Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 14615–14620

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Synthesis of TiO_2 hollow spheres with tunable pore structure and enhanced photocatalytic activity

Ruiping Liu[a,*], Feng Ren[a], Weiming Su[a], Peng He[a], Chao Shen[a], Lei Zhang[b,**], Chang-an Wang[c]

[a]Department of Materials Science and Engineering, China University of Mining & Technology (Beijing), Beijing 100083, China
[b]Department of Mechanical Engineering, PO Box 755905, University of Alaska Fairbanks, Fairbanks, AK 99775, USA
[c]School of Materials Science and Engineering, State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China

Received 21 July 2015; received in revised form 24 July 2015; accepted 27 July 2015
Available online 4 August 2015

Abstract

Titania hollow spheres were fabricated successfully by using tetrabutyl titanate as titanium precursor and colloidal carbon spheres as hard templates. The microstructure, textural properties, structure regulation approach, as well as the photocatalytic properties of the hollow spheres were investigated. The results show that the hollow spheres possess the perfect spherical shape, monodispersity, and hierarchically pore structures which endow them with high specific surface area and pore volume. The wall thickness and textural properties of the hollow spheres can be easily tailored by adjusting the concentration of tetrabutyl titanate. Evaluation of the titania hollow spheres for the photo-decomposition of methylene blue (MB) under visible-light irradiation reveals that they exhibit excellent photocatalytic activity and durability.

Keywords: A: Powders chemical preparation; B: Microstructure-final; D: TiO_2; E: Functional applications

1. Introduction

Titania (TiO_2) is considered to be one of the most useful semiconducting metal oxides for applications ranging from sensors to photonic crystals, energy storage, and photocatalysis [1]. Its wide band gap energy (E_g, 3.0–3.2 eV) allows absorption of UV light, generating electrons (e^-) and holes (h^+), which can subsequently induce red-ox reactions. To utilize solar energy efficiently, TiO_2 should be of high crystallinity and high surface area to promote charge separation as well as electron transport.

In order to improve the photocatalytic activity of titania, many investigations have been reported by researchers [2–4]. Doping and morphology control are considered as two very promising strategies. On one hand, it has been extensively demonstrated that anion-doping (such as nitrogen, sulfur and carbon) was an effective approach to improve the visible light photocatalytic activity of titania [5–10], and the same effect can also be obtained by doping of Ag [11], ZnO [12], and Ce [13], etc. On the other hand, it is well known that morphology and microstructures are very important to the photocatalytic activity of titania. Therefore, there are many studies focused on the new structures of titania, such as nanorods [14,15], nanowires [16,17], and nanotubes [18,19], etc.

Recently, fabrication of titania hollow spheres has attracted enormous attention because of their low density, large surface area, good surface permeability as well as high light-harvesting efficiencies [20]. It is also expected that higher energy conversion efficiency and photocatalytic activity could be achieved using titania hollow spheres as photocatalysts. Various methods, such as templating method [21], sonochemical method [22], and hydrothermal method [23], etc., have been reported for the preparation of inorganic materials with hollow spherical structures. However, most of the methods mentioned above required surface modification of the templates before the deposition of precursor materials of hollow spheres. Furthermore, the microstructures were hard to regulate and the process was deleterious to the environment. Therefore, in the present work, we aimed to

*Corresponding author. Tel.: +86 10 62339175; fax: +86 10 62339081.
**Corresponding author. Tel.: +1 907 474 6135; fax: +1 907 474 6141.
E-mail addresses: bjlrp165@126.com (R. Liu), lzhang14@alaska.edu (L. Zhang).

http://dx.doi.org/10.1016/j.ceramint.2015.07.181
0272-8842/

prepare titania hollow spheres with tunable structure by using colloidal carbon spheres as the hard template. The fabrication techniques, microstructure, and photocatalytic properties of the titania hollow spheres were investigated systematically.

2. Experimental procedure

2.1. Synthesis of carbon spheres

The carbon spheres used in the present study were prepared by hydrothermal treatment of glucose. 9 g of glucose (Beijing Chemical Reagent Factory, analytical purity) were dissolved in 90 mL deioned (DI) water to form a clear solution, which was then placed in a 100-mL Teflon-sealed autoclave and maintained at 180 °C for 12 h. The black products were seperated and purified by centrifugation and repeatly washed in DI water and ethanol for at least three times, followed by drying in a vacuum oven at 80 °C for 6 h.

