Synthesis of TiO_2 nanoparticles with pure brookite at low temperature by hydrolysis of $TiCl_4$ using HNO_3 solution

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Nanocrystalline materials are currently receiving much attention by virtue of their special chemical, physical, and mechanical properties. Of these materials, nanosized titanium dioxide has been of great interest because it exhibits many modified electronic and optical properties as well as extensive application, including photocatalysis and photoelectrochemical solar cells [1–4]. Titania has three naturally occurring polymorphs: rutile, anatase, and brookite. The rutile and anatase phases are well known and many studies on their synthesis and application have been reported [1, 5–8]. However, it has been reported that pure brookite-type TiO_2 without a mixture of rutile or anatase phase is difficult to prepare and the difficulty in preparing brookite having high purity and large surface area is probably one of the reasons for its limited application [3, 10]. Recently, pure brookite-type TiO_2 particles have been synthesized by hydrothermal method, in which the autoclave with high temperature and pressure as well as complexing agents are required [2–4, 10]. Other researchers reported that brookite is sometimes observed as a by-product when the precipitation is carried out in an acidic medium at low temperatures [2, 7, 10, 11]. We therefore describe a relatively simple method that leads to synthesis of pure brookite-type TiO_2 nanoparticles without adding complexing agents at low temperature.

In this study, $TiCl_4$ used as a starting material was hydrolyzed using HNO_3 solutions with various so that TiO_2 nanoparticles could be obtained by merely heating it at temperatures ranging from 60 °C to 150 °C, from that reaction condition for the formation of pure brookite-type TiO_2 particles from aqueous $TiCl_4$ solution was investigated. A typical procedure for making nanocrystalline TiO_2 particles was as follows. $TiCl_4$ was hydrolyzed by adding 1.0 M HNO_3 dropwise to prepare a stock solution, in which the concentration of titanium was 5.45 M. During the reaction, the yellow cakes of $TiO(OH)_2$ were formed first, which were then dissolved with added HNO_3 solution to form an aqueous $TiCl_4$ solution. This stock solution remained in a stable state without precipitation even after 6 months at room temperature. Finally, HNO_3 solution with concentration of 1.0–8.0 M was added to the stock solution to prepare transparent aqueous $TiCl_4$ solutions with various concentrations of Ti^{4+} for precipitation. This solution was poured into reactor and placed in the oven at the temperature of 60–150 °C for precipitation. TiO_2 precipitates were repeatedly cleaned by distilled water and dried at 70 °C for 48 hr or more to obtain the final particles.

TiO_2 particles obtained by heating the aqueous $TiCl_4$ solution with 0.8 M of Ti^{4+} prepared using 4.5–5.0 M HNO_3 at 70 °C for 20 hr were confirmed to be pure brookite by X-ray diffraction (XRD) as shown in Fig. 1 and analysis of diffraction line widths indicated that the particles size is less than 20 nm. However, TiO_2 particles with pure rutile structure were obtained when not more than 2.0 M HNO_3 or not less than 5.5 M HNO_3 was added to the stock solution whereas a mixture of the rutile and brookite was produced at 2.5–4.0 M HNO_3. The volume fraction of brookite in the mixture of brookite and rutile, which was calculated by the K.N.P. Kumar equation using intensities of the (1 1 0) main peak of rutile phase and the (1 2 0) main peak of brookite phase in Fig. 1, was maximum value of about 90% at 4.0 M HNO_3 but reduced to about 50% at 2.5 M HNO_3, disappeared to yield only rutile at 2.0 M HNO_3, showing that it is very dependent on the concentration of added HNO_3 solution for dilution of stock solution. These results mean that the concentration of HNO_3 in the solution play an important role in determining the crystal structure of TiO_2 precipitates. In this regard, based on the conditions producing pure brookite, the range of HNO_3 concentration for formation of pure brookite was obtained from HNO_3 concentration in the aqueous $TiCl_4$ solutions prepared using 4.5 and 5.0 M HNO_3, respectively. The so-obtained range of HNO_3 concentration is about 3.89–4.32 M.

