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Nanoparticulate titanium dioxide synthesized by sol–gel and solution combustion techniques

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Abstract

Nano-sized titanium dioxide is renowned for its prominent photocatalytic properties. Various synthesis techniques have been successfully employed in production of nano-titanium dioxide. Some of the techniques require expensive initial reagents as well as extensive preparation time. A rapid, simple and cost-effective technique capable of producing high quality nano-particles is highly desirable. This study, therefore, aims at examining effects of synthesis techniques and initial reagents on chemical compositions and particle sizes of titanium dioxide. A solution combustion technique as well as a sol–gel method using Titanium (IV) isopropoxide (TTIP) and submicrometer-sized titanium dioxide as initial reagents were employed as synthesis techniques. Experimental results indicated that all synthesized powders contained pure anatase titanium dioxide. Average particle sizes of powders prepared by the solution combustion technique from TTIP and submicrometer-sized titanium dioxide were 44 and 77 nm whereas, powder sizes prepared by the sol–gel method averaged at 48 and 85 nm respectively.

Keywords: A. Ceramic processing; B. Nanoparticles; C. TiO_2; D. Combusted synthesis; E. Sol–gel

1. Introduction

In the last few decades, nanomaterials have drawn worldwide attention because of their unique properties. Nano-sized titanium dioxide is one of the materials renowned for its prominent photocatalytic properties [1,2]. It has been accepted that titanium dioxide is a polymorph materials, which exists in three main structures, anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Pure anatase or mixture of anatase and rutile at ratio of 80:20 is desirable for photocatalytic applications due to their high reactivity [3]. In addition to crystalline structures, particle size is also a factor contributing to high catalytic activities of the titanium dioxide particles.

Small particles in the range of nanometer have high specific surface area, which greatly enhance reactivity. To attain the desirable characteristics, nano-sized powders with high quantities of the anatase phase needs to be carefully monitored during titanium dioxide synthesis. Common techniques employed in the synthesis process of nano-sized titanium dioxide include hydrothermal [4], co-precipitation [5], sol–gel [1,6] and solution combustion technique [7]. The solution combustion and sol–gel methods are simple and effective synthesis techniques of obtaining nanometer or sub-micrometer-sized powders with high compositional homogeneity. In addition, both techniques require cost-effective initial reagents and low energy supplies during the synthesis. The techniques also accommodate doping of various cations and anions [8,9].

As mentioned previously, numerous research works have reported techniques related to the synthesis of nanoparticulate titanium oxide. Some of the techniques, however, require expensive initial reagents as well as extensive preparation time. Rapid, simple and cost-effective techniques capable of producing high quality nano-particles are highly desirable. This study, therefore, aims at examining effects of synthesis techniques and initial reagents on chemical compositions and particle sizes of titanium dioxide. Simple routes that require low energy supply during the synthesis, specifically the sol–gel and the combustion techniques were employed as synthesis techniques of titanium dioxide in this

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study. To reduce processing cost, cost-effective and commercially available titanium (IV) isopropoxide and submicrometer- sized titanium dioxide were used as initial reagents.

2. Materials and methods

The solution combustion technique and the sol–gel technique were employed in the synthesis of TiO_2 powders. To synthesize the powders by the solution combustion technique, aqueous solutions containing titanium ions were prepared. Titanium (IV) isopropoxide (TTIP) (Aldrich chemistry®, 97%) and micron-sized titanium dioxide (TiO_2) (Sigma-Aldrich®, 99%) were used as initial reagents for the combustion synthesis. For the combustion process prepared from Titanium (IV) isopropoxide, deionized water was added to the TTIP to obtain a 2.5 M concentration solution. For the process prepared by micron-sized titanium dioxide, the titanium dioxide powder was dissolved in sulfuric acid (H_2SO_4, Emsure®, 95–97%), and subsequently diluted with deionized water to obtain a 6 M concentration solution. Glycine (NH_2CH_2COOH, Fluka analytical®, 99%), acting as combusting fuels, at a ratio of 1:1 glycline:titanium was added to the prepared TTIP and titanium dioxide solutions. The mixtures were subsequently stirred by a magnetic stirrer and placed in an ultrasonic bath for 10 min. A low heating temperature of less than 400 °C was applied to the solution to initiate combustion. Upon completion of the combustion reaction, the powder products were collected and calcined at 250 °C and 500 °C for 2 h.

