



Simple fabrication of mesoporous TiO₂ microspheres for photocatalytic degradation of pentachlorophenol

Juan Xie^{a,b}, Li Bian^a, Lan Yao^a, Yongjing Hao^a, Yu Wei^{b,*}

^a College of Science, Hebei University of Engineering, Handan 056038, China

^b Key Laboratory of Inorganic Nanomaterials of Hebei Province, Hebei Normal University, Shijiazhuang 050024, China

ARTICLE INFO

Article history:

Received 15 July 2012

Accepted 20 September 2012

Available online 5 October 2012

Keywords:

TiO₂

Porous materials

Powder technology

Photocatalysis

Pentachlorophenol

ABSTRACT

Mesoporous TiO₂ microspheres of sizes varying from 0.5 to 4.5 μm, which are composed of numerous pure anatase TiO₂ nanoparticles of diameter ~18 nm were successfully synthesized via a facile route without any template or structure-directing agent. XRD, FESEM, UV–vis DRS and N₂ adsorption–desorption analysis were used to characterize the product. A possible auto-orientation assembly formation mechanism of the TiO₂ spherical structure has been proposed. Experimental results show that the obtained mesoporous TiO₂ microspheres can be used as photocatalyst to effectively degrade persistent organic pollutant pentachlorophenol under UV irradiation, and the photocatalytic activity of them is much higher than that of commercial P25.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Pentachlorophenol (PCP) is a ubiquitous soil and water contaminant because of its widespread application in agriculture, industry, and commercial product formation and preservation [1]. This compound can not only alter the electrical conductivities of biomembranes and inhibit cellular enzymes, but also produce mutations in animal (including human) cells and exhibit teratogenic, carcinogenic, and reproductive effects [2,3]. Unfortunately, conventional physicochemical and biological processes are not efficient for degradation of PCP due to its stable aromatic ring system and chlorine substituents. In recent years, advanced oxidation processes (AOPs) have been employed to treat chlorinated phenols, especially photocatalytic method in which TiO₂ is the most commonly used photocatalyst [4,5].

It is well known that photocatalytic activity of TiO₂ is related to its morphology besides crystal structure, since the photocatalytic reactions often take place on the surface of catalysts. So far, various structures of TiO₂ have been reported, including tubes, wires, rods, fibers, microspheres and so on. Among them, three-dimensional (3D) TiO₂ spheres have received increasing attention owing to their excellent performances and intrinsic properties [6,7]. However, most approaches employed to fabricate TiO₂ spheres involve cumbersome processes and are prone to generate by-products, because they usually adopt templates or structure-directing agents, such as PEG 200, FC-4, nonanoic acid and so on

[8–10]. Therefore, it is scientifically and practically significant to develop simple, mild, and environmental friendly methods for the synthesis of spherical TiO₂ photocatalysts.

In this work, mesoporous TiO₂ microspheres were prepared via a facile route, only using water and Ti(OC₄H₉)₄ as reactants. Photocatalytic activity of the sample was evaluated by measuring the photodegradation of PCP. To the best of our knowledge, there is not any similar report about mesoporous TiO₂ microspheres for the photocatalytic degradation of pentachlorophenol at present.

2. Experimental

All chemicals were of analytical grade and used as received without further purification. TiO₂ used for comparison was Degussa P25 (Frankfurt, Germany), whose surface area and particle size were reported 50 m² g⁻¹ and 21 nm, respectively [11].

0.5 mL distilled water was introduced into 50 mL anhydrous alcohol to get a mixture solution, which was treated in an ultrasonic cleaning bath (250 W) for 30 min, and then was stirred violently at room temperature for 5 h. After that, 3.40 mL Ti(OC₄H₉)₄ diluted in 6.6 mL anhydrous alcohol was added into the aforementioned solution, followed by mild continuous stirring for 5 h. White product was collected by filtration, washed with anhydrous alcohol, air-dried at ambient temperature, and finally calcined at 500 °C for 2 h in air.

The X-ray diffraction (XRD) pattern was examined using a Bruker D8 Advance diffractometer, equipped with a Cu-Kα radiation. Morphology of the product was characterized by field

* Corresponding author. Tel.: +86 311 8626 8342; fax: +86 311 8589 3425.
E-mail address: hbsdweiyu@163.com (Y. Wei).

emission scanning electron microscopy (FESEM, HITACHI S-4800). N_2 adsorption–desorption isotherms were obtained at 77 K on an Omnisorp 100CX instrument, and pore size distributions were determined from desorption branch of the isotherms with the BJH method.

Photocatalytic experiments were carried out by adding 0.1 g photocatalyst powders into 100 mL PCP aqueous solution (10 mg L^{-1} , pH 9–10) with ultrasonic treatment for 15 min. Before illumination, the suspension was stirred continuously in dark for 30 min to ensure adsorption equilibrium. A 125 W low-pressure mercury lamp with main wavelength of 253.7 nm was used as light source, and the distance between the lamp and the solution is about 10 cm. Aqueous suspension, containing PCP and powder catalyst taken out at regular intervals, was centrifugally separated and filtrated through millipore filter to remove the catalyst. The kinetic photodecomposition process was monitored by measuring the residuary concentration of PCP with a UV–vis spectrophotometer (TU1900, Beijing Purkinje General Instrument Co. Ltd., China) at 220 nm, and each concentration was repeatedly determined at least three times.