On the other hand, in order to investigate the effect of reaction temperature on morphology of TiO_2 particles, they were obtained from aqueous $TiCl_4$ solution with 0.8 M of Ti^{4+}, which was prepared by adding 4.5 M HNO_3 to the $TiCl_4$ stock solution, at 60–150 °C for 20 hr and the XRD patterns of these products are shown in

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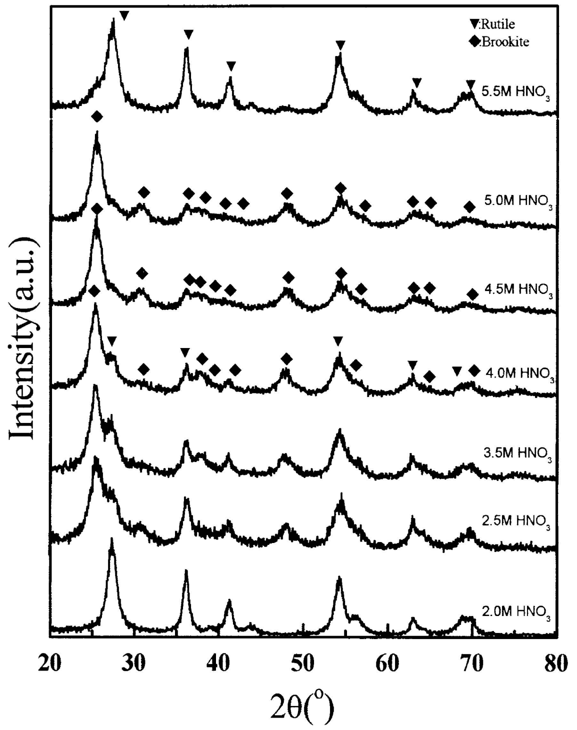

Figure 1 The XRD patterns of TiO_2 particles obtained from aqueous $TiCl_4$ solution with 0.8 M Ti^{4+} prepared by adding various HNO_3 concentrations at 70 °C for 20 hr.

Fig. 2. TiO_2 particles obtained at 60 and 70 °C consisted of pure brookite without mixture of rutile or anatase phase. However, the particles formed at 80 °C were a mixture of brookite and rutile phases, whose ratio of brookite to rutile by volume was 87 to 13, whereas a mixture of anatase and rutile phases at 100–120 °C, in which the volume fraction of anatase was about 82% at 100 °C but decreased to about 56% at 120 °C, forming rutile at 150 °C. In particular, it is very interesting to note that the particle structure mixed with rutile is changed from brookite to anatase with increase of reaction temperature. Judging collectively from both of the above results, it can be said that the concentration of HNO_3 in the solution and reaction temperature play an important role in determining the crystal structure of TiO_2 precipitates.

Fig. 3 shows XRD patterns of TiO_2 particles obtained from aqueous $TiCl_4$ solutions with various concentrations of titanium, which were prepared by adding 4.5 and 5.0 M HNO_3 solution to the $TiCl_4$ stock solution, for 20 hr at 70 °C, respectively. In the case of using 4.5 M HNO_3, pure brookite particles were obtained at not more than 1.2 M of titanium, whereas a mixture of predominant rutile and small brookite at 1.4 M (Fig. 3A). However, at 5.0 M HNO_3, pure brookite particles were obtained at not more than 0.8 M while two polymorphs of TiO_2, brookite

