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Ceramics International 33 (2007) 915–918

CERAMICS INTERNATIONAL

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Low temperature synthesis of nano-sized $(Sn_{0.25},Ti_{0.75})O_2$ photocatalysts by a molten salt method

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Received 6 December 2005; received in revised form 18 December 2005; accepted 14 February 2006
Available online 18 April 2006

Abstract

Nano-sized $(Sn_{0.25},Ti_{0.75})O_2$ photocatalysts were successfully synthesized by a molten salt (MS) method at 260 °C for 2 h, where a homogeneous precipitate containing titanium and tin cations as a precursor. The synthesized powders were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and UV–vis, respectively. The results show that the products are composed of homogeneously spherical particles with an average size of ca.10 nm, and have better UV absorption and visible light response when the reaction temperature is increased to 400 °C.

Keywords: D. TiO_2; Sn; Molten salt method; Nano-sized photocatalyst

1. Introduction

SnO_2–TiO_2 coupled oxides have received considerable attention as gas sensor [1–3] and varistor ceramic [4], which is mainly due to the mass transport properties of the $Sn_xTi_{1-x}O_2$ system [5,6]. In addition, SnO_2–TiO_2 coupled photocatalyst is well known to be one of the most effective photocatalysts, and its photocatalytic behavior has been studied extensively in recent years [7–11]. Compared with SnO_2 or TiO_2, the binary TiO_2–SnO_2 as a photocatalyst improves the photocatalytic activity due to an increase of charge separation of photo-generated electrons and holes [9–12]. Moreover, the previous study has showed that a smaller crystalline size and a better symmetrical shape of particles also mean a better photo-catalytic activity [13].

SnO_2–TiO_2 coupled oxides have been synthesized by various methods: the solid-state reaction [2], CVD method [9], and homogeneous precipitation [11]. But there are still many limitations such as high reaction temperature [2,9] and large particle size and irregular particle shape [2,12]. Recently, the molten salt (MS) method has been widely used for the preparation of unitary oxide and multicomponent oxides [14–18], and it can offer a good reaction condition with a high ion concentration and the quick pervasion [19]. There have been few reports on the preparation of SnO_2–TiO_2 coupled oxides by the MS method except Naidu and Virkar [20], who have studied TiO_2–SnO_2 phase diagram using the MS method at 400 °C for a very long reaction time (180 d).

In this work, we choose $(Sn_{0.25},Ti_{0.75})O_2$ as an investigation target of the SnO_2–TiO_2 system. A nano-sized $(Sn_{0.25},Ti_{0.75})O_2$ photocatalyst could be readily synthesized by the MS method at 260 °C for 2 h, which is lower than the lowest synthetic temperature reported in the previous literature [20] to our knowledge. Furthermore, a $(Sn_{0.25},Ti_{0.75})O_2$ photocatalyst powder with better absorption to the UV light and visible light could be obtained by our MS method when the reaction temperature is increased to 400 °C.

2. Experimental

The reagents ($SnCl_4{\cdot}5H_2O$, $Ti(OC_4H_9)_4$, $LiNO_3$, ammonia) were all analytical grade. $SnCl_4{\cdot}5H_2O$ and $Ti(OC_4H_9)_4$ were used as the raw materials, and HCl solution (37 wt.%, analytical grade) as a reaction medium and ammonia solution (25 wt.%)

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0272-8842/$32.00
doi:10.1016/j.ceramint.2006.02.006

as a co-precipitator. $SnCl_4{\cdot}5H_2O$ and $Ti(OC_4H_9)_4$ in a molar ratio of 1:3 were dissolved in the HCl solution (pH 1). Then, the ammonia solution was slowly added to the above mixed solution containing titanium and tin cations to adjust the pH value until 8, and a white precipitate was formed. The precipitate was filtered and washed with the ammonia solution for several times. Then, the precipitate was dried at 70 °C in air overnight as a precursor for $(Sn_{0.25},Ti_{0.75})O_2$ powders.

The $(Sn_{0.25},Ti_{0.75})O_2$ precursor was mixed by ball milling in absolute ethanol with $LiNO_3$ salt whose melting point is 254 °C [19]. The weight ratio of $LiNO_3$ salt to the $(Sn_{0.25},Ti_{0.75})O_2$ precursor was selected as 4:1. After the mixture was dried at 70 °C in air, it was placed in an alumina crucible, and heat treated at 260, 300 and 400 °C for 2 h, respectively. Finally, the resulting products were washed with distilled water for several times to remove the alkali metal salt, washed with absolute ethanol, and dried at 70 °C for 3 h.