To synthesize the powders from TTIP by the sol–gel technique, ethanol at the volumetric ratio of 1:2 ethanol: titanium isopropoxide (TTIP), was added to TTIP. High acidic condition (pH 2) was generally required for synthesis of titanium oxide. This could be achieved by adding nitric acid (Univar®, 70%) into the prepared solution. The solution mixture was subsequently stirred by a magnetic stirrer for 30 min. To synthesize titanium dioxide nanoparticles from the micron-sized titanium oxide, the titanium dioxide powder was dissolved in sulfuric acid, and subsequently diluted with deionized water to obtain a 2.3 M concentration solution. Polyacrylic acid $(C_3H_4O_2)_n$ (Carbopol®), acting as gelling agent was added to the prepared solution. Starting when gelation of the titanium (IV) isopropoxide and micron-sized titanium dioxide mixtures occurred, the process was allowed to continue for 24 h. Heating the gels to 300 °C, the gels were transformed into fine powders, which were then collected and calcined at 250 °C and 500 °C for 2 h.

The composition of the calcined powders were investigated using an x-ray diffractometer (Bruker, D8 Advance), over angles ranging from 20° to 80° in 2θ, at a step size of 0.02° and a scanning rate of 1.3°/min. A scanning electron microscope (FEI Quanta 450) was employed in the morphological examination of the particles. Particle sizes were determined using Image J Software and the Scherrer equation.

3. Results and discussion

3.1. Chemical compositions

X-ray diffraction analysis of the calcined powders, as shown in Figs. 1 and 2, indicated that all powders exhibited complete formation of anatase phase TiO_2 (JCPDS 01-086-1157) with the predominant peak at 2θ=25.4, 37.8, 48.0, and 54.5 which corresponded to the planes (101), (004), (200), and (105), respectively. Neither rutile nor brookite TiO_2 phase was evident in the diffraction patterns obtained.

Single phase of the anatase titanium dioxide appeared in the x-ray diffraction patterns of the powders prepared by the solution combustion technique. Pure anatase phase obtained from the solution combustion technique might be attributed to appropriate quantities of combustion fuels and appropriate calcination temperature used in this experiment. It has been reported that inadequate amount of fuels led to incomplete reaction, which consequently resulted in powders with initial reagents still remaining. On the contrary, excessive quantity of fuel could promote formation of undesired carbon compounds [10].

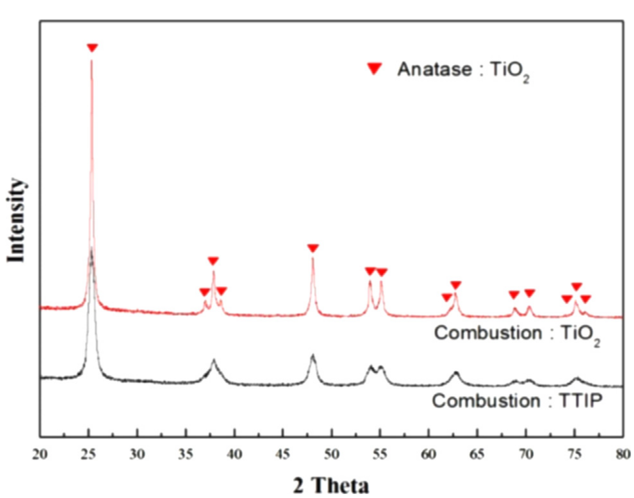

Fig. 1. X-ray diffraction patterns of powders synthesized by the solution combustion technique, prepared from titanium (IV) isopropoxide (TTIP) and sub-micrometer titanium oxide.

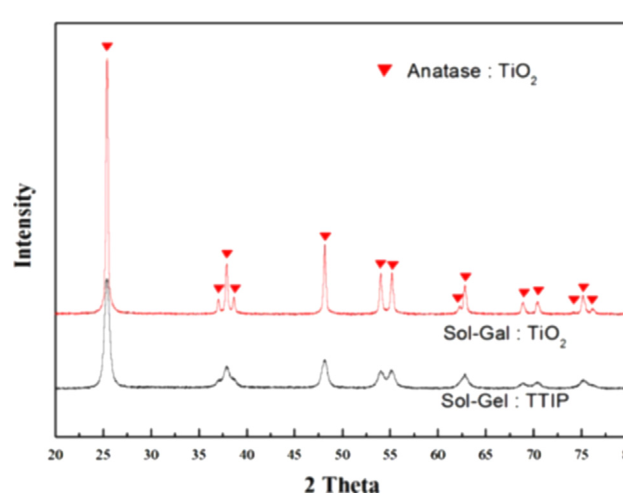

Fig. 2. X-ray diffraction patterns of powders synthesized by the sol–gel technique, prepared from titanium (IV) isopropoxide (TTIP) and sub-micrometer titanium oxide.

