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Titanium dioxide powder prepared by a sol-gel method

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Titanium dioxide (TiO_2) powder was prepared by a sol-gel method. Titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$) and citric acid (($C_3H_5O(COO)_3)H_3 \cdot H_2O$) were used as the starting precursors with a mole ratio of 1 : 3. Ammonium hydroxide (NH_4OH) was added to adjust the pH of the mixed final solutions. Co-precipitation powder was obtained with the final solutions at pH = 2, 4 and 6. The powder was dried at 80 °C for 24 h and calcined at 400 and 800 °C for 2 h with a heating rate of 5 K.minute^{-1}. The phase transformation was investigated by an X-ray diffractometer (XRD). The anatase structure of titanium dioxide was obtained after calcination at 400 and 800 °C for 2 h. The microstructure was characterized by a scanning electron microscope (SEM). The range of particle size was 0.1-0.5 μm with an irregular particle shape.

Key words: TiO_2, Sol-gel method, XRD, SEM.

Introduction

Titanium dioxide (TiO_2) is a very useful semiconducting transition metal oxide material and exhibits unique characteristics such as low cost, easy handling, non-toxicity, and resistance to photochemical and chemical erosion. These advantages make TiO_2 a material in solar cells, chemical sensors, for hydrogen gas evolution, as pigments, self cleaning surfaces, and environmental purification applications [1]. The photocatalytic activity of TiO_2 is one of its most distinctive features, and it is largely determined by properties such as the crystalline phase, crystallite size, and specific surface area. The effect of these properties on the photocatalytic activity of TiO_2 has been studied [2]. TiO_2 exists in both crystalline and amorphous forms and mainly exists in three crystalline polymorphs, namely, anatase, rutile and brookite. Anatase and rutile have a tetragonal structure, whereas brookite has an orthorhombic structure [3]. There are different routes that can be used to synthesize titanium dioxide. These include a conventional solid state route [4-6], precipitation [7, 8], sonochemical [9], hydrothermal [10-12], microwave hydrothermal [13], solvothermal [14, 15] and sol-gel methods [16-18]. In chemical processes for the synthesis high quality powders, of high purity, homogeneity, controlled morphology and finer particles are also obtained. The sol-gel method has been considered to be a promising route for the synthesis of powders for photocatalytic materials. In this study, titanium dioxide (TiO_2) powder was prepared by a citric sol-gel method. The phase transformation was investigated by an X-ray diffractometer (XRD). The microstructure was characterized by a scanning electron microscope (SEM).

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Experimental Procedure

Titanium dioxide (TiO_2) powder was prepared by a sol-gel method as shown in Fig. 1 Titanium isopropoxide

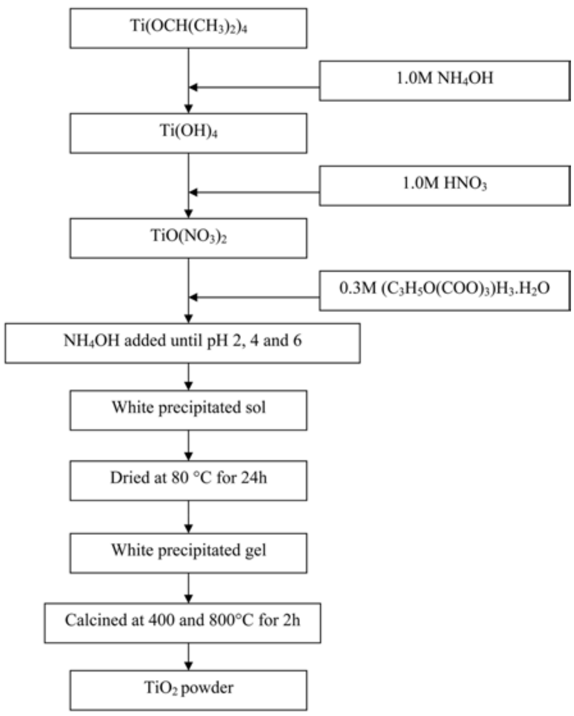

Fig. 1. Schematic diagram for the synthesis of TiO_2 powder by a sol-gel method.

