Macrostructure-controlled titania ceramics derived from particle-stabilized emulsions: Preparation and photocatalysis performance

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HIGHLIGHTS
- Porous TiO₂ ceramics with high porosity and uniform pore structure were prepared by particle-stabilized emulsions method.
- The prepared samples have high adsorption capacity and excellent photocatalysis performance for Rhodamine B.
- The adsorption and photocatalytic degradation rate were obviously improved by covering the TiO₂ surface with a carbon layer.

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ABSTRACT

To enhance the photocatalytic efficiency and resolve the titania recovery problem, we studied the processing of particle-stabilized emulsions for preparing porous TiO₂ ceramics in this study. The samples were synthesized with different solid contents from 15 vol% to 30 vol%. The solid content markedly affected the pore structure and morphology. When the solid content in the precursor was controlled at 30 vol%, the sample had the three-dimensional interpenetrating structure with high porosity and uniform pore structure and the average pore size was about 3–18 μm. With excellent pore structures, the samples show the high adsorption capacity and excellent photocatalysis performance for Rhodamine B. Furthermore, when porous TiO₂ ceramic was covered by a 2 nm carbon film layer (C/TiO₂), the adsorption efficiency and photocatalytic degradation rates were efficiently improved.

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1. Introduction

In recent years, solar energy has become one of the effective ways to reduce environmental pollutants. Semiconductor photocatalysis has been extensively studied as a promising alternative technology for environmental purification. Since 1972, Fujishima et al. [1] found that under light irradiation, TiO₂ experienced continuous redox reaction to generate hydrogen. Therefore, TiO₂ has received increasing attention for its unique optical and chemical properties, and its photocatalytic performance may be obviously enhanced through surface modification or nanominiaturization [2,3]. However, the use or recycling of nano-TiO₂ is not convenient. It is necessary to study the recycling methods of nano-TiO₂. Over the years, the most widely used method is to load TiO₂ on some porous materials, such as diatomite, charcoal, silica, and montmorillonite [4–6]. With the more active TiO₂ sites and more gas and light channels, porous TiO₂ ceramics show the high photocatalytic efficiency [7]. However, when it is loaded on other porous materials, the photocatalytic effect will be largely decreased because of the decreased specific surface area and the negative influence of ionic species from the porous materials [8].

Porous TiO₂ ceramics with various structures and functions in powder, film, or bulk forms have been widely applied in photocatalysis, catalytic reaction, biological materials, refractory materials, filtration, reaction electrode, and environmental purification owing to their high permeation, high specific surface area, high catalytic activity, high thermal stability, high chemical stability, low
thermal conductivity, low bulk density, low specific heat, and other excellent properties. Different engineering applications of porous TiO\(_2\) ceramics require different pore macrostructures and shapes [9–13]. Various methods have been developed to synthesize the porous TiO\(_2\) ceramics with desired pore architectures. Compared with other methods, the micro-emulsion method has the following advantages. Firstly, the particle adsorption leads to the stabilization of the dispersed system of two immiscible fluids and particle-stabilized emulsions and foams can be prepared. Secondly, the prepared porous materials (foams) have the longer stable period than surfactant-stabilized foams because the surfactant can be more easily removed from the liquid/gas interface than the weakly hydrophobic particle. When water was used as the continuous phase in particle-stabilized emulsions, similar hydrophobic particles also exist in oil-in-water (o/w) emulsions. Therefore, the hydrophobic particles can be encased in the surfaces between the emulsion drops and water and oil-in-water (o/w) materials may be prepared [14–20].

Porous TiO\(_2\) ceramics not only overcome the shortcoming of difficulty recycling, but also distinctly enhance the photocatalysis rate compared with the commercial P25 TiO\(_2\). Moreover, when porous TiO\(_2\) ceramics were covered with a thin carbon film, the adsorption and photocatalytic rate of the obtained porous TiO\(_2\) ceramics were further improved.

2. Material and methods

2.1. Preparation of porous TiO\(_2\) ceramics

Porous TiO\(_2\) ceramics were synthesized according to the modified particle-stabilized emulsion method. The TiO\(_2\) ceramic suspension was prepared according to the following procedure. Firstly, commercial TiO\(_2\) (P25) (anatase: rutile = 80:20, Evonik Industries AG, Germany) was dissolved in de-ionized (D.I.) water containing the appropriate amount of dispersing agent (the ammonium salt of polyacrylicacid; Adamas Reagent, Ltd.). Afterward, ammonia (4 M) and hydrochloric acid (2 M) was added into the TiO\(_2\) solution to adjust the pH and prevent the agglomeration of TiO\(_2\) particles. During the addition of TiO\(_2\) powder, the suspension pH was maintained above 9.9.