For the powders prepared by the sol–gel technique, pure anatase phase was also observed. In addition, diffracted peaks appeared sharp with low noise. No amorphous hump was observed in the patterns. The results indicated that amorphous phases developed during the hydrolysis and condensation reactions transformed it into crystalline anatase and that organic phases in the precursor completely decomposed.

The results also suggested that calcination temperature of 500 °C was appropriate for the formation of high purity crystalline anatase phase. Insufficient calcination temperature might results in undesired amorphous phase still remaining. On the contrary, excessive calcination temperature might result in particle coarsening and phase transformation. Effects of calcination temperature on phase transformation were observed by Paola et. al and Mahshid et. al [11,12]. Phase transformation of anatase into rultile at temperature from 500 to 800 °C was also reported by Han et. al [13].

3.2. Particle sizes and morphology

Scanning electron micrographs of the powders, as shown in Figs. 3 and 4, indicated that all powders contained equiaxed particles. Image analysis also provided information related to particle sizes of the powders. The results indicated that average particle sizes ranging from 43.5 to 76.9 nm and 48.4 to 84.6 nm were observed in powders prepared by the solution combustion technique and the sol–gel technique, respectively.

The solution combustion process involved aqueous solution of initial reagents and fuels. Particle sizes of the combusted powders were generally limited to the size of the liquid droplets before combustion. The titanium oxides powders with particles in nanometer range were, therefore, commonly observed.

The sol–gel process involved preparation of colloid containing titanium compounds. To retain the size of the particles, reagglomeration of the nano-particles should be prevented. Stabilization of particles are generally achieved by electrostatic, steric or electrosteric interactions. To achieve electrostatic stabilization, highly negative or positive values of zeta potential (more than 30 mV or less than −30 mV) should be attained [14]. Zeta potential is strongly influenced by pH of the colloidal system. For the titanium dioxide system, highly positive values of zeta potential are observed at highly acidic condition, as is shown in Fig. 5 [15,16].

Scherrer's equation (Eq. (1)) was also applied to determine crystallite size of the powders. Broadening of the prominent peaks was employed in the calculation of particle sizes as shown below

$$D_p = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where

D_p is the mean diameter of particles
λ is wavelength of x-ray
θ is the Bragg angle
β is the line broadening at half the maximum intensity (FWHM).

Results from the calculation indicated that average particle sizes ranging from 51.86 to 65.77 nm and 58.60 to 99.24 nm were obtained for powders prepared by the solution combustion technique and the sol–gel technique, respectively. The results from Scherrer's equation were in agreement with those obtained from the image analysis technique. The differences of particle sizes between the two analysis techniques were lower than 20%, as are shown in Table 1.

The particle size analyzes revealed that synthesis techniques did not have a pronounced effect on particle sizes of the powders. Initial reagents, however, had a significant effect on particle sizes. Powders prepared from titanium (IV) isopropoxide (TTIP) had finer particle sizes than powders prepared from titanium dioxide. This might be attributed to the solubility of the initial reagents. TTIP was in the form of solution while submicrometer-sized titanium dioxide, on the other hand, was in solid form that needed to be dissolved in sulfuric acid. It might also be possible that titanium dioxide particles were not completely dissolved in sulfuric acid, which thus contributed to the slight enlargement of the particles.

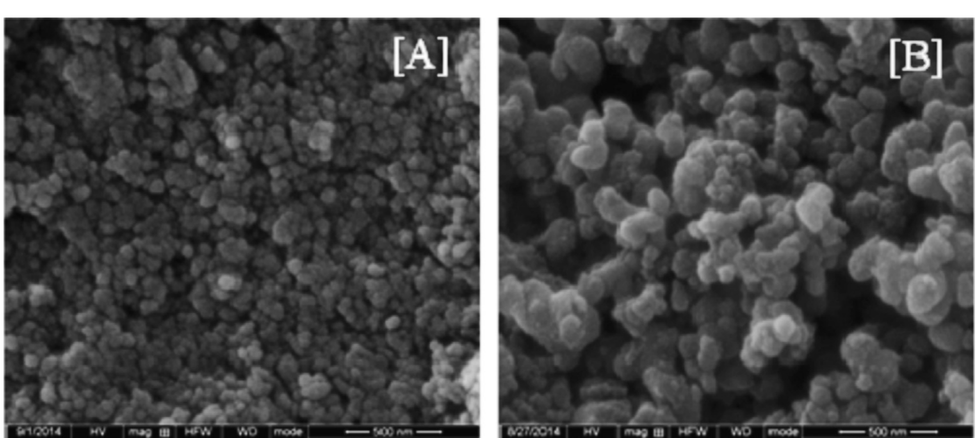

Fig. 3. Scanning electron micrograph showing titanium dioxide powders prepared by the solution combustion technique, using titanium(IV)isopropoxide (A) and sub-micrometer sized titanium dioxide (B) as initial reagents.

