



Synergistic effects of hollow structure and surface fluorination on the photocatalytic activity of titania

Kangle Lv^{a,b,*}, Jiaguo Yu^{b,**}, Kejian Deng^a, Jie Sun^a, Yanxi Zhao^a, Dongyun Du^a, Mei Li^a

^a Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, South-Central University for Nationalities, Wuhan 430074, China

^b State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

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ABSTRACT

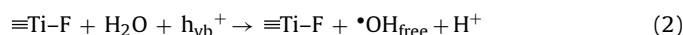
To study the synergistic effects of hollow structure and surface fluorination on the photoactivity of TiO₂, TiO₂ hollow microspheres were synthesized by a hydrolysis–precipitate method using sulfonated polystyrene (PS) as templates and tetrabutylorthotitanate (TBOT) as precursor, and then calcined at 500 °C for 2 h. The calcined samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and N₂ sorption. Photocatalytic activity was evaluated using reactive brilliant red X3B, an anionic organic dye, as a model pollutant in water. The results show that the photocatalytic activity of TiO₂ hollow microspheres is significantly higher than that of TiO₂ nanoparticles prepared in the same experimental conditions. At pH 7 and 3, the apparent rate constants of the former exceed that of the latter by a factor of 3.38 and 3.15, respectively. After surface fluorination at pH 3, the photoactivity of hollow microspheres and nanoparticles further increases for another 1.61 and 2.19 times, respectively. The synergistic effect of surface fluorination and hollow structure can also be used to prepare other highly efficient photocatalyst.

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1. Introduction

A great deal of effort has been devoted in recent decades in solving the widespread problem of contamination of effluent from urban and agricultural industries with biorecalcitrant and organic pollutants [1–9]. Various catalytic techniques have been applied in the field of environmental protection. Among which, TiO₂ photocatalysis has attracted increasing attention due to its biological and chemical inertness, strong photooxidation power, cost effectiveness, and long-term stability against photo and chemical corrosion [8–12]. However, a vital problem, i.e., low quantum efficiency (~4%), hampers its widespread practical applications [10,13,14]. To improve these properties, the morphologies and macroscopic structures of TiO₂ have been intensively studied [13,15–17]. For example, a three-dimensional porous structure of TiO₂ with a large surface area is known to exhibit an enhanced photocatalytic performance [18,19]. The submicron-scale hollow spheres of TiO₂ are promising because of their potential to provide a large

surface/volume ratio [17,19]. In addition, the diffractions on the hollow spheres and the reflections due to the shell structure would improve the functional properties of TiO₂ [13,19]. It has been recently reported that surface fluorination can result in significant enhancement in the photocatalytic activity of TiO₂, ascribed to the enhanced production of free •OH radicals in solution as a result of fluoride displacement of surface hydroxyl groups (Eqs. (1) and (2)) [11,12,20,21]. Interestingly, Choi and co-workers have demonstrated that the surface fluorination of TiO₂ also results in the enhanced photocatalytic degradation of stearic acid [22] and acetaldehyde [23] in gaseous phase, and they ascribed this to the enhanced generation of airborne free •OH radicals.



However, the synergistic effects of hollow structure and surface fluorination on the photoactivity of TiO₂ have not been reported yet. In the present work, we prepared hollow spheres of TiO₂ using sulfonated polystyrene (PS) as template, and the effect of surface fluorination on the photoactivity of hollow microspherical TiO₂ is examined, using reactive brilliant red X3B [10], an anionic organic dye, as the target organic pollutant.

* Corresponding author at: State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Luoshui Road 122#, Wuhan 430070, China. Tel.: +86 27 87952410; fax: +86 27 87952410.

** Corresponding author. Tel.: +86 27 87871029; fax: +86 27 87879468.

E-mail addresses: lvkangle@mail.scuec.edu.cn (K. Lv), jiaguoyu@yahoo.com (J. Yu).

