

Article

Phase Control of TiO₂ Prepared by TiCl₄ Hydrolysis and Electrochemical Method

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Abstract. The phase structure of TiO₂ dependent on applications. It is importat to develop an effective method to control the phase structure of TiO₂. In this study, the TiO₂ was synthesized by TiCl₄ hydrolysis method. The control of hydrolysis was done by electrochemical method in a cell consisting of two plate carbon as electrodes. The electrodes distance was set to 2.6 to 4 cm and immersed in solution at dimensions of (5 × 2) cm. The electrodes were connected to the positive and negative terminals of a DC power supply for 1 to 2.5 hours. The voltage was varied from 5 to 15 V at constant stirring and room temperature. The resulted suspension was aged for 48 hours. The solution was filtered. The powder dried directly in an oven at 150°C for 2 hours, washed 2 times, and dried again 60 °C for 6 hours. In this work, the voltage, electrode distance, and TiCl₄ initial concentration can control the phase structure of TiO₂.

Keywords: TiO₂, phase control, hydrolysis, electrochemical

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1. Introduction

Titanium dioxide (TiO_2) has attracted great attention due to its unique physical and chemical properties for the great potential applications. TiO_2 is applied as pigments, cosmetics, adsorbent, solar cell, photocatalysts, photovoltaic, sensors and electrochemistry [1–8]. The phase structure of TiO_2 is anatase, rutile and brookite. Rutile is stable phase at all temperature and pressures. Anatase is metastable but it be stabilised at lower temperatures [9].

The anatase phase of TiO_2 can be applied in solar cells and photocatalyst [10,11]. The rutile phase of TiO_2 is suitable for lithium-ion batteries, pigments and adsorption [12-15]. The brookite phase is used in electrochromic smart windows [16]. The applications of TiO_2 particle depends on the phase structure so it is importance to develop an effective method to control the phase structure of TiO_2 .

The conventional method to phase control is the calcination temperature [9,17]. Cao, et.al. [18] reported that the key factor determining the crystal phase is the molar ratio of TiCl_4 to butanol. The phase structure of TiO_2 were also controlled by the concentration of aqueous TiCl_4 solution and dopants [9,19].

The control of the parameters such as temperature, the concentration of the precursor, pH, and dopants is greatly required to promote phase structure [20-22]. The complexity of the method and the different variables make the product difficult to control. In this study, the electrochemical method was developed to control of the TiO_2 particle that synthesized by hydrolysis. The control of powders by electrochemical method is a attractive method. In the electrochemical method, the product can be controlled by current or potential [23-25]. In this work, the phase structure of TiO_2 prepared by hydrolysis was controlled by electrochemical method.

2. Experimental

The homogeneous solution for synthesis of TiO_2 powders was prepared by diluting TiCl_4 (Merck) in 50%v ethanol (Merck) at concentration 0.1 and 0.2 M TiCl_4 . All chemicals were used as supplied with no further treatment. The control of hydrolysis was done by electrochemical method in a cell consisting of two plate carbon as electrodes. The electrodes distance was set to 2.6 to 4 cm and immersed in solution at dimensions of (5 × 2) cm. The electrodes were connected to the positive and negative terminals of a DC power supply (Zhaoxin PS-3005D) for 1 to 2.5 hours. The voltage was varied from 5 to 15 V at constant stirring and room temperature. The solution was filtered. The powder dried directly in an oven at 150°C for 2 hours, washed 2 times, and dried again 60 °C for 6 hours. The morphologies of the particles and energy dispersive X-ray spectrometry (EDX) analysis were observed using scanning electron microscopy (Inspect S40, FEI). The phase structure of TiO_2 particle was analysed by X-ray diffractometer (Shimadzu 6000) to investigate the influence of time electrolysis, voltage, distance of electrode and the concentration of aqueous TiCl_4 solution.

3. Result and Discussion

Gas bubbles appeared immediately at the surface of anode and cathode in electrochemical cell. Gas bubbles are hydrogen and oxygen from the reduction and oxidation of water. A white precipitate was obtained by electrochemical cell under the conditions described above. The EDX measurements were carried out to investigate the resulted particle. The EDX patterns clearly show distinct peaks of Ti, O and Cl elements. The product contains TiO_2 with Cl as impurity from residual reactant (Fig. 1).

