

Selective synthesis of anatase and rutile *via* ultrasound irradiation

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A simple and efficient methodology has been established for the selective synthesis of anatase and rutile as well as their mixtures with various precursors using ultrasound irradiation; the products, the particle sizes of which are nanometric (< 9 nm), are dependent both upon the reaction temperature and the precursor used; a substantial reduction in reaction time as well as reaction temperature is observed as compared to the corresponding hydrothermal processes.

Since Fujishima and Honda¹ discovered the photocatalytic splitting of water on titania electrodes, intensive, world-wide research activity based on titania has ensued. Titania has three crystalline phases: rutile, anatase and brookite, of which rutile is the most stable while anatase exhibits the highest photocatalytic activity.² Up to now, many methods have been established for the synthesis of titania,^{3–8} the sol–gel technique being the most often used. Unfortunately, the sol–gel derived precipitates are amorphous in nature, which requires further treatment to induce crystallization.^{9,10} The hydrothermal technique is widely employed to enhance crystallinity in laboratory and commercial preparations. However, many factors, *e.g.* reaction temperature, reaction time and the medium, may influence the crystallization process. A recent paper demonstrated that the optimum temperature for the hydrothermal treatment is 473–493 K.¹¹ In order to obtain crystalline titania at lower temperature, a longer aging time is required. On the other hand, the photocatalytic activity of titania is particle size dependent, *i.e.* the smaller the titania particles, the higher their photocatalytic activity.¹² Hence, it is of great importance to improve the synthesis methodology. Here we describe a new, simple route for the direct, selective synthesis of nanosized anatase and rutile employing ultrasound irradiation for a short reaction time.

The sonochemical synthesis has been described elsewhere,¹³ which has been employed to prepare amorphous metals^{14,15a} and oxides.^{15b} In the present work, it has been found that ultrasound irradiation can also accelerate the crystallization process of titania. The most important result of this investigation is the dependence of the product phase on both the used precursor and the reaction temperature. Under the same reaction conditions, anatase was formed when tetraisopropyltitanate (TPT) was employed as the precursor, rutile was obtained when titanium tetrachloride (TTC) was used, while a mixture of anatase and rutile was obtained when the precursor was a mixture of TPT and TTC.

Table 1 Synthesis conditions for samples A–H and their crystalline phases

Sample	Precursor	Synthesis conditions ^a	Sample phase	Particle size ^b /nm	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$
A	TTC	Hydrolyzed in water, sonicated for 3 h	Rutile	8.2	103.5
B	TPT	Hydrolyzed in water, sonicated for 3 h	Anatase	3.5	201.5
C	TPT+TTC	Hydrolyzed in water, sonicated for 3 h, TPT:TTC = 63.4:36.6 (molar ratio)	Rutile + anatase (52.4:47.6)	6.8	
D	TPT+TTC	Hydrolyzed in water, aged at 353 K for 3 h	Poorly crystalline	—	
E	TPT	Hydrolyzed in water, sonicated at 303 K for 3 h	Brookite + anatase	2.5	
F	TTC	Hydrolyzed in water, sonicated at <i>ca.</i> 283 K for 3 h	Rutile	5.9	
G	TPT	Hydrolyzed in 0.2 mol/L HCl (pH = 0.7), sonicated for 3 h	Rutile + anatase	6.5	
H	TPT	Precipitated the supernatant of G at pH 8.6 with $\text{NH}_3 \cdot \text{H}_2\text{O}$ (24% aq.), sonicated for 3 h	Anatase	2.9	289.8

^a Sonication was carried out under atmospheric pressure without cooling if no other conditions are specified. ^b Average particle size was estimated from PXRD line-broadening employing Scherrer formula.

In a typical synthesis, 110 mL of deionized water was sonicated by employing a direct immersion titanium horn (Sonics and Materials, VC-600, 20 kHz, 100 W cm^{-2}) for 10 min. At this stage 10 mL of the precursor (TPT, TTC or TPT+TTC, Aldrich) was injected into the sonication cell. The mixture was further sonicated continuously for 3 h. The sonication was conducted without cooling so that a temperature of 353 K was reached at the end of the reaction. The precipitates were separated by centrifugation and washed twice with deionized water and once with ethanol. The product was further dried under vacuum overnight. The detailed synthesis conditions for various samples are summarized in Table 1.

