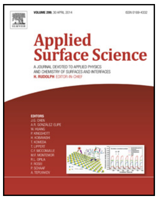
Applied Surface Science 299 (2014) 35–40

Contents lists available at ScienceDirect

Applied Surface Science

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



Preparation and characterization of N-doped visible-light-responsive mesoporous TiO_2 hollow spheres

Qiong Wu, Wei Li, Dianping Wang, Shouxin Liu*

Key Laboratory of Bio-Based Materials Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, Heilongjiang, PR China

ARTICLE INFO

Article history:
Received 13 November 2013
Received in revised form 27 January 2014
Accepted 27 January 2014
Available online 6 February 2014

Keywords:
TiO_2 hollow sphere
Visible-light response
Hard template
Carbon sphere

ABSTRACT

Visible-light-responsive N-doped TiO_2 mesoporous hollow spheres were prepared by acid-catalyzed hydrolysis, using carbon spheres obtained by glucose hydrothermal carbonization as a hard template. The spheres were characterized using scanning electron microscopy, transmission electron microscopy, N_2 adsorption–desorption isotherms, X-ray diffraction, ultraviolet-visible diffuse reflectance spectroscopy, and X-ray photoelectron spectroscopy. The effects of the N content and calcination temperature on the morphology and photocatalytic activity of TiO_2 were investigated. A visible-light response was obtained with TiO_2 hollow spheres of diameter 700–850 nm, shell thickness 100 nm, and a bimodal mesoporosity concentrated at 4–6 and 12–14 nm. Phenol degradation of 79.6% was achieved using a catalyst consisting of TiO_2 hollow spheres prepared with a Ti:N mass ratio of 1:0.5, and calcined at 600 °C.

1. Introduction

The controlled preparation of mesoporous structures with specific TiO_2 morphologies has attracted much attention in recent years [1]. Hollow-sphere particles can be regarded as nanoreactors [2], and can improve the catalytic performance by varying the internal microreaction environment. Recently, various chemical and physicochemical methods, including template methods [3], self-assembly techniques [4], super living chemical methods [5], and solvent thermal growth [6], have been developed for the preparation of TiO_2 hollow spheres. Among these techniques, template methods have several merits such as being simple and cheap, and enabling size control [7]. Syoufian et al. [8] prepared TiO_2 hollow spheres with smooth surfaces and controllable shell thicknesses by a sol-gel method, using polystyrene as the template; the achieved degradation of methylene blue under visible light was much higher than that obtained with commercial TiO_2. Ao [9] prepared hollow TiO_2 microspheres using carbon spheres (HCs) as a template, followed by treatment with hydrazine hydrate at 120 °C. The microspheres exhibited relatively high photocatalytic activity for X-3B degradation. In our previous study [10], size and morphology controllable HCs were prepared via glucose hydrothermal carbonization; they showed promise as hard templates for inorganic particle preparation.

Materials doped with nonmetals such as N [11], C [12], S [13], and N–F [14] have been found to have high photocatalytic activity under visible-light irradiation. According to the calculated densities of state in anion-doping of anatase TiO_2 crystals, N-doping is the most effective [15–17]. Asahi et al. [18] prepared N–TiO_2 with high visible-light catalytic activity, showing that N (2p) and O (2p) orbital hybridization can narrow the energy gap, leading to a visible-light response. Nakamura et al. [19] showed that N-doping can form an N_{2p} middle band gap above the valence band of O, in which visible light can activate electrons and induce visible-light catalytic activity. Peng et al. [20] showed that N entered the TiO_2 lattice, forming N–Ti–O and O–N–O, present as $(TiO_2)_m$–$(Ti_{1-y-m}O_{2-x-2m}N_{x+y})$, and the degradation of methyl orange under visible light achieved with this material was much higher than that obtained with P25.

Mesoporous N-doped TiO_2 hollow spheres were prepared by acid-catalyzed hydrolysis, using HCs as a hard template and urea as an N source. The effects of the N content and calcination temperature on the morphology, structure, crystalline phase, and photocatalytic activity of TiO_2 were investigated.

2. Experimental

2.1. Synthesis of HCs hard template

In a typical HCs synthesis [21], a glucose solution (0.7 mol/L, 40 mL) was placed in a stainless-steel autoclave of capacity 50 mL, and autoclaved at 180 °C for 5 h. The solution was then cooled

---

* Corresponding author. Tel.: +86 451 82191204; fax: +86 451 82191204.
E-mail address: liushouxin@126.com (S. Liu).

0169-4332/$ – see front matter © 2014 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.apsusc.2014.01.176

to room temperature. The black precipitate was collected and sequentially washed with water, pure ethanol, and acetone. The precipitate was dried at 80 °C for 6 h.

2.2. Preparation of N-doped TiO_2 hollow spheres

As-prepared carbon spheres (1.5 g) and a certain amount of urea were suspended in 150 mL of distilled water by continuous stirring (the mass ratios of Ti:N were 1:0.25, 1:0.5, 1:1, 1:1.5, and 1:2.0). $TiCl_4$ (1.5 mL) was then added dropwise to the stirred solution, which was maintained at a temperature of 5 °C. After vigorous stirring at 300 r/min for 1 h, a solution of $(NH_4)_2SO_4$ and HCl was added, and the mixture was stirred for 30 min, keeping the mass ratio of $TiCl_4$:$(NH_4)_2SO_4$:HCl at 1:2:10 during the reaction. The mixture was heated to 98 °C at a rate of 5 °C/min and kept at this temperature for 1 h. $NH_3{\cdot}H_2O$ was used to adjust the pH of the mixture to 8, and then the mixture was maintained at 98 °C for 1 h. After standing in air at room temperature for 12 h, the TiO_2 composite particles were washed several times with distilled water and ethanol. Finally, the prepared samples were heated in an air atmosphere to a certain temperature (500, 600, 700, 800, or 900 °C) at a heating rate of 25 °C/min, and held at this temperature for 2 h to remove the template. The obtained samples were labeled HTN_m-n, where m represents the reciprocal of the Ti:N mass ratio and n is the calcination temperature. TiO_2-600 samples without urea and templates were prepared for comparison.

