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Effect of raw materials for the synthesis of TiO_2 powders by a hydrothermal processing

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Abstract TiO_2 nanoparticles were prepared under high temperature and pressure conditions by precipitation from titanium tetrachloride ($TiCl_4$) and titanium isopropoxide (TTIP). TiO_2 powders were obtained in the temperature range of 150°C~190°C for 4 h. The microstructure and phase of the synthesized particles were studied by TEM and XRD. TEM and X-ray diffraction pattern shows that the synthesized particles were crystalline. The average sizes of the synthesized particles from titanium tetrachloride and titanium isopropoxide were below 20 nm and 10 nm, respectively. The average size of the synthesized particles increased with increasing reaction temperature. The effects of synthesis parameters, such as the reaction temperature and pH value are discussed.

Key words TiO_2 nanoparticles, Powders morphology, Titanium precursors, Hydrothermal processing

1. Introduction

Recently, the synthesis of nanometer-sized particles has been investigated extensively because of their novel electrical, optical, magnetic, and chemical properties [1]. The effect of particle size on the electronic and optical properties of these nanosized particles during the growth of the crystallite from the molecular level to the bulk material is an area of fundamental interest [2].

Nano-sized titania as a semiconductor photocatalyst has proved to be the most suitable for widespread environment application, such as air purification, water disinfections, hazardous waste remediation and water purification. This is due to its biological and chemical inertness, strong photo oxidization power, cost effectiveness and long-term stability against photo and chemical corrosion [3-13]. Many studies on the synthesis of superfine TiO_2 powder have been done using titanium compounds, such as titanium alkoxides ($Ti(OR)_4$) [14, 15] or titanium tetrachloride ($TiCl_4$) [16] as the starting materials.

Hydrothermal processe is widely applied to obtain metal oxide nanoparticles [17]. The method have a potential for the direct preparation of crystalline ceramic powders and offer a low-temperature alternative to conventional powder synthesis techniques in the production of oxide powders [18]. This process can produce fine, high-purity, stoichiometric particles of single and multicomponent metal oxides. Furthermore, if process conditions such as solute concentration, reaction temperature, and reaction time are carefully controlled, a desire shape and size of the particles can be produced [19, 20]. These powders could be sintered at low temperature without calcination and milling steps [21].

The object of this study was to prepare TiO_2 nanoparticles using titanium tetrachloride ($TiCl_4$) and titanium isopropoxide (TTIP) as precursor via a hydrothermal method.

2. Experiment

The preparation TiO_2 nanoparticles were schematically illustrated in Fig. 1. TiO_2 precursors were precipitated from 0.1 M $TiCl_4$ solution or 0.1 M TTIP solution by slowly adding KOH with rapid stirring. pH value of starting solutions varied between 7 and 11. After 30 min of stirring the solution was placed in a 1000 ml stainless steel pressure vessel. Hydrothermal treatment was carried out at 150~190°C for 4 h and cooled naturally to room temperature. The reaction products were washed five times by repeated centrifugation, and then dried at 80°C for 24 hours in air.

The recovered powders were analyzed for phase composition using X-ray diffraction (XRD, Philips X'pert

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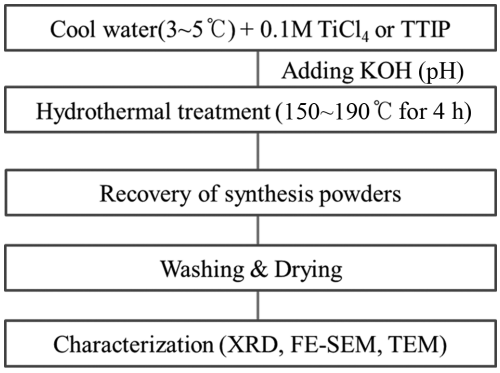

Fig. 1. Experimental flow chart of synthesized titanium dioxide (TiO_2) powders by hydrothermal processing.

MPD PW3040, Holland) over the 2θ range from 20° to 80° at the scan speed of 2° min^{-1}. The morphology of the synthesized particles was observed using transmission electron microscope (TEM, Jeol 2000FXII, Japan). For TEM studies, samples were prepared by adding drops of freshly prepared cluster solution on a carbon film supported on a Cu grid.

