Controlled Nanophase Development in Photocatalytic Titania

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Acid catalyzed hydrolysis of titanium butoxide was used to synthesize homogenous titania gels, which were converted to the anatase and rutile polype types through controlled firing. The mechanism of this phase transformation was investigated by quantitative powder X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). Condensation to titania is a function of annealing time, temperature and atmosphere. In air, calcinations below 600°C favored the formation of anatase, with rutile only appearing at > 600°C. However, in situ transformation where titania nanoparticles were treated under vacuum in the TEM required heating at higher temperatures up to 900°C. This is may be due to the formation of surface layers of reduced titanium oxide that passivate and retard the anatase to rutile transformation. Grain growth and specific surface area varied inversely, with especially rapid crystallization observed at and beyond the transformation temperature. Potential photocatalytic activity was identified with ultraviolet-visible (UV-Vis) spectroscopy. A red shift of the absorption edge for nano-titania was observed due to quantum size effects.

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1. Introduction

Semiconductor photocatalysts are widely regarded as potential low cost and environmentally friendly materials for air and water purification.¹,² Amongst them, titania is considered a promising candidate due to its oxidation strength, high photostability, and nontoxicity.³,⁴ Nonetheless, widespread implementation is restricted as the band-gap is in the ultraviolet range, substantially increasing the operating costs of titania-based systems. To overcome this limitation, current research is focused on improving efficiency using titania-nanometal composites,⁵,⁶ electrochemically enhanced catalysis,⁷ band-gap shifted doped-titanias⁸ or porous composite ceramics.⁹ For all these variants, high catalytic performance is strongly dependent on crystallinity, particle size and the surface structure of the titania.⁸,⁹ ‘These in turn are controlled through precise synthesis of the semiconductor.¹⁰ For example, Ito et al.¹¹ reported the water-to-ethanol ratio was the key factor controlling crystallinity of the as-grown titania nanoparticles. Moreover, there are contradictory reports of the most active photocatalytic phase - the semiconductor band gaps of bulk anatase and rutile are 3.2 eV and 3.0 eV respectively - due to factors ranging from surface chemistry to quantum effects to incomplete characterization.¹² Further, it is rare that consideration is given to other titania phases including brookite, TiO₂(B), TiO₂(II), TiO₂(H) amongst others, although these can be present as transient, or nanoencapsulated structures within the commonly recognized polytypes.¹³

For the past two decades, sol-gel routes have been an important source of nanocrystalline titania.¹⁴,¹⁵ The critical amorphous to anatase phase transition is controlled fundamentally by preparative conditions, that in turn, dictate photocatalytic efficiency.¹⁶,¹⁷ In particular, the agglomeration of crystal nuclei must be avoided to obtain a homogeneous product at the smallest possible scale (<10 nm). In this study, we describe and validate a simple sol-gel process for the synthesis of 3–5 nm anatase crystals.

2. Experimental Methods

Acid catalyzed hydrolysis of an alcohol solution of titanium tetrabutoxide Ti(OBu)₄ was used to synthesize nanosized titania powders. The alkoxide was diluted with ethanol by thorough stirring in air with a magnetic mixer. Dilution was accomplished in two stages. First a portion of absolute alcohol was introduced, and then H₂O and HCl dissolved in the remaining ethanol were added dropwise with continuous stirring to form homogenous sol. The process of hydrolysis was controlled carefully. Through a sequence of hydrolysis and polycondensation reactions, the sol-gel transition was permitted to proceed gradually. The wet gel was dried at 60°C under vacuum for 5 h. Finally, calcinations were completed by firing at 200–800°C for 2 h in air.