The phase compositions in the coupled oxides prepared was analyzed using an X-ray diffractometer (XRD, Bruker D8, Germany). A transmission electron microscope (TEM, JEM-1200 EX) was used to observe the morphology and particle size of the prepared photocatalysts, and their UV–vis absorption spectra recorded on a U-3010 spectrophotometer.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $(Sn_{0.25},Ti_{0.75})O_2$ photocatalysts obtained by the MS method at different temperatures. All the peaks could be indexed as

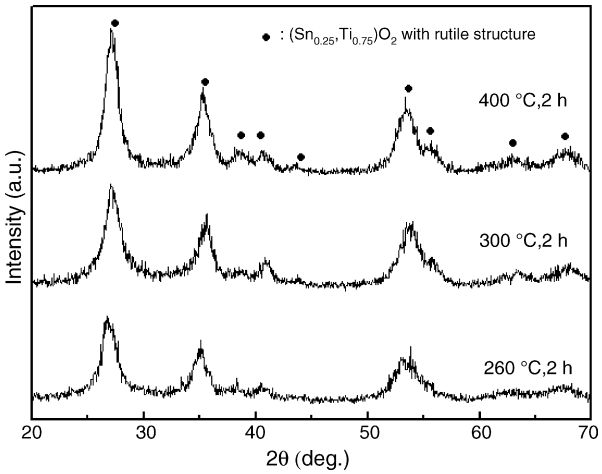

Fig. 1. XRD patterns of $(Sn_{0.25},Ti_{0.75})O_2$ photocatalysts obtained by the MS method at different reaction temperatures.

$(Sn_{0.25},Ti_{0.75})O_2$ phase with rutile structure, which is consistent with the literature [5]. The diffraction peaks are getting sharper and stronger with the increase of reaction temperature. It reveals that crystallites with the rutile structure have already begun to form at 260 °C for 2 h, and have better crystallinity with increasing reaction temperature.

Fig. 2 shows the TEM micrographs of $(Sn_{0.25},Ti_{0.75})O_2$ photocatalysts obtained by the MS method at 260, 300 and 400 °C for 2 h, respectively. It displays that the as-prepared powders are composed of nano-sized particles, which are nearly spherical in shape with the average size about 10 nm, and are of

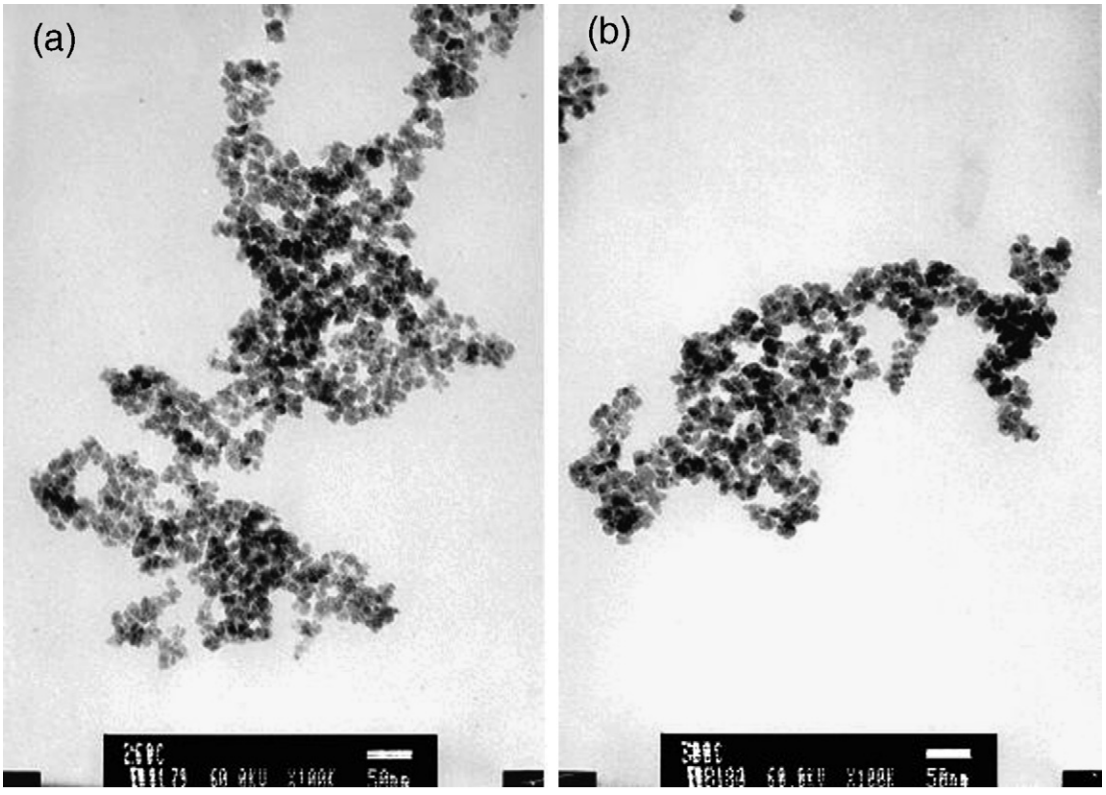

Fig. 2. The TEM photographs of $(Sn_{0.25},Ti_{0.75})O_2$ photocatalysts obtained by the MS method at different reaction temperatures for 2 h: (a) 260 °C; (b) 300 °C; and (c) 400 °C.