3. Results and Discussions

Fig. 2 shows X-ray diffraction patterns of the synthesized TiO_2 nanoparticles as a function of pH value. The XRD data of the particles synthesized at pH 11 indicate that they are amorphous. The particles synthesized at pH 7~9 were identified as nanocrystalline anatase (JCPDS no. 21-1272). At lower temperature, very small nanosized TiO_2 powders are synthesized. As the pH

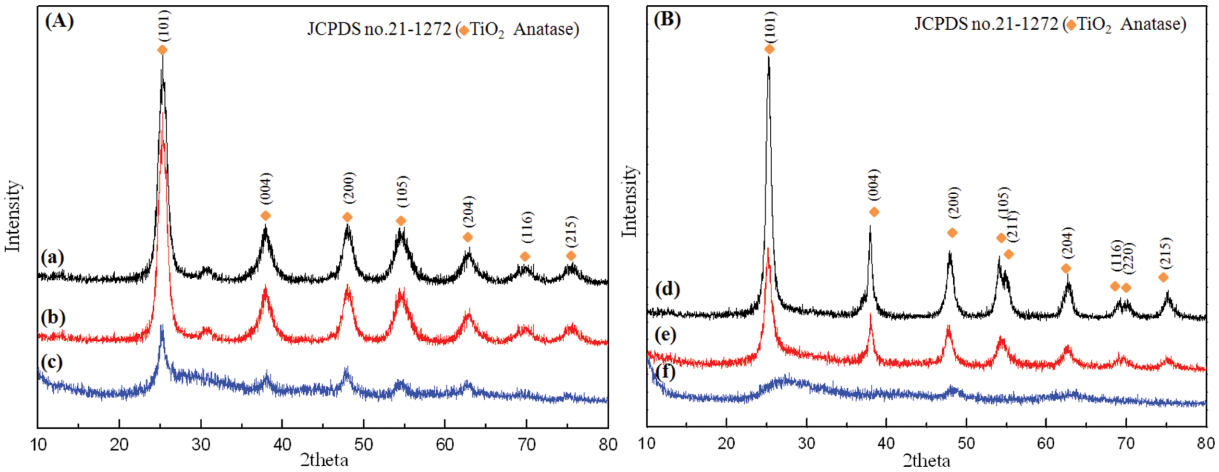

Fig. 2. X-ray diffraction patterns of the synthesized TiO_2 nanoparticles by hydrothermal reaction at 150°C for 4 h as a function of pH value: (A) [(a) pH 7, (b) pH 9, (c) pH 11 (TTIP)], (B) [(d) pH 7, (e) pH 9, (f) pH 11 ($TiCl_4$)].