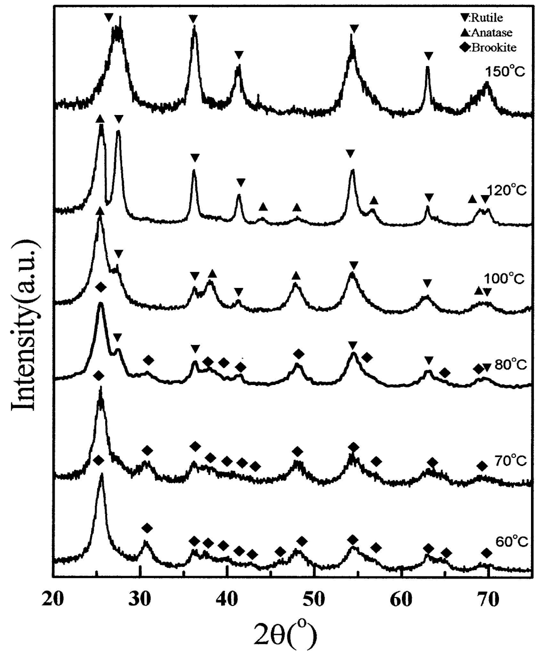

Figure 2 XRD patterns of TiO_2 particles obtained from aqueous $TiCl_4$ solution with 0.8 M Ti^{4+} prepared by adding 4.5 M HNO_3 at the temperature of 60–150 °C for 20 hr.

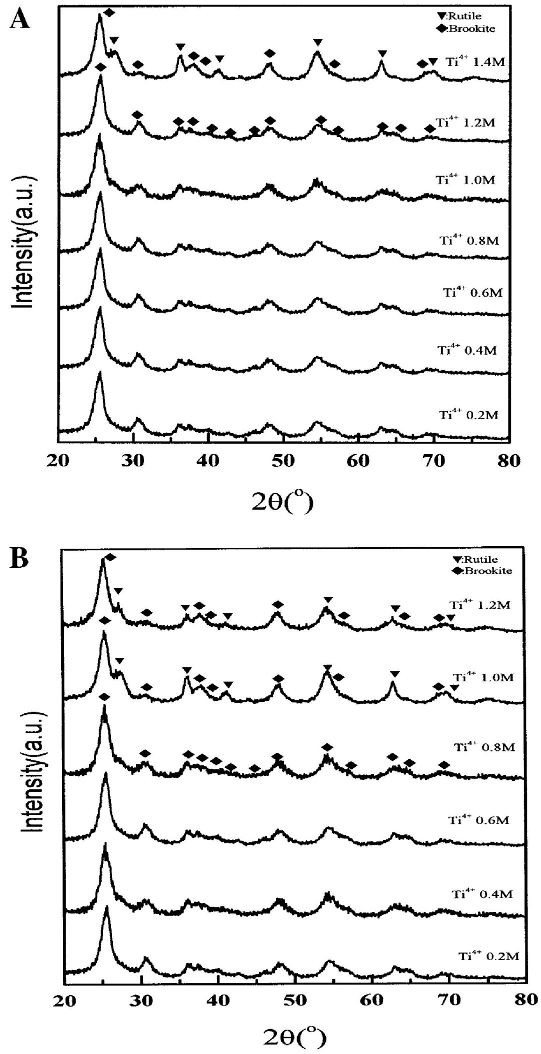

Figure 3 The XRD patterns of TiO_2 particles obtained from aqueous $TiCl_4$ solution with various concentrations of Ti^{4+} prepared by adding 4.5 M and 5.0 M HNO_3 at 70 °C: (A) 4.5 M HNO_3, (B) 5.0 M HNO_3.

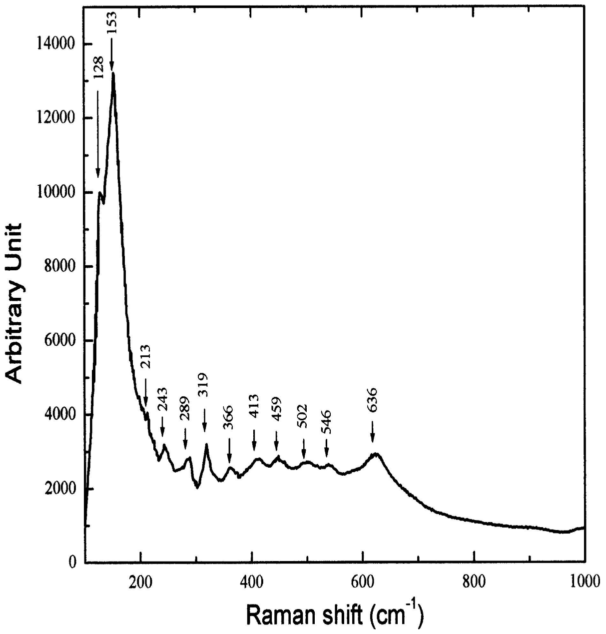

Figure 4 Raman spectrum of as-prepared brookite-type TiO_2.

