Materials Letters 129 (2014) 50–53

Contents lists available at ScienceDirect

Materials Letters

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

One-pot synthesis of foamed titania–silica composite and its photocatalytic performance

Jinxi Zhang, Baoshan Li*, Chunying Han, Jianjun Liu

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

ARTICLE INFO

Article history:
Received 14 February 2014
Accepted 1 May 2014
Available online 9 May 2014

Keywords:
Nanoparticles
Nanocomposites
Photocatalytic degradation
One-step method
Porous materials

ABSTRACT

A novel foamed titania–silica composite (FTSC) with hierarchical porous structures was prepared by a one-pot microemulsion method using tetrabutyl titanate and tetraethyl orthosilicate as titania and silica precursors. The as-prepared FTSC was characterized by powder X-ray diffraction, scanning electron microscope, transmission electron microscopy, energy dispersive X-ray spectroscopy and N_2 adsorption–desorption isotherms. The results show that the FTSC possesses foam like structures with cavities and mesoporous shells, and the anatase-phase titania in FTSC was confirmed. The specific surface area of FTSC is 354 m^2/g and the average pore diameter is about 7.6 nm. The obtained FTSC shows promising efficiency in the photocatalytic degradation of methylene blue under UV light.

1. Introduction

As one of the advanced oxidation processes, photocatalytic oxidation has been widely used in environmental protection and waste water treatments [1,2]. Nanosized TiO_2 is one of the most promising candidate photocatalyst because of its superior physicochemical properties, excellent UV absorbency, high photocatalytic activity, low toxicity and low cost. It has been demonstrated that the photocatalytic activity of TiO_2 depends on its phase structure, specific surface area, crystal size, crystallinity and pore structure [3]. To maximize TiO_2 photoactivity, much effort has been devoted to design nanosized TiO_2 particles with high photocatalytic activity [4].

On the other hand, with the rapid development of nanotechnology, materials with special dimensionality and size have brought novel and promising properties. Thus, various hierarchical structured TiO_2 photocatalysts have been synthesized, such as porous TiO_2 [5], hierarchical TiO_2 microspheres [6], TiO_2 nanorod array [7], TiO_2 hollow nanocages [8], TiO_2 hollow spheres [9] and TiO_2 foams [10]. Among them, the hierarchical porous TiO_2 foams would give a new opportunity for high performance in the course of catalytic reactions [10–14].

In the present work, we reported a simple route for the production of novel foamed titania–silica composite (FTSC) with hierarchical porous structures by one-pot method. The photocatalytic properties of the samples were studied with the decomposition of methylene blue (MB) under UV irradiation. The positive effect of the foamed porous structures on the photocatalytic activity was discussed.

2. Experiments

The titania–silica precursor was prepared as follows: 2.35 g of tetrabutyl titanate was added into a mixture of 2 mL of acetylacetone and 5 mL of octane. The resulting mixture was stirred for 20 min at room temperature to obtain a yellow solution. Then 7.2 mL of tetraethyl orthosilicate (TEOS) was added into the solution with stirring for another 20 min to obtain titania–silica precursor. In a typical synthesis of FTSC, 1.4 g of CTAB was dissolved in a mixture of 70 mL of deionized water, 15 mL of aqueous ammonia (3 mol/L) and 20 mL of octane. After the mixture was vigorously stirred for 30 min at 283 K, the titania–silica precursor was dropped slowly. The resulting mixture was vigorously stirred at room temperature for another 60 min. Then the mixture was transferred into a Teflon–lined autoclave and heated at 383 K for 48 h. The product was separated by filtration, washed with deionized water and ethanol, and dried at 333 K in air for 24 h and finally calcined at 923 K for 6 h to obtain FTSC.

The photocatalytic experiments were carried out in a 200 mL cylindrical glass reactor equipped with a 50 W high-pressure mercury lamp using 100 mL of methylene blue (MB) aqueous solution with an initial concentration of 20 mg/L and 0.1 g of FTSC photocatalyst. The concentrations of MB during the photodegradation were determined by spectroscopic analysis at 665 nm. For a comparison purpose, photocatalytic activity of the commercial

* Corresponding author. Tel./fax: +86 10 64445611.
E-mail address: bsli@mail.buct.edu.cn (B. Li).

http://dx.doi.org/10.1016/j.matlet.2014.05.006
0167-577X/

AEROXIDE TiO_2 P25 powders with average particle size of 21 nm was also measured.

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2500 VBZ+/PC diffractometer using Cu-Kα radiation. N_2 adsorption–desorption isotherms were obtained using a Micromeritics ASAP2020M instrument. The morphology of the sample was examined by transmission electron microscope (TEM) on a JEM-3010. The scanning electron microscope (SEM) photographs of the samples were obtained using a Hitachi S-4700 electron microscope and the elemental analysis was performed by an energy dispersive X-ray spectroscopy (EDS) attached to the SEM.

3. Result and discussion

The SEM image of FTSC (Fig. 1a) reveals that the FTSC sample possesses hollow structure similar to foam. The magnified SEM image (Fig. 1b) shows that the FTSC consisted of agglomerated broken hollow spheres with a diameter of ca. 100 nm. By TEM image (Fig. 1c), the hollow structure with mesoporous shells can be clearly observed. The results of SEM and TEM show that the FTSC possesses a foamed structure with agglomerated thin mesoporous shells and cavities. The element content of Ti in FTSC was detected by EDS analysis (Fig. 1d) and the molar ratio of Ti/Si is1:4.6, which is nearly the same as the theoretical molar ratio of Ti/Si (1:4) calculated by the dosage of the precursors tetrabutyl titanate and TEOS.