Crystallinity was investigated by powder X-ray diffraction (XRD) using a Siemens diffractometer (D5005) fitted with a copper tube and using a 2-theta stepping size of 0.02°. The titania powders were lightly compacted into XRD specimen discs for data collection. Average grain sizes for anatase and rutile were estimated from diffraction peak widths determined by Rietveld refinement. Two types of transmission electron microscope analysis were undertaken. In the first, a JEOL JEM-3010 transmission electron microscope (TEM) operated at 300 kV was used to collect selected area electron diffraction patterns (SAD), microdiffraction patterns (MD), and high-resolution transmission electron micrographs (HRTEM). For these observations, the powders were floated on ethanol, dispersed ultrasonically, and several drops of the suspension collected on lacey carbon films supported by copper grids. In the second experiments, high temperature annealing of air-calcined 200°C powder was conducted in situ with a Gatan hot stage inserted into a Philips EM 430 TEM using an accelerating voltage of 300 kV. For this study, the powders were suspended in distilled water and collected on holey carbon films supported by a molybdenum grid. Convergent beam electron diffraction (CBED), bright field imaging (BF) and SAD were used to monitor the phase
transformation processes in the powders. Observations were carried out close to the grid bars where thermal conductivity and temperature measurement are better correlated. The dried titania gels were also examined by thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a Netzsch (STA 409) thermal analyzer. The surface area of the samples was estimated by N₂ chemisorption using a Brunauer-Emmett-Teller (BET) in a flow of inert gas (helium) at 200°C. A Shimadzu UV-1601 spectrophotometer was used to collect the UV-Vis spectra. FTIR spectra were recorded at room temperature with a Biorad spectrometer (Excalibur Series) in the frequency range of 400–4000 cm⁻¹.

3. Results and Discussion

3.1 Thermal analysis and phase stability

Thermal analysis (DSC/TGA) revealed that the dry gel undergoes endothermic dehydration in the temperature range 80–150°C, while exothermic reactions localized between 250°C and 550°C, are attributable to the evaporation and combustion of organic compounds (Fig. 1).²⁰ The phase changes accompanying calcination of the gel are summarized in Fig. 2 where X-ray diffractograms are presented over the temperature range of 200–800°C. Below 500°C all peaks correspond to anatase, with rutile beginning to appear (at a level detectable by XRD) only at 600°C, beyond which the quantity of this latter phase increased rapidly until transformation was complete at 800°C. For anatase, Bragg peak widths gradually decreased with increasing temperature due to crystallization, however even at 500°C the reflections remain relatively broad. Figure 3 illustrates the trend in anatase particle size as determined from Rietveld analysis. Using this method, the particle diameter for the dried gel is ~3 nm. After heat treatment at 200°C the size increased to 9 nm but below 500°C (less than the anatase → rutile transition) crystallization was slow. Beyond this growth was rapid for both anatase and rutile reaching 140 nm and 100 nm at 700°C respectively. The XRD results are consistent with the BET surface area analysis (Fig. 3) where the titania dry gel showed a specific surface area of 248.3 m²/g that decreased rapidly from 171.2 m²/g at 300°C to 2.0 m²/g at 700°C.

3.2 Microstructural characteristics

The SAD pattern of titania heat treated at 200°C is shown in Fig. 4(a) to indicate the polycrystallinity of the sample. The first five diffraction rings, counting out from the forward-scattered beam, have lattice spacings of 0.35, 0.24, 0.19, 0.17, and 0.15 nm, respectively, that correspond to anatase reflections {011}, {013}, {200}, {1011}, and {123}. SAD patterns of TiO₂ samples calcined at 200, 300, 400 and 500°C were not significantly different. Direct observation of crystalline nanodomains was achieved using lattice images collected at underfocus conditions that allowed an accurate estimate of crystallite size. For example, a HRTEM image of the 200°C titania sample (Fig. 4(b)) revealed crystalline nanodomains ~6–10 nm in diameter in good agreement with XRD results (9 nm). During hot stage in situ TEM, the 200°C air-calcined powder was slowly raised to 700°C and maintained at temperature for 4 h to allow thermal equilibration, after which the temperature was increased to 900°C. In contrast to the ex situ calcinations in air, anatase proved far more persistent at high temperatures for in situ TEM experiments. Whereas air calcinations lead to rapid transformation to the high temperature polytype beyond 500°C (see Fig. 2), no transformation was observed in the TEM even after treatment.
at 700°C for half an hour. Although the temperature distribution across the grid may not be homogeneous, the long duration of the experiment and the selection of crystals close to grid bars to ensure better thermal conductivity, suggest there is genuine retardation.