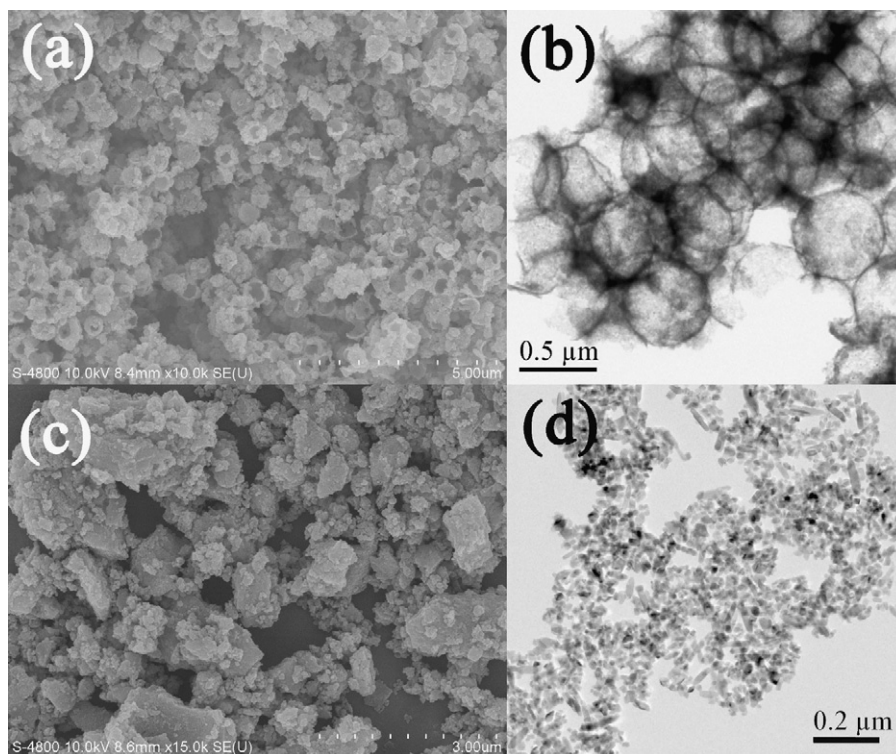


Fig. 1. SEM and TEM images of TiO₂ hollow microspheres (A and B) and nanoparticles (C and D).

2. Experimental

2.1. Preparation

Template of sulfonated PS with a diameter of 0.5 µm is prepared according to the literature [24], then 25 mL ethanol solution containing 0.3 mL tetrabutylorthotitanate (TBOT) was added dropwise to 15 mL of the sulfonated PS spheres ethanol solution (0.1 g/mL) under magnetic stirring. After that, 25 mL of ethanol solution containing 3.4 mL ammonia solution was dropped into the mixed solution. The resulted solution was stirred at 60 °C for another 2 h before it was refluxed for another 1.5 h. The solution was then filtered and the cake was washed with ethanol and water. TiO₂ hollow spheres were obtained after the cake was heated in air at 500 °C for 2 h to remove the PS templates. TiO₂ nanoparticles were also prepared accordingly in the absence of sulfonated PS template.

2.2. Characterization

The X-ray diffraction (XRD) patterns obtained on a D8 advance X-ray diffractometer (German Bruker) using Cu K α radiation at a scan rate of 0.02°/s were used to determine the crystallite size and identity. The accelerated voltage and applied current were 200 kV and 20 mA, respectively. The average crystallite size of the catalyst was determined according to the Scherrer equation using FWHM data after correcting for the instrumental broadening. The BET surface area (S_{BET}) of the powders was analyzed using nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen-adsorption apparatus (USA). The BET surface area was determined by a multi-point BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.3. Pore volume and average pore size (APS) were determined by nitrogen-adsorption volume at the relative pressure of 0.994. All the samples were degassed at 180 °C prior to the nitrogen-adsorption measurements. The morphologies of TiO₂ powders were observed on a field emission scanning electron microscope (SEM) (Hitach, Japan) with an acceleration voltage of

20 kV and transmission electron microscope (TEM) (Tecnai G20, USA) using an acceleration voltage of 200 kV.

2.3. Adsorption and photoactivity evaluation

Photocatalytic reactions were carried out using a high-pressure mercury lamp (375 W, Shanghai Yamin) as light source, emitted mainly at 365 nm. The reactor (80 mL) was made of a Pyrex glass, and positioned at a fixed distance of ca. 10 cm from the lamp. X3B was used as the target organic pollutant. HClO₄ and NaOH were used to adjust the solution pH, and NaF (1.0 mM), if necessary, was added in the solution for surface fluorination of TiO₂. Prior to illumination, a suspension containing 50.0 mg of catalyst and 50 mL of 1.0×10^{-4} mol/L X3B was continuously stirred in the dark for 12 h. The concentration of substrate in bulk solution at this point was used as the initial value for the adsorption and the further kinetic treatment of the photodegradation processes. During the photoreaction, the reactor was thermostated at 25 °C through a water recycle system and stirred mechanically at a constant rate. At given intervals of illumination, small aliquots of the suspension were withdrawn by syringe, centrifuged, and then filtered through a Millipore filter (pore size 0.45 µm). The filtrates were monitored by a UV–vis spectroscopy at 510 nm.

3. Results and discussion

3.1. Morphology and crystalline phase

Fig. 1A and B shows SEM and TEM images of the titania hollow microspheres prepared in the presence of spheric sulfonated PS template, respectively. In this preparation approach, TBOT is firstly adsorbed into the negatively charged sulfonated shell layer of PS templates [13]. After hydrolysis in a basic solution and calcinations, the PS template is removed and the hollow spheres of TiO₂ are obtained. The prepared TiO₂ hollow microspheres are monodispersed in a diameter of 0.5 µm and a shell thickness of 10–20 nm

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