Advanced Powder Technology 24 (2013) 972–979

Contents lists available at SciVerse ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Effect of processing methods on physicochemical properties of titania nanoparticles produced from natural rutile sand

S. Arunmetha, P. Manivasakan, A. Karthik, N.R. Dhinesh Babu, S.R. Srither, V. Rajendran *

Center for Nano Science and Technology, K.S. Rangasamy College of Technology, Tiruchengode 637 215, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 22 August 2012
Received in revised form 19 December 2012
Accepted 29 January 2013
Available online 13 February 2013

Keywords:
Natural rutile sand
Titania nanoparticles
Sol–gel process
Sonication method
Spray pyrolysis technique
Bandgap studies

ABSTRACT

Titania (TiO_2) nanoparticles were produced from natural rutile sand using different approaches such as sol–gel, sonication and spray pyrolysis. The inexpensive titanium sulphate precursor was extracted from rutile sand by employing simple chemical method and used for the production of TiO_2 nanoparticles. Particle size, crystalline structure, surface area, morphology and band gap of the produced nanoparticles are discussed and compared with the different production methods such as sol–gel, sonication and spray pyrolysis. Mean size distribution (d_{50}) of obtained particles is 76 ± 3, 68 ± 3 and 38 ± 3 nm, respectively, for sol–gel, sonication and spray pyrolysis techniques. The band gap (3.168 < 3.215 < 3.240 eV) and surface area (36 < 60 < 103 $m^2\,g^{-1}$) of particles are increased with decreasing particle size (76 > 68 > 38 nm), when the process methodology is changed from sol–gel to sonication and sonication to the spray pyrolysis. Among the three methods, spray pyrolysis yields high-surface particles with active semiconductor bandgap energy. The effects of concentration of the precursor, pressure and working temperature are less significant for large-scale production of TiO_2 nanoparticles from natural minerals.

1. Introduction

Mass production of titania (TiO_2) nanoparticles with high-surface area and free-flowing structure has attracted much attention due to their wide variety of applications such as in beam splitters, optical and anti-reflection coatings, catalysis, gas sensors, ultraviolet (UV) absorbers, lithium batteries, optical, electronic and electrochromic devices [1–5]. Owing to their high-photocatalytic activity and chemical stability, nano-TiO_2 is used in clean technologies such as environmental remediation, self-cleaning glasses, pigments, paints, ceramics, cosmetics and solar energy conversion [6–8]. Titania has three polymorphic crystalline forms namely rutile, anatase and brookite, of which first two forms exist in nature commonly with tetragonal symmetry [9]. Optoelectronic properties and photocatalytic activity of TiO_2 strongly depend on the phase and size of crystallites. Both anatase and rutile TiO_2 nanoparticles with high-surface area and low crystallite size are significantly important for unique applications such as photocatalysts, optoelectronics, paints and pigments. Nano-TiO_2 with anatase phase has been widely used for optoelectronic and photocatalytic applications [10,11]. However, rutile phase TiO_2 nanoparticles have been significantly used as white pigment materials, because of their good visible light-scattering property along with effective absorption of UV light [11].

A variety of synthesis methods are being explored and developed for the production of TiO_2 nanoparticles, such as thermal decomposition [12], precipitation and hydrolysis [13], sol–gel [14], hydrothermal [15], solvothermal [16], sonication [17], ball milling [18], chemical vapour deposition [19], and spray pyrolysis [20]. Among them, sol–gel, sonication and spray pyrolysis are the most common and significant methods for mass production of high-surface area TiO_2 nanoparticles with controlled particle size and morphology. In general, sol–gel process is considered as an excellent method to synthesise a large variety of nanosized metallic oxides with controlled size, structure and morphology [14].

Sonication method enables considerable changes in surface morphology with controlled particle size ranging from nanometres to millimetres. Ultrasound is an important tool for the synthesis of metal oxide nanoparticles with controllable morphologies. The advantages of ultrasound irradiation for the synthesis of mesoporous materials are drastic reduction in fabrication time and aggregation of nanoparticles into porous structures without destroying the micellar structure [17]. The atomised spray pyrolysis technique is used to form ultrafine and uniform ceramic powders. Wide variety of multi-component system and homogeneous mixture of powders over a range of particle sizes are made possible through spray method [20]. The morphology of particles produced by spray pyrolysis method can be controlled by the choice of precursors,

* Corresponding author. Tel.: +91 4288 274741–4/274880; fax: +91 4288 274880 (direct), 274860.

E-mail address: veerajendran@gmail.com (V. Rajendran).

0921-8831/$ - see front matter
http://dx.doi.org/10.1016/j.apt.2013.01.011

concentration, droplet size and the residence time in the furnace [18].

The aim of this work was to investigate in detail the process and to understand the key issues for production of TiO_2 nanoparticles from natural mineral rutile. The hydrolysis behaviour of titanium sulphate in an aqueous solution was investigated by changing the production method. It was also aimed to achieve large-scale production of high-surface area TiO_2 nanoparticles from inexpensive precursors through solution-based chemical process. Understanding the chemistry of particle formation is expected to play an important role in designing new techniques and developing new processes that can be used economically for the mass production of high-surface area TiO_2 nanoparticles. In this article, the results based on spray pyrolysis, sonication and sol–gel processes are discussed in detail for the mass production of high-surface area TiO_2 nanoparticles. The principal objective of this work was to optimise the production method in terms of production rate, particle size, surface area and bandgap for photocatalytic and energy conversion applications.

