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Short communication

A novel method for the preparation of $Bi_4Ti_3O_{12}$ nanoparticles in w/o microemulsion

Lijin Xie [a], Junfeng Ma [a,b,*], Zhongqiang Zhao [a], Hua Tian [a], Jun Zhou [a], Yonggang Wang [b], Jiantao Tao [b], Xiaoyi Zhu [b]

[a] *College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266003, China*
[b] *Institute of Materials Science and Engineering, Ocean University of China, Qingdao 266003, China*

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Abstract

Nanometer-sized $Bi_4Ti_3O_{12}$ particles have been prepared by chemical reaction of bismuth nitrate pentahydrate, titanium sulfate and ammonia solution in a reverse microemulsion system consisting of water, OP (*P*-octyl polyethylene glycol phenylether, non-ionic surfactant), *n*-butanol (co-surfactant), and cyclohexane (oil). Precursor hydroxides precipitated in the droplets of water-in-oil (w/o) microemulsion were calcined at 800 °C for 4 h to form $Bi_4Ti_3O_{12}$ nanoparticles. The samples were investigated with X-ray diffraction (XRD), transmission electron microscopy (TEM), fourier transform infrared spectrophotometer (FT-IR) and ultraviolet visible spectrophotometer (UV–vis). It was found that the as-prepared $Bi_4Ti_3O_{12}$ nanoparticles had small particle sizes (35 nm), high crystallinity, narrow size distributions and strong light absorption properties not only in the ultraviolet light but also in the visible light region.

Keywords: $Bi_4Ti_3O_{12}$ nanoparticles; Water-in-oil microemulsions; Synthesis

1. Introduction

As a member of the Aurivillius family compounds, which are well known as ferroelectric materials, bismuth titanate $Bi_4Ti_3O_{12}$ is of particular interest due to its unique electro-optic switching behavior. Generally, it is useful for various applications such as memory storage, optical display, piezoelectric converters or pyroelectric devices over a wide range of temperatures [1–6]. $Bi_4Ti_3O_{12}$ is also an important photocatalyst material [7]. It is well known that the photocatalytic properties can be improved by decreasing the particle size of the photocatalyst material in order to increase the number of active sites on its surfaces. Thus, for the application of $Bi_4Ti_3O_{12}$ as photocatalyst material, nanosized particles are desirable. Up to now, several methods, including solid state reaction [8,9], coprecipitation method [10], and hydrothermal synthesis [11], molten salt process [12], citrate method [13], laser sintering [14], were developed for the synthesis of $Bi_4Ti_3O_{12}$ powders. However, these methods still have some drawbacks.

Reverse microemulsions are colloidal nanodispersions of water in oil stabilized by a surfactant film. These thermodynamically stable dispersions can be considered as true nanoreactors, which can be used to carry out chemical reactions and, in particular, to synthesize nanomaterials. The synthesis of nanoparticles in microemulsions, the formation mechanisms and growth control in recent years have been reviewed by MP. Pileni [15] and López-Quintela et al. [16,17]. Now, water-in-oil (w/o) microemulsions have been successfully used to synthesize colloidal metals [18,19], superconducting materials [20,21], and magnetic materials [22,23]. Unfortunately, no descriptions concerning the preparation of $Bi_4Ti_3O_{12}$ powders by the use of water-in-oil microemulsions have appeared. In this paper, for the first time, some results on the synthesis of $Bi_4Ti_3O_{12}$ nanoparticles in water-in-oil microemulsions are presented.

2. Experimental

2.1. Chemicals

Bismuth nitrate pentahydrate (analytic reagent), titanium sulfate (analytic reagent) were supplied by Shanghai Chemical

* Corresponding author. Tel.: +86 53282031623; fax: +86 53282031623.
E-mail address: majf@mail.ouc.edu.cn (J. Ma).

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Table 1
Composition of the microemulsion system used for the synthesis reactions

	M I	M II	wt.%
Aqueous phase	0.1 M $Bi(NO_3)_3$ and $Ti(SO_4)_2$	1.0 M NH_4OH	20
Surfactant	OP	OP	17
Co-surfactant	*n*-Butanol	*n*-Butanol	10
Oil phase	Cyclohexane	Cyclohexane	55

Reagent Corporation. Ammonia water (28 wt.%), OP (analytic reagent), *n*-butanol (Analytic reagent) and cyclohexane (analytic reagent) were obtained from Laiyang Chemical Reagent Corporation. All reagents were used without further purification. The water used throughout this work was distilled water.

