HRTEM Study of Phase Transformation from Anatase to Rutile in Nanocrystalline TiO_2 Particles

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Abstract

The anatase particle was facetted at the free surface and a neck formation between the anatase particles prior to the phase transformation occured. This resulted in the severe lattice distortion at the region of the interface near the neck and this can act as the nucleation sites for the phase transformation. The grain growth of rutile particles after the phase transformation grew very fast by the sweeping phenomena of grain boundary. Therfore, It leaded to the microstructure without the rutile phase located in anatase particle.

Keywords: Anatase, rutile, nucleation, growth, phase transformation, phase boundary

1. Introduction

The titania (TiO_2) is widely used for photocatalyst, gas sensor, and solar cell, since it is n-type semiconductor containing donor-like oxygen vacancies [1]. A major issue in such applications is the control of the optimum anatase to rutile phase ratio during phase transition. It is reported that TiO_2 consists of a rutile ($P4_2/nmm$) and two polymorphic metastable phases, anatase ($I4_1/amd$) and brookite (Pbca). The mixture of two phases generates a phase boundary and it changes the resident time of electrons that are separated from the hole. However, there is little understanding on the position of phase boundary and morphological change during phase transition [2].

Several researchers have reported that the nucleation sites for the anatase-to-rutile phase transformation [3-5]. However, the exact nucleation site and growth behavior using high resolution transmission electron microscopy (HRTEM) is not known. In the present work, the transformation of rutile phase from anatase nanoparticle was investigated by HRTEM observation.

2. Experimental and Results

We manufactured anatase nanoparticle (~50 nm) by flame method, in which titanium tetraisopropoxide (TTIP) was used as a precursor [6]. The as-manufactured anatase nanoparticles were heat-treated up to 900°C (HT900) in air and were kept for 1 hr at each temperature.

Figure 1 shows the variation of X-ray diffraction [Philips XRD 3003] of TiO_2 nanoparticle during the heat treatment. The phase transformation from anatase to rutile started around 700°C and almost finished at 900°C. However, the particle size of anatase phase calculated by Scherer equation scarcely changed during the phase transformation and even increased a little.

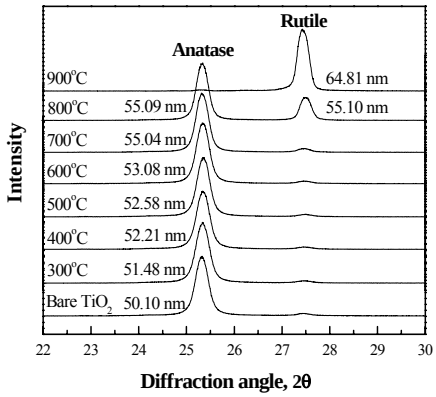

Fig. 1. XRD spectra obtained from the heat-treated TiO_2 nanopowders. The numbers above indicates the particle size of anatase phase in diameter.

The morphological change of the heat-treated TiO_2 nanoparticle was observed by TEM [FEI, Tecnai F20] as shown in Fig. 2. A significant variation of HT700 is a neck formation and the surface-faceting phenomena of TiO_2 nanoparticle without the particle growth, maintaing the anatase phase.

The HT800 sample shows a rutile phase of 30%, while the remaining anatase particle still keeps the small size of 50 nm and is agglomerated locally. Meanwhile, the transformed

rutile particles became coarse and round. Here, we could not find the rutile grain which embeds in the anatase particle. The rutile phase always independently exists with a single crystal or bicrystal. The HT900 sample has a rutile content of >99% and consists of a different particle shape from HP800. It shows an elongated structure well known as a vermicular structure. It usually appears when the very rapid phase transformation or grain growth takes place during heating [7, 8]. It seems that the fast grain growth of a rutile particle is attributed to the big difference of surface tension between anatase and rutile, γ^{Rutile}=2.2 J/m^2; $\gamma^{Anatase}$=0.4 J/m^2 [9].

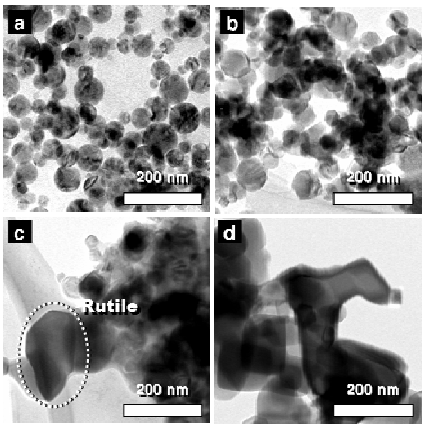

Fig. 2. TEM micrographs of the as-manufactured and heat-treated TiO2 nanoparticles: (a) as-manufactured TiO2, (b) HT700, (c) HT800, and (d) HT900.

Fig. 3 shows (a) the HRTEM micrograph of HP800 sample and (b) an image enlarging the circle region in Fig. 3(a) which was processed by HRTEM image → FFT → inverse FFT treatments. In HP800, the two contact particles kept the anatase phase and the stress field by a lattice distortion was generated around the interface (see the arrows in Fig. 3(b)). In general, it has been reported that the interface has the lowest activation energy for the phase transformation [10]. Therefore, the lattice distortion developed at the interface can act as the nucleation sites from anatase to rutile. Unfortunately, however, we could not find the rutile grain nucleated in the anatase particle. It is possibly due to the very fast grain growth of rutile phase based on the fact that the particle size of anatase phase did not decrease during the phase transformation in Fig. 1. Furthermore, rutile particles imbedded in anatase particle were not observed in the HRTEM analysis. If the rutile grain is imbedded and trapped in the anatase particle after the phase transformation, the grain size of anatase should become smaller and smaller with the formation of rutile phase.

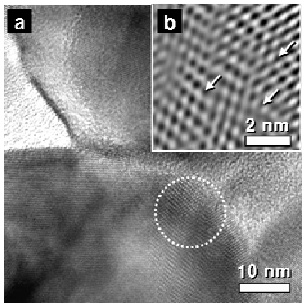

Fig. 3. (a) The HRTEM micrograph of HP800 sample and a IFFT image(b) enlarged at the circle region in (a).

3. Summary

In this study, we have investigated the transformation behavior from anatase to rutile using X-ray measurement and TEM observation. The anatase particle prior to the phase transformation was facetted at the free surface and formed the neck between the anatase particles. It resulted in the severe lattice distortion at the region of interface, which acts as the nucleation sites. Unfortunately, however, we could not find the rutile grain nucleated or imbedded in anatase particle due to a very fast grain growth.

The nucleation of rutile phase was suppressed but the transformed rutile particle grew very fast by the sweeping phenomena of grain boundary. The coarse rutile particle with the round shape was formed at the relatively low temperature and at the high temperature, formed an elongated vermicular structure by the rapid grain growth.

4. References

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