2. Materials and methods

2.1. Synthesis of titanium sulphate precursor

Titanium sulphate precursor was prepared as discussed in our previous report [18]. Rutile sand (89–96%) was used as the starting material for precursor synthesis. The chemical composition of the rutile sand is given in Table 1. The sand was digested with concentrated H_2SO_4 in the temperature range 200–250 °C for 3 h in a muffle furnace. After digestion, the mixtures were changed into dry cake. The mixture that contains water-soluble titanium sulphates was leached with double-distilled water. The reaction of rutile sand with concentrated H_2SO_4 is given in Eq. (1).

$$\text{Rutile Sand} + \text{Conc. } H_2SO_4 \rightarrow Ti(SO_4)_2 + \text{Rutile Sand} \tag{1}$$

2.2. Synthesis of TiO_2 nanoparticle using sol–gel method

Extracted titanium sulphate (250 ml) was used as the precursor for the synthesis of TiO_2 nanoparticles. One millimolar concentration of acetyl trimethyl ammonium bromide (99%; Loba, India) was added to the filtrate of titanium sulphate. Then, aqueous ammonia solution (5 N) was added drop by drop into the filtrate until it reached the pH value of 7. The reaction of aqueous ammonia with titanium sulphate is given in following equations:

$$\underset{\text{Titanium Sulphate}}{Ti(SO_4)_2} + C_{19}H_{49}BrN + 4NH_4OH \rightarrow \underset{\text{Sol}}{Ti(OH)_4} + C_{19}H_{42}BrN + 2(NH_4)_2SO_4 \tag{2}$$

$$Ti(OH)_4 + \underset{\text{Sol}}{C_{19}H_{42}BrN} \rightarrow \underset{\text{Gel}}{Ti(OH)_4]_n \cdot xC_{19}H_{42}BrN} \tag{3}$$

$$\underset{\text{Gel}}{Ti(OH)_4]_n \cdot xC_{19}H_{42}BrN} \rightarrow \underset{\text{Amorphous gel}}{Ti(OH)_4 + C_{19}H_{42}BrN} \tag{4}$$

After the reaction, titanium hydroxide was obtained in the solution. It was digested at 80 °C for 32 h followed by drying at 120 C for 3 h in a hot-air oven. Digestion led to the control of gel nucleation. The obtained gel was washed with double-distilled water to remove the ammonium sulphate. Finally, the dried gel was sintered at 400 °C for 3 h in a muffle furnace to convert the titanium hydroxide gel into nanosized TiO_2 particles as given in following equation:

$$\underset{\text{Titanium hydroxide}}{Ti(OH)_4} \rightarrow \underset{\text{Particle}}{TiO_2} + 2H_2O \uparrow \tag{5}$$

2.3. Synthesis of TiO_2 nanoparticle using sonication method

Aqueous ammonia (5 N) solution was added drop by drop into titanium sulphate solution under sonication with constant ultrasound irradiation (35 kHz). The solution was added until the pH value of 7 to achieve complete hydrolysis of titanium sulphate precursor. The ultrasound irradiation was performed with a high-intensity probe immersed directly in diluted solution under ambient air for 3 h with regular time interval (to reduce the heat of the solution, which was produced during the reaction). After the sonication process, the obtained solution of hydrous TiO_2 was dried at 80 °C for 48 h in a hot-air oven. Further, hydrous TiO_2 was calcined at 400 °C for 3 h to obtain nanosized TiO_2 particles as given in Eq. (5).

2.4. Synthesis of TiO_2 nanoparticle using spray pyrolysis method

The hydrous TiO_2 was precipitated at pH 7 using 250 ml of titanium sulphate precursor and aqueous ammonia (5 N) solution. The obtained solution was diluted with double-distilled water to get transparent solution. It was used as the starting phase in spray pyrolysis. The black diagram of the automated spray pyrolysis experimental set-up was as shown in Fig. 1. The details such as atomisation, decomposition and formation process of the nanoparticles through spray pyrolysis technique are shown in Fig. 1. In the spray pyrolysis method, reaction often takes place in solution droplets, followed by solvent evaporation. The hot air was introduced into the reaction chamber followed by the precursor spray into the chamber with use of a two-fluid nozzle pressurised with compressor air. The feed pump was used to control the flow rate of precursors. Atomiser formation was controlled by controlling the pressure of compressed air. The sprayed and atomised nanosized entities of hydrous TiO_2 were decomposed at 400 °C to obtain nanosized TiO_2 particles. After the completion of one full cycle, the produced nanosized TiO_2 particles were collected from the cyclones. The decomposition reaction of hydrous TiO_2 is shown in Eq. (6).

$$\underset{\text{Colloidal Solution}}{Ti(OH)_4} \rightarrow \underset{\text{Particle}}{TiO_2} + 2H_2O \uparrow \tag{6}$$

2.5. Characterisation

Crystalline phases of all powder samples were detected by powder X-ray diffraction (XRD) patterns (X'Pert PRO, PAN analytical, the Netherlands) using Cu Kα as a radiation source (λ = 1.54060 Å). The diffractometer was operated at 40 kV and the scans were performed over a range from 10 ° to 80 ° of angle 2θ, with an increase in scanning rate of 10 ° per min. The crystallite size is calculated from XRD peak analysis using Debye–Scherrer equation [21]. Fourier transform infrared (FTIR) spectra of all the samples were obtained on a spectrometer (Spectrum 100;

Table 1
Chemical composition of natural rutile sand.

Composition	TiO_2	SiO_2	Fe_2O_3	P_2O_5	ZrO_2	NbO	Cr_2O_3	ThO_2	ZnO
Rutile sand									
wt.%	89.62	3.86	2.05	1.93	1.89	0.36	0.20	0.05	0.01