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STM and STS investigations of Ce-doped TiO_2 nanoparticles

HOU Tinghong, MAO Jian, ZHU Xiaodong, and TU Mingjing

College of Materials Science and Engineering, Sichuan University, Chengdu 610064, China

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Abstract: Ce-doped titanium oxide nanoparticles were investigated in the paper. The surface structures of undoped and Ce-doped TiO_2 nanoparticles were observed by scanning tunneling microscopy (STM). The experimental results of scanning tunneling spectroscopy (STS) show that the surface electronic structures of TiO_2 nanoparticles are modified by introducing new electronic states in the surface band gap through cerium ion doping. The results are discussed in terms of the influence of doping concentration on the surface band gap of TiO_2.

Key words: semiconductor materials; TiO_2 nanoparticle; STM/STS; Ce-doping

1. Introduction

Environmental pollution and destruction is a growing global problem that cannot be neglected as it is a grave threat to our world and daily life. Compared with existing pollution remediation technologies, semiconductor photocatalysis is an environmental-friendly method with many advantages such as no secondary pollution, self-regeneration and low energy consumption.

In 1972, Fujishima and Honda [1] discovered the photocatalytic splitting of water using a rutile titanium dioxide (TiO_2) photoanode and Pt counter electrode. This event marked the beginning of a new era in semiconductor photocatalysis. Since then, TiO_2-based photocatalysts have gained more and more importance and this is reflected in the extensive research that deals with theoretical aspects and practical applications in recent years [2]. However, TiO_2 displays high photoactivity only when it is irradiated by ultraviolet light due to its wide band gap (~3.2 eV for anatase). Doping with impurities has been widely used to modify the properties of TiO_2 by introduction of new states in its electronic structure [3-4]. In particular, because of the unique 4f electron configuration, lanthanide metal ions, such as cerium (Ce^{3+}), are ideal dopants to modify the electronic structure of TiO_2. The knowledge about electronic features of TiO_2 surface is necessary for the development and design of highly reactive photocatalysts. Although there have been some reports on lanthanide-doped TiO_2 nanoparticles, their electronic properties have seldom been thoroughly investigated [5-7].

Scanning tunneling microscopy (STM) combined with scanning tunneling spectroscopy (STS) can provide the information on surface topography and surface electronic properties in a nanometer scale resolution. Therefore, it is a powerful tool in characterization of semiconductor nanoparticles. Although numerous studies had been conducted on TiO_2-based materials [8-11], there has been no detailed STM/STS analysis in literatures concerning the experimental STM and STS of lanthanide-doped TiO_2 nanoparticles.

In the present study, we report the application of STM/STS technique to the investigation of Ce-doped TiO_2 nanoparticles and to the determination of their surface structural and electronic properties. The influence of cerium ion concentration on the surface electronic structure is also discussed.

Corresponding author: MAO Jian **E-mail:** scucm_mj@163.com

2. Experimental

2.1. Sample preparation

The Ce-doped TiO_2 nanoparticles were prepared by impregnation method. In a typical process, a required amount of pure TiO_2 (anatase) powders was added into a given amount of $Ce(NO_3)_3 \cdot 6H_2O$ solution with different concentrations of Ce^{3+} ions. The slurry was dispersed in an ultrasonic bath for 15 min. After impregnated for 3 h, it was filtered and then dried at 373 K. Finally it was calcined in an electric resistance furnace at 773 K for 3 h.

The concentration of Ce^{3+} ion in the sample was determined using complexometric titration method, which uses ethylene-diaminetetraacetic acid (EDTA) as a titrant and xylenol orange as an indicator. The filtrate was adjusted to the range of pH 5-6 and the volume of the standard solution of EDTA used in titration was measured. The crystal structure of the samples was characterized by X-ray diffraction (XRD). XRD patterns were recorded using a powder diffractometer (Model DX-2000) and Cu K_α radiation. Data were collected at room temperature over the range of $20° < 2\theta < 80°$ in 0.03° 2θ steps. The observed diffraction angles were calibrated using SiO_2 as the standard reference material.

2.2. STM/STS measurement

All STM and STS measurements were performed using a home-built scanning tunneling microscope (STM.IPC-205B) in Science School of Chongqing University under constant current operation at room temperature. In the STS measurements, the tip-sample distance was kept constant with a current of 0.1 nA and a bias voltage of 1.0 V, the scanning voltage range of –3.0 V to + 3.0 V with a scanning rate of 400 mV/s.

3. Results and discussion

3.1. Concentration of Ce^{3+} ion and XRD analysis

Table 1 shows the calculated concentration of Ce^{3+} ion in the samples based on the result of complexometric titration. As shown in Table 1, nano-TiO_2 powders show extremely strong absorption for Ce^{3+} ion and the absorption rate is close to 100%.

Table 1. Concentrations of Ce^{3+} ion in the samples

Sample	CDT0.5	CDT1.0	CDT1.5	CDT2.0	CDT2.5
Doping value / at.%	0.5	1.0	1.5	2.0	2.5
Calculated value / at.%	0.495	0.994	1.496	1.994	2.497

Fig. 1 shows XRD patterns of the doped samples. It reveals the presence of peaks (2θ = 25.4°, 37.8°, and 48.2°), which are regarded as an attributive indicator of anatase TiO_2. All samples do not appear any other new crystal phase apart from crystal titania. Based on the Laue integral width of the peaks in the XRD patterns, the calculated average grain sizes of the samples are shown in Table 2. The grain size of undoped and Ce-doped samples shows no obvious change and has a diameter of about 16 nm. It implies that the dopants may not enter the TiO_2 lattice.

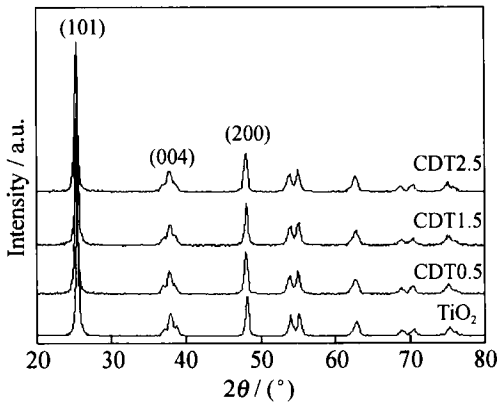

Fig. 1. XRD patterns of the Ce-doped TiO_2.

Table 2. Average grain sizes of the samples

Ce^{3+} content / at.%	0.0	0.5	1.5	2.5
Average grain size / nm	16.4	16.2	16.3	16.1

3.2. STM Images

Figs. 2(a) and 2(b) show the three-dimensional and the topographic STM images (273 nm × 273 nm) of the undoped TiO_2 nanoparticles respectively. Some isolated spherical TiO_2 nanoparticles can be clearly identified. From the STM image, it is observed that the sample shows little aggregation.