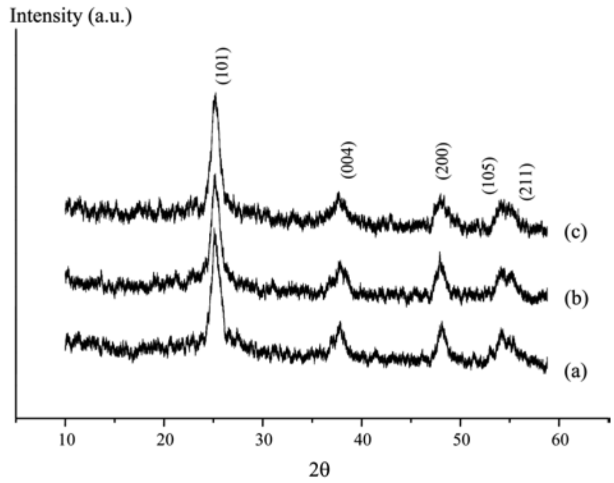

Fig. 2. X-ray diffraction patterns of TiO_2 powder calcined at 400 °C for 2 h at pH (a) 2, (b) 4, and (c) 6.

[$(Ti(OCH(CH_3)_2)_4$] (97% Aldrich, England), ammonium hydroxide [NH_4OH] (30% BDH, England), nitric acid [HNO_3] (65% Merck, Germany) and citric acid monohydrate [$(C_3H_5O(COO)_3)H_3 \cdot H_2O$] (99% Ajax, Australia) were used as the starting materials. 1.0 M NH_4OH solution was added to $Ti(OCH(CH_3)_2)_4$ in an ice bath at 10 °C to form titanic acid [$Ti(OH)_4$] and then dissolved with 1.0 M HNO_3 to form titanyl nitrate [$TiO(NO_3)_2$]. Deionized water containing 0.3 M $(C_3H_5O(COO)_3)H_3 \cdot H_2O$ and 1.0 M NH_4OH were added to adjust the pH value of the solutions. The white precipitated sol was obtained after adjusting the final range of pH of the solution to 2-6. This was then washed, filtered and dried in an oven (Gallenkamp, England) at 80 °C for 24 h. The white gel was calcined in the muffle furnance (Control-2416, Carbolite, England) at 400 and 800 °C for 2 h with a heating rate of 5 K·minute^{-1}. The phase transformation was investigated by an X-ray diffractometer (modified D-500, SIEMENS, Germany) using Ni-filtered monochromatic CuK_α radiation. The detection range was 10° and 60° with a step size of 0.10° (2θ/s/s) and a continuous mode. The powder was obtained and the structure confirmed with the Joint Committee on Powder Diffraction Standards (JCPDS) Card File No. 21-1272 [19] and 21-1276 [20]. The powder was dispersed with ethanol [C_2H_5OH] (99.9% Merck, Germany) medium in an ultrasonic bath (Model 5880, Cole-Parmer, England) for 20 minutes, and gold [Au] coated with a fine coater (JSC1200, JEOL, Japan) for 1 minute. The microstructure was characterized by a scanning electron microscope (JSM5410-LV, JEOL, Japan) with a tungsten (W) filament K type, an acceleration voltage of 25 kV, and a working distance of 18 mm.

Results and Discussion

Figs. 2(a-c) show X-ray diffraction patterns of TiO_2 powder prepared by the sol-gel method calcined at 400 °C for 2 h with a heating rate of 5 K·minute^{-1} at pH 2-6. At the lower pH value of 2, Fig. 2(a), a single-phase anatase structure of the TiO_2 powder after calcining at 400 °C for 2 h was obtained by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) Card File No. 21-1272 [19]. With an increase in the pH value, the line width and intensity of diffraction lines slightly decrease and increase at pH 4 and 6, respectively. At the higher pH of 4 and 6, Fig. 2(b, c), a single-phase anatase structure of TiO_2 powder after calcining at 400 °C for 2 h was obtained by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) Card File No. 21-1272 [19]. This is in good agreement with a previous report [21].

