Nanocrystalline TiO₂ by three different synthetic approaches: A comparison

T V ANURADHA* and S RANGANATHAN

Department of Materials Engineering, Indian Institute of Science, Bangalore 560 012, India

MS received 5 December 2006; revised 13 April 2007

Abstract. A comparison of the efficiency of three different synthetic routes viz. sol–gel method involving templating, mechanochemical synthesis and combustion synthesis for the production of nanostructured TiO₂, is reported. In the sol–gel method, nanocrystalline TiO₂ is produced when titanium tetraisopropoxide is templated onto dodecylamine which forms the liquid crystalline hexagonal structure and the template is then extracted using 1 : 1 solution of ethanol–hydrochloric acid mixture. Mechanochemical synthesis of nanocrystalline TiO₂ involved mechanical milling of stoichiometric amounts of titanium and cupric oxide in a planetary ball mill using stainless steel vial with wear resistant stainless steel balls. Nanocrystalline TiO₂ is produced by the combustion reaction involving titanyl nitrate and fuels like glycine and citric acid. Nanostructured TiO₂ with an average particle size of ~14 nm is produced by the sol–gel method whereas the mechanochemical reaction between titanium and cupric oxide resulted in the formation of nanocrystalline TiO₂ with an average particle size of ~20 nm after 12 h of milling. On the other hand, combustion synthesis resulted in the formation of nanocrystalline TiO₂ with an average particle size of less than ~50 nm. The microstructures of nanocrystalline TiO₂ produced by the above three methods are analysed.

Keywords. Nanocrystalline; templating; surfactant; mechanochemical; planetary ball mill; combustion.

1. Introduction

Mesoporous materials based on transition metal oxides are generally produced by the sol–gel method involving templating (Ying *et al* 1999). Some of the attempts to produce mesoporous materials have resulted in the formation of nanoparticles which in turn involved the reverse micelles that acted as the micro-reactor for the hydrolysis and condensation of organometallic precursors like titanium tetraisopropoxide i.e. Ti(*i*-OC₃H₇)₄. The synthesis of TiO₂ based mesoporous molecular sieve by using neutral amine surfactants like decylamine and hexadecylamine as templates was earlier reported (Ulagappan and Rao 1996). Earlier attempts to produce stable mesostructure of TiO₂ using dodecylamine as template have failed but resulted in the formation of wormhole like structures which were found to crumble during extraction of the template (Wang *et al* 2004). There are also some efforts to stabilize the mesoporous network by the addition of 12 wt% sodium chloride solution (Antonelli 1999) or by subsequent insertion of lithium (Lerouse *et al* 2001) or by chemical vapour deposition (Yoshitake *et al* 2002) or by microwave induced hydrothermal synthesis (Wang *et al* 2006). Dodecylamine is used here as the template with sodium chloride solution to produce stable mesoporous structure of titania.

In a mechanochemical synthesis, the product is formed by the chemical reaction induced by mechanical milling (Murty and Ranganathan 1998; Suryanarayana 2001). Here, nanocrystalline TiO₂ is produced by the mechanochemical reaction between metal titanium (Ti) and cupric oxide (CuO). The milling experiments are carried out using planetary ball mill (FRITSCH-p7). Schaffer and McCormick (1989a, b, 1990) are the first to report the reduction of metal oxides by reactive metals. They studied the mechanochemical reduction of cupric oxide by a variety of metallic reducing agents in a SPEX 8000 mixer/mill using a hardened steel vial and three 10 mm diameter/8 g steel balls and they found that the reaction proceeded in a controlled manner in the presence of a liquid process agent like toluene whereas an unstable combustion reaction occurred when no such control agent was used. The mechanical solid state reduction (MSSR) of cuprous oxide (Cu₂O) using elemental Ti as reducing agent is reported which in turn involved rod milling (El-Eskandarany 1995). El-Eskandarany (1995) showed that there is no remarkable change till 43 ks (~12 h) of milling and the rate of reaction is found to increase with milling time beyond 43 ks and MSSR reaction is found to have come to an end by 360 ks (~101 h) of milling. In our investigations, the MSSR reaction of CuO with metallic Ti is studied by using planetary ball mill without using any process control agent (PCA) like toluene since it is understood that material characteristics affects ignition of the com-

*Author for correspondence (anu_guhan@yahoo.co.in)

bustion reactions by ball milling (Mingliang *et al* 2001) like cupric oxide (CuO) system which showed shorter incubation periods than cuprous oxide (Cu₂O) which required longer milling time (Mulas *et al* 2001).