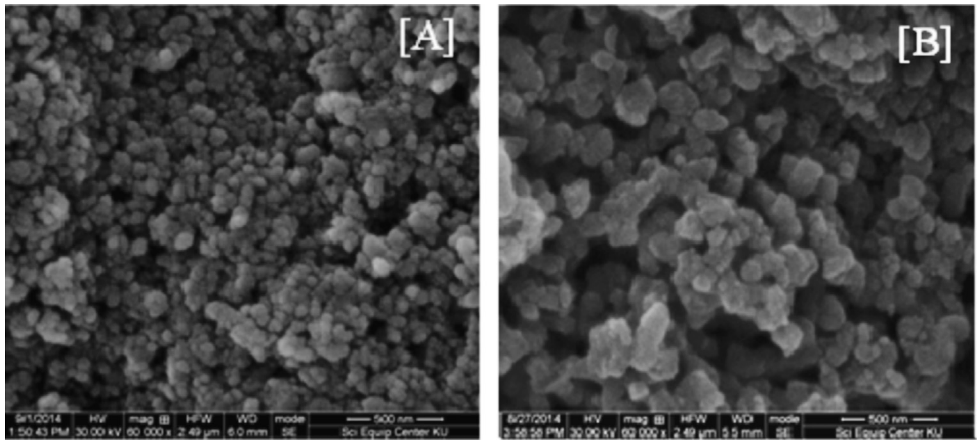

Fig. 4. Scanning electron micrograph showing titanium dioxide powders prepared by the sol–gel technique, using titanium (IV) isopropoxide (A) and sub-micrometer sized titanium dioxide (B) as initial reagents.

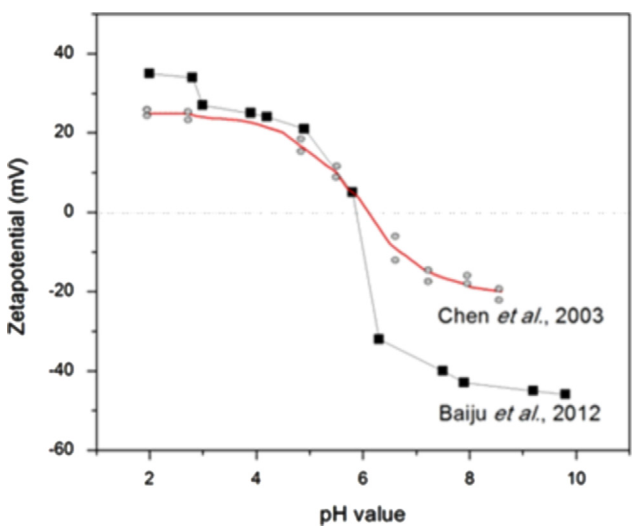

Fig. 5. Zeta potential of titanium dioxide as a function of pH. The plot was reconstructed from raw data reported by [15,16].

Table 1
Particle sizes of the powders prepared by the solution combustion and the sol–gel techniques.

Synthesis technique	Initial reagent	Particle size		
		Image analysis (nm)	Scherrer's equation (nm)	Difference (%)
Combustion	**TTIP**	43.53	51.86	17.40
	TiO_2	76.94	65.77	15.60
Sol–gel	**TTIP**	48.36	58.6	19.10
	TiO_2	84.64	99.24	15.80

4. Conclusions

Pure anatase phase titanium dioxide powders were successfully synthesized by simple and cost-effective techniques, specifically the solution combustion and the sol–gel techniques. Cheap and highly available initial regents such as Titanium (IV) isopropoxide (TTIP) and submicrometer-sized titanium dioxide proved to be good candidates for initial reagents of the synthesis process. The synthesized powders had average particle sizes ranging from 44 to 85 μm. Particle size analyses revealed that synthesis techniques did not produce a pronounced effect on the powders' particle sizes. However, initial reagents had an effect on particle sizes. Powders prepared from Titanium (IV) isopropoxide (TTIP) were finer than powders prepared from sub-micrometer sized titanium dioxide, which might have been attributed to the higher solubility of the TTIP.

Conflict of interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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