The powder X-ray diffraction (PXRD) patterns of the as-prepared samples are presented in Fig. 1. The reflections in Fig. 1(a) can be indexed to rutile (JCPDS 21-1276) while those in Fig. 1(b) are indexed to anatase (JCPDS 21-1272), which correspond to the as-prepared products using TTC and TPT as precursors, respectively. The sonication of a TPT and TTC mixture yielded sample C, which was a mixture of anatase and rutile [Fig. 1(c)]. Unlike the sol–gel method, the as-prepared products of the sonication process are always perfectly crystalline. For comparison, sample D was synthesized by employing the same precursor and reaction conditions (353 K) as sample C except that the reaction was carried out without sonication. Sample D is poorly crystalline or amorphous as shown in Fig. 1(d).

By employing the well-known formula¹⁶ $X_A = [1 + 1.26(I_R/I_A)]^{-1}$, where X_A is the fraction of anatase in the mixture, and I_R and I_A are the intensities of reflections (110) of rutile and (101) of anatase, respectively, it is estimated that sample C contains 47.6% anatase and 52.4% rutile. This is quite surprising because the molar ratio of TPT to TTC in the irradiated solution is 63.4:36.6. Taking into account that rutile and anatase were the sole corresponding products when TTC and TPT acted as the precursors, separately, it is obvious that part of rutile formed at the expense of TPT.

The strong influence of the reaction temperature and the acidity of the medium on the crystallization of titania were further demonstrated in the syntheses of samples E–H. When TPT was used as precursor and sonication was carried out at 303 K, sample E was obtained as a mixture of brookite (JCPDS 29-1360) and anatase [Fig. 1(e)] while for TTC sonicated at *ca.* 283 K the product obtained (*i.e.* sample F) was mainly rutile [Fig. 1(f)]. However, at the same temperature when TTC was

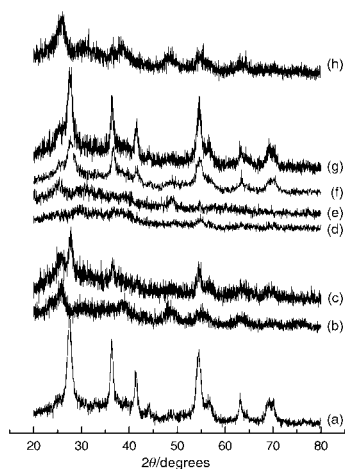


Fig. 1 PXRD patterns of the as-prepared samples A–H (from bottom to top).

hydrolyzed and aged, no precipitates appeared without sonication. It is interesting that when TPT was dissolved in a dilute HCl solution ($\text{pH} = 0.7$) and sonicated, only little solid product (sample G) was obtained showing a rutile phase [Fig. 1(g)]. However, after adjustment of the pH of the above supernatant to 8.6 by addition of ammonia, a white precipitate appeared, and further sonication resulted in the formation of sample H, which was pure anatase [Fig. 1(h)]. These results imply that, although the ultrasonic irradiation promotes the crystallization process of titania, the final crystalline phase of the product is also determined by the acidity of the medium. The particle sizes of samples A, B, C, E, F, G and H, were below 9 nm (Table 1) and were calculated using the Scherrer formula. A TEM image of sample H is shown in Fig. 2, and reveal particles of 4–6 nm diameter.

The results from liquid- N_2 adsorption measurements may aid understanding of the formation of the products. Fig. 3 shows the N_2 adsorption isotherms and pore size distributions of samples A, B and H. The isotherms are characteristic of types H2 (for samples B and H) and H3 (for sample A).¹⁷ Many porous absorbents tend to give a type H2 loop. For sample B a very broad pore size distribution with an average pore size of 5.0 nm was measured, while for sample H a narrower pore size distribution was observed. However, unlike the mesoporous samples B and H (anatase) the results obtained for sample A (rutile) indicate its non-mesoporous nature. The mesopores in samples B and H may be constructed through the aggregation of particles.

A close examination of the PXRD patterns reveals a curious phenomenon. The reflections assigned to anatase are always broader than those for rutile, which implies smaller mean

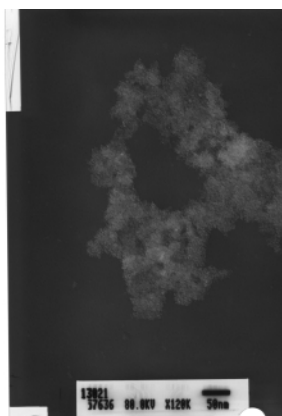


Fig. 2 TEM image of sample H obtained on a JEOL-JEM1200EX electron microscope.

