Research Article

Fabrication and Characteristics of Macroporous TiO\textsubscript{2} Photocatalyst

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Macroporous TiO\textsubscript{2} photocatalyst was synthesized by a facile nanocasting method using polystyrene (PS) spherical particles as the hard template. The synthesized photocatalyst was characterized by transmission electron microscope (TEM), scanning electron microscopy (SEM), thermogravimetry-differential thermogravimetry (TG-DTG), X-ray diffraction (XRD), and N\textsubscript{2}-sorption. TEM, SEM, and XRD characterizations confirmed that the macroporous TiO\textsubscript{2} photocatalyst is composed of anatase phase. The high specific surface area of 87.85 m\textsuperscript{2}/g can be achieved according to the N\textsubscript{2}-sorption analysis. Rhodamine B (RhB) was chosen as probe molecule to evaluate the photocatalytic activity of the TiO\textsubscript{2} catalysts. Compared with the TiO\textsubscript{2} materials synthesized in the absence of PS spherical template, the macroporous TiO\textsubscript{2} photocatalysts sintered at 500°C exhibits much higher activity on the degradation of RhB under the UV irradiation, which can be assigned to the well-structured macroporosity. The macroporous TiO\textsubscript{2} material presents great potential in the fields of environmental remediation and energy conversion and storage.

1. Introduction

For the environment protection purpose, the disposal of various toxic dyes from the textile industry has attracted extensive attention. Rhodamine B (RhB) is widely used as a colorant in textiles and food stuffs and is also a well-known water tracer fluorescent [1]. It is harmful to human beings and animals and causes irritation of the skin, eyes, and respiratory tract.

Owing to high photocatalytic efficiency, good oxidation capability, stable chemical reaction, low cost, and nontoxicity, titanium dioxide (TiO\textsubscript{2}) has been applied widely in wastewater treatment [2–4], environment purification [5, 6], solar energy transfer [7, 8], chemical sensing [9, 10]. Recently, it was found that incorporation of well-defined porosity of TiO\textsubscript{2} materials could greatly enhance the photoactivity in the area of environmental remediation and energy conversion [11–13]. For a variety of practical applications, the fabrication of desired structure with network is important as well as control in grain size, crystallinity, and composition [14–16].

At present, porous TiO\textsubscript{2}, combining the outstanding properties of TiO\textsubscript{2} with their porous structure, has gained great research interests, and various synthetic techniques had been developed. For example, Liu et al. prepared anatase TiO\textsubscript{2} porous thin films by sol-gel method with CTAB surfactant as a pore-forming agent, and many factors were studied [17]. Bala et al. fabricated hollow spheres of anatase TiO\textsubscript{2} by spherical CaCO\textsubscript{3} nanoparticles as a template and investigated the photocatalytic activity [18]. Zheng et al. synthesized rutile and anatase TiO\textsubscript{2} mesoporous single crystals with diverse morphologies by silica-templated hydrothermal method [19]. Dong et al. prepared highly ordered transparent TiO\textsubscript{2} macropore arrays via a glass-clamping method and investigated the potential application in degradation of organic dyes [20]. However, the general synthesis usually involved complicated multistep to obtain porous skeleton. Firstly, it is required to assemble spheres into colloidal crystals as templates, and then the precursor is filled into interstices among the crystals for several times [21–23]. Moreover, for an efficient photodegradation catalyst, the macroporous structure is essential due...
to the run-through-macropore network which maximizes the uptake and the diffusion of the organic molecules [24–26]. Additionally, the porous structures are propitious to enhance the light scattering and improve the utilization rate of irradiation light [27–29].

Herein, a simple method without assembly and filling steps was introduced in this work for the preparation of macroporous TiO$_2$ through a sol-gel process using polystyrene spheres as sacrificial templates. Compared with the TiO$_2$ materials synthesized in the absence of PS spherical template [30, 31], the macroporous TiO$_2$ photocatalyst sintered at 500°C exhibits much higher activity on the degradation of RhB under the UV irradiation. The macroporous TiO$_2$ material present great potential in the fields of environmental remediation and energy conversion and storage.

2. Experiment

2.1. Materials. Tetrabutyl titanate (Ti(OC$_4$H$_9$)$_4$), sodium styrene sulfonate, sodium hydrogen carbonate, potassium persulfate, ethanol, Rhodamine B (RB), acetic acid, and nitric acid were all analytical grade and used without further purification. Styrene was washed by 5% NaOH solution several times to remove polymerization inhibitor. All of the reagents were purchased from Shanghai Chemical Reagent Ltd. Co.

2.2. Preparation of PS Microspheres. PS spheres were obtained by emulsion polymerization of styrene according to previous reports [32–34]. At first, 150 g deionized water was poured into a 300 mL jacket reactor, which was kept at 85°C until the end of the reaction. Then, 0.08 g sodium styrene sulfonate as the emulsifier and 0.0633 g sodium hydrogen carbonate as the buffer were dissolved in the deionized water. Under constant stirring, 18.30 mL styrene monomer was added to this solution, accompanied with nitrogen protection. After 1 h, 0.0833 g potassium persulfate as an initiator was introduced into the solution. After 18 h polymerization, the monodispersed PS spheres with the average diameter of 278 nm were obtained, and the standard deviation of spheres was less than 2.76%.

