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One-dimensional growth of TiO_2 nanorods from ilmenite sands

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ABSTRACT

Growth mechanisms of TiO_2 nanorods synthesized from mineral ilmenite using ball milling and annealing method have been systematically investigated. Two annealing processes are needed to grow the nanorods. The heating rate and gaseous environment in the first annealing step are critical to the formation of intermediate phases; these and the annealing atmosphere in the second heating play very important roles in nanorod growth. One-dimensional growth of the nanorods induced by low-temperature annealing in nitrogen plus hydrogen is possibly driven by atom vacancy diffusion in addition to surface diffusion.

1. Introduction

Titanium oxide (TiO_2) nanorods and nanowires have unique one-dimensional structures and excellent photocatalytic properties with substantial applications in photocatalysis, nanoelectronics and photo-electrochemistry [1]. Mass production at low cost has not been achieved but is a critical issue for future industrial applications. We recently reported a new synthesis technique of TiO_2 nanorods with the potential to be scaled up for large quantity production [2]. TiO_2 nanorods are extracted from mineral ilmenite sands through a ball milling and two-step annealing process. Powder mixtures of ilmenite and activated carbon are first milled for mechanical activation [3,4], the milled samples are then heated twice at two different temperatures and in different gases. The resultant nanorods have a rutile tetragonal structure with diameters in the range of 100–500 nm, and lengths of a few micrometers. Their growth direction is parallel to the ⟨0 0 1⟩ direction. Ilmenite is a naturally occurring iron titanate (nominally $FeTiO_3$) and thus significantly reduces the production cost of rutile nanorods. Although a catalytic role of the Fe has been observed [2], detailed growth mechanisms and phase changes during each annealing step are not well understood. In this study, the critical conditions for producing intermediate metastable titanium oxide phases in the first high-temperature annealing were investigated. Mechanisms of one-dimensional growth of the nanorods from the coarse intermediate particles during the second annealing were also revealed.

2. Material and methods

The starting ilmenite used in this study is a naturally occurring iron titanate ($FeTiO_3$) which is abundant in nature. High-purity ilmenite was provided by Consolidated Rutile Limited located in Australia. Chemical composition (wt.%) of the ilmenite are TiO_2 (dry basis) 49.6, iron (total) 35.1, FeO 32.8, Fe_2O_3 13.7, Al_2O_3 0.47, Cr_2O_3 0.25, SiO_2 0.45). Several grams of the mixture of ilmenite ($FeTiO_3$) and activated carbon (weight ratio of 4:1) were milled in a Fritsch planetary ball mill with 10 steel balls (diameter 1 cm) for 50 h in vacuum at room temperature. Isothermal annealing was conducted in a horizontal tube furnace at different temperatures (700–1200 °C) and in different atmospheres (Ar, Ar–5%H_2 or N_2–5%H_2) at a flow rate of 100 ml/min. Milled and annealed samples were characterized by using an X-ray diffraction (XRD) spectrometer with a cobalt Ka radiation ($\lambda = 0.1789$ nm). Scanning electron microscopy (SEM) was conducted using a field-emission Hitachi S4500 instrument.

3. Results and discussion

Fig. 1 displays the SEM images of the starting ilmenite sand particles (Fig. 1a), the milled powders (Fig. 1b), and the intermediate product formed after the first annealing (Fig. 1c). Rutile nanorods can be produced by further annealing of the intermediate product at 700 °C in N_2–5%H_2. The following systematic investigation has been conducted to clarify the critical conditions in each

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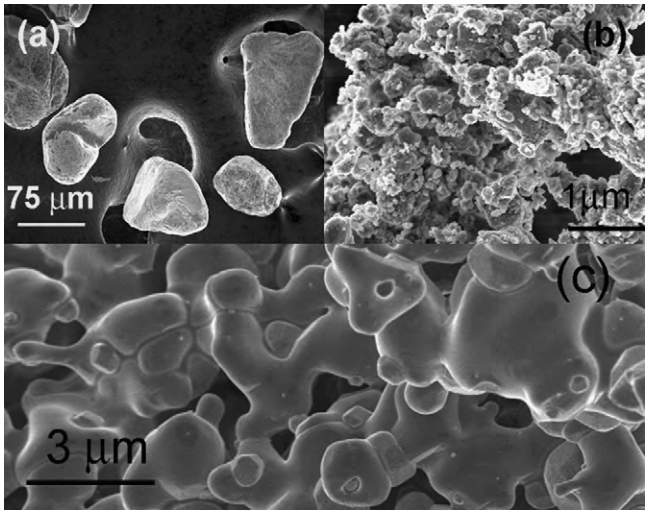

Fig. 1. SEM images of starting ilmenite (a), milled ilmenite (b), morphology of the milled sample after annealing at 1200 °C in Ar–5%H_2 for 8 h (c).

annealing step for producing the intermediate structures and final nanorods.