and rutile, were formed at not less than 1.0 M (Fig. 3B). The oxidation ratio of Ti^{4+} to TiO_2 was more than 99% at and less than 0.8 M of the Ti^{4+} concentration but abruptly decreased to less than about 46% at and more than 1.0 M, showing that the kinetics of oxidation is very dependent on the concentration of titanium. Also, when the reaction time was extended to more than 40 hr the two polymorphs of TiO_2, brookite and rutile, were formed, indicating that reaction time should be properly controlled to obtain pure brookite even though the HNO_3 concentration in solution has been kept in the range for brookite formation. When the reaction time was sufficiently extended, brookite as a metastable structure transformed to rutile as a stable one. The as-prepared crystalline TiO_2 nanoparticles with pure brookite structure were stable in terms of phase purity and morphology up to about 500 °C but transformed to rutile at about 800 °C.

The identity of brookite-type structure was verified by Raman spectrum of as-prepared pure brookite as shown in Fig. 4, in which there are 12 peaks. All of the peaks are consistent with Raman spectrum of natural brookite [3, 12, 13] though the peak positions shift a little, except the absence of two weak peaks.

Fig. 5 shows TEM micrograph of as–prepared brookite. The crystallite with pure brookite structure obtained by adding 4.5 M HNO_3 at 70 °C is spherical shape with the size of less than 20 nm.

Considering all of the above results and efficiency in oxidation of Ti^{4+} to TiO_2, crystalline TiO_2 nanoparticles with pure brookite structure are efficiently prepared by heating the aqueous $TiCl_4$ solution with not more than 0.8 M of Ti^{4+}, in which the concentration of HNO_3 is kept in the range of about 3.9–4.3 M, at the temperature of not more than 70 °C within 40 hr. This preparation method of TiO_2 nanoparticles with pure brookite would provide opportunities for developments of the brookite formation and its application fields although it was difficult to exactly determine reaction condition for brookite formation because of possible errors in experiment and insufficient experimental data in subdivided range of reaction parameters such as reaction temperature, HNO_3 and titanium concei

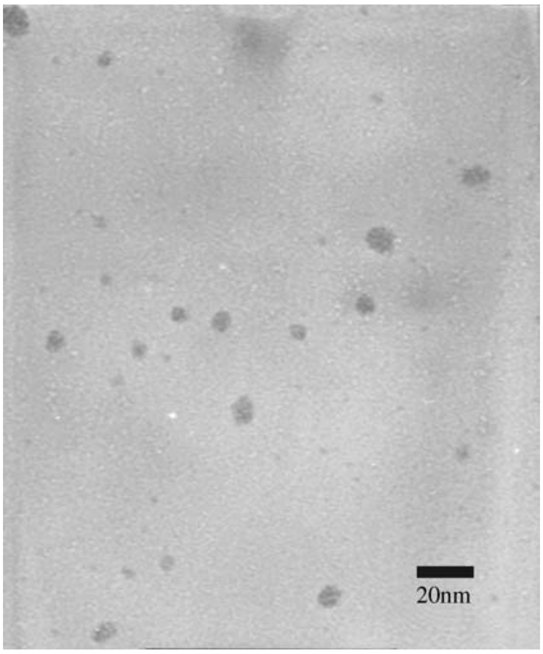

Figure 5 TEM photograph for pure brookite TiO_2 particles obtained from aqueous $TiCl_4$ solution with 0.8 M of Ti^{4+} prepared by adding 4.5 M HNO_3 at 70 °C. (Scale bar = 20 nm).

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