Combustion synthesis involves the use of low temperature (< 500°C) initiated gas-producing exothermic reactions which are self-propagating and yield voluminous fine particle oxides in a few minutes which in turn required combustible redox compounds or the redox mixtures (oxidizer-fuel) which when ignited undergo self-propagating combustion (Patil 1993; Mimani and Patil 2001; Prakash *et al* 2002; Patil *et al* 2002). Nanocrystalline TiO₂ is produced here by the combustion reaction of TiO(NO₃)₂ with mild fuels like citric acid (CA), and glycine (GLY) which enhances the formation of nanoparticles with uniform pore sizes.

It is proposed to compare the links among three different processing routes viz. sol-gel method involving templating, mechanochemical synthesis and combustion synthesis. It is also planned to study the size effect of the materials produced by the above mentioned processing routes. Another objective is to study the links between nanostructured and mesoporous materials since many attempts to produce mesoporous materials could result in the formation of nanostructured materials and *vice versa*.

2. Experimental

In the sol-gel process, 5 ml of Ti(*i*-OPr)₄, 1.25 g of dodecylamine, 3.9 g of NaCl, 3 ml of ethanol and 30 ml of distilled water were taken. Dodecylamine was added to Ti(*i*-OC₃H₇)₄ followed by the addition of 30 ml of ethanol. 3.9 g of NaCl in 30 ml of distilled water was then added to the above to form a sol which was then kept overnight at room temperature. The titania gel thus obtained was then subjected to digestion in a hot water bath at 100°C for 3 h and washed repeatedly to eliminate the salt i.e. NaCl, completely. Then the sample was further treated with *p*-toluene sulphonic acid (PTSA) which eliminated the salt completely.

In the mechanochemical synthesis, stoichiometric amounts of micron-sized CuO (Ranbaxy, AR grade) and Ti (Sigma-Aldrich, 100 mesh, 99%) with the ball-charge ratio of 8 : 1 were milled in the planetary ball mill. The reactants were taken in a stainless steel vial with wear resistant stainless steel balls. Milling of stoichiometric amounts of CuO and Ti in air was combustible in nature and hence called combustion ball milling.

In the combustion synthesis, the amounts of reactant materials viz. titanyl nitrate (TiO(NO₃)₂) and fuels like glycine (C₂H₅O₂N) or citric acid (C₆H₈O₇) were chosen based on the total oxidizing and reducing valency of the oxidizer and the fuel, which served as a numerical coefficient for the stoichiometric balance so that the equivalence ratio was equal to unity (i.e. total oxidizing valency/

total reducing valency (O/F) = 1) and the energy released was maximum. Ammonium nitrate (NH₄NO₃) was sometimes added for the complete balance of total oxidizing and reducing valency of the oxidizer and the fuel. According to concepts used in propellant chemistry, the elements, C, H, and Ti⁴⁺ have the valencies of +4, +1, and +4, respectively. The element oxygen was considered as an oxidizing element with a valency -2. The valency of nitrogen was considered to be zero.

TiO(NO₃)₂ was produced *in situ* by the hydrolysis of Ti(*i*-OPr)₄ followed by treatment with HNO₃.

The combustion reactions are represented by the following balanced equations:

3. Characterization

3.1 X-ray diffraction studies

Figure 1(a) shows the X-ray diffraction (XRD) pattern of as obtained titania gel which indicated it to be amorphous in nature. The amorphous phase could be hydrous TiO₂ i.e. TiO₂·*n*H₂O. The XRD pattern of titania after washing and subsequent heat treatment at 100°C for 3 h is shown in figure 1(b) which indicated the presence of sodium chloride (NaCl). Figure 1(c) shows the X-ray diffraction pattern of titania after treatment with PTSA followed by subsequent washing which indicated the complete extraction of NaCl. Sodium chloride could have been removed completely as a sodium salt of *p*-toluene sulphonic acid. XRD studies indicated the formation of nanocrystalline TiO₂ in the form of rutile (JCPDS card no. 82-0514) with an average crystallite size of ~14 nm as determined by Debye Scherrer's equation. Figure 2 shows the XRD patterns of samples obtained by mechanochemical synthesis which in turn involved milling of stoichiometric amounts of CuO and Ti (ball-charge ratio, 8 : 1) for different milling intervals of 0 h, 2 h, 4 h, 8 h and 12 h in air. XRD studies of the sample indicated complete reaction even after 2 h of milling and grain refinement occurred thereafter. XRD studies of the sample after 4 h indicated the formation of nanocrystalline Cu (JCPDS card no. 85-1326) and rutile form of TiO₂ (JCPDS card no. 82-0514) with a crystalline size of TiO₂ being 30 nm which reduced to 20 nm after 12 h of milling. It is also observed by XRD that the intensity of TiO₂ peaks are suppressed compared to that of copper as