The reasons for the enhanced stability of anatase in the microscope experiments are likely to be complex, however, the conditions in the electron microscope differ in two significant respects compared to the usual laboratory syntheses described above. First, the materials are heated in vacuum, rather than air, and observations are carried out in the flux of a relatively intense electron beam. Both these factors are significantly reducing in nature. It is well known that titanates can be reduced in situ during HRTEM, even in the absence of heating. Relevant examples include the conversion of tianate hollandite20) (actually an alkali-stuffed version of TiO₂(H)) to rutile and the conversions of titanate perovskites to titanium monoxide.21) It is also known that semiconductors can readily undergo electron-beam-induced decomposition at energies near their band gap.22,23) Such mechanisms are especially effective close to the surfaces of solids, since an anion (or a cation) may acquire extraordinary charge states and be ejected from the surface due to the consequent electrostatic instability of its interatomic bonds with neighbouring ions. Such effects, while presently observed only on macroscopic titanate crystals, could conceivably play an even more important role in nanocrystalline material. It is postulated under HRTEM conditions nonstoichiometric titanium monoxide (TiO) may passivate the anatase surfaces to allow their persistence to high temperatures than under oxidizing conditions. This matter is currently the subject of detailed study by atomic resolution microscopy.

For the same sample, the temperature was then increased to 900°C and held constant with observations being recorded after 1, 2, 3 and 4 h (Fig. 5). The anatase diffraction rings began to blemish after 1 h. However, the phase transformation took place slowly, with weak mottled diffraction rings corresponding to rutile forming after 2 h. At longer times, as grain growth continued, and the transformation progressed, ring intensity gradually reduced and random Bragg diffraction spots appeared that were attributable to anatase and rutile. BF contrast of the nano-agglomerates changed correspondingly, with very fine crystals appearing that were distributed throughout and possessed darker contrast than the anatase phase. Strong diffraction rings from those areas corresponded to rutile. Under CBED mode, and by moving the probe carefully, micro-diffraction patterns from the newly formed particles could be indexed as rutile (Fig. 6).
3.3 FTIR and UV-Vis spectra

FTIR of the as-prepared titania gel gave a broad band between 3600 and 3100 cm\(^{-1}\) that was assigned to fundamental stretching vibrations of different hydroxyl groups (free or bounded) (Fig. 7). The absorption peak at 1620 cm\(^{-1}\) in each spectrum below 400 °C was due to physisorbed H\(_2\)O molecules,\(^{11,24}\) while the absorption peaks from 1280–1450 cm\(^{-1}\) that form at 300–400 °C can be identified as the vibrations of carbonates and bicarbonates.\(^{25}\) These are the thermal decomposition products of organic residuals.

The UV-Vis absorption spectra of TiO\(_2\) powders heat-treated at 200–400 °C is shown in Fig. 8. The abrupt increase of the absorption in each spectrum below ~400 nm results from the transition of electrons from the valence band to the conduction band, and is the basis for the photocatalytic functionality of titania. The absorption band edge of the 200 °C treated TiO\(_2\) can be estimated as 337 nm (3.7 eV) by extrapolating the steep slopes in the curve to the long-wavelength side. As expected, this is larger than the bulk value for anatase (3.2 eV) due to significantly enhanced surface quantum effects in the nanoparticles. Indeed, by comparing the UV-Vis absorption spectra it can be seen that the absorption shifts to longer wavelengths (i.e. smaller band gaps) with increasing temperature. This red shift is attributable to increasing crystal size and a reduced quantum size effect.\(^{26,27}\)

4. Conclusions

Nanosized titanium powders with particle sizes down to 3 nm were synthesized through a sol-gel method at low temperatures (<60 °C). Ex-situ calcination in air below 500 °C yielded a stability field favorable to the formation of anatase with the phase transformation accelerating above 600 °C, however under the reducing conditions found in the TEM the reaction required long annealing at 900 °C. It is postulated that the transformation is delayed due to partial reduction of titania that permits surface passivation and phase stabilization by reduced titanium oxide monolayers. The particle size of both anatase and rutile increased with temperature, leading to a red shift of the UV-Vis absorption edge due to quantum confinement.

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REFERENCES