

Size effect on phase transition sequence of TiO₂ nanocrystal

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Abstract

Titanium dioxide nanocrystal with a mixture of anatase and brookite was prepared by sol–gel method. The effects of the grain size and the phase content on the transition were studied for TiO₂ nanocrystal annealed in air for 1 h at the temperature range 200–650 °C. The experimental results indicate that the phase transition sequence depends on relative grain size between anatase and brookite. Under the same grain sizes anatase, brookite, and rutile is the most stable at the size smaller than 4.9 nm, between 4.9 and 30 nm, and larger than 30 nm, respectively. Thermodynamic analysis gives an empirical expression on a critical grain size of brookite D_c , which dominates the transition sequence between anatase and brookite. As the size of brookite D_b reaches D_c , brookite and anatase phases transform directly to rutile. When $D_b > D_c$, anatase phase transforms to brookite and then brookite to rutile and/or directly to rutile; when $D_b < D_c$, brookite phase transforms to anatase and then anatase to rutile and/or directly to rutile. The origin of the transition sequence was discussed from the view of free energy. © 2005 Elsevier B.V. All rights reserved.

Keywords: TiO₂ nanocrystal; Phase transition; Size effect; X-ray diffraction

1. Introduction

Titanium dioxide nanocrystal has received great attention in recent years for its unusual physical/chemical properties in comparison with its bulk properties and for its potential applications in conventional catalyst support, photocatalytic substrate, photochemical/photoelectrochemical, solar cell and so on [1–5]. Titanium dioxide has three phases in nature, rutile, anatase, and brookite. Rutile has high refraction index, visible transparency and ultraviolet absorptivity, thus it has been widely applied in pigments and opacifiers. Anatase is chemically and optically active, suitable for catalyst support and photoelectrochemical material [2–4]. Brookite is rare in nature, but recently it has been found that it is more electrochemically active than anatase and is a good candidate for photovoltaic devices [5]. A mixture of 70%/30% anatase/rutile is best photocatalyst for the oxidation of organics in the treatment of wastewater [6]. Therefore, it is interesting to investigate the phase stability and phase transition of

TiO₂ nanocrystal. In bulk material, rutile is stable, whereas brookite and anatase are metastable and easy to transform to rutile when heated. Thermodynamics indicates that phase stability for three polymorphs is in decreasing sequence of rutile, brookite, and anatase [7], which suggests that the phase transition from anatase to brookite may take place. However, phase relationships and transition kinetics may be dramatically modified, when the grain size is enough small. This is because the phase stability depends upon surface energy differences among three phases. Anatase with the grain size below 14 nm is more stable than rutile [8]. This explains that anatase phase is preferable to be synthesized at nanometer size, which is similar to the case that usually γ -Al₂O₃ phase is synthesized in nanosized case; whereas α -Al₂O₃ phase is formed in bulk [9]. Anatase phase is more stable than brookite in nanocrystal with the size smaller than 11 nm [10], which suggests that the phase transition from brookite to anatase also may take place. The phase transition between anatase and brookite happens in TiO₂ nanocrystal aggregations, instead of the single anatase or brookite phase. Usually TiO₂ nanocrystal is mixed with two phases of anatase and brookite or three phases of anatase, brookite, and rutile

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[3,5,10], so phase transition in such system is quite complicated. It was reported that different phase transitions occurred from anatase to brookite and to rutile and/or directly to rutile [10], from brookite to anatase and then to rutile [11], and from anatase and brookite directly to rutile [12]. Although many factors, such as impurity, grain size, reaction atmosphere and synthesis condition, may affect phase transition [10,13–17], it remains unclear what is main cause for dominating the phase transition sequence in TiO₂ nanocrystal aggregations. Under the assuming that the grain sizes in the three phases are equal, the phase stability dependence on the grain size in TiO₂ nanocrystal was investigated [10]. However, the grain sizes of three phases are practically not equal, as the grain gets coarsened during the process of phase transition. Therefore the relative grain size among three phases in TiO₂ nanocrystal mixture is crucial to the phase transition sequence.

In this paper, we report the preparation of three samples of TiO₂ nanocrystal with different grain sizes of anatase and brookite. We study the influence of the transition by the grain size and the phase contents change by heat treatment. We discuss their interaction between the phase transition sequence and both the grain size and phase content on the basis of thermodynamic analysis.