the milling continues and this might be due to the maximum peak broadening of TiO_2 peaks which in turn indicates its rapid grain size reduction. XRD studies of the samples produced by combustion synthesis involving the reaction of $\text{TiO}(\text{NO}_3)_2$ with glycine and citric acid, respectively (figure 3) indicated the formation of rutile phase (JCPDS card no. 82-0514) of nanocrystalline TiO_2 with an average crystallite size of ~ 50 nm. It is thus clear that all the above methods resulted in the formation of same rutile form of TiO_2 (JCPDS card no. 82-0514).

3.2 Scanning electron microscopic studies

Figure 4 shows the scanning electron microscopic (SEM) image of TiO_2 obtained after treatment with PTSA in a

sol-gel process which showed spherical morphology of the particles with agglomerates as big as a few hundreds of a micron resembling that of a cauliflower in one of its cross sections. Figure 5 shows SEM images of the products during mechanochemical synthesis after milling stoichiometric amounts of CuO and Ti for 2 h, 4 h, 8 h and 12 h. SEM studies indicated the particle morphology to be spherical. The formation of agglomerates is seen at every stage of milling as indicated by SEM studies. Figure 5(c) shows the agglomerate to be as big as $25\ \mu$. Figure 6 shows the SEM micrographs of the combustion derived

Figure 1. XRD patterns of sol-gel derived titania: (a) as obtained, (b) after heat treatment at 100°C for 3 h and (c) after treatment with *p*-toluene sulphonic acid.

Figure 2. XRD patterns of the samples during mechanochemical synthesis after milling stoichiometric amounts of CuO and Ti for different milling intervals of (a) 0 h, (b) 2 h, (c) 4 h, (d) 8 h and (e) 12 h.

TiO₂ using glycine (a) and citric acid (b), respectively. SEM studies indicated the presence of pores with sizes <0.25 μ and 4 μ , respectively.

3.3 Transmission electron microscopic studies

Figure 7 shows the bright field transmission electron microscopic (TEM) image of sol-gel derived TiO₂ in rutile form obtained after treatment with PTSA with its corresponding selected area electron diffraction (SAED) pattern. Figure 7(a) indicates the honeycomb structure corre-

Figure 3. XRD patterns of combustion-derived TiO₂ using glycine and citric acid as fuels, respectively.

Figure 4. SEM micrograph of sol-gel titania produced after treatment with PTSA where NaCl is used.

sponding to that of hexagonally organized mesostructure of amorphous organic template i.e. DDA with pore size of the order of ~ 57 Å, though it is not highly ordered. The SAED pattern showed the presence of only TiO₂, thus confirming the amorphous nature of the mesostructure of DDA (figure 7(b)). TEM studies indicated the formation of nanoparticles of TiO₂ with particle size < 50 nm inside the pore regions and thus demonstrating the presence of closed pores. The bright field TEM image of the sample during mechanochemical synthesis after 4 h of milling indicated the formation of nanocrystalline TiO₂ in rutile form with an average particle size of < 30 nm (figure 8), where the difference in mass contrast clearly indicates the formation of dark TiO₂ particles and bright copper particles. Figure 9 shows TEM bright field image of combustion derived TiO₂ using citric acid as fuel with its corresponding selected area diffraction pattern and TEM studies are indicative of average particle sizes of < 50 nm. The difference in mass contrast in the TEM bright field image of the sample produced by the combustion reaction of TiO(NO₃)₂ with citric acid indicated the presence of bright particles of citric acid (organic) together with dark particles of TiO₂ (inorganic) confirming the incomplete combustion reaction. The region labeled 'M' in figure 9(a) shows the rotational Moiré fringes.

