Journal of Physics and Chemistry of Solids 71 (2010) 971–975

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Lanthanide absorption spectral probe in titania nanoparticles synthesized by ultrasonic assistant sol–gel method

Wang Hai-Yan, Yang Yue-Tao*, Chen Wan-Song, Wang Yue, Liu Xiao-Jun, Zhang Shu-Yi

Key Laboratory of Modern Acoustics, Ministry of Education, Institute of Acoustics, Nanjing University, Nanjing 210093, China

ARTICLE INFO

Article history:
Received 12 September 2009
Received in revised form
27 January 2010
Accepted 30 March 2010

Keywords:
A. Nanostructures
B. Sol-gel growth
D. Phase transitions

ABSTRACT

Titania nanoparticles were obtained by an ultrasonic assistant sol–gel method. The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermal analysis. The optical absorption of the samples has been measured by photoacoustic (PA) spectroscopy, which is powerful for detecting small amount of strongly scattering materials. The structural variations of the sample during the phase transitions were firstly studied using Nd^{3+} as an absorption spectral probe. The PA results show that the TiO_2 gel heated at 50 °C is basically amorphous and still contains abundant trapped water and ethanol, which makes the environment around Nd^{3+} similar with that of its aqueous ion. For the sample calcined at higher temperature, the f–f transitions of Nd^{3+} exhibit a continuous red shift along with the gel-to-anatase transformation, indicating an increase of the “degree of covalency” for Nd^{3+} bonding. For the sample calcined at 1100 °C, however, the f–f transitions of Nd^{3+} show blue shifts and the hypersensitive transition intensities of Nd^{3+} decrease, indicating an increase of ionicity for Nd^{3+} bonding. This can be attributed to the segregation of Nd^{3+} ions to the external surface, forming $Nd_4Ti_9O_{24}$ during the anatase-to-rutile transition.

1. Introduction

The nanocrystalline titania as a kind of photocatalysis has attracted considerable attentions for its potential use in environmental cleaning [1–3]. The sol–gel method, as a new wet chemical technique, has been successfully applied to prepare TiO_2 powders, films and fibers [4–6]. Generally, the sol–gel process includes two stages: the sol-to-gel transition and the gel-to-crystal transition [7,8]. The latter stage is exceedingly complex. Many techniques have been used to study this process, such as thermal analysis, microscopy, XPS, NMR and so on. Spectroscopy has played a surprisingly limited role. Only IR and Raman spectroscopy have been routinely employed for the studying structural changes at the molecular level [9,10].

Although light absorption is the first step of the complex processes leading to photocatalysis, there are few results on light absorption for TiO_2 powders because of the difficulty in the use of conventional methods due to the scattering and opaque properties of the samples. Photoacoustic (PA) spectroscopy detects the heat generated through the non-radiative transitions in the sample after absorbing an incident light [11]. It has been widely used to investigate the chemical and physical properties of many samples. The PA technique enables to obtain spectra of any type of solids, whether it be crystalline, powder or gel [12–16]. So PA method may be a suitable tool to study the structural variation of titania powders.

Lanthanide ions exhibit sharp absorption bands in the visible and ultraviolet region of the spectrum due to the Laporte forbidden f–f transitions. Their absorption bands are sensitive to the local environment and the ligand binding. These ions are frequently used as spectroscopy probes in systems of biological importance. Applications include the study of discrete equilibrium structures under specific physical and chemical conditions, distributions of structure types in a heterogeneous system [17–19]. It is interesting to study the structure variations of titania powders treated at different temperatures using lanthanide absorption probe. Additionally, this can also be helpful for the better design of lanthanide doped titania for various applications [20–22].

In this paper, the neodymium (III) ion is used as a spectral probe of the structural variations for titania powders during the gel-to-anatase and the anatase-to-rutile transformation firstly. The absorption edges of TiO_2 samples are investigated by PA spectroscopy. The f–f transitions of Nd^{3+} in the samples calcined between 50 and 1100 °C are investigated by the PA method, which reflect the structural variation of the samples.

2. Experimental

2.1. Preparation of the samples

Tetra-n-butyl titanate $Ti(OC_4H_9)_4$ was used as a titanium source. Solution A containing a desired amount of $NdCl_3 \cdot 6H_2O$,

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* Corresponding author. Tel.: +86 25 83686048; fax: +86 25 83315557.
E-mail address: yyang@nju.edu.cn (Y.-T. Yang).

0022-3697/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jpcs.2010.03.043

20 ml of ethanol, 0.8 ml of HCl and 9.0 ml of distilled water was added dropwise to solution B containing 50 ml of $Ti(OC_4H_9)_4$ and 200 ml of ethanol under 50 W 20 kHz ultrasonic irradiation (Sonics-VCX750) for 30 min at room temperature. All chemicals were analytically pure, and the Nd^{3+}/Ti^{4+} mole ratio was 0.05. The resulting sols were cast into cylindrical-shaped plastic boxes and sealed with wax film, then set aside at room temperature. One week after gelation, holes were poked in the wax film to allow solvent escape. Then the gels were treated at 50 °C for 3 days. The obtained gels were grounded into ultrafine powder and washed by acetone and distilled water, followed by calcination for 1 h in a box furnace operating between 50 and 1100 °C in an ambient atmosphere. The neodymium concentration in the TiO_2 sample was checked by inductively coupled plasma analysis and it was found to be 4.4% with respect to titanium. The samples were dry ground separately, and passed dry through a set of sieves. The mean diameter of the samples was 115 μm. The samples were then pressed to have a disklike shape with a thickness of 2 mm for photoacoustic measurement.

