogen peroxide was added to the dye solution. The dye solutions were stirred for 15 min before the Ushio UXL-500DO-500 W broad spectrum Xe lamp was switched on. The light was switched on and the solution was stirred for two hours. 3 mL samples were removed every 15 min for the first hour and then every half an hour for the second hour. Each sample removed was centrifuged at 15,000 rpm for three minutes, twice. Then the remaining dye solution’s was determined using ultraviolet visible light spectroscopy (UV-Vis) and measuring absorption at $\lambda = 593$ nm.

3 Results and discussion

The phase of titania synthesised showed a strong dependence on the number of equivalents of NH$_4$F added. When the PXRD spectra (supplementary information S1) were fitted the results revealed (Figure 1(a)) that at less than or equal to 0.25 equivalents of NH$_4$F added the titania produced was phase pure rutile. As more NH$_4$F was added anatase phase titania began to dominate reaching a peak at 0.5 equivalents. As more NH$_4$F was added the anatase phase content remained stable at approximately 60%. The literature states that when NH$_4$F is present anatase phase would dominate [15], however as we previously reported oxalic acid in sols favours rutile phase at the higher temperature of hydrothermal treatment [13]. It would appear that above 0.25 equivalents NH$_4$F the influence of the F ion overcomes that of the oxalate.
We have shown previously that the oxalic acid content influences crystallite sizes [13] here we found the concentration of NH$_4$F also influenced the crystallite sizes of each phase independently. Figure 1(b) shows rutile phase crystallites grew larger with increasing NH$_4$F equivalency until anatase phase titania begun to appear *ca* up to 82 nm.
This could be owing to a lack of TiO₂ building blocks to grow the rutile. Anatase phase crystallites show much dependency on the NH₄F equivalency, ca 33 to 19 nm.

SEM images revealed that the rutile produced in the absence of NH₄F were elongated rods as previously reported [13]. However when 0.25 equivalents of NH₄F was added the shape of the rutile crystallites dramatically changed to isotropic pyramid like crystallites, compare Figure 2(a) and (b). The shape of the anatase crystallites produced did not show any well-defined shape. This is in part owing to the small size of the crystallites made it very difficult to accurately resolve the crystallites shape. Nonetheless it can be seen in Figure 2(c) that the rutile present amongst the anatase crystallites is of a similar shape to those observed in sample 0.25 F. The F⁻ ion is binding to a facet of the growing rutile phase crystallites and inhibiting or enhancing growth in specific crystallography directions.

**Figure 2** SEM images of titania synthesised with: (a) 0 equivalents (0 F) NH₄F, (b) 0.25 equivalents NH₄F (0.25 F) and (c) 1 equivalent NH₄F (1 F)

The most interesting effect of the NH₄F when compared to our previously synthesised titania from hydrothermal treating of oxalic acid sols, was that titania produced in all samples bar sample 0 F was a dark blue colour. UV-DRS shown in Figure 3 revealed the titania produced has a shifted absorption edge and an red light absorbing tail. The initial shift in the absorption edge can be explained by the phases produced. Rutile phase titania has a smaller bandgap ca 3.0 eV then anatase phase titania ca 3.2 eV [1]. However the phase change does not explain the absorption of red light. Blue titania has previously be synthesised by other groups were reducing conditions have been used to produce
Ti$^{3+}$ defects [16]. In other papers, reducing conditions were induced by adding reducing gases or reducing agents [17,18]. However, in our synthesis no reducing agents were added deliberately. Previously reported [13] we had noticed the oxalic acid decomposes at the high temperatures used for the hydrothermal synthesis. Secondly, it was noticed the rutile synthesised without any NH$_4$F added did not turn blue.

Figure 3 UV-Vis – DRS results showing shift in bandgap and red light absorption of samples synthesised with zero, 0.25, 0.5 and one equivalent of NH$_4$F (see online version for colours)

To investigate what could potentially be causing the reducing conditions that induce defects generating the blue colour. Mass spectrometry was used to analyse the gases released from the hydrothermal synthesis. Looking at the mass spectra below in Figure 4, it can be seen that there are many decomposition products. First there is more CO$_2$ present than in air, this confirms what we had suspected in our previous paper that oxalic acid decomposes to form CO$_2$ and water [13]. Secondly, there are traces of what we suspect are organic decomposition compounds with masses between 40 g mol$^{-1}$ and 45 g mol$^{-1}$. These peaks also appear lower in the spectrum as doubly charged masses. Lastly and most importantly, we detected the presence of hydrogen. Hydrogen is a well-known reducing agent that has been used to synthesise blue titania before [17]. What we propose is the elevated temperatures thermally decompose the organic components (ethanol, propanol and oxalic acid) to hydrogen and other products. At the high temperatures and high pressures inside the autoclave the hydrogen can reduce Ti$^{4+}$ to Ti$^{3+}$ which is incorporated into the growing crystallites. Interestingly hydrogen is also detected in the synthesis of 0 F yet blue titania was not formed. We suspect that the presence of the F$^-$ ion is necessary to either assist in the formation or stabilise the defect possibly by replacing an oxygen to localise the Ti$^{3+}$ state.
A photocatalytic study was carried out to see how the phase, shape, size and colour had affected the photoactivity of the titania synthesised. In all cases the photocatalytic activities of the hydrothermally prepared samples are lower than commercial P-25,
see Figure 5. The two rutile samples, 0 F and 0.25 F show the lowest activities as would be expected, while the 0.5 F sample, containing the highest proportion of anatase showed the highest activity, being almost equivalent to the P-25 sample. However, if the results are normalised for surface area, the 0.25 F sample showed surprisingly high activity (three times the P-25). Note the BET measured surface area for 0 F, 0.25 F, 0.5 F, 1 F and P-25 are 23.95, 4.81, 35.47, 43.78 and 50.10 m²/g, respectively. This is surprising as rutile phase titania is generally believed to be tens of times less photoactive than anatase phase titania [1]. The high activity of sample 0.25 F may be owing to the increased crystallinity of the large crystallites, the exposed facets or the combination of Ti³⁺ and fluorine doping. Visible light studies were not yet performed on these titania samples. A future report will focus on the full examination of measurement of defect sites and Ti³⁺ concentrations, magnetic measurements, and UV and visible light photoactivity.

4 Conclusion

In conclusion we found that NH₄F can be used to change the morphology of titania produced when hydrothermal treating oxalic acid sols. At low concentrations of NH₄F rutile phase is produced. The NH₄F both alters the shape of the crystallites produced and generates some defects, possibly Ti³⁺, giving the titania a dark blue colour. At higher NH₄F concentrations anatase phase crystallites are produced. The shape of the crystallites produced appears to be unaffected by the NH₄F nonetheless the same blue colour is observed. The possible cause of the blue colour is a hydrogen reducing atmosphere generated by the decomposition of the organics present in the sol. The NH₄F also affects the photoactivity of the titania. Anatase phase rich titania produced at 0.5 equivalents of NH₄F is the most photoactive yet the shape modified blue rutile has the highest activity per surface area unit.

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References


Supplementary information

Figure S1  PXRD diffractograms of key samples (0 F, 0.25 F, 0.5 F and 1 F)