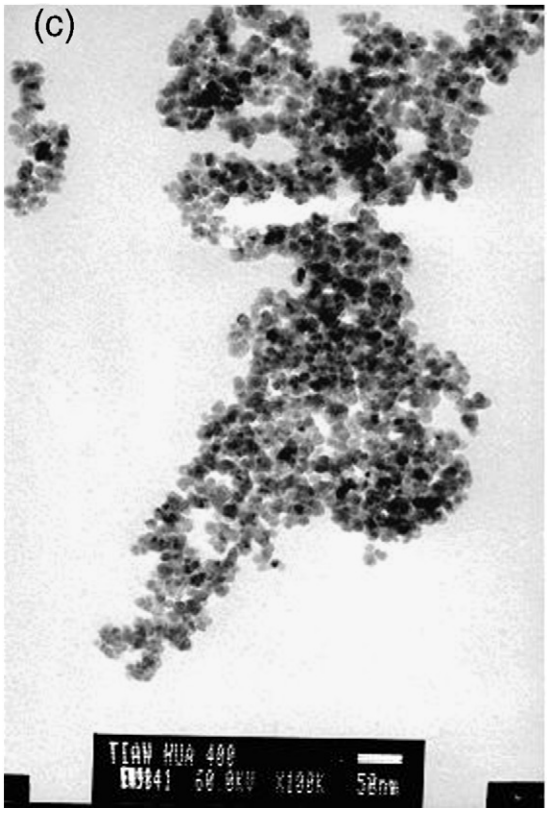

Fig. 2. (*Continued*).

narrow particle size distribution and a little soft aggregation with the increase of the reaction temperature.

The UV–vis absorption spectra of $(Sn_{0.25},Ti_{0.75})O_2$ photocatalysts synthesized by the MS method at different temperatures, are given in Fig. 3. It shows that with increasing reaction temperature, the UV absorption of the $(Sn_{0.25},Ti_{0.75})O_2$ photocatalyst becomes stronger and the UV absorption edge wavelength has a red shift. These results reveal that the UV absorption of the $(Sn_{0.25},Ti_{0.75})O_2$ photocatalyst is obviously influenced by the reaction temperature. As shown in Fig. 2, a better crystalline morphology could be found in the case of higher reaction temperature (400 °C), corresponding to a better crystallinity even though the average particle size of the powders has no significant change. This observation is in a good agreement with the results from XRD.

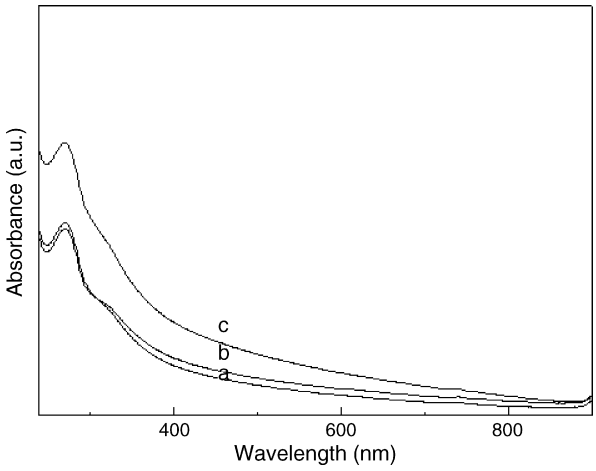

Fig. 3. The UV-VIS spectra of $(Sn_{0.25},Ti_{0.75})O_2$ photocatalysts obtained by the MS method at different reaction temperatures for 2 h: (a) 260 °C; (b) 300 °C; and (c) 400 °C.

It is well known that a smaller crystalline size, better shape of particle and stronger UV absorption are avail to improve the photocatalytic activity [19]. Our experimental results demonstrated that $(Sn_{0.25},Ti_{0.75})O_2$ photocatalysts synthesized by the MS method at the low temperature could allow a better photocatalytic activity.

4. Conclusions

A low temperature MS method is developed to synthesize nano-sized $(Sn_{0.25},Ti_{0.75})O_2$ photocatalyst, and the sample at 260 °C for 2 h exhibited a good UV absorption and visible light response. Further elevation the reaction temperature to 400 °C would promote the ctystallization of the $(Sn_{0.25},Ti_{0.75})O_2$ phase to improve its photocatalytic activity.

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