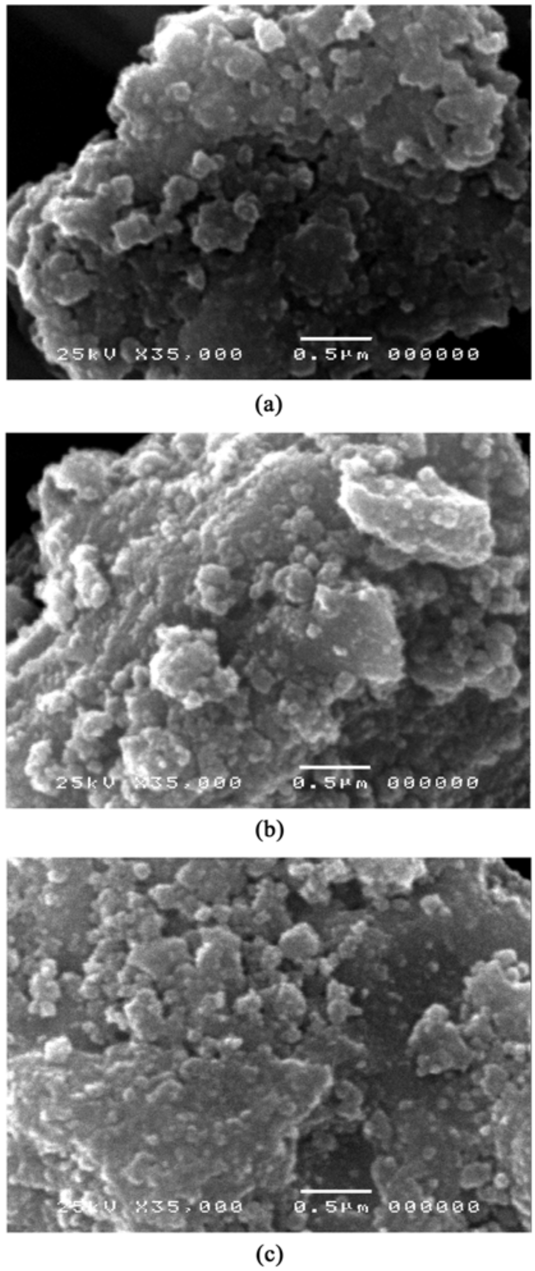

Fig. 3. SEM micrographs of TiO_2 powder calcined at 400 °C for 2 h at pH (a) 2, (b) 4, and (c) 6.

Figs. 3(a-c) show SEM micrographs of the TiO_2 powder

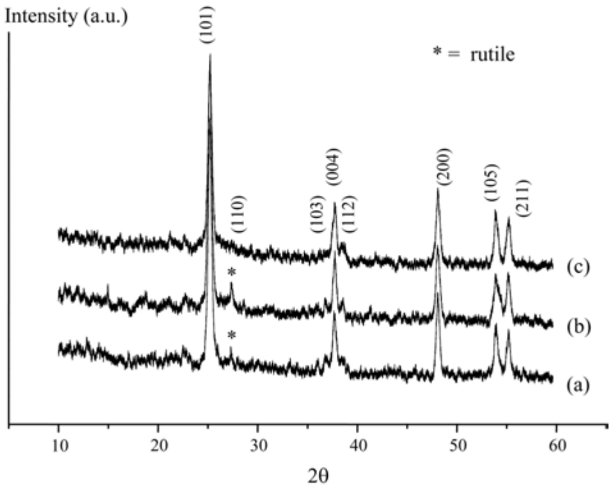

Fig. 4. X-ray diffraction patterns of TiO_2 powder calcined at 800 °C for 2 h at pH (a) 2, (b) 4, and (c) 6.

prepared by the sol-gel method calcined at 400 °C for 2 h with a heating rate of 5 K·minute^{-1} at pH 2-6. The particle size increased as the pH values increased. The powders consisted of small and soft agglomerates. The SEM micrograph of the powder using a pH of 2 and calcined at 400 °C for 2 h, Fig. 3(a), showed a highly agglomerated fine powder irregular in shape and 0.1 μm in diameter. At a pH of 4, Fig. 3(b), the powder was agglomerated and become slightly larger with an average size of 0.2 μm. At a pH of 6, Fig. 3(c), the powder was agglomerated, fused together and some particle growth occurred with an average size of 0.4 μm. These particle sizes are smaller than those previously reported [22].

