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Letter

Low-temperature wet-chemical preparation of titania nanocrystallines by utilizing γ-Al_2O_3 as fluorion scavenger

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ABSTRACT

Herein, we utilized γ-Al_2O_3 as the fluorion scavenger to prepare anatase titania nanocrystallines at low temperatures (<100 °C). The prepared products were characterized by X-ray powder diffraction (XRD), thermogravimetric (TG) analysis, Fourier transform infrared spectroscopy (FTIR), and transmission electron microscope (TEM). The crystal growth of products was very sensitive to reaction temperatures and starting fluorion scavengers. When the reaction took place at 80 °C and 90 °C for 3 h, single-phase spindle-shaped anatase titania nanocrystallines were obtained. Furthermore, the formation mechanism of as-prepared titania nanocrystallines was investigated.

1. Introduction

Titania, a wide band-gap semiconductor oxide, is an exceptional material that is widely applied in photocatalysis, electrochromic devices, gas sensors, self-cleaning coatings and dye-sensitized solar cells [1–5].

Various methods, including flame spray pyrolysis, solution combustion, hydrothermal treatment, sol–gel, anodic oxidation, reverse micelle, and hydrolysis in water–acid systems, have been developed to prepare nanostructured titania [6–12].

From a green chemistry point of view, the energy-saving, economic, low-cost method for synthesis of nanostructured materials is a widely popular synthetic method.

Recently, the synthesis of nanostructured titania using the liquid phase deposition (LPD) method has received much attention, as the LPD method can realize the crystallization of titania at low temperature (<100 °C). Ding et al. prepared titania thin films for degradation of benzotriazole by using boric acid as the fluorion scavenger [13]. Zhang et al. synthesized the photoelectroactive mesoporous TiO_2/DNA hybrid film by using boric acid as the fluorion scavenger [14]. Wen et al. fabricated V-doped titania nanocrystalline film with room-temperature ferromagnetism by using boric acid as the fluorion scavenger and vacuum annealed treatment [15]. Charoensirithavorn et al. prepared titania nanotube arrays for high-performance dye-sensitized solar cells by using boric acid as the fluorion scavenger and using ZnO nanorod arrays as a template [16,17]. Generally, as with the LPD method, boric acid (H_3BO_3) and aluminum foil were utilized as the fluorion scavengers [18]. As is well known, γ-Al_2O_3 is highly effective in removing excessive fluorion from drinking water [19], which strongly triggers our interest to investigate whether γ-Al_2O_3 can be utilized as a fluorion scavenger to synthesize nanostructured titania.

In this study, we utilized γ-Al_2O_3 powder as the fluorion scavenger, and prepared crystallized anatase titania nanocrystallines at low temperatures. The advantages of this method are energy-saving, one-step, rapid, low cost, easy to large-scale, and without using any organic additive. The possible formation mechanism of titania nanocrystallines prepared by utilizing γ-Al_2O_3 powder as the fluorion scavenger was also studied.

2. Experimental procedures

All chemicals were analytically pure and were used without further purification. Titania nanocrystallines were synthesized by the following procedures. Firstly, 2.8 g ammonium hexafluorotitanate ($(NH_4)_2TiF_6$) was completely dissolved into 240 ml of de-ionized water, to form an aqueous solution of $(NH_4)_2TiF_6$. Secondly, 0.4 g γ-Al_2O_3 powders (AKP-G015, Sumitomo Chemicals Co. Ltd., Japan, specific surface area of 184 $m^2\,g^{-1}$) were added to the $(NH_4)_2TiF_6$ solution. After strongly stirring and homogeneously mixing, the mixture was divided into four solutions of equal quantities. These solutions were heated at 60 °C, 70 °C, 80 °C and 90 °C for 3 h, respectively. The final products were obtained by centrifugation, washing several times with de-ionized water and drying at about 80 °C. For comparison, α-Al_2O_3 (AKP-53, Sumitomo Chemicals Co. Ltd., Japan, specific surface area of 10.5 $m^2\,g^{-1}$) was also used as a fluorion scavenger, and the experimental procedures were the same as with γ-Al_2O_3.