4. Discussion

The sol-gel process with templating involved the formation of reverse hexagonal mesoporous structure which in turn composed of reverse micellar rods of DDA that could act as template to produce nanoparticles. The addition of salt in this experiment is found to stabilize the liquid crystalline structure of DDA. Thus, an attempt to synthesize mesoporous TiO₂ resulted in the formation of nanocrystalline TiO₂ (rutile) which involved controlled hydrolysis of Ti(*i*-OPr)₄ in the reverse micelles of dodecylamine of the liquid crystalline phase (mesostructure). The production of nanoparticles of amorphous titania is already demonstrated using dodecylamine which formed the reverse micelles without the mesostructure (Anuradha and Ranganathan 1999).

In the case of mechanochemical synthesis involving combustion, the amounts of initial reactant powders are carefully chosen so as to avoid extensive damage to the mill since the above reaction is combustive in nature. This experiment differs from the earlier reports with respect to the milling conditions. Thus the reaction can be written as follows

Though dry milling results in faster reaction, it is observed that it always will result in the coating of the milling media (inner vial surface and balls) with the reactant powders which perhaps may limit the microstructural evolution.

Figure 5. SEM micrographs of the samples after milling the mixture of CuO and Ti for different intervals of time: (a) 2 h, (b) 4 h, (c) 8 h and (d) 12 h.

Figure 6. SEM micrographs of combustion-derived TiO₂ using fuels: (a) glycine and (b) citric acid.

According to thermodynamics, the reaction of CuO and Ti is found to be feasible because of its standard free energy being negative. Standard free energies of formation of CuO and Ti (elemental) are -128.292 and 0 kJ mol^{-1} , respectively whereas standard free energies of formation of rutile and anatase are -889.406 and $-883.266 \text{ kJ mol}^{-1}$, respectively with the standard free energy of formation of copper (elemental) as 0 kJ mol^{-1} (Chase Jr *et al* 1985). Hence the standard free energy of reaction ($\Delta G_{\text{f(rxn)}}^{\circ}$) of

CuO and Ti (5) is $-632.822 \text{ kJ mol}^{-1}$ in accordance with the following expression,

$$\Delta G_{\text{f(rxn)}}^{\circ} = \Delta G_{\text{f(products)}}^{\circ} - \Delta G_{\text{f(reactants)}}^{\circ}.$$

Earlier, the synthesis of nanosized anatase TiO₂ ($< 50 \text{ nm}$) with high surface areas was reported using combustion of redox mixtures containing stoichiometric amounts of titanyl oxalate ($\text{TiOC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)– NH_4NO_3 and titanyl nitrate ($\text{TiO}(\text{NO}_3)_2$)–carbohydrazide ($\text{CH}_6\text{N}_4\text{O}$)/oxalyldihydrazide

Figure 7. (a) TEM bright field of sol-gel TiO_2 after treatment with *p*-toluene sulphonic acid where NaCl is used and (b) its corresponding SAED pattern.

Figure 8. The bright field TEM image of sample after milling CuO and Ti for 4 h; Inset: the corresponding selected area electron diffraction pattern (R, rutile and C, copper).

($\text{C}_2\text{H}_6\text{N}_4\text{O}_2$) and the high surface areas are indicative of the liberation of large amounts of gases which dissipate the heat and inhibit sintering (Aruna and Patil 1996). Unlike in earlier reports, the synthesis of nanocrystalline TiO_2 is described here which uses milder fuels like glycine and

citric acid thereby reducing the flame temperatures drastically enhancing the formation of nanosized TiO_2 with uniform pore sizes.

The combustion-derived TiO_2 has an average particle size in the range 10–40 nm whereas TiO_2 produced by the sol-gel method has an average particle size of < 10 nm. The formation of agglomerates is evident in both methods. However, the particle size distribution is rather broad in the combustion-derived samples compared to that derived from the sol-gel method. TiO_2 obtained by mechanical milling was found to have a near spherical morphology with an average particle size of < 50 nm. It is more likely that combustion synthesis with reasonably high flame temperatures and mechanical milling often results in the formation of defect microstructures. However, more exhaustive TEM studies are required to study these defects in detail. Titania is found to be stable in rutile form when the particle size exceeds 14 nm and below this critical size, anatase phase was stable (Zhang and Banfield 1998). All the three methods resulted in the formation of rutile phase of TiO_2 indicating the average particle size exceeding 14 nm though TEM studies confirm the particle sizes of < 10 nm in the case of sol-gel process involving templating.