2.2. Synthesis of $Bi_4Ti_3O_{12}$ nanoparticles

$Bi_4Ti_3O_{12}$ powders were prepared via two processing methods: (i) the conventional co-precipitation method and (ii) the microemulsion method. In the co-precipitation method, ammonia water (28 wt.%) was added to aqueous solution including Bismuth and Titanium cations (molar ratio of Bi/Ti = 4/3) until the pH of the mixture reached 8, where a white precipitate was produced. The precipitate was filtered, washed with distilled water and dried in a drying oven at 100 °C for 24 h. Then the dried precipitate was calcined for 4 h at 800 °C in an electric furnace in air.

For the microemulsion method, cyclohexane was used as the oil phase, OP was used as the surfactant and *n*-butanol was used as the co-surfactant. Two kinds of microemulsions (M I and M II) with different aqueous phase were obtained (see Table 1). The aqueous phase in the M I was a solution of Bismuth and Titanium cations (molar ratio of Bi/Ti = 4/3), while the aqueous phase in the M II containing the precipitating agent, NH_4OH (1.0 M). These two microemulsions were mixed for 3 h under constant stirring speed. The opaque appearance of the mixture upon vigorous stirring indicated the formation of the particles. Powder samples were obtained by flocculating the colloids with acetone and followed by separation in a centrifuge. The precipitates were washed with acetone and ethanol to eliminate excess OP, and then dried at 100 °C for 24 h. The dried precipitates were calcined at 800 °C for 4 h in an electric furnace in air.

2.3. Characterization

X-ray diffraction (XRD, D/max, Rigaku, Japan) employing Cu Kα radiation was used to identify the crystalline phase of the prepared powders. JEM-1200 EX transmission electron microscope (Tokyo, Japan) was employed to examine the morphology and size of the nanoparticles, operated at 60.0 kV. Samples were prepared by adding ethanol to a fraction of the powders synthesized, ultrasonic dispersing for 10 min and droplet of it was dropped on a carbon-coated copper grid. The fourier transform infrared (FT-IR) spectra were recorded on samples in KBr tablets using an AVATAR360 FT-IR spectrophotometer (Nicolet, America). Their ultraviolet visible (UV–vis) absorption spectra were recorded on a U-3010 spectrophotometer (Tokyo, Japan). The UV–vis absorption spectra of the as-prepared $Bi_4Ti_3O_{12}$ powders were recorded in the wavelength range of 200–1000 nm using a U-3010 spectrophotometer (Tokyo, Japan). Samples for UV–vis absorption characterization were prepared by dispersing the as-prepared powders in the ethanol by ultrasonic, and the pure ethanol was used as a reference sample.

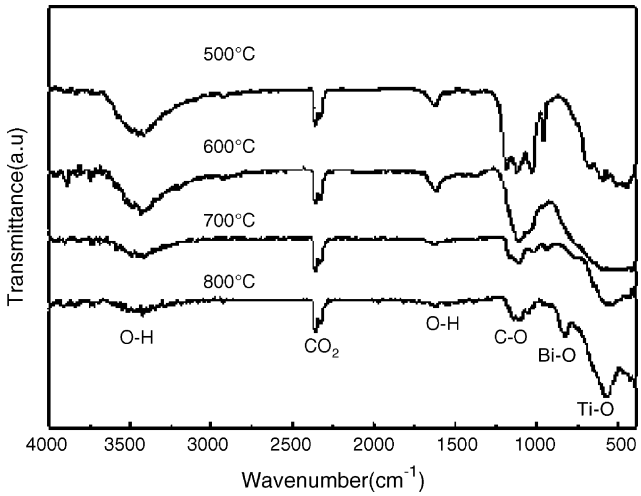

Fig. 1. FT-IR spectra for $Bi_4Ti_3O_{12}$ powders calcined at various temperatures after preparation by microemulsion method.

3. Results and discussion

3.1. FT-IR analysis

Fig. 1 shows FT-IR spectra for the powders prepared by microemulsion method calcined at various temperatures in the range of 500–800 °C. The calcination was carried out at each temperature for 2 h in air. The peaks around 1628 and 3421 cm^{-1} correspond to the bending vibrations of absorbed molecular water and *n*-Butanol and the stretching vibrations of –OH groups, respectively [24]. The weak peaks at 2362 cm^{-1} belong to the stretching vibrations of CO_2, and the ones at 1119 cm^{-1} correspond to the bending vibrations of –C–O, which shows that a few organic groups are absorbed on the surfaces of the powders. As the calcination temperature increased, it is seen that these peaks reduced gradually. As the calcination temperature increased to 800 °C, these absorption peaks were almost disappeared, denoting that most of organics were removed. There exist only two strong peaks near 795 and 578 cm^{-1} agreeing with the stretching vibrations of Bi–O and Ti–O [25,26], which indicate that the products are well crystallized.

3.2. XRD study

Fig. 2 shows the X-ray diffraction patterns of the calcined powders prepared in the co-precipitation method. As shown in Fig. 2, all characteristic peaks for the stable phase $Bi_4Ti_3O_{12}$