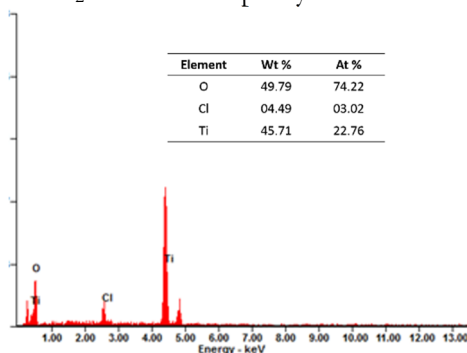


Fig. 1. EDX spectra of the particle resulted

The influence of time electrolysis to phase structure of TiO_2 was investigated from 1 to 2.5 hrs. The Fig. 2 shows the XRD patterns obtained by electrolysis at different time electrolysis. The XRD patterns show the similar diffraction patterns, indicating that the particle is three phase mixed TiO_2 , which consist of brookite, anatase, and rutile. The rutile phase can be identified located at 27.3° (2θ) from its (110) plane diffraction (JCPDS No 75-1753). The existence of brookite in the XRD patterns is evidenced form the presence of the (121) peak at 30.8° (2θ) (JCPDS No 72-0100), since no overlapping of this peak with any other peaks from anatase or rutile. Although the strongest diffraction from (110) anatase peaks at 25.3° (2θ) (JCPDS No. 84-1286) is overlapped with the (120) and (111) peaks of brookite at 25.1° and 25.3° (2θ), the relative amount of the three polymorphs can be evaluated. The ideal brookite has a (121) peak/(120) peak rasio of ~ 0.9 . In the XRD patterns showed that the rasio (121) peak/(120) peak very low. This condition evidenced the existence of anatase.

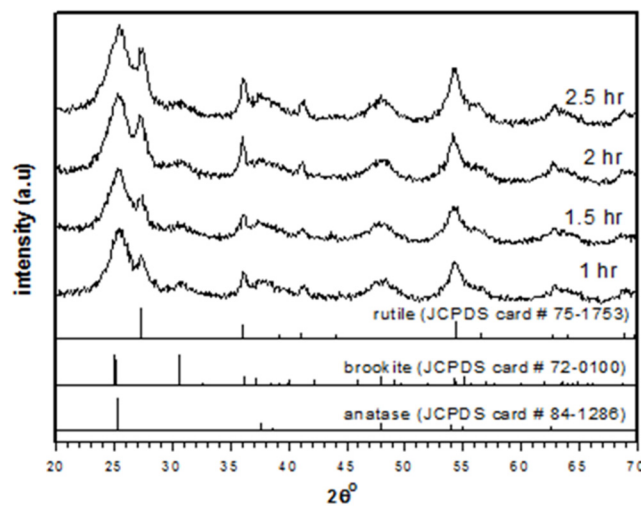


Fig. 2 XRD patterns for particles prepared using various time electrolysis

The time electrolysis from 1 h to 2.5 hrs resulted the different particle size (Fig. 3). The SEM micrograph of synthesized TiO_2 particles show that dense agglomeration of particles and irregular shape. The longer the electrolysis time, the smaller the size of particles obtained.

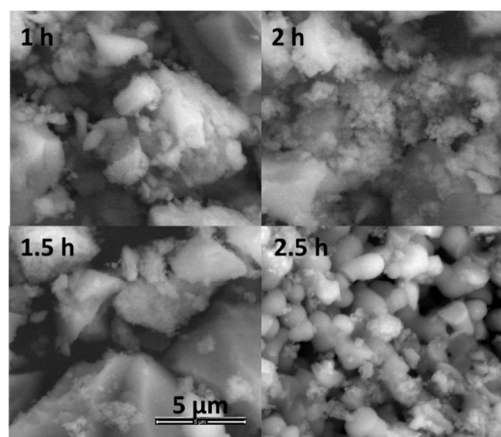


Fig. 3 SEM images of the particles prepared using various electrolysis time

Further the phase structure of TiO_2 particles was controlled by voltage. The XRD patterns resulted are shown in Fig. 4. The rutile phase appear in 5 V according the presence of the (110) peak at 27.3° (2θ), the (101) peak at 36.0° (2θ), and the (211) peak at 54.4° (2θ). The peaks of rutile decrease at 10 V and disappear at 15 V. The voltage can control the rutile phase. The smaller the voltage increasingly tend to form rutile phase. The brookite phase didn't appear at 5 V, but they increase at 10 and 15 V evidenced the presence of the (121) peak at 30.8° (2θ). The bigger the voltage increasingly tend to form brookite phase. Anatase peaks

at 25.3° (2θ) (JCPDS No. 84-1286) is overlapped with the (120) and (111) peaks of brookite at 25.1° and 25.3° (2θ) making it difficult to evaluate the effect of voltage on anatase phase.