2.3. Preparation of TiO$_2$ Sol. With the Ti(OC$_4$H$_9$)$_4$ as precursor, ethanol as solvent and glacial acetic acid as inhibitor, TiO$_2$ sol was synthesized by sol-gel method according to references elsewhere [35, 36]. The procedure can be divided into three steps. At first, solution A was prepared by mixing 3 mL deionized water and 16 mL absolute ethyl alcohol. And then solution B was obtained by adding 10 mL Ti(OC$_4$H$_9$)$_4$ and 2 mL glacial acetic acid into 32 mL ethanol slowly with the rapid stirring. At last, solution A was dripped slowly into solution B under rapid stirring. The homogeneous and transparent solution of TiO$_2$ sol was thus obtained.

2.4. Preparation of Macroporous TiO$_2$. In a typical synthesis of macroporous TiO$_2$, 11 mL PS spheres suspension with the concentration of 5.88 wt% was added slowly into 10 mL as-prepared TiO$_2$ sol. The intimate mixture was obtained by stirring and ultrasonication. Then, the mixture was placed in an oven at 70°C for 12 h and then TiO$_2$/PS sphere composites were obtained. To prepare macroporous TiO$_2$, the as-obtained composites were sintered in muffle furnace at 500°C for 2 h in air. The ultima product was denoted as m-TiO$_2$. For contrast, the synthesis of TiO$_2$ nanoparticles was the similar to the preparation of macroporous TiO$_2$ without adding the PS spheres, which was labeled as r-TiO$_2$.

2.5. Characterization. Field emission scanning electron microscopy (FE-SEM) was carried out on FEI Sirion-200 and transmission electron microscopy TEM was taken on JEM JEM-2100. The XRD patterns of the synthesized samples were obtained by a Bruker-AXS D8 Advance diffractometer with CuK$_α$ radiation ($\lambda = 0.15418$ nm). To determine the proper sintering temperature and analyze the weight content of PS spheres in the TiO$_2$/PS composites, both the as-prepared PS spheres and TiO$_2$/PS composites were investigated by thermogravimetry and derivative thermogravimetry (TG-DTG), which was operated at a program-controlled temperature elevation rate of 10°C/min in the air. N$_2$ adsorption-desorption isotherms were measured on a Quantachrome NOVA 2000e sorption analyzer at liquid nitrogen temperature (77 K). The samples were degassed at 120°C overnight prior to the measurement. The surface areas were calculated by the multipoint Brunauer-Emmett-Teller (BET) method.

2.6. Photocatalytic Experiment. The photocatalytic activity tests of the synthesized TiO$_2$ were performed by the degradation of Rhodamine B (RhB) under UV light irradiation under ambient conditions. The experiment was performed in a water-jacket reactor operated at 20°C. The light source was a 450 W high-pressure mercury lamp (Foshan Electrical and Lighting Co. Ltd.) with a strong peak centered at 362 nm. The distance between the sample and the lamp was about 10 cm. In a typical process, 0.1 g of the obtained product was placed into 100 mL of RhB aqueous solution ($2 \times 10^{-5}$ mol/L) under magnetic stirring. 5 mL of the mixture was collected at a given time interval of 15 min and was then centrifuged to discard any sediment. Then the concentration of RhB was determined on a TU-1810 UV-vis spectrophotometer at $\lambda_{max} = 553$ nm [37, 38]. The decomposition efficiency of RhB was calculated by the following formula:

$$\text{Decomposition efficiency} = \frac{A_0 - A_t}{A_0} \times 100\%, \quad (1)$$

where $A_0$ and $A_t$ represent the absorbance of the RhB solution before irradiation and the absorbance at time $t$, respectively.

3. Results and Discussion

3.1. Material Characterization. TG-DTG curves of both PS spheres and the TiO$_2$/PS composites are shown in Figure 1. For PS spheres, three weight loss stages, below 300, 300–400, and 400–500°C, can be observed. The PS spheres undergo endothermic desorption of physically adsorbed water and
residual solvent at low temperature below 300°C. The major weight loss of about 90% between 300 and 400°C can be assigned to the thermal decomposition of the polystyrene, which was decomposed from long chain to shorter chain and then depolymerized into volatile monomers with low molecular weight. While, the third stage in the range of 400–500°C can be attributed to the combustion of the residual coke. With respect to the TiO$_2$/PS nanocomposite, it is found that PS spheres can be completely removed at 500°C (Figure 1(b)). Thus, 500°C was selected as the calcination temperature to prepare the macroporous TiO$_2$ photocatalyst. The weight content of TiO$_2$ in the TiO$_2$/PS nanocomposite is calculated to be 43.2%.