Figs. 4(a-c) show X-ray diffraction patterns of the TiO_2 powder prepared by the sol-gel method calcined at 800 °C for 2h with a heating rate of 5 K·minute^{-1} at pH 2-6. At the pH value of 2 and 4, Fig. 4(a, b), a multi-phase anatase and rutile structure of the TiO_2 powder after calcining at 800 °C for 2 h was obtained by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) Card File No. 21-1272 [19] and 21-1276 [20]. At the highest pH of 6, Fig. 4(c), a single-phase anatase structure of the TiO_2 powder after calcining at 800 °C for 2 h was obtained by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) Card File No. 21-1272 [19]. With an increase in the pH value, the line width and intensity of diffraction lines slightly decrease and increase at pH 4 and 6, respectively. This is in good agreement with a previous report [21].

Figs. 5(a-c) show SEM micrographs of the TiO_2 powder prepared by the sol-gel method calcined at 800 °C for 2 h with a heating rate of 5 K.minute^{-1} at pH 2-6. The SEM micrograph of powder produced using a pH of 2 and calcined at 800 °C for 2 h, Fig. 5(a), shows an agglomerate of fine powder which is irregular in shape with 0.2 μm in diameter. At a pH of 4, Fig. 5(b), the powder was agglomerated and become slightly larger with an average size of 0.4 μm. At a pH of 6, Fig. 5(c),

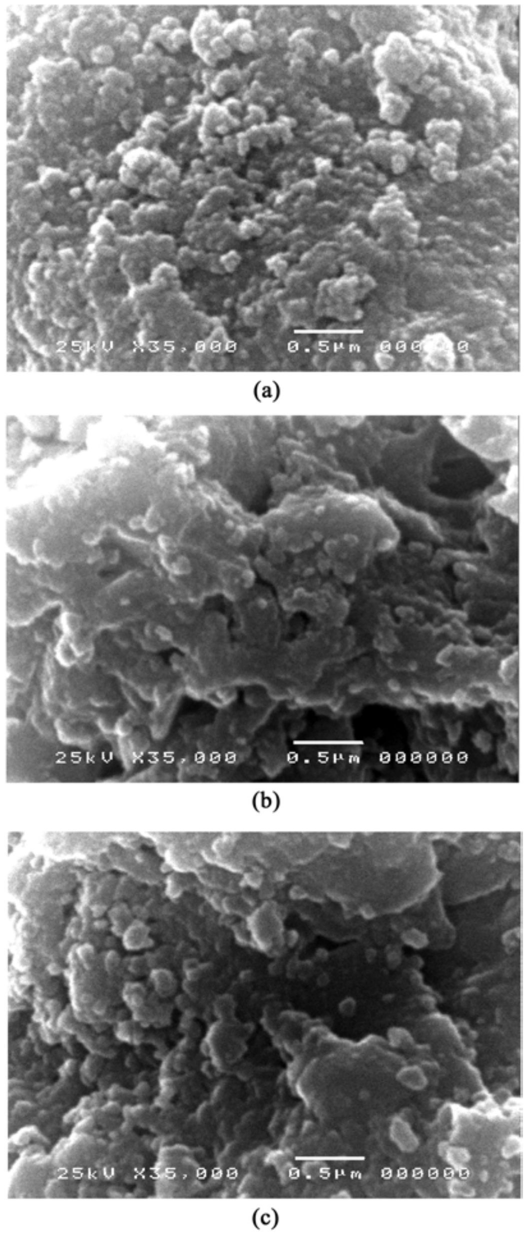

Fig. 5. SEM micrographs of TiO_2 powder calcined at 800 °C for 2 h at pH (a) 2, (b) 4, and (c) 6.

the powder was agglomerated, fused together and some particle growth occurred giving an average size of 0.5 μm. These particle sizes are smaller than those previously reported [22].

Conclusions

Titanium dioxide (TiO_2) powder was prepared by a sol-gel method. At all pH values from 2 to 6, the anatase structure of TiO_2 was obtained after calcination at 400 °C for 2 h with a heating rate of 5 K·minute^{-1}. At a higher calcining temperature of 800 °C for 2 h with a heating rate of 5 K·minute^{-1}, a multi-phase of the anatase and rutile structures of TiO_2 was obtained at pH values of 2 and 4. The particles of TiO_2 were highly agglomerated and irregular in shape with the particle sizes in the range of 0.1-0.5 μm. The size of both the rutile and anatase phases increased the pH values and calcination temperatures increased from 2 to 6 and 400 °C to 800 °C, respectively.

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