3.1. First high-temperature annealing

The same quantity of ball milled ilmenite was annealed at three different temperatures (900, 1100 and 1200 °C) for 6 h using the same heating rate of 20 °C/min. XRD spectra of the heated samples are presented in Fig. 2a. When the annealing temperature is less than 1100 °C, rutile is the dominant phase, which is consistent with a previous report [3,4], but the rutiles remain as particles after the second annealing treatment. At temperatures of 1100 °C and above, the metastable Ti_3O_5 phase is dominant, which is an important intermediate structure for the formation of 1D rutile nanorods.

The heating rate is also critical for the formation of the desired intermediate phase. As shown by the XRD spectra in Fig. 2b, annealing at 1200 °C after different heating rates produced different phases. When heating at a high rate of 20 °C/min in the first annealing, ilmenite was quickly reduced to Ti_3O_5; lower heating rates of 5 and 10 °C/min lead to the formation of two metastable phases, Ti_2O_3 and Ti_3O_5, after the first annealing. The XRD spectra of Fig. 2b indicate that the ratio of Ti_2O_3 to Ti_3O_5 approaches 1:1 at 5 °C/min which is higher than the ratio obtained at 10 °C/min. Slow heating favors the formation of the Ti_2O_3 phase. The chemisorption energy for one Ti_2O_3 group is 5.4 eV per unit cell, which is very similar to the bonding energy between Ti_2O_3 and TiO_2 (6.3 eV) [5]. Therefore, Ti_2O_3 can be converted to TiO_2 more easily than Ti_3O_5 during the second annealing, which is in excellent agreement with our experiments.

The appropriate annealing atmosphere in the first annealing step is another crucial requirement for the formation of the intermediate phase. When the annealing was conducted in pure argon gas for 8 h at 1200 °C, ilmenite was only partially reduced by activated carbon into TiO_2 and Fe, as revealed by the XRD spectrum of Fig. 2c. Prolonged annealing at such a high temperature could lead to reactions between TiO_2 and Fe to form FeTi alloys. When 5% of H_2 in Ar was used, the hydrogen, which is also a reducing agent, increases the formation of metastable oxides as the intermediate phase, which can be seen from the XRD spectra of Fig. 2c. Nitrogen cannot be used in the first annealing as iron nitride could be produced. Therefore, high annealing temperatures, low heating rates and hydrogen gas are important to the formation of the required intermediate phase.

