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A Facile Synthesis of Hierarchically Porous TiO_2 Microspheres with Carbonaceous Species for Visible-light Photocatalysis

Weigang Liu, Yingming Xu, Wei Zhou, Xianfa Zhang, Xiaoli Cheng *, Hui Zhao, Shan Gao, Lihua Huo **

Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China

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Hierarchically porous anatase TiO_2 microspheres composited with carbonaceous species (TCS) have been successfully fabricated by a one-step template-free solvothermal method, combined with subsequent low temperature dried process. In this configuration, the TCS microspheres are constructed by the interconnected porous nanosheets, which are further assembled with abundant nanoparticles and carbonaceous species. Such composite microspheres possess a large specific surface area of 337 m^2 g^{-1}, uniform mesopores of 3.37 nm and high total pore volumes of 0.275 cm^3 g^{-1}. The materials exhibit the enhanced photocatalytic properties and stability for degradation of rhodamine B (RhB) under visible-light irradiation. The enhanced photocatalytic degradation performance may be ascribed to their abundant porous structure, large specific surface area and the unique assist-function of the carbonaceous species.

1. Introduction

In the face of the energy shortage and the destruction of ecological balance, how to take advantage of environmentally friendly solar energy is one of the most extremely urgent works to the researchers[1]. Since Fujishima and Honda[2] firstly utilized UV illuminant for photoelectrochemical water-splitting on the TiO_2 electrode in 1972, TiO_2 has been widely used as a kind of photocatalyst for solar energy conversion and environmental applications due to its high chemical stability, non-toxicity, large titanium source and low cost[3]. In recent years, hierarchically porous TiO_2 exhibited remarkable and highly efficient photocatalysis for the decomposition of toxic organic pollutants in view of their high specific surface area and more activated sites on the surface[4,5]. For instance, Zhu et al.[6] reported a facile one-step template-free hydrothermal method to synthesize hierarchically nanoporous structures of TiO_2 with large specific surface area of 170 m^2 g^{-1}, which performed good degradation capacity under UV light irradiation. Zhou and his group[7] prepared mesoporous anatase TiO_2 through an evaporation-induced self-assembly technique for degradation of toxic 2,4-dichlorophenol under UV irradiation, and this catalyst also possessed high specific surface area of 122 m^2 g^{-1}. It implies that the TiO_2 nanomaterials with high specific area will show good photocatalytic degradation property. However, the application of pure TiO_2 is limited due to its wide band gap (anatase titanium is 3.2 eV, rutile titanium is 3.0 eV)[8], it can be activated only under the UV light illumination which makes up only a small fraction (<4%) of the total solar spectrum[9,10].

To overcome the shortcoming of the wide band gap energy of the pure TiO_2 and make full use of solar energy, considerable efforts have been carried out, for instance, metallic ions doped (e.g. V, Cr, Fe, Co, Mn, Mo, Ni, Cu, Y, Ce and Zr)[11–13], noble metals loaded (Au, Ag, Pt)[14,15], nonmetallic element doped (e.g. N, S, C, F, B)[16–20], and nonmetallic material modified[21–23] TiO_2 materials were studied. Among these decorated TiO_2 materials, metallic ion doped materials lacked the necessary thermal stability and exhibited low photocatalytic efficiency. Nonmetallic element doped or nonmetallic material modified TiO_2 materials demonstrated a significant improvement of the visible-light photocatalytic efficiency[24], especially carbon material modification has been proved to be an excellent candidate for extending the absorption spectrum of TiO_2 to the visible light region.

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* Corresponding author. Ph.D.; Tel.: +86 451 86608426; Fax: +86 451 86608426.
E-mail address: xiaolicheng@foxmail.com (X. Cheng).

** Corresponding author. Ph.D.; Tel.: +86 451 86608040; Fax: +86 451 86608040.
E-mail address: lhhuo68@yahoo.com (L. Huo).

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Recently, carbonaceous modified materials have attracted intensive research attention, which is an efficient method to overcome the disadvantages of pure anatase TiO_2. This is mainly because carbonaceous species can facilitate electron transfer and bind with TiO_2 by forming coordination bonds between functional groups and Ti^{4+} centers[25]. And they can also efficiently compensate for the disadvantages of the individual component, and induce a synergistic effect, such as an efficient charge separation and improvement of photostability[26]. An et al.[27] used a novel method to prepare TiO_2/MWCNT composites for phenol degradation with the irradiation light range of 450–900 nm. Sampaio et al.[28] fabricated GO-TiO_2 composites, comprising of 4 wt% carbon through multistep reaction, which exhibited the efficient degradation of microcystin-LA under simulated solar light and visible light irradiation. Zhao et al.[24] synthesized porous dyad structure of anatase phase TiO_2@carbon by adding furfural as carbon precursor via one-step solvothermal method. The as-synthesized materials possessed a surface area of 120 m^2 g^{-1} and visible light photocatalysis for degradation of methyl orange. Recently, Liu et al.[29] utilized $Ti(BuO)_4$ as a source for both Ti and carbon to obtain two carbon states (graphite-like and carbonate-like species) modified mesoporous anatase TiO_2 powders through xerogel carbonization in a hypoxic atmosphere (5% O_2, 95% N_2) at 400 °C. The obtained samples showed a high activity for degradation of methyl orange and phenol under visible light irradiation because the graphite-like and carbonate-like species narrowed the band-gap of anatase TiO_2. Although carbon modified TiO_2 has been prepared under special conditions, most of these methods needed high temperature, or complicated synthetic process with more than two steps. This is very complex and expensive to scale up for practical applications. Thus, it is still a challenge to realize a one-step synthesis of carbon modified TiO_2 with high specific surface area and uniform mesoporosity, especially maximizing light absorption in the visible-light region.