3. Results and discussion

XRD pattern of the as-synthesized sample is shown in Fig. 1a. All the diffraction peaks are well assigned to anatase phase TiO_2 (JCPDS 21-1272). Diffraction peaks are a little broadened, suggesting the nanocrystalline feature of the sample. Average crystallite size of TiO_2 particles calculated by applying Debye–Scherrer's equation is approximately 17.2 nm, which is smaller than that of Degussa P25. As shown in Fig. 1b and c, the sample consists of TiO_2 microspheres in sizes varying from 490 nm to 4.5 μm . Pits on the product surface and some discernible fragments may result from the ultrasonic treatment before FESEM observation. High magnification FESEM images (Fig. 1d and e) demonstrate that the surface of big spheres is much smoother than that of small spheres. It is noteworthy that no matter how big the sphere is, it is assembled from numerous nanoparticles of diameter $\sim 18 \text{ nm}$, which is in good agreement with XRD calculating result.

Fig. 2 depicts the N_2 adsorption–desorption isotherm and the BJH pore size distribution of as-synthesized TiO_2 microspheres. As

can be seen, the isotherm belongs to type IV with H2 hysteresis-loop, indicating the existence of porous structure. The corresponding BJH analysis reveals that these porous TiO_2 microspheres have very narrow pore size distribution (2.0–10.0 nm) centered 4.0 nm (Fig. 2b). According to the BET method, the sample has a specific surface area of $112.6 \text{ m}^2 \text{ g}^{-1}$, which is much higher than that of Degussa P25.

Based on the above characterization results, consulting the aggregation growth theory put forward by Shi et al. [12], a possible auto-orientation assembly formation process is proposed in Scheme 1. Ultrasonic treatment and stirring process make trace water uniformly dispersed in ethanol solvent. The $H_2O:Ti(OC_4H_9)_4$ M ratio is extremely low, so that hydrolysis reaction is limited, and plenty of TiO_2 nuclei of several nanometers in diameter (i.e. primary particles) form after introducing $Ti(OC_4H_9)_4$. To minimize the overall energy of the reaction system, primary particles tend to aggregate together and form 3D structures (i.e. secondary particles). Because aggregation growth mode can occur between nuclei, large particles, even nucleus and large particle with the increase of reaction time, some primary particles continuously incorporate into secondary particles, making them become more spherical aggregates (I), while some secondary particles rotate and rearrange to find a suitable place to further reduce the surface energy, leading to much larger aggregates (II). Finally, TiO_2 aggregates with spherical (III), pseudo-spherical (IV), and even multisphere connective (V) structures are obtained. In addition, with the formation of 3D structures, the diameter of each individual TiO_2 particle also increased to some extent. Massive pores of the as-synthesized TiO_2 microspheres would probably come from the agglomeration of TiO_2 nanoparticles.

Fig. 3 displays the degradation efficiency of PCP versus irradiation time over as-synthesized TiO_2 microspheres. For comparison, the well-known and highly active Degussa P25 photocatalyst was investigated under the same conditions. Blank study (absence of catalyst) was carried out as a background check. It could be observed that without catalyst, only $\sim 40\%$ of PCP was degraded even after 135 min. In contrast, the degradation efficiency of PCP enhanced greatly in the presence of catalysts. In 135 min, the removal of PCP on P25 was $\sim 80\%$, while porous TiO_2 microspheres showed much higher catalytic activity, and PCP was almost completely eliminated within 120 min. Furthermore, TiO_2

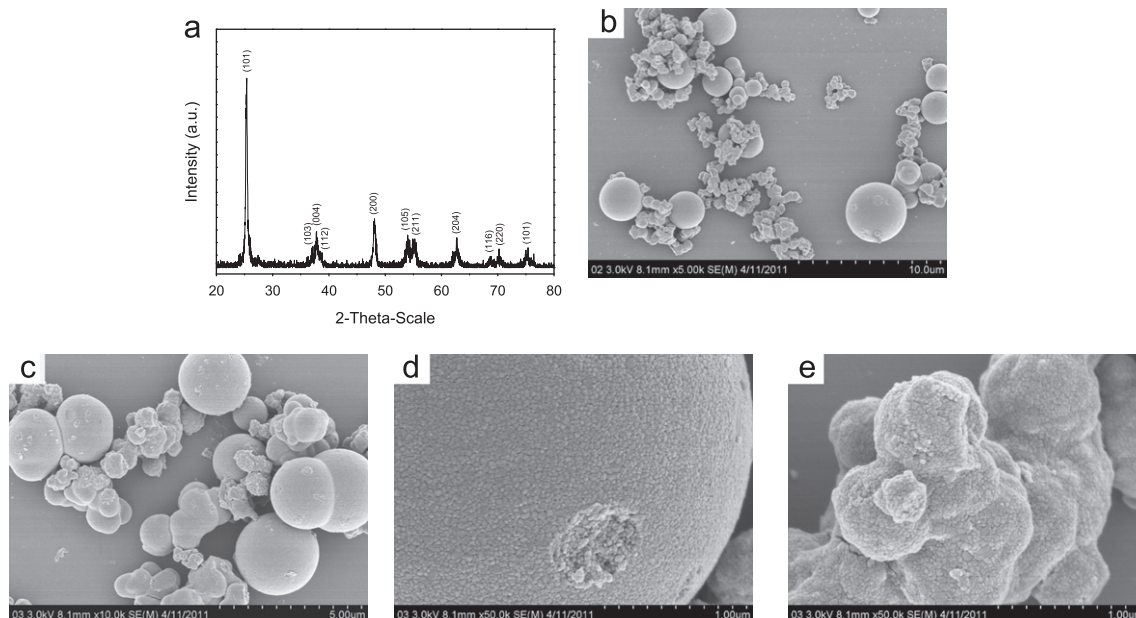


Fig. 1. (a) XRD pattern, (b and c) low and (d and e) high-magnification FESEM images of TiO_2 microspheres.

Download English Version:

<https://daneshyari.com/en/article/1646072>

Download Persian Version:

<https://daneshyari.com/article/1646072>

[Daneshyari.com](https://daneshyari.com)