The crystalline phases of specimens were determined by powder X-ray diffraction (XRD, RINT-2100, Rigaku Corporation). Thermogravimetric (TG) analysis of the specimen was conducted (Thermo Plus TG8120, Rigaku). The infrared (IR) spectrum

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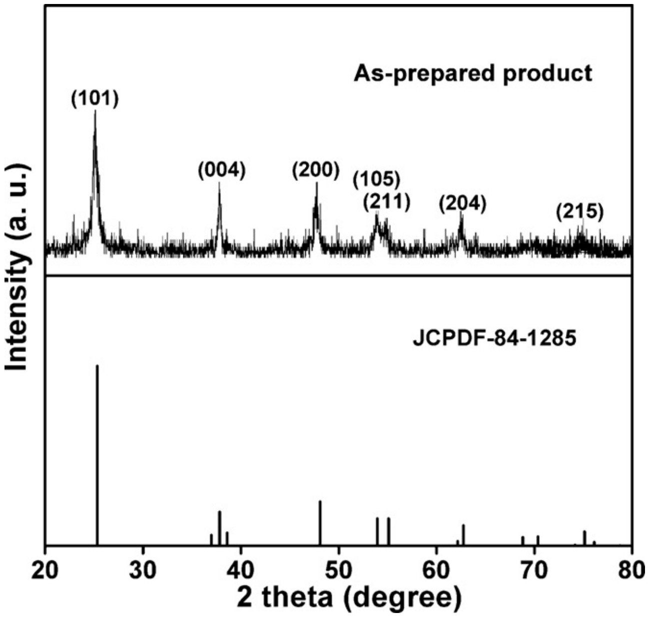

Fig. 1. XRD pattern of the product prepared at 80 °C for 3 h.

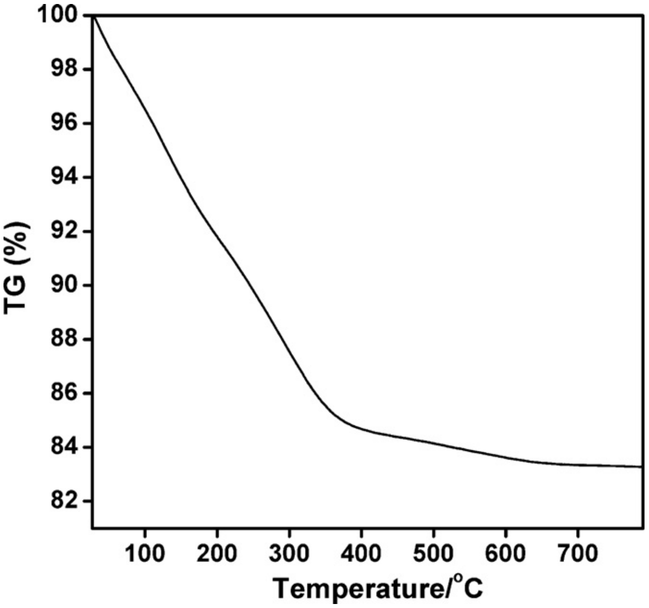

Fig. 2. TG curve of the product prepared at 80 °C for 3 h.

of the specimen was recorded in the range of 400–4000 cm^{-1} by Fourier transform infrared spectroscopy (FTIR, V570, JASCO Corporation). The morphologies of samples were observed by using a transmission electron microscope (TEM, H-7600, Hitachi Corporation).

3. Results and discussion

Fig. 1 displays a typical XRD pattern of the product prepared at 80 °C for 3 h. The prepared product shows clear X-ray diffractions at $2\theta = 25.3$, 37.8, 48.1, 53.9, 55.1, 62.7, and 75.1°. All peaks of the pattern can be assigned to diffractions from the (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), and (2 1 5) crystal planes of anatase TiO_2 with lattice constant $a = 0.378$ nm and $c = 0.951$ nm (ICSD No. 202242, JCPDS No. 84-1285). No impurity peak is observed, which indicates that high-purity anatase titania was successfully synthesized by using γ-Al_2O_3 powder as the fluorion scavenger.

