Sonochemical synthesis and microstructure investigation of rod-like nanocrystalline rutile titania

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Abstract

Rod-like and star-like nanocrystalline rutile titania were prepared by a sonochemical method in TiCl\textsubscript{4}/HCl solution. The product was investigated by XRD, TEM, SAED, and HRTEM. The results indicate that the product is purely rutile. The formation of rutile titania may be due to rutile’s inherent high-temperature stability. The appearance of star-like structures should be attributed to the conditions of sonochemical method.

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1. Introduction

TiO\textsubscript{2} continues to attract much interest, because of its uses as catalyst, support in environmental photocatalysis, membranes and sensors. Primarily, it has three forms: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Among them, rutile is the most thermodynamically stable phase. Rutile TiO\textsubscript{2} is an important material for optical communication and energy resources. Because of its unique physical properties and chemical behavior in photosensitive reactions, pure rutile has high catalytic activity. It has been used in the electronics industry for its high dielectric constant and high electrical resistance [1]. Rutile titania is difficult to obtain at normal conditions. Generally, it can be prepared by calcination of anatase titania at high temperature. Recently, in hydrothermal synthesis, pure rutile titania has been obtained at less than 160 °C. However, the hydrothermal method is difficult to carry out. Yang et al. [2] have prepared rutile at room temperature by precipitating and peptizing method. Shu et al. [3] have also obtained rutile at low temperature by LTDRP method. But their product is not very pure.

Currently, there has been considerable interest in the preparation of semiconductor nanorods or nanofibers and the investigation of their properties. Control over both nanocrystalline morphology and the crystal size is a new challenge for synthetic chemists and materials scientists. Ultrasound has become
an important tool in nanocrystalline synthesis in recent years. It has shown very rapid growth in its application to materials science due to its unique reaction effects. When solutions are exposed to strong ultrasound irradiation, bubbles are implosively collapsed by acoustic fields in the solution. High-temperature and high-pressure fields are produced at the centers of the bubbles. This effect is known as acoustic cavitation. The advantages of this method include the rapid formation of nanoparticles with narrow size distributions, and high purities. This method has been successfully applied to the preparation of various nanosized materials including metals [4–7], metal carbides [8], oxides [9,10] and chalcogenides [11].

In this paper, we extended the sonochemical method to the synthesis of rod-like rutile titania and star-shaped rutile nanocrystals, which have rarely been reported up to now. And we investigate the microstructure and the growth of the product.

2. Experiment

In a typical procedure, 2 ml of pure TiCl₄ was added to 100 ml of hydrochloric acid (10 ml 38% HCl diluted by 90 ml distilled water) solution dropwise. Ultrasound irradiation was accomplished with a high-intensity ultrasonic probe (Xinzhi; 0.6 cm diameter; Ti-horn, 20 kHz, 600 W) immersed directly in the reaction solution under ambient air for 50 min. When the reaction was finished, white precipitates were obtained. The precipitates were centrifuged, washed with distilled water, and dried in air at 60 °C. The final products were collected for the phase analyses carried out with XRD, and TEM, select area electron diffraction (SAED), and HRTEM. The samples used for TEM observations were prepared by dispersing some powder products in ethanol followed by ultrasonic vibrations for 10 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. The microstructure observation was carried out in the JEM-4000EX high-resolution transmission electron microscope.

3. Results

The powder XRD pattern of the product is shown in Fig. 1. All the diffraction peaks can be indexed as the pure rutile phase for TiO₂. The intensities and positions of the peaks are in good agreement with literature values (JCPDS Card Files, No. 77-0441, \( a = 0.4601 \) nm, \( c = 0.2964 \) nm). No peaks of anatase or brookite phase are detected, indicating the high purity of the product.

The size and morphology of the product are analyzed by TEM measurements. The TEM images (Fig. 2a) reveal that the product consists of short nanorods (or corn-shaped). The width of the nanorods...
is in the 20–50 nm range, and the length is about 100–200 nm. The end of the rod is some spine. The crystallinity of the product is also proven by SAED and HRTEM. Transmission electron diffraction performed in a set of such nanorods leads to a pattern as shown in Fig. 2b. The SAED measurements show that the particles are well crystallized and the diffraction rings match the XRD peaks very well. Fig. 3 shows a HRTEM image of one rod-like crystal, the strias are clear (110) plane of rutile. In addition, we find some star-shaped nanocrystals (Fig. 2c) in the sample.

4. Discussion

Ultrasound waves that are intense enough to produce cavitation can drive chemical reactions such as oxidation, reduction, dissolution, decomposition and hydrolysis. These reactions can occur in three different regions [12] surrounding the collapsing bubble in aqueous media. They are: (a) the interior region (gas environment) of the collapsing bubbles, where high temperature (about 5000 K) and high pressure (over 1800 atm) are produced. And the cooling rate is over $10^7$ K/s when the bubbles implode. Here, H$_2$O was pyrolyzed into H$^\cdot$ and OH$^\cdot$, (b) the interfacial liquid region between the bubbles and bulk solution. The temperature in this region is lower than that of the interior of the bubbles. But it is still high enough to satisfy the needs of pyrolysis and hydrolysis; (c) the bulk resolution region, at ambient temperature where the reaction between molecules and surviving OH$^\cdot$ or H$^\cdot$ can still take place. In our case, the sonochemical reaction should take place mostly in the interfacial liquid region. This is because TiCl$_4$ is ionic, and the reaction needs a liquid environment, so it will not occur in region (a). We consider that during an aqueous sonochemical process, the elevated high temperature in region (b) makes the new nucleus directly rutile phase as rutile is the high-temperature stable phase of titania.

Fig. 3 (HETEM image) shows that the (110) lattice fringe is parallel to the rod axis, which indicates that
the growth velocity of [001] direction is faster than the [110] direction. This is because of rutile’s inherent growth habit; rod-like rutile’s growth habit is shown in Fig. 4a [13]. Its growth orientation is along c-axis. The structure of rutile consists of chains of TiO₆ octahedra, in which each octahedron shares a pair of opposite edges in the (001) plane. Thus, the rod morphology is due to the rutile chain type fast growth along the c-axis. Otherwise, we observed some star-like nanocrystals in the sample as Fig. 2c indicates; this may be a twin structure. In nature, twinning is rutile’s general form. Fig. 4b shows the typical twin structure of rutile, and {101} is the twin crystal’s association plane. Our experimental environment offers the possibility for forming twin crystals. During the sonication process, the temperature gradient in the solution will cause the local stress that may be advantageous to the formation of twins. In addition, the growth units non-homogeneously disperse in the solution, which is also a factor for the formation of twins. Once the nuclei form, there are a large number of defects and traps on the nuclei surface. In our experimental condition, twin formation is a possible mechanism to decrease the density of defects and reduce the system energy as the crystal grows. In Fig. 4a, we can see that there are eight exposed {101} equal planes with different directions. Therefore it is reasonable that the star-shaped structures which occur are made up of several twins. Star-like crystals can increase surface-to-volume ratio and prevent product agglomeration, which is advantageous to increase the photocatalysis efficiency of the sample. The details of the formation of star-like structure are being investigated deeply.

5. Conclusion

Pure rod-like rutile titania nanocrystallines were prepared by sonochemical method in HCl/TiCl₄ solution. TiCl₄ is cheap and easily obtained and the sonochemical method is convenient. The formation of rutile phase is due to rutile’s inherent high-temperature stability. The rod morphology of rutile is due to the rutile chain type fast growth along the c-axis. Otherwise, we observed the star-like crystal structure of rutile, which may be due to the sonication environment.

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