2.3. Characterization

The morphologies and sizes of the products were observed using environmental scanning electric microscopy (SEM; Quanta 200, FEI, Hillsboro, OR, USA). The hollow morphologies were characterized using transmission electron microscopy (JEOL 2011, FEI Holland). The pore structure was characterized using N_2 adsorption–desorption isotherms measured at −196 °C with an ASAP 2020 instrument (Micromeritics, American). Prior to the gas adsorption measurements, the carbon was degassed at 120 °C under vacuum for 4 h. The Brunauer–Emmett–Teller (BET) surface area was calculated from the N_2 adsorption isotherms using the BET equation. The total pore volume was estimated at a relative pressure of 0.01–1.0. X-ray diffraction (XRD) measurements were performed with a Rigaku D/Max-rB diffractometer (Tokyo, Japan) using Cu-Kα radiation (45 kV, 40 mA, $\lambda = 1.54178$ Å). The absorption wavelength and energy gap were characterized using ultraviolet-visible (UV-vis) spectroscopy (TU-1900, Beijing) in the wavelength range 200–700 nm. X-ray photoelectron spectroscopy (XPS) was performed with a Physical Electronics PHI5700 spectrometer (Chanhassen, MN, USA), using Al-Kα radiation ($h\nu = 1486.6$ eV). The binding energies were referenced to the C_{1s} line at 284.6 eV. Quantitative analyses of C and O were based on the peak intensities of the C_{1s} and O_{1s} signals, respectively.

2.4. Photocatalytic activity tests

The photocatalytic activity tests [27] were carried out in a cylindrical quartz photoreactor (275 mL), using phenol as the model compound, with a 380 W Xe lamp (510 nm, Shanghai Hualun Lamp Factory, China) positioned inside the reactor as the light source. Photocatalyst powder (0.25 g) was added to an aqueous solution of phenol (100 mg/L, 250 mL). Before photocatalytic degradation, the suspension was magnetically stirred in the dark for 30 min to establish a phenol adsorption–desorption equilibrium. Samples (5 mL) were collected from the suspension and were immediately centrifuged at 1000 r/min for 10 min. The concentration of phenol after illumination was determined spectrophotometrically using a TU-1900 UV-vis spectrometer at 270 nm.

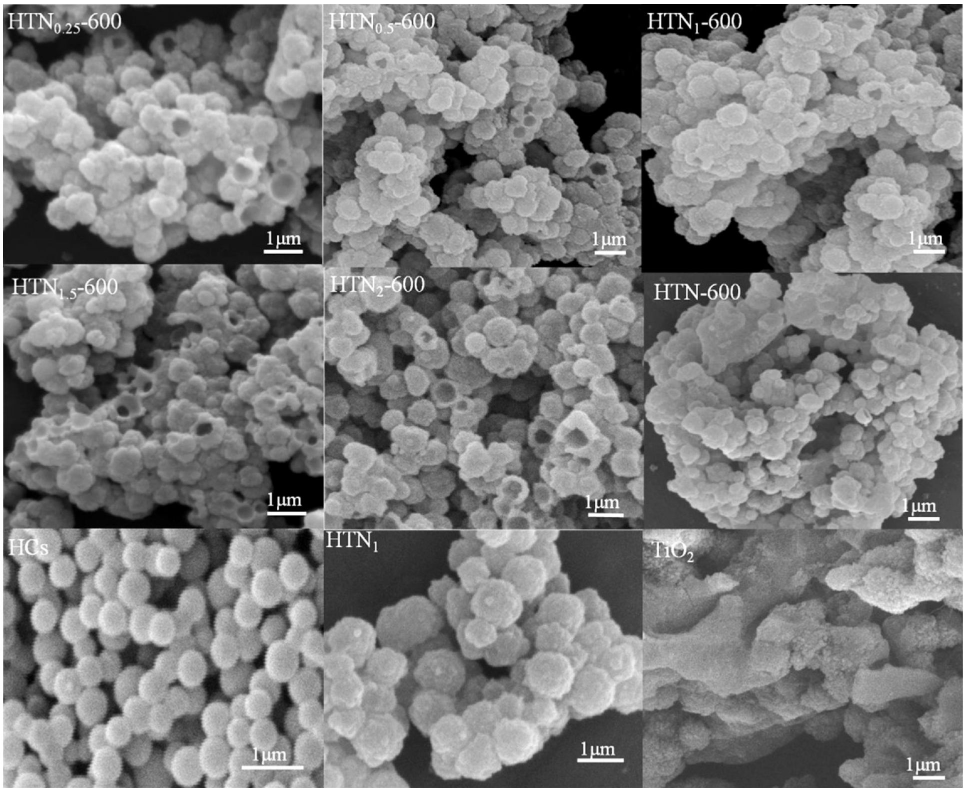


Fig. 1. SEM images of HTN_m-600, HCs, and TiO_2.