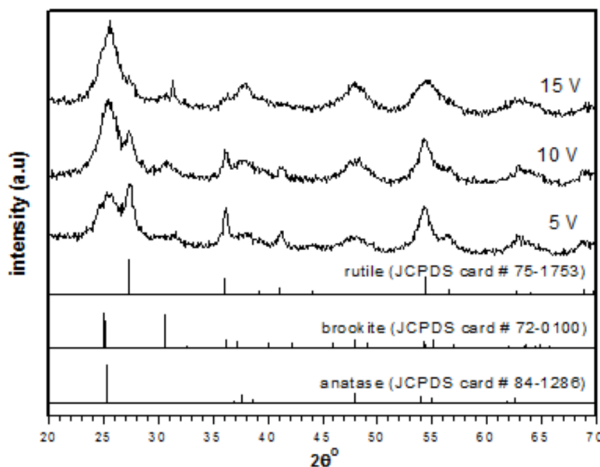


Fig. 4 XRD patterns for particles prepared using various voltage

The effect of electrode distance on the XRD patterns are shown in Fig. 5. The peaks of rutile phase increases with larger electrode distance. In 4 cm electrode distance, the pure rutile phase was resulted. The peaks of brookite appear at 2.6 cm electrode distance but disappear at 3 and 4 cm electrode distance. The peaks of anatase appear at 2.6 cm electrode distance, decrease at 3 cm electrode distance, and disappear at 4 cm electrode distance. The larger the electrode distance increasingly tend to form rutile phase and the smaller the electrode distance increasingly tend to form anatase and brookite phase.

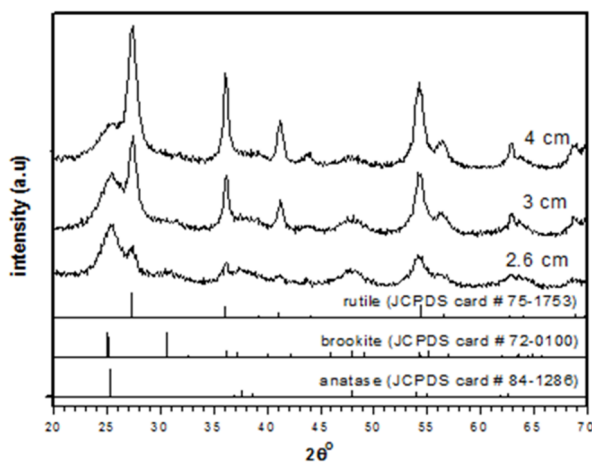


Fig. 5 XRD patterns for particles prepared using various electrode distance

Fig. 6 shows the comparison of XRD patterns from 0.1 M and 0.2 M TiCl_4 initial concentration. At 0.1 M TiCl_4 initial concentration the peaks of brookite, anatase, and rutile appears. The peaks of rutile increase while the peaks of anatase and brookite decrease at 0.2 M TiCl_4 initial concentration.

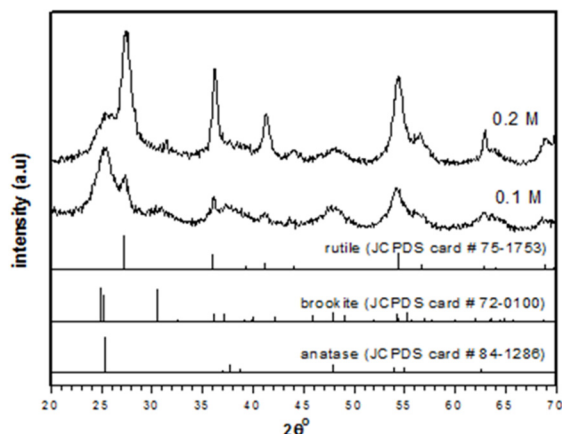


Fig. 6 XRD patterns for particles prepared using various TiCl_4 initial concentration

4. Conclusions

The phase structure of TiO_2 particles can be controlled by voltage, electrode distance, and TiCl_4 initial concentration. The larger the voltage increasingly tend to form anatase and brookite phase while smaller the voltage increasingly tend to form rutile phase. The larger the electrode distance and TiCl_4 initial concentration increasingly tend to form rutile phase while the smaller the electrode distance and TiCl_4 initial concentration increasingly tend to form anatase and brookite phase.

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