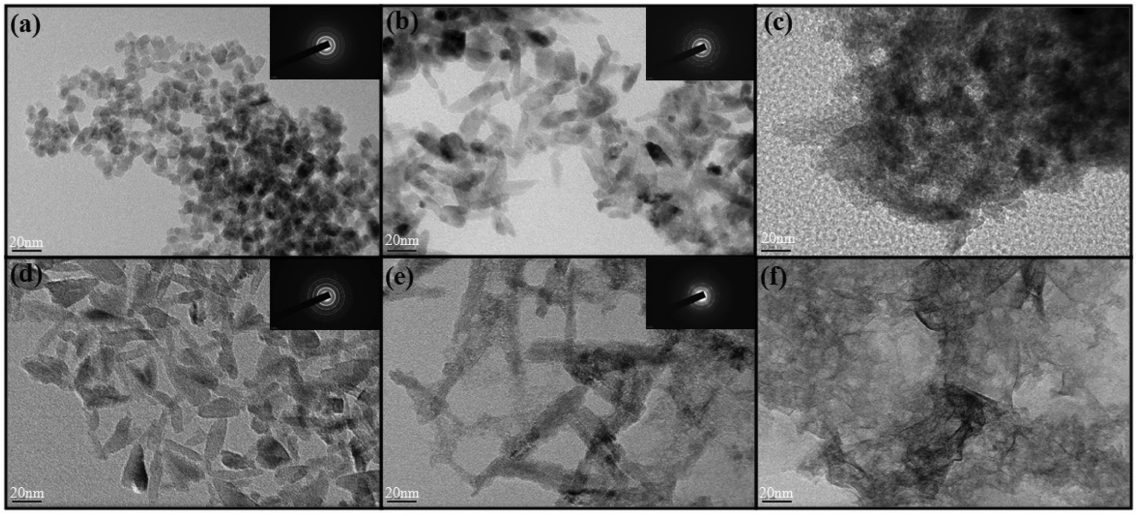

Fig. 3. TEM images (inset SAED patterns) of the synthesized TiO_2 nanoparticles by hydrothermal reaction at 150°C for 4 h as a function of pH value: TTIP [(a) pH 7, (b) pH 9 (c) pH 11], $TiCl_4$ [(d) pH 7, (e) pH 9, (f) pH 11].

value is increased, the crystallinity and the size of TiO_2 are decreased.

The morphology of the obtained TiO_2 nanopaticles was characterized by transmission electron microscope (TEM) observations. Fig. 3 shows TEM images and select area aperture diffraction (SAED) patterns of the TiO_2 nanopaticles. As shown in Fig. 3, the average crystalline sizes of the synthesized TiO_2 nanoparticles increased with pH value increased from 7 to 9. With increasing pH value, the crystallinity of the synthesized nanoparticles is decreased.

The morphology of powders using TTIP as precursor shows spherical or spheroid-shaped TiO_2 nanoparticles. On the other hand, the morphology of powders using $TiCl_4$ as precursor shows needle or rod-shaped TiO_2 nanoparticles. The average sizes of the synthesized particles from titanium tetrachloride and titanium isopropoxide were below 20 nm and 10 nm, respectively. The SAED patterns indicate the prepared TiO_2 nanopaticles were well crystalline.

Fig. 4 shows X-ray diffraction patterns of the synthesized TiO_2 nanoparticles as a function of reaction temperature. All the diffraction peaks can be readily indexed to anatase TiO_2 structure (JCPDS no. 21-1272).

Fig. 5 shows TEM images and SAED patterns of the synthesized TiO_2 nanoparticles by hydrothermal reaction at pH 7 for 4 h as a function of reaction temperature. As shown in Fig. 4, the average crystalline sizes of the synthesized TiO_2 nanoparticles increased with reaction temperature increased from 150°C to 190°C. With increasing reaction temperature, the crystallinity of the synthesized nanoparticles is increased.