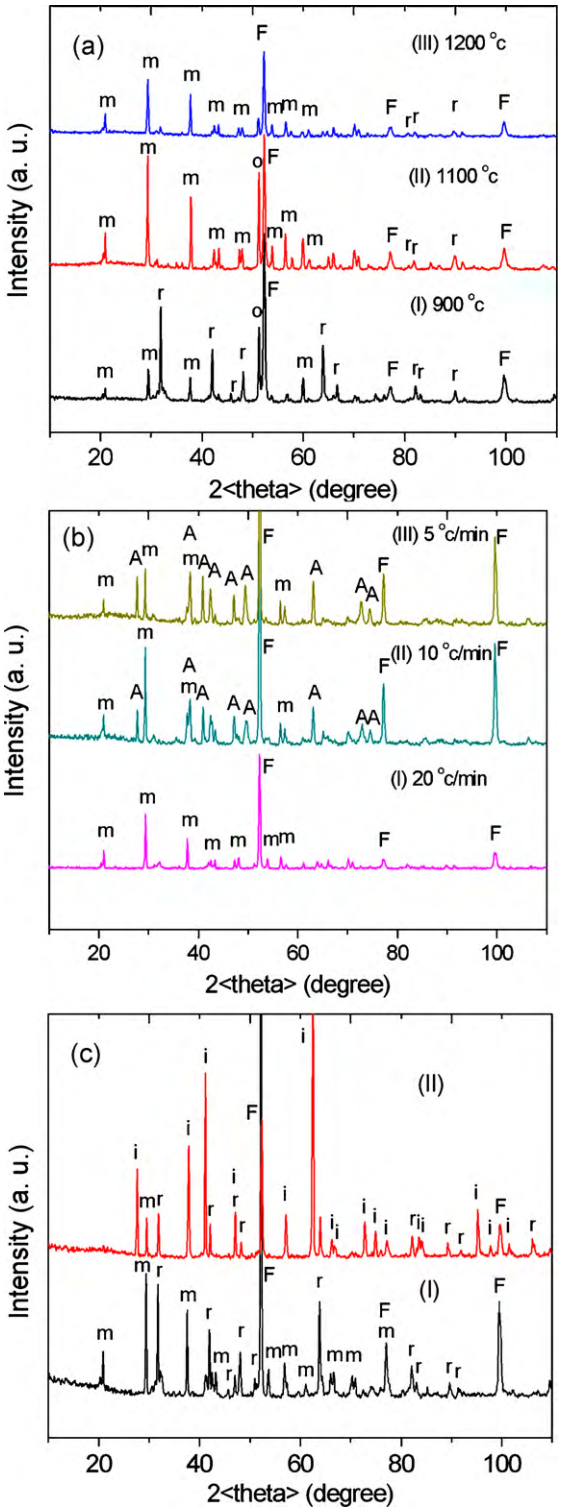

Fig. 2. XRD spectra of milled ilmenite and carbon annealed under different conditions: (a) annealing for 6 h, with the same heating rate of 20 °C/min, at (I) 900 °C, (II) 1100 °C, (III) 1200 °C; (b) annealing for 8 h at 1200 °C with different heating rates (I) 20 °C/min, (II) 10 °C/min, (III) 5 °C/min; (c) annealing at 1100 °C in Ar–5%H_2 for 24 h (I); annealing at 1200 °C in Ar for 8 h (II); r: rutile, A: Ti_2O_3, m: Ti_3O_5, i: $FeTiO_3$, F: Fe, o: FeO.

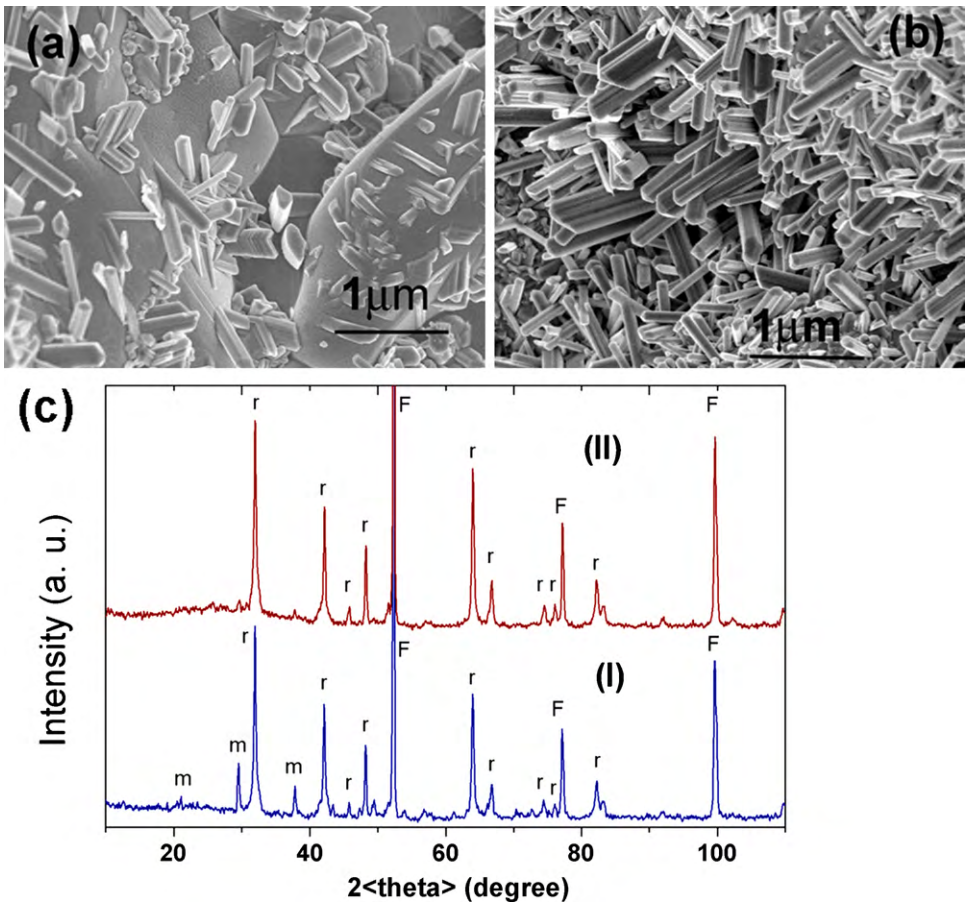

Fig. 3. (a) SEM image of the intermediate product after the second annealing step in N_2–5%H_2 for only 4 h at 700 °C; (b) SEM image after the second annealing in N_2–5%H_2 for 8 h at 700 °C; (c) XRD spectra after the second annealing in N_2–5%H_2 at 700 °C for (I) 6 h and (II) 16 h; r: rutile, F: Fe.