Fig. 2 shows the TG analysis of the product prepared at 80 °C for 3 h. The TG curve can be divided into two stages. The first stage is from room temperature to 370 °C, over which the greatest mass loss (up to 15%) was observed. The mass loss is mainly caused by the evaporation and dehydration of the physically adsorbed water. The second stage is from 370 °C to 700 °C, where the mass loss is about 1.5%. This can be attributed to the thermal decomposition of some intermediate compounds containing NH_4^+ and F^- in the as-prepared TiO_2 powders [20].

Fig. 3 shows the FTIR spectrum of the product prepared at 80 °C for 3 h. The broad band at 3150 cm^{-1} and medium intense band at 1630 cm^{-1} are attributed to the stretching mode and bending mode of adsorbed water and hydroxyl groups [21]. The presence of water may result from adsorption of water vapor from the atmosphere due to the high surface area of the prepared nano-sized product. A strong absorption peak at 450–700 cm^{-1} is attributed to the stretching mode of Ti–O [22], which clearly denotes the presence of titania. No other functional groups was detected through FTIR, combined with XRD patterns, which further indicates that single-phase titania has been synthesized by using γ-Al_2O_3 powder as the fluorion scavenger.

Fig. 4 shows the XRD patterns of the products prepared at different temperatures for 3 h. It can be clearly seen that when the reaction was carried out at 60 °C, no titania peak was detected. When the reaction temperature was increased to 70 °C, in addition to the γ-Al_2O_3 peak, an anatase titania peak was also detected, which indicated that the prepared product was a mixture of anatase titania and γ-Al_2O_3. When the reaction was carried out at 80 °C, only the anatase titania peak could be detected, which indicated that the prepared product was pure anatase titania and all γ-Al_2O_3 powders had been exhausted. Increasing the reaction temperature to 90 °C, the crystallinity of the prepared anatase nanocrystalline increased correspondingly. The morphology of the prepared anatase nanocrystallines was carried out using transmission electron microscope (TEM). Fig. 5 shows TEM images of titania prepared at 80 °C and 90 °C for 3 h. From Fig. 5(a), it can be clearly seen that titania nanocrystalline prepared at 80 °C for 3 h is spindle-shaped, with a lateral width of 30–40 nm. Fig. 5(b) shows the selected-area electron diffraction (SAED) pattern obtained by

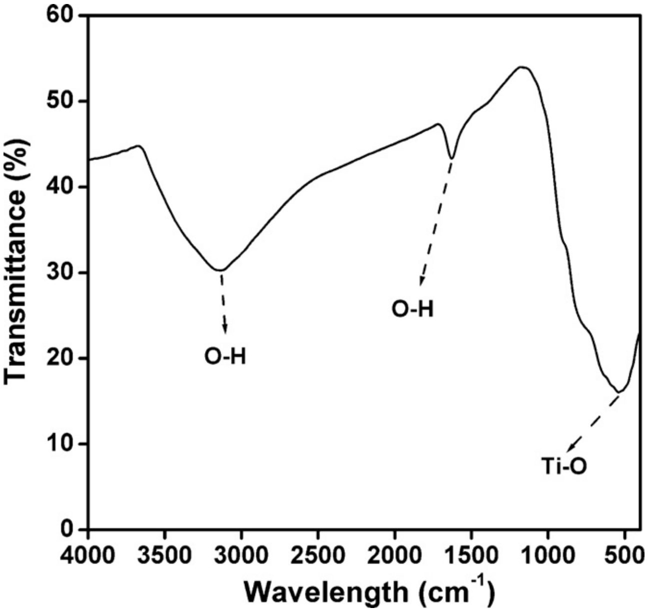

Fig. 3. FTIR spectrum of the product prepared at 80 °C for 3 h.