Herein, we report a facile one-pot template-free solvothermal method for the fabrication of 3D hierarchically porous TiO_2 microspheres composited with carbonaceous species (TCS) which are only dried at low temperature of 150 °C. Moreover, the as-prepared TCS possesses high-performance for the photocatalytic decomposition of RhB, which is attributed to their abundant porous structure, the larger specific surface area and strong adsorption ability. It can be reused for 5 times and the porous structure still preserves well without collapse and deformation.

2. Experimental

2.1. Chemicals

In this work, all of the materials were analytic reagent, directly used without further purification. Water was deionized (DI) water (18.2 MΩ cm) purified by Millipore (PL5122, USA). Commercial TiO_2 nanoparticles (P25) with a phase composition of 80% anatase and 20% rutile were purchased from Degussa Chemicals (Hanau, Germany).

2.2. Preparation of hierarchically porous TCS

Titanium diisopropoxide bis(acetylacetonate) (TDAA) was used as the titanium source and carbonaceous species source. In a typical synthesis, 0.458 mL TDAA was slowly dissolved in 30 mL isopropyl alcohol under continuously magnetic stirring, and then 0.2 mL glacial acetic acid was further slowly injected. The as-obtained mixed solution was constantly stirred for another 1 h to ensure homogeneous, and then transferred to a Teflon-lined stainless steel autoclave with 50 mL volume, followed by solvothermal treatment at 150 °C for 12 h. After being cooled to room temperature, the gray powders were isolated by a centrifuge with 9000 rotational speed per min, washed with deionized water and ethanol twice, respectively. Then the TCS were dried at 60, 100, 150 and 200 °C in an electric oven for 24 h, respectively (hereafter referred to as TCS-60, TCS-100, TCS-150 and TCS-200 in order). Especially, additional two portions of the TCS were calcined at 300 and 500 °C for 1 h, respectively (hereafter referred to as TCS-300 and TCS-500).

2.3. Materials characterization

The surface morphology of the obtained samples treated at different temperatures was measured by using scanning electron microscope (SEM, Hitachi S-4800, Japan). The crystalline phase of the samples was investigated by X-ray diffraction meter (XRD, Bruker D8 Advance, Germany) using Cu$K\alpha$ radiation with $\lambda = 0.15405$ nm, the voltage is 40 kV and the current is 100 mA. Thermogravimetric-differential thermal analysis (TG-DTA) was carried out using Perkin-Elmer model Pyris-Diamond thermal analysis equipment (Perkin Elmer, USA) from room temperature to 800 °C at a heating rate of 10 °C min^{-1} under air, severally. Transmission electron microscope (TEM, FEI Tecnai G2 F20 S-Twin, Japan) was also employed to examine the morphology and fine structure of the products, operating with 200 kV accelerating voltage. Fourier transform infrared (FT-IR) spectra were recorded in the region of 400–4000 cm^{-1} by an FT-IR spectrometer (Bruker, Equinox55, Germany) using KBr as reference. UV-vis diffuse reflectance spectra (DRS) were recorded through a UV-vis spectrometer (BWS002, BWTEK, USA) with $BaSO_4$ pellets. Compositional analysis of the samples was performed using X-ray photoelectron spectroscope (XPS) (VG Scientific, ESCALAB 250, England) with a standard and monochromatic source (Al$K\alpha$) radiation ($h\nu = 1486.6$ eV) within ±0.2 eV deviation in the binding energy position. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C 1s line to 284.5 eV. Brunauer–Emmett–Teller (BET) specific surface area and Barrett–Joyner–Halenda (BJH) pore structure of the obtained products were completed at 77 K on a TriStar3000 gas adsorption instrument (Micro-metrics Instruments, TriStar II 3020, USA) via N_2 adsorption–desorption process.

2.4. Photo-degradation measurement

The photocatalytic properties of the samples to rhodamine B (RhB) were evaluated under visible light irradiation. A 150 W xenon lamp equipped with optical filters (≥420 nm) was used to ensure the wavelengths more than 420 nm, the distance between the dye and the light source was 18 cm and the optical irradiance at the sample was 250 μw cm^{-2}. For a comparison experiment under UV light irradiation, a light source of 160 W Hg lamp was also used. The irradiation distance was also kept 18 cm. Fifteen milligrams of the obtained catalyst was dissolved in 15 mL of RhB solution with a concentration of 20 mg L^{-1}, which was sonicated for about 1 min. Before the photocatalytic reaction, the suprasil quartz cylindrical bottle was placed 18 cm apart from the lamp source, the optical irradiance at the sample was 2000 μw cm^{-2} and the whole reaction process was kept under continuously stirring. The photocatalytic reaction was initiated in dark for 30 min to reach adsorption–desorption equilibrium between the RhB and the photocatalyst. During the experiment, roughly 4 mL solution was extracted into a small centrifugal tube at certain time intervals of 30 min and centrifuged to separate from catalyst, and then the RhB filtrates were measured with a UV-vis spectrophotometer (Agilent 8453, USA).

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