2.2. Preparation of TiO_2 hollow spheres

Firstly, 5 mL tetrabutyl titanate was dissolved in 50 mL ethanol to form a clear solution, and then 0.1 g of the newly prepared carbon spheres were dispersed in the above suspension with the aid of ultrasonication. After stirred for 2 h, the mixed solutions of ethanol and DI water with the volume ratio of 5:1 were added dropwise to the suspension with vigorous stirring. The mixture was aged for 1 h, and then subjected to four centrifugation/water wash/re-dispersion cycles to remove impurities, and finally dried in a vacuum oven at 60 °C for 5 h. After synthesis, the carbon–titania composites were calcined in air at 450–850 °C (heating rate of 2 °C/min) for 4 h to strengthen the shell structure and remove the carbon core, leading to hollow titania particles.

2.3. Characterization

The calcination procedure was determined by the thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses. FTIR spectra of carbon spheres were measured by using Nicolet Magna 750 in the wave number region of 4000 to 500 cm^{-1} with 64 scans at 8 cm^{-1} resolution. X-ray diffraction (XRD) patterns were taken on a Bruker D8-Advance diffractometer using Ni filtered Cu Kα radiation. The applied current and voltage were 40 mA and 40 kV, respectively. During the analysis, the samples were scanned from 20 to 80° at a speed of 4°/min. Scanning electron microscopy (SEM) images were collected using a Carl Zeiss Jena scanning microscope, and transmission electron microscopy (TEM) images were taken using a JEOL JEM-2011 system operated at 200 kV. BET-surface area was measured by N_2 adsorption at liquid nitrogen temperature using a NOVA4000 automated gas sorption system.

2.4. Photocatalytic test

The photocatalytic experiment was carried out in a photo reaction system (Shanghai Bilon Instrument Co., Ltd, BL-GHX-V) by using methylene blue (MB) as a model pollutant. A 500 W Xe lamp equipped with a 420 nm cut-off glass filter (removing the UV irradiation below 420 nm wavelength), positioned in the center of a water-cooled quartz jacket, was used as the visible light irradiation source. At the side of quartz jacket, five 100-mL cylindrical vessels were used as the reactive bottle to load reaction solution. 25 mg of photocatalyst powder was added into 50 mL of 10 mg/L MB aqueous solution to form suspension. Then, the suspension was irradiated with visible light (wavelength longer than 420 nm). During the irradiation, the suspension was stirred continuously. For comparison, the commercial Degussa P25 was also examined under the same conditions. At a given time interval, 3 mL of suspension was taken out and immediately centrifuged to eliminate the solid particles. The absorbance of the filtrate was measured by a spectrophotometer at the maximum absorbance peak of 664 nm.

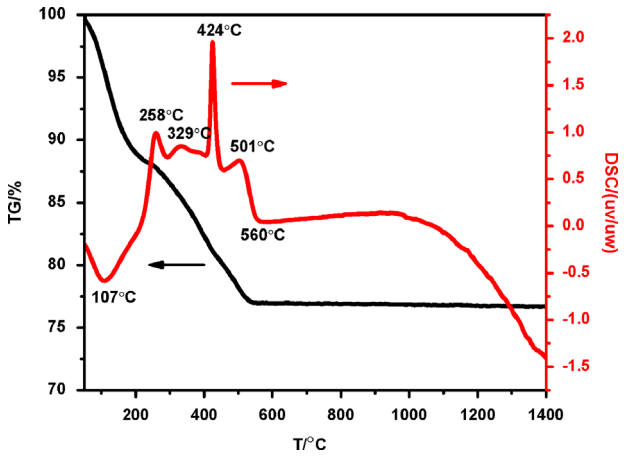

Fig.1. TG-DSC curves of the as-prepared carbon–titania composite.

3. Results and discussion

The calcination procedure was determined by the TG-DSC curve of the as-prepared carbon–titania composite (Fig. 1). It can be seen that the weight loss was about 12% when the temperature elevated from the ambient temperature to 217 °C, corresponding to the endothermic peak located at 107 °C in the DSC curve, and it was due to the volatilization of the residual H_2O and ethanol. The exothermic peak located at 258 °C and 329 °C in the DSC curve was attributed to the removal of carbon spheres and decomposition of tetrabutyl titanate, respectively. The exothermic peak at 424 °C was attributed to the crystallization of TiO_2, and the minor endothermic peak at 560 °C was associated with the transformation of anatase TiO_2 to rutile TiO_2.

To determine the crystal phase of the as-prepared samples calcined at different temperatures, XRD measurements were carried out and the results are shown in Fig.2. It can be seen that after the calcination of carbon–titania composite spheres at 450 °C, the titania precursor was transformed into anatase TiO_2, and with increasing calcination temperature, the crystallization degree increased. Once the carbon–titania composites spheres were calcined at 650 °C, most of the titania precursor was transformed into anatase TiO_2, and a small portion was transformed into rutile TiO_2 (the peak at $2\theta = 27.5°$ can be