XRD are employed to characterize the crystallite structure of the synthesized TiO$_2$ catalysts. It can be seen from Figure 2(a) that the diffraction peaks of TiO$_2$ after being calcinated at 450°C can be indexed to anatase phase TiO$_2$ (JCPDS NO. 21-1272) and rutile phase TiO$_2$ (JCPDS NO. 21-1276), indicating that the sample calcined at 450°C is composed of bicrystalline phase. When the calcination temperature was increased to 500°C, all diffraction peaks can be indexed to pure anatase phase (JCPDS NO. 21-1272), and no characteristic peaks of other impurities can be detected. Thus, 500°C is a proper sintering temperature to prepare anatase phase macroporous TiO$_2$, which is in accordance with the TG-DTG analysis (Figure 1). The sharp diffraction peaks in Figure 2(b) illustrate the well crystallization of m-TiO$_2$ after the heat treatment. The crystallite size ($D$) was calculated to be about 10 nm according to the Scherrer formula $D = K\lambda/\beta\cos\theta$ [39], where $K$ is a constant (shape factor, about 0.9), $\lambda$ is the X-ray wavelength (0.15418 nm), $\beta$ is the full-width at half-maximum, and $\theta$ is the diffraction angle. The values of $\beta$ and $\theta$ were taken from TiO$_2$ (101) diffraction line.

TEM images of the PS spheres and m-TiO$_2$ are given in Figure 3. Figure 3(a) shows the TEM image of the PS spheres. The size of the PS spheres is about 278 nm, and the standard deviation of monodispersed spheres is less than 2.76%. This indicates that the PS spheres are suitable to be employed as macroporous templates. As shown in Figure 3(b), the PS spheres are wrapped by TiO$_2$ nanoparticles before being sintered. Figure 3(c) shows the low-magnification TEM image of macroporous TiO$_2$ sintered at 500°C in air, from which macropores can be clearly seen, suggesting that PS spheres have been completely removed after calcination at 500°C in air. And the SEM image (Figure 3(e)) also demonstrates well-defined macroporous structure. The size of the hollow spheres is about 240 nm, which is smaller than the size of original PS spheres template, suggesting the significant shrinkage after the PS removal via calcination. Additionally, Figure 3(c) also illustrates that run-through-macropore network structure was formed. And the SEM images in Figure 3(e) further confirm that the macropores left by the templates are interconnective with neighboring hollow
spheres. High-resolution TEM image (Figure 3(d)) displays that the crystalline size of TiO$_2$ nanoparticles is about 10 nm, which is in good agreement with the XRD analysis.

N$_2$ adsorption-desorption measurements were performed to investigate the textural properties of the macroporous TiO$_2$. The N$_2$ adsorption-desorption isotherms of r-TiO$_2$ and m-TiO$_2$ are shown in Figure 4. One can see that the isotherm of the r-TiO$_2$ is of typical type IV, characteristic of mesoporous materials, according to IUPAC classification. The adsorbed nitrogen volume for m-TiO$_2$ becomes steep in the $P/P_0$ range of 0.8–1.0, which indicates the presence of large macropores. Based on the Brunauer-Emmett-Teller (BET) equation, the specific surface areas of r-TiO$_2$ and m-TiO$_2$ were evaluated to be about 91.2 and 87.8 m$^2$/g, respectively.

3.2. Photocatalytic Activity Test. The photocatalytic activities of the prepared TiO$_2$ samples were examined through the photodegradation of RhB under UV light irradiation. The degradation efficiency was illustrated by the change of the RhB concentration during the photodegradation process and the results were shown in Figure 5. The photocatalytic results reveal that the photocatalytic activity of the macroporous TiO$_2$ was significantly improved as compared to that of the traditional TiO$_2$ nanoparticles. For the macroporous TiO$_2$, 92.63% of the RhB was decomposed after 2h irradiation.
However, as to the r-TiO₂ sample, the degradation percentage is only 81.66%. Here, the macroporous structure is believed to facilitate the transportation of reactant molecules and products through the interior space due to the run-through-macropore networks [40–43] and to favor the harvesting of exciting light due to enlarged surface area and multiple scattering within the porous framework [43, 44]. So the enhanced photoactivity of m-TiO₂ could be achieved.

4. Conclusions

In summary, macroporous TiO₂ photocatalyst was successfully synthesized via a simple sol-gel method using polystyrene spheres as sacrificial templates. The prepared macroporous TiO₂ exhibited higher photocatalytic activity than the TiO₂ sample through a template-free approach in catalyzing the degradation of RhB under UV light illumination. And the superior photocatalytic performance can be related to the run-through-macropore network structure. Considering the facile preparation and high photocatalytic activity, the macroporous TiO₂ materials display a good potential in the fields of environmental remediation and energy conversion and storage.

Conflict of Interests

The authors have no conflict of interests in relation to the instrumental companies directly or indirectly.

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