Fig. 2a shows the XRD patterns of the FTSC and the commercial AEROXIDE TiO_2 P25 (P25). The XRD peaks of P25 are indexed as the mixed phases of anatase (JCPDS File no. 21-1272) and rutile (JCPDS card no. 21-1276). Compared with the P25, only anatase phase was detected for FTSC. The average particle size of TiO_2 in FTSC is 3.9 nm from the XRD peak at $2\theta=25.3^\circ$ by using the Debye–Scherrer formula. Fig. 2b shows the N_2 adsorption–desorption isotherm of the FTSC. It gives type-IV isotherms with a hysteresis loop, indicating the presence of mesopores in the wall of FTSC. The specific surface area (BET) of FTSC is 354 m^2/g. The pore size distribution of FTSC is shown in the inset of Fig. 2b. The result of pore size distribution shows that the average diameter of mesopores of FTSC is about 7.6 nm. Fig. 2c shows the N_2 adsorption–desorption isotherm of P25. The specific surface area of P25 is 59 m^2/g. The pore size distribution of P25 (inset of Fig. 2c) shows a wide pore size distribution range from 2 to 100 nm with an average diameter of about 16.9 nm, and the formation of its pore structure could be attributed to the aggregations of TiO_2 crystallites.

Fig. 3 displays the results of degradations of MB solution. In the absence of the catalyst, 20 mg/L of methylene blue was photolyzed only up to 1.2% in 3 h. On the contrary, the MB degradation rate increases obviously with the irradiation time using either FTSC or P25. Additionally, the photodegradation of MB with FTSC (78.8% in 3 h) was much more effective than that with P25 particles (46.7%

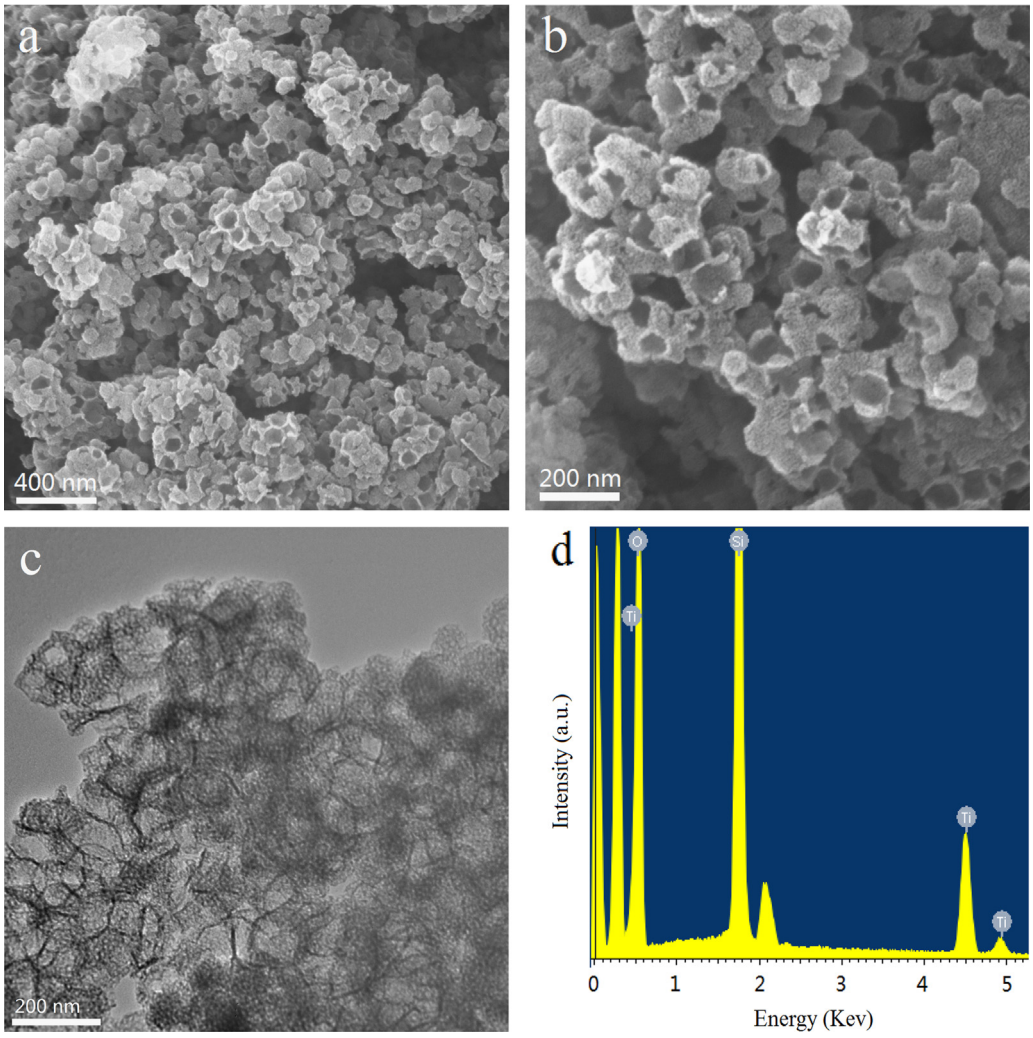

Fig. 1. (a) and (b) SEM images of FTSC, (c) TEM image of FTSC and (d) EDS pattern of the FTSC.