3.2. Second low-temperature annealing

The SEM image in Fig. 3a indicates that nanorods start to grow from the surface of big clusters of the intermediate phase and Fig. 3b shows a high yield of nanorods after annealing at 700 °C in N_2–5%H_2 for 8 h. Fig. 3c shows XRD spectra of samples heated at 700 °C in N_2–5%H_2 for 6 and 16 h, respectively which reveal the formation of TiO_2 and Fe phases in the final sample. After a certain number of hours, all intermediate phases are completely converted to TiO_2 and Fe phases. The nanorod length depends on the annealing time, but overheating could lead to the sintering of nanorods into coarse particles. In the second annealing, heating atmospheres also play an important role. In N_2–5%H_2 gas, highly crystalline nanorods can be produced as both Ti_2O_3 and Ti_3O_5 are metastable and can be easily decomposed to TiO_2 in nitrogen atmosphere than other gases [6].

3.3. One-dimensional growth mechanism

It seems that oxygen is required for the transformation from the intermediate oxides Ti_2O_3 and Ti_3O_5 to TiO_2, but in our case, TiO_2 nanorods formed after annealing at 700 °C in a N_2–5%H_2 gas mixture. The oxygen needed here may have come from the absorption of air between the two annealing steps as the sample was exposed to air. The intermediate sample was very fine powder which might have a strong ability to absorb gases from the environment.

Both Ti_2O_3 and Ti_3O_5 phases contain increased concentrations of O vacancies and Ti interstitials. Low-temperature annealing causes a net flux of both Ti and O atoms to achieve the stable TiO_2 structure on the crystal surface and this favors crystal growth along a certain direction even without additional oxygen [7]. In addition, the presence of hydrogen gas during the annealing enhances the above process by increasing surface oxygen vacancies and helps the atomic rearrangement.

The big clusters of titanium oxide phases consist of long strips running along the [0 0 1] crystal direction. When they decompose in the nitrogen and hydrogen gas mixture, it is more likely they split and move along the 0 0 1 direction. Several models of phase transformation of TiO_2 during heating in high vacuum with a large number of oxygen vacancies have been proposed [5,8–11]. The suggested possible atomic-scale mechanisms for the 1D growth process are: (1) a missing-row of oxygen atoms in TiO_2 [9] where bridging oxygen atoms were absent; (2) an added-row model [10] with a Ti_2O_3 stoichiometry where the Ti cations move to octahe-

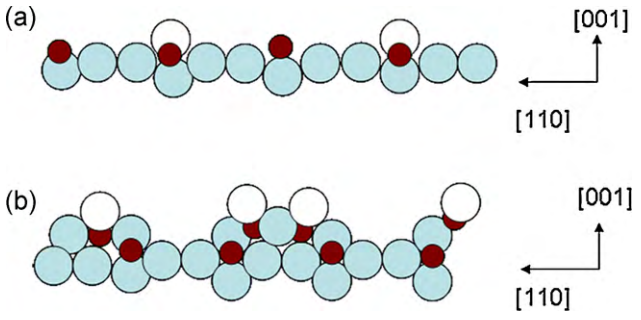

Fig. 4. Examples of proposed models for the TiO_2 phase transitions. Large circles represent O atoms, Ti atoms are represented by small filled circles. (a) Missing O-row model in which alternate bridging-O rows are absent; (b) the added Ti_2O_3 structure proposed by Onishi and Iwasawa [10].

dral sites and oxygen atoms stay near their bulk-like positions; (3) an added-row model with a Ti_3O_5 stoichiometry [11] where all the atoms remain near their bulk positions, and (4) a stoichiometric model where the added rows proposed by Pang et al. [11] have been modified by adding oxygen to create an added row of Ti_3O_6. Fig. 4 is a drawing displaying the missing-row (Fig. 4a) and added-row (Fig. 4b) models of Ti_2O_3. These models can explain various cross sections of the nanorods (Fig. 3a and b).

4. Conclusions

The growth mechanisms of TiO_2 nanorods produced by the ball milling and annealing method have been investigated. The formation of TiO_2 nanorods requires heating to 1100 °C or higher at a slow heating rate and appropriate gas environment in the first annealing step and a suitable annealing atmosphere in the second step. One-dimensional growth at low-temperature annealing in nitrogen plus hydrogen is possibly driven by atom vacancy diffusion in addition to a surface diffusion.

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