5. Conclusions

The attempts to synthesize mesoporous TiO_2 by sol-gel process involving templating have resulted in the formation of nanocrystalline TiO_2 with an average crystallite size of ~ 14 nm. The above synthesis involved the reverse micellar rods of DDA which in turn formed the liquid crystalline structure (mesostructure) that acted as the

Figure 9. (a) The bright field TEM image of combustion-derived TiO_2 with citric acid (CA) as the fuel and (b) its corresponding SAD pattern. 'M' shows the Moire fringes.

template for the production of nanoparticles. The use of salt in the medium is found to stabilize the mesostructure that is formed with DDA. Combustion ball milling of CuO and metal Ti in air is successful and it has resulted in the formation of nanocrystalline TiO_2 with an average particle size of < 50 nm after 4 h of milling which is further reduced to ~ 20 nm after 12 h of milling. Nanocrystalline TiO_2 (rutile) with an average particle size of ~ 10 – 30 nm is obtained by the combustion reactions involving $\text{TiO}(\text{NO}_3)_2$ and fuels like citric acid and glycine.

All the three synthetic methods have resulted in the formation of nanostructured TiO_2 . Sol–gel method involved temperatures as high as 100°C whereas mechanochemical and combustion syntheses involved flame temperatures as high as 1000°C , but the flame appears to be momentary and thus inhibiting the grain growth. The combustion-derived TiO_2 has an average particle size in the range 10 – 40 nm whereas TiO_2 produced by the sol–gel method has an average particle size of < 10 nm. The formation of agglomerates is evident in both methods. However, the particle size distribution is rather broad in the combustion-derived samples compared to that derived from the sol–gel method. The combustion-derived TiO_2 was found to form the defect structure with stacking faults and dislocations whereas the sol–gel derived TiO_2 was free from defects.

Acknowledgements

The support of the Council for Scientific and Industrial Research (India) through a Senior Research Fellowship is gratefully acknowledged which helped in carrying out this research. The guidance by Prof. K C Patil for this research is also gratefully acknowledged.

References

- Antonelli D M 1999 *Microporous & Mesoporous Mater.* **33** 209
- Anuradha T V and Ranganathan S 1999 *Nanostruct. Mater.* **12** 1063
- Aruna S T and Patil K C 1996 *J. Mater. Syn. Process* **4** 175
- Chase Jr M W, Davies C A, Downey Jr, Frurip D J, McDonald R A and Syverud A N 1985 *J. Physical & Chemical Reference Data*, Supplement #1, 14, JANAF Thermochemical Tables, Third Edition, Parts I & II
- El-Eskandarany M S 1995 *Mater. Trans. JIM* **36** 182
- Lerouse F, Dewar P J, Intissar M, Ovrard G and Nasar L F 2002 *J. Mater. Chem.* **12** 3245
- Mimani T and Patil K C 2001 *Mater. Phys. Mech.* **4** 134
- Mingliang M, Xinkuan L, Shengqi X, Donglang C and Jingen Z 2001 *J. Mater. Process. Technol.* **116** 124
- Mulas G, Monagheddu M, Doppiu S, Cocco G, Maglia F and Anselmi Tamburini U 2001 *Solid State Ionics* **141** 649
- Murty B S and Ranganathan S 1998 *Inter. Mater. Rev.* **43** 101
- Patil K C 1993 *Bull. Mater. Sci.* **16** 533
- Patil K C, Aruna S T and Mimani T 2002 *Curr. Opinion Solid State & Mater. Sci.* **6** 507
- Prakash A S, Khadar A M A, Patil K C and Hegde M S 2002 *J. Mater. Syn. Process* **10** 135
- Schaffer G B and McCormick P G 1989a *Scr. Metall.* **23** 835
- Schaffer G B and McCormick P G 1989b *Appl. Phys. Lett.* **55** 45
- Schaffer G B and McCormick P G 1990 *Metall. Trans.* **A21** 2789
- Suryanarayana C 2001 *Prog. Mater. Sci.* **46** 1
- Ulagappan N and Rao C N R 1996 *Chem. Commun.* 1047
- Wang H W, Kuo C H, Lin H C, Kuo I T and Cheng C F 2006 *J. Am. Ceram. Soc.* **89** 3388
- Wang Y, Zhang S and Wu X 2004 *Nanotechnology* **15** 1162
- Ying J Y, Mehnert C P and Wong M S 1999 *Angew. Chem. Int. Ed.* **38** 56
- Yoshitake H, Sugihara T and Tatsumi T 2002 *Chem. Mater.* **14** 1023
- Zhang H and Banfield J F 1998 *J. Mater. Chem.* **8** 2073