The suspension was ball-milled in the polyethylene bottles for 20 h with alumina milling balls (10 mm in diameter) to obtain homogeneously deagglomerated TiO\(_2\) suspension. In addition, the weight ratio of ball to suspension was 2. After the ball milling, the pH value of the suspension was far below 9.9. Therefore, it was important to adjust pH to the optimal value of 9.9. Alumina milling balls were separated from the ball-milled suspension and the suspension was then transferred to a glass beaker for adding propyl gallate (C\(_{10}\)H\(_{12}\)O\(_5\)) (AR, Sinopharm Chemical Reagent Co., Ltd; a short amphiphilic molecules act as the surface modifier). Propyl
gallate was dissolved in ethyl alcohol according to the propyl gallate/ethyl alcohol mass ratio of 1. Then the resultant alcoholic solution was added dropwise into the suspension under magnetic stirring. The suspension was changed from white to orange red immediately after dropping the first alcoholic solution. After 5-min magnetic stirring, the pH of the suspension subsequently adjusted to 9.9. Then the solution stood for 30 min. After the preparation of suspensions with the desired solids and surfactants described above, the pH value of the TiO2 suspension was re-adjusted to 9.9. Then, Octane (C8H18) (CP, Sinopharm Chemical Reagent Co., Ltd.) was added into TiO2 as oil phase suspensions according to the different solids concentrations. The volume concentration (\(\phi\)) in 60 mL of de-ionized water ranged from 15 vol% to 30 vol%. Emulsification was performed by vigorously stirring the suspension and octane for 3 min with a household mixer at full power to introduce octane into the suspension and produce the foam.

After foaming, wet foams were transferred into culture dishes (90 mm in diameter and 20 mm in height), which were maintained 24 h at room temperature.

The completely dried samples were respectively calcined at different temperatures (400 °C, 500 °C, 600 °C, 700 °C, and 800 °C) for 2 h in air and the heating rate was 5 °C min\(^{-1}\).

Fig. 3. SEM micrographs of porous TiO2 foams sintered at different temperatures. (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C.

Fig. 4. SEM micrographs of porous TiO2 foams sintered at 500 °C with different solid contents \(\phi\) from 15 vol% to 30 vol%, (a) 15 vol%, (b) 20 vol%, (c) 25 vol%, (d) 30 vol%.
2.2. Preparation of porous C/TiO₂ ceramics

According to the above similar method with the modification that an appropriate amount of sucrose (C₁₂H₂₂O₁₁) (AR, Sinopharm Chemical Reagent Co., Ltd.) was added into the aqueous ceramic suspension as the origin of carbon, the porous C/TiO₂ ceramics were synthesized. The solid concentration of the initial TiO₂ suspension was maintained at 30 vol% and the addition concentration of the sucrose was 30 wt%. The detailed procedures and principles of which are shown in Fig. 1, moreover, without adding sucrose is the schematic of the preparation of porous TiO₂ ceramic.

After drying at 50 °C for 24 h, the samples were sintered at 500 °C in N₂ (99.99%) for 2 h and the heating rate was 5 °C min⁻¹.

2.3. Characterization of the catalysts

In the photocatalysis experiments of TiO₂ porous ceramics, 50 mg catalysts was added into 50 mL of 10 mg L⁻¹ Rhodamine B (Rhb) solution in the vessel and maintained in suspension by a magnetic stirrer. A 500 W Hg lamp used in the experimental with the wavelength centered at 365 nm was about 10 cm above the photo-reactor. Prior to illumination, the suspension was magnetically stirred for 120 min in dark to ensure the adsorption–desorption equilibrium. Then, UV light was turned on for 50 min to test photocatalytic activity. The photocatalytic experiments of C/TiO₂ porous ceramics were processed according to the same method. However, in order to display the change in the photocatalytic efficiency after loading C on TiO₂ porous ceramics, the Rhb content was increased to 30 mg L⁻¹ and the dark reaction period and illumination period were respectively changed to 60 min and 48 min. The concentrations of Rhb solution was monitored by UV–Visible spectrophotometer (Varuan, US). Photocatalytic activity of the synthesized TiO₂ porous ceramics was characterized by the degeneration rate of Rhb solution. According to Langmuir law, there is a linear relation between the absorbance and the density at the characteristic wavelength. The degeneration rate was calculated as:

\[ \eta = 100\% \times \frac{(A_0 - A_t)}{A_0} \]

where \( \eta \) represents the Rhb solution degeneration rate; \( A_0 \) represents the initial concentration of Rhb solution; \( A_t \) represents the concentration of Rhodamine B solution after adsorption equilibrium; \( A_t \) represents the concentration after irradiation.

The phases of the ceramic samples were determined by X-ray diffraction (XRD) analyses (D’Max-Ra 12 kW, Ouyatu, Japan) using Cu-Kz radiation and the scanning rate was 8.0 ° min⁻¹. The microtopography of the ceramic samples was investigated by scanning
electron microscopy (SEM) (S-4800, Hitachi, Japan). Electronic Differential System (EDS) was used to analyze the compounds and element contents of the C/TiO2 samples. The microstructure of the C/TiO2 ceramics was characterized by transmission electron microscope (TEM) (JEM-2100). Surface areas of the porous ceramics were calculated from the adsorption isotherms of nitrogen at 77 K on the Autosorb iQ Station 2 system (Quantachrome Instruments, US) according to Brunauer–Emmett–Teller (BET) method.

3. Results and discussion

3.1. Effects of temperature on TiO2 ceramics

Fig. 2 shows the XRD patterns of P25 and the prepared samples. As shown in Fig. 2(a), the main peaks of P25 were clearly observed. Within the temperature range of 400 °C-600 °C, these porous TiO2 samples had the similar crystal composition to P25. However, the diffraction peaks turned wider, stronger and sharper during the temperature increased from 600 °C to 800 °C, as shown in Fig. 2(b). When the temperature reached 800 °C, the characteristic peak of anatase TiO2 disappeared, indicating that the anatase TiO2 in the porous ceramics was completely converted into rutile TiO2, thus losing the photocatalytic activity. As shown in Fig. 3, the porous structure of the TiO2 ceramics was obviously observed and pores are in the spherical shape. Meanwhile, the porous structures of prepared TiO2 ceramics showed no apparent change when sintering at temperature (400 °C-700 °C) from Fig. 3(a)-(d).

3.2. Effects of solid contents on the morphology of TiO2 ceramics

Fig. 4 shows the SEM images of the samples sintered at 500 °C with different solid contents (φ) between 15 vol% to 30 vol% at pH 9.9. It is proved that the solid content significantly influences the morphology of the porous TiO2 ceramics. The reason is that the particle-stabilized emulsion is greatly affected by the concentration of particles. Moreover, higher concentrations will increase the emulsion stability. In fact, an amphiphilic surfactant was added in the suspension to retain the hydrophilic TiO2 particles in the octane droplets. One end of amphiphilic surfactant molecule is hydrophilic, whereas the other end is hydrophobic. In this oil in water system, since the hydrophobic group has a tendency to remain in the oil phase, the amphiphilic part of the surfactant molecule will gather on the oil surface. As a result, the hydrophilic end is hydrophilic. In this oil in water system, since the hydrophobic group has a tendency to remain in the oil phase, the amphiphilic part of the surfactant molecule will gather on the oil surface. As a result, the hydrophilic end is hydrophilic. In this oil in water system, since the hydrophobic group has a tendency to remain in the oil phase, the amphiphilic part of the surfactant molecule will gather on the oil surface. As a result, the hydrophilic end is hydrophilic. In this oil in water system, since the hydrophobic group has a tendency to remain in the oil phase, the amphiphilic part of the surfactant molecule will gather on the oil surface. As a result, the hydrophilic end is hydrophilic.
were gradually changed to the regular spherical shape and the loosely packed porous structure was densely packed. In addition, increasing the \( \phi \) value from 15 vol\% to 30 vol\% also decreasing the pore size, as shown in Fig. 4(b)–(d). Because of the octane droplets in the system with lower particle concentration were more instability than that with higher particle concentration, so that they were generated coalescence to form larger droplets. Meanwhile, the BET results indicated that the surface area was 46.2 m\(^