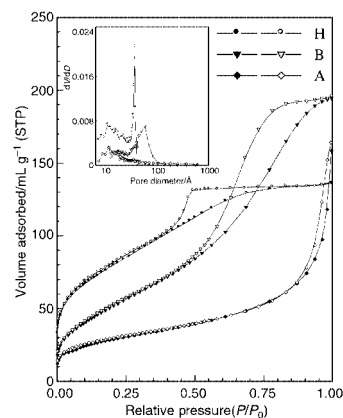


Fig. 3 Adsorption (filled)–desorption (open) isotherms of N_2 for samples A, B and H. Inset: pore size distributions of samples A, B and H.

particle sizes of the bulk anatase products. In fact, according to the Scherrer formula, the particle sizes of all rutile samples are almost twice that of the anatase samples (Table 1). As TTC hydrolyzes violently in water, part of the titanium hydroxide precipitates before dissolving in the acidic solution. Meanwhile, some of the titanium ions that exist as titanyl can be further coordinated by chloride anions. In contrast, the hydrolysis of TPT in water is slower, which results in a nearly neutral, partly condensed and more homogeneous gel. In the latter case, ultrasound irradiation generates many localized hot spots within the gel, outside which the polycondensation of $\equiv\text{Ti}-\text{OH}$ species is promoted. This further causes the homogeneous formation of a large number of seed nuclei, which leads to a smaller particle size. We propose that the interactions caused by sonication amongst the titanium species in the gel is stronger than those in the mixture containing $\equiv\text{Ti}-\text{Cl}$ species, which leads to the formation of anatase, a less condensed metastable phase.

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Notes and references

- 1 A. Fujishima and K. Honda, *Nature*, 1972, **37**, 238.
- 2 J. Ovenstone and K. Yanagisawa, *Chem. Mater.*, 1999, **11**, 2770.
- 3 R. W. Siegel, S. Ramasamy, H. Hahn, Z. Li, T. Lu and R. Gronsky, *J. Mater. Res.*, 1988, **2**, 1367.
- 4 P. W. Morrison, Jr., R. Raghavan, A. J. Timpone, C. P. Artelt and S. E. Pratsinis, *Chem. Mater.*, 1997, **9**, 2702.
- 5 Q. Chen, Y. Qian, Z. Chen, G. Zhou and Y. Zhang, *Mater. Lett.*, 1995, **22**, 77.
- 6 Y. Murakami, T. Matsumoto and Y. Takasu, *J. Phys. Chem. B*, 1999, **103**, 1836.
- 7 P. D. Moran, J. R. Bartlett, G. A. Bowmaker and J. L. Woolfrey, *J. Sol–Gel Sci. Technol.*, 1999, **15**, 251.
- 8 S. Komarneni, R. K. Rajha and H. Katsuki, *Mater. Chem. Phys.*, 1999, **61**, 50.
- 9 C. C. Wang and J. Y. Ying, *Chem. Mater.*, 1999, **11**, 3113.
- 10 E. A. Barringer and H. K. Bowen, *J. Am. Ceram. Soc.*, 1982, **65**, c199.
- 11 H. Cheng, J. Ma and L. Qi, *Chem. Mater.*, 1995, **7**, 663.
- 12 Z. Zhang, C. C. Wang, R. Zakaria and J. Y. Ying, *J. Phys. Chem. B*, 1998, **102**, 10 871.
- 13 K. S. Suslick, *Ultrasound: its Chemical, Physical and Biological Effects*, VCH, Weinheim, 1988.
- 14 K. S. Suslick, S. B. Choe, A. A. Cichowlas and M. W. Grinstaff, *Nature*, 1991, **353**, 414.
- 15 (a) Yu. Koltypin, X. Cao, G. Kataby, R. Prozorov and A. Gedanken, *J. Non-Cryst. Solids*, 1996, **201**, 159. (b) X. Cao, Yu. Koltypin, R. Prozorov, G. Kataby and A. Gedanken, *J. Mater. Chem.*, 1997, **7**, 2447.
- 16 R. A. Spurr and H. Myers, *Anal. Chem.*, 1957, **29**, 760.
- 17 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, 1985, **57**, 603.