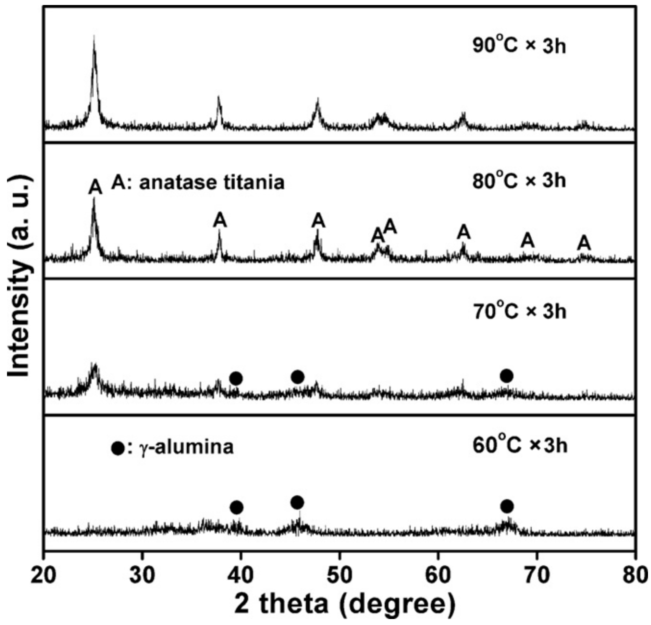

Fig. 4. XRD patterns of products prepared at different reaction temperatures for 3 h.

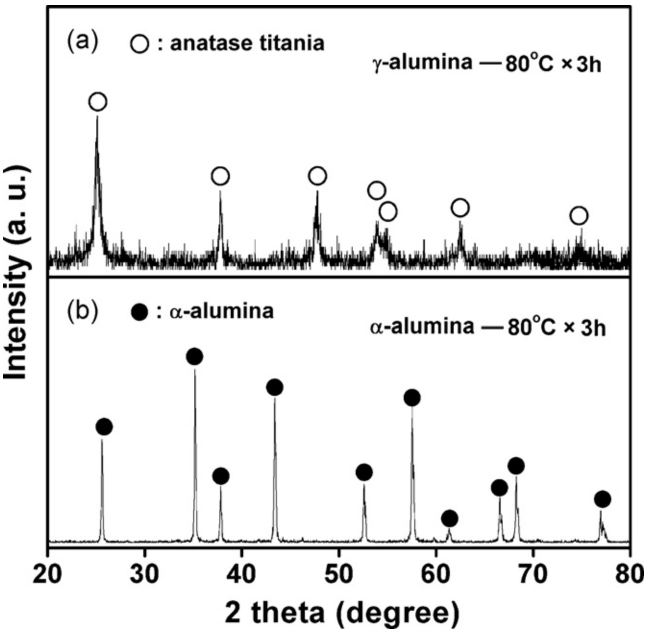

Fig. 6. XRD patterns of as-prepared products with different starting fluorion scavengers: (a) γ-Al_2O_3; (b) α-Al_2O_3.

focusing the electron beam on many nanoparticles in Fig. 5(a). The reflections, corresponding to the (1 0 1), (0 0 4), (2 0 0) and (1 0 5) crystal planes of anatase titania, clearly indicate the crystalline nature of the product. Increasing the reaction temperature to 90 °C, larger spindle-shaped titania nanocrystallines were obtained (Fig. 5(c)), which indicated that Ostwald ripening was an underlying mechanism operative in this crystal growth process [23]. The above-mentioned phenomena convincingly indicates that the crystal growth of products is very sensitive to the reaction temperature, which may be due to the fact that a high reaction temperature provides increased driving force for the reaction and crystallization process via Ostwald ripening [24].