2.2. *Characterization*

The PA spectra were measured on a single-beam spectrometer constructed in our laboratory. The excitation source was a 500 W Xenon lamp. The optical system contained a monochromator and an EG&G mechanical chopper at a frequency of 33 Hz, which was used to modulate the light source intensity. The acoustic signal was monitored with the sample placed in an indigenous photoacoustic cell fitted with an electret microphone. The output signal from the microphone was amplified by a preamplifier, and then fed to a SR830 lock-in-amplifier with a reference signal imputed from the chopper. The final signal was normalized for the changes in lamp intensity using carbon black as a reference. The PA spectra of all the samples were recorded at room temperature in the region of 300–800 nm.

X-ray diffractograms (XRD) were obtained on an ARLX'TRA X-ray diffractometer using Cu Kα radiation. The XRD revealed that the anatase phase was fairly stable up to 900 °C. For the sample calcined at 1100 °C, diffraction peaks of a rutile phase appeared. The morphology of the samples was investigated by transmission electron microscopy (TEM) using a JEM-200CX microscopy.

The thermogravimetric analysis was performed on a STA-449C thermal analyzer in air at a heating rate of 10 °C min^{-1}. The thermogravimetric analysis (TGA) presented a mass loss corresponding to the loss of water and solvent molecules (50–200 °C), and another relating to a loss of organic groups (300–400 °C). Differential scanning calorimetry (DSC) revealed structural changes occurred from 450 to 700 °C and from 950 to 1050 °C, with an exothermic peak and an endothermic peak in the above two temperature ranges, respectively.

3. Results and discussion

The photoacoustic signal is obtained by detecting the heat generated through non-radiative transitions by the sample after absorbing a periodically varying incident light. Fig. 1 shows the PA absorption spectral of the title samples calcined at different temperatures. The broad absorption edge from 340 to 420 nm is attributed to the band edge transition. Anatase TiO_2 is an indirect gap semiconductor. The band gap energy of the anatase samples has been evaluated according the Ref. [6]. It is found that there is almost no deviation of the determined values from that of the bulk anatase (band gap = 3.2 eV). The photoacoustic spectra modify considerably the shape in Fig. 1. This can be attributed to the unusual variation of the oscillator strength of the first allowed direct transition, for anatase TiO_2 samples with different sizes [6]. While for the sample calcined at 1100 °C, a remarkable shift to higher wavelength of 413 nm can be attributed to the smaller band gap of rutile phase than that of anatase phase. It should be noted in the region where the energy of incident light is higher than the band gap of TiO_2, photoacoustic saturation occurs in Fig. 1 due to the strong absorption of the semiconductor.

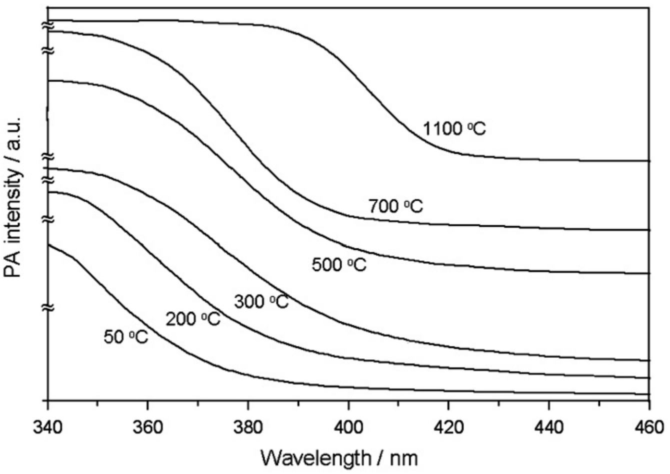

Fig. 1. PA spectra of the Nd^{3+} doped TiO_2 powders calcined at different temperatures.

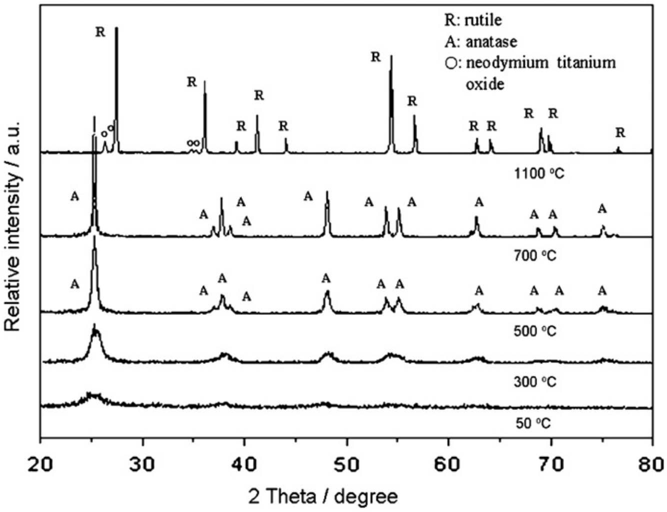

Fig. 2. XRD patterns of the Nd^{3+} doped TiO_2 powders calcined at different temperatures.

XRD spectrum of the samples are shown in Fig. 2. For the sample treated at 50 °C, only weak and broad diffraction peaks of anatase phase appear, indicating that the grain size is very small and the amount of crystal grains is little. The diffraction peaks of anatase phase become more clearly for the samples treated at higher temperatures. The anatase phase is fairly stable up to 900 °C in the case of Nd^{3+} doped titania. On the other hand, the anatase-to-rutile transformation starts as early as 650 °C in the case of pure titania. The presence of interstitial Nd^{3+} ions increases the diffusion barrier at the titania–titania grain contact, which is needed for the grain growth process [23]. Additionally, Nd^{3+} ions that may have replaced the Ti^{4+} sites will have a stabilizing effect on the Ti–O bond. This further retards the anatase-to-rutile transformation temperature [23,24]. While for the sample calcined at 1100 °C, diffraction peaks of a rutile phase