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Rapid Communication

The role of NH_3 atmosphere in preparing nitrogen-doped TiO_2 by mechanochemical reaction

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Abstract

NH_3 atmosphere in ball milling plays an important role in preparing $TiO_{2-X}N_X$ by a simple mechanochemical reaction. The results show that the structure transformation of titania milled in NH_3 is greatly delayed compared with that in air. The specific surface area of titania milled in NH_3 for 2 h is two times larger than that in air. It was also found that titania prepared in NH_3 has obvious absorbance for visible light. Mechanochemical milling in NH_3 atmosphere offers a new route to prepare $TiO_{2-X}N_X$ with high surface area.

Keywords: Titania; Nitrogen doping; Mechanochemical reaction; Phase transformation; Visible light absorption

1. Introduction

Titania (TiO_2) has been extensively studied as a photocatalytic material because of its unique properties (high redox ability, good stability and ready availability, etc.) [1–3]. However, its application has been mainly limited to UV light due to its large band gap. Many efforts have been made to extend its light absorption into the visible range by doping trace elements and formation of oxygen vacancies [4–6]. In recent years anion doping (C, N, S, F, Cl) has attracted much attention, especially since $TiO_{2-X}N_X$ by sputtering a TiO_2 target in an N_2 (40%)–Ar gas mixture followed by annealing in N_2 gas and carbon doping of *n*-TiO_2 to $TiO_{2-X}C_X$ were reported [7,8]. The optical absorption of both samples shifted to the visible region of $\lambda < 535$ nm. Meanwhile, varieties of methods to dope anions have been attempted in recent years [9–12].

Mechanical alloying as an effective technique of synthesizing a variety of nanocrystalline materials is also used to prepare nitrogen-doped titania or strontium titanate [13,14]. Conventionally, the organic substance (containing nitrogen element) and titania powder is milled together to prepare $TiO_{2-X}N_X$ by mechanochemical reaction in air atmosphere. During the process of ball milling in air, the anatase to srilankite and the srilankite to rutile transformations occur [17]. Fresh oxygen-rich surfaces are formed due to the mechanical breakage. Electrons are transferred from the fresh surfaces to the organic substance, as a result leading to the destruction of weak bonds in the organic substance and the formation of new bonds between the oxide and nonmetallic elements [17,18]. During this process NH_3 is released from the organic substance. It is generally believed that NH_3 is adsorbed on the surfaces of titania and reacts with activated surfaces, thus causing the growth of nitrogen-doped titania [13,15]. NH_3 released from organic substance seems to be an effective nitrogen source to dope nitrogen in mechnochemical reaction. During ball milling phase transformation from anatase to srilankite and then to rutile occurs [16]. However, it is still unclear how NH_3 affects the structure transformation of nitrogen-doped titania by mechanochemical reaction. The agglomeration caused by high surface energy of fresh surfaces can reduce surface area of titania. To increase the specific surface area, it is necessary to segregate the fresh surfaces from each

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other. It is thought that by introducing more active NH_3 to the ball-milling vial, strong interaction with fresh surfaces can occur. Meanwhile, gaseous NH_3 as a nitrogen source can avoid the residual organics remaining in titania which is the case where organic nitrogen sources are used.

In this paper, anatase titania powder is milled in gaseous NH_3 and air. The effects of gaseous NH_3 on the phase transformation, surface area, doping of nitrogen and UV–VIS absorbance of titania are investigated.

2. Experimental

Commercial anatase titania powder (99%, 8 wt% rutile) was used as the precursor material. A high-energy mill (Spex 8000 M) was used for grinding of the samples. Two Φ15 mm and four Φ5 mm hard steel balls with 1 g of titania powder were introduced to a hard steel vessel of 50 cm^3 inner volume. Prior to filling NH_3 gas in the vessel, the vial was evacuated to less than 20 Pa by a mechanical pump.

The phases of the samples were determined by X-ray diffraction (XRD). The relative content of srilankite was determined by the XRD peak intensity ratio as follows:

$$S\% = I_{S1\,1\,1}/(I_{S1\,1\,1} + I_{A1\,0\,1} + I_{R1\,1\,0}), \qquad (1)$$

where $S\%$ is the fraction of the peak intensity of srilankite $d_{1\,1\,1}$, $I_{S1\,1\,1}$, $I_{A1\,0\,1}$ and $I_{R1\,1\,0}$ are the intensities of srilankite $d_{1\,1\,1}$, anatase $d_{1\,0\,1}$ and rutile $d_{1\,1\,0}$, respectively.