2. Experimental details

Titanium dioxide nanocrystal with a mixture of anatase and brookite phases was synthesized by sol–gel method [18]. An ethanol solution of tetrabutyl titanate, Ti(OC₄H₉)₄, was slowly added into deionized water which was vigorously stirred. At same time, dilute nitric acid was added to the solution to decrease reaction rate in order to get nanocrystal with different grain sizes. The resulting titania gel was washed with deionized water three times, followed by evaporation in atmosphere at room temperature for several days. Three as-prepared nanocrystal samples A, B and C with mixed anatase and brookite were prepared. For sample A the hydrolysis rate was the slowest, whereas for sample C it was the fastest. To examine the heat effect the samples were treated in air for 1 h in 200–650 °C.

The phase contents and the grain sizes of anatase, brookite, and rutile are determined by X-ray diffraction (XRD). The diffraction patterns were collected using a D/Max-RA diffractometer with Cu K α radiation (40 kV, 100 mA) in the step-scanning mode.

Micrographs of TiO₂ nanocrystal were recorded on transmission electron microscope (TEM) of JEM-200CX. The samples were prepared by dispersing the TiO₂ nanocrystal powder in alcohol by ultrasonic treatment, dropping onto a carbon film supported by a copper grid, and then dried in air.

The phase contents was determined from XRD pattern according to the following equations [10]:

$$W_a = \frac{0.884A_a}{0.884A_a + A_r + 2.721A_b} \quad (1a)$$

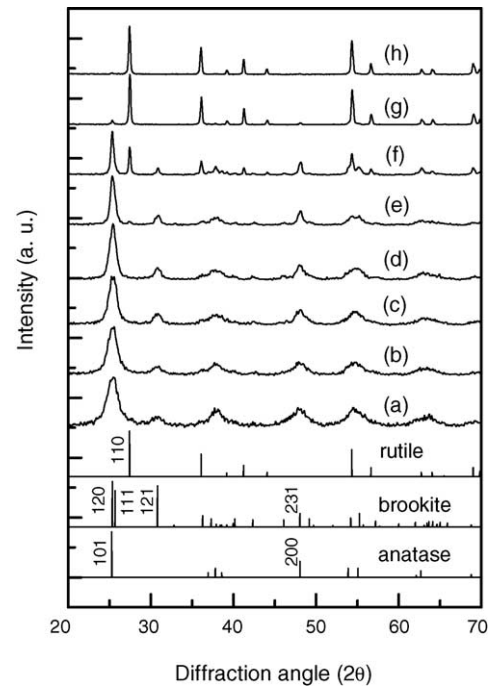


Fig. 1. XRD patterns of sample A of TiO₂ nanocrystal at various temperatures. Curve (a) stands for the result from the as-prepared sample, and curves (b)–(h) present the results annealed at 200, 300, 400, 500, 550, 600 and 625 °C, respectively.

$$W_r = \frac{A_r}{0.884A_a + A_r + 2.721A_b} \quad (1b)$$

$$W_b = \frac{2.721A_b}{0.884A_a + A_r + 2.721A_b} \quad (1c)$$

where W_a , W_r and W_b represent the weight fractions of anatase, rutile, and brookite, respectively. A_a , A_r and A_b are the individually integrated intensity for anatase (1 0 1), rutile (1 1 0), and brookite (1 2 1) peaks. Fig. 1 clearly shows X-ray diffraction patterns for sample A under different heat treatments. Below pattern (a) standard XRD patterns of anatase, brookite, and rutile from JCPDS cards were also plotted, and their relatively characteristic peaks can be used to identify the measured diffraction peaks clearly. It is clearly seen that anatase (1 0 1) peak overlaps with the brookite (1 2 0) and (1 1 1) peaks. Because the 2θ difference between anatase (1 0 1) and brookite (1 2 0) peaks is as small as 0.078° (Ref. JCPDS cards Nos. 21-1272 and 29-1360) and the full width at half maximum of diffraction lines are broaden in nanophase, it is difficult to deconvolute these three peaks from the overlapped peak. We calculated the integrated intensity of anatase (1 0 1) peak based on assuming that anatase (2 0 0) peak overlaps completely with brookite (2 3 1) peak (2θ difference is 0.038°) and the intensities of all the peaks in TiO₂ nanocrystal are proportional to their standard intensities in JCPDS cards (nanocrystal grains are approximately randomly oriented in the sample). According to data in JCPDS cards of anatase and brookite, we have an integrated intensity expression for

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