Moreover, an interesting phenomenon was found when the starting fluorion scavenger, γ-Al_2O_3, was replaced by α-Al_2O_3. In this case, no titania nanocrystalline was generated, which can be proved by XRD patterns (Fig. 6). As is well known, γ-Al_2O_3 is an extremely important material in catalysis [25]. Compared with α-Al_2O_3, γ-Al_2O_3 has a higher surface area and is quite active both as a solid contact material for adsorption and as a catalyst per se for many reactions [26,27]. In other words, γ-Al_2O_3 is alumina in an active form, with high surface area and high catalytic surface activity. Higher surface activity of γ-Al_2O_3 than α-Al_2O_3 may be the main reason for that, under the same reaction conditions, titania nanocrystallines can be obtained only by using γ-Al_2O_3 powder as the fluorion scavenger, but not α-Al_2O_3.

With respect to the hydrolysis of $(TiF_6)^{2-}$ complex in aqueous solution, the following chemical reaction equilibrium can been carried out [28].

$$[TiF_6]^{2-} + 2H_2O \rightleftharpoons TiO_2 + 4H^+ + 6F^- \tag{1}$$

As with γ-Al_2O_3, a very effective adsorbent for fluorion removal [19], Al (III) ions have good combining affinity with fluorion. Thus fluorion can react with the very active γ-Al_2O_3 by forming chemical bridges between two cations (one from the fluoride and one from the γ-Al_2O_3 lattice) [29]. The chemical reaction between γ-Al_2O_3 and fluorion can be formulated as follow:

$$\gamma - Al_2O_3 + 12F^- + 6H^+ \rightarrow 2AlF_6^{3-} + 3H_2O \tag{2}$$

Thus, under the mass action principle, the chemical equilibrium can be shifted to the right by the addition of γ-Al_2O_3 as the fluorion scavenger. The addition of γ-Al_2O_3 leads to the consumption of non-coordinated fluorion, accelerates the hydrolysis reaction of $(TiF_6)^{2-}$ complex, and finally forms titania in the aqueous solution, according to Eq. (1).

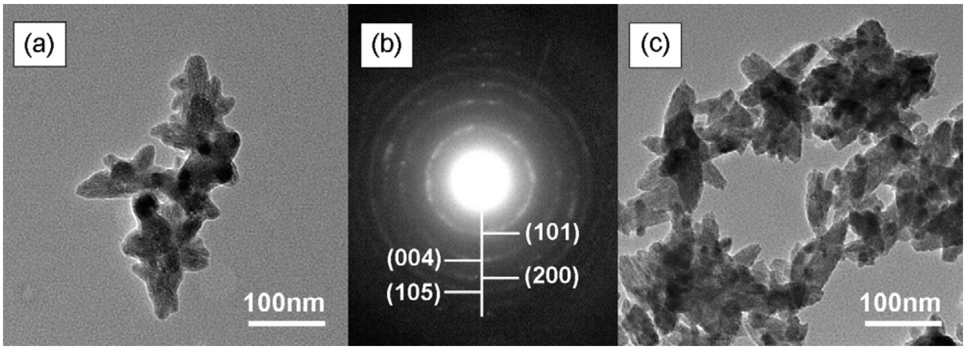

Fig. 5. TEM images of products prepared under different conditions: (a) 80 °C for 3 h; (b) SAED pattern taken from (a); (c) 90 °C for 3 h.

4. Conclusions

In this paper, we reported a novel and direct approach for preparing crystallized titania at low temperatures by utilizing γ-Al_2O_3 powder as the fluorion scavenger. The crystal growth of as-prepared products was very sensitive to the reaction temperatures and the starting fluorion scavengers. When the reaction was carried out at 80 °C and 90 °C for 3 h, single-phase anatase titania nanocrystallines were generated. The prepared anatase titania nanocrystallines was spindle-shaped with very uniform crystal size. An interesting phenomenon was found, by using γ-Al_2O_3 as the fluorion scavenger, titania nanocrystallines were obtained, but titania nanocrystallines could not be generated by using α-Al_2O_3 as the fluorion scavenger, which was mainly due to the higher surface activity of γ-Al_2O_3 than α-Al_2O_3.

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