The absorption edge and band gap energy of the samples was determined from the onset of diffuse reflectance spectrum of the sample measured using a UV–VIS spectrophotometer (Shimadzu, UV-2550). The binding energy was identified by X-ray photoelectron spectroscopy (XPS) with Mg-$K\alpha$ radiation (PHI5300). The specific surface area (BET) was determined by nitrogen adsorption–desorption isotherm measurements at 77 K (ASAP 2010).

3. Results and discussion

3.1. Effect of NH_3 on the phase transformation

XRD patterns for the milled titania in air and NH_3 are shown in Figs. 1 and 2, respectively. It is obvious that the phase transformations of both anatase to srilankite and srilankite to rutile in NH_3 are delayed compared with that in air. The milled titania in air for 3 h mainly consists of rutile titania; however, much anatase and srilankite titania still exist when milled in NH_3 for 3 h. The relative content of srilankite rapidly reaches its maximum then decreases when titania is milled in air compared with that in NH_3. However, the content of srilankite in NH_3 is higher than that in air at 0.5 h from Fig. 3.

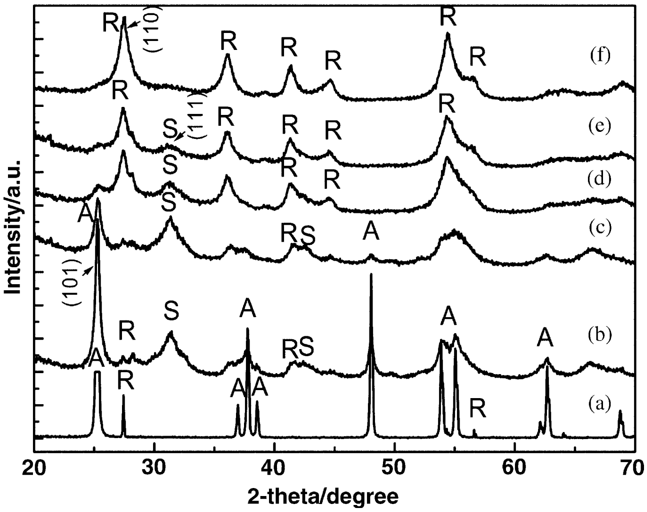

Fig. 1. XRD patterns of the samples milled in air: (a) raw, (b) 0.5 h, (c) 1 h, (d) 2 h, (e)3 h and (f) 5 h. A represents anatase, S srilankite and R rutile structure.

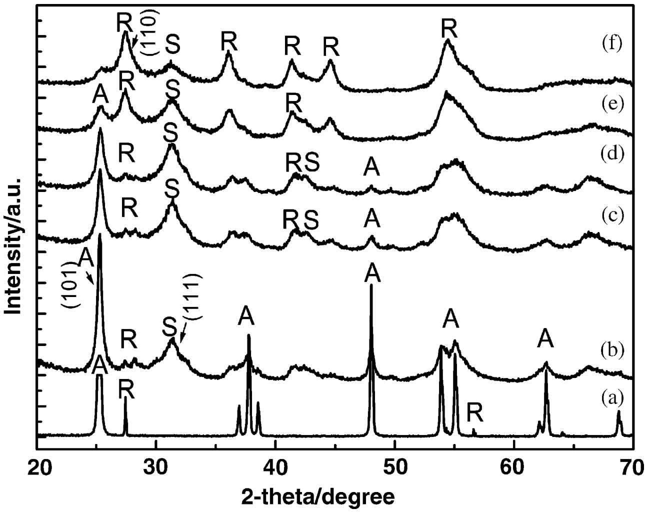

Fig. 2. XRD patterns of the samples milled in NH_3: (a) raw, (b) 0.5 h, (c) 1 h, (d) 2 h, (e) 3 h and (f) 5 h. A represents anatase, S srilankite and R rutile structure.

To understand the whole process of phase transformation, two factors are considered: oxygen partial pressure [19] and interaction of NH_3 with fresh surfaces. It has been proposed that the removal of oxygen ions, which generates oxygen vacancies, accelerates the anatase to rutile transformation because it involves an overall contraction of the oxygen structure, accompanied by shrinkage in volume, and breaking of two of the six Ti–O bonds [20]. Therefore the high oxygen partial pressure is not beneficial to the production of oxygen vacancies and the transformation rate of anatase in the high oxygen partial pressure is significantly slowed. On the other hand, the following process occurs when the mixture of titania and organic substance is milled. The mechanical stressing induces the formation of fresh oxygen-rich surfaces, which results in electron transfer from O^{2-} on the oxide surfaces to the organic substance. As a result, it leads to the destruction of weak bonds in the organic substance and the formation of new bonds between the oxide and non-metallic element [17,18]. The bond energies of N–N and N–H are 946 and