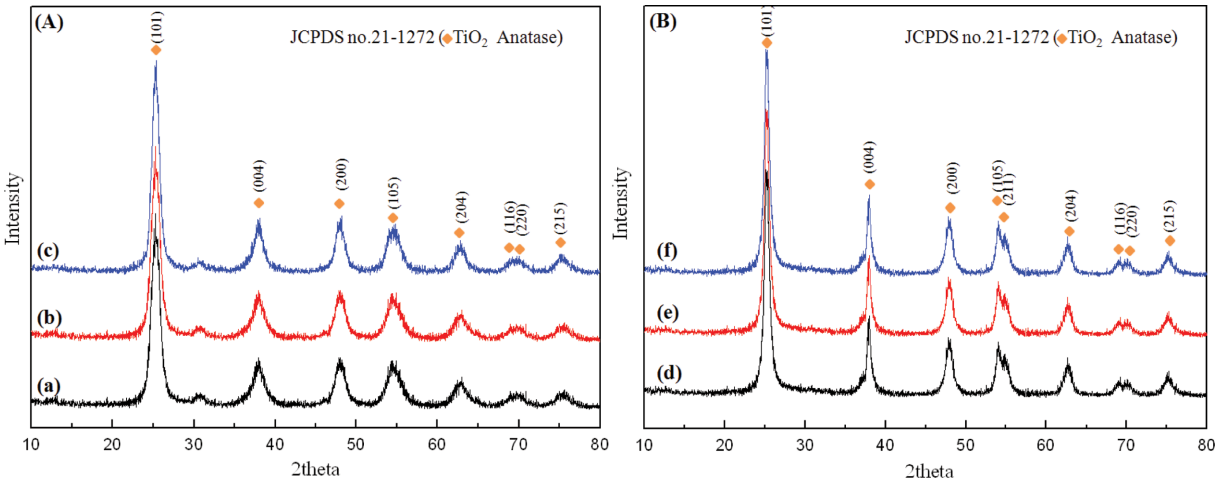

Fig. 4. X-ray diffraction patterns of the synthesized TiO_2 nanoparticles by hydrothermal reaction at pH 7 for 4 h as a function of reaction temperature: (A) [(a) 150°C, (b) 170°C, (c) 190°C (TTIP)], (B) [(d) 150°C, (e) 170°C, (f) 190°C ($TiCl_4$)].

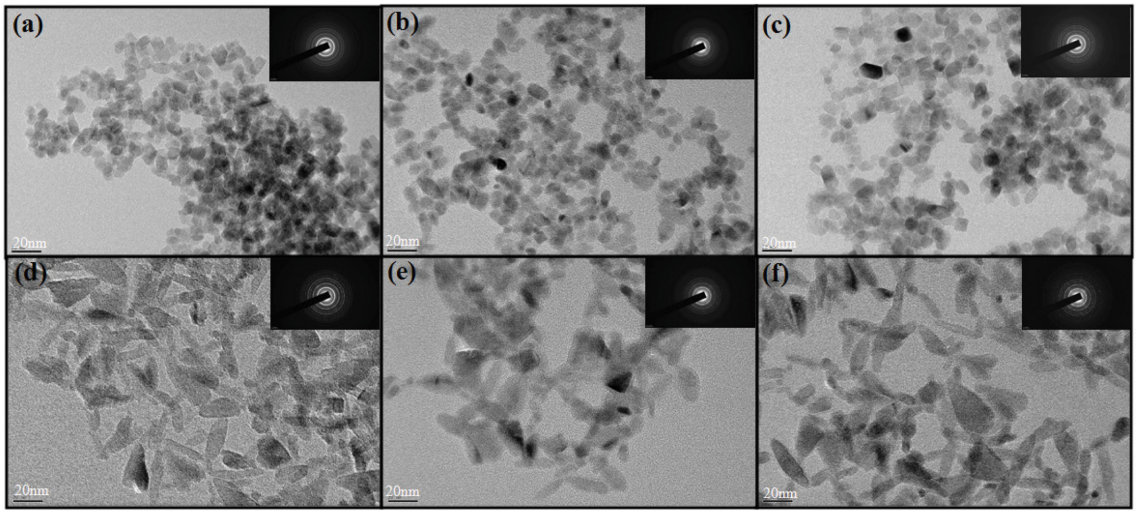

Fig. 5. TEM images (inset SAED patterns) of the synthesized TiO_2 nanoparticles by hydrothermal reaction at pH 7 for 4 h as a function of reaction temperature: TTIP [(a) 150°C, (b) 170°C, (c) 190°C], $TiCl_4$ [(d) 150°C, (e) 170°C, (f) 190°C].

4. Conclusions

TiO_2 nanoparticles were prepared under mild temperature and pressure conditions by precipitation from $TiCl_4$ and TTIP. The particles synthesized at pH 7~9 were identified as nanocrystalline anatase. As the pH value is increased, the crystallinity and the size of TiO_2 are decreased. The morphology of powders using TTIP as precursor shows spherical or spheroid-shaped TiO_2 nanoparticles. on the other hand, the morphology of powders using $TiCl_4$ as precursor shows needle or rod-shaped TiO_2 nanoparticles. The average sizes of the synthesized particles from titanium tetrachloride and titanium isopropoxide were below 20 nm and 10 nm, respectively. From X-ray analysis and TEM, the synthesized particles were crystalline. The size and morphology of the synthesized TiO_2 nanoparticles can be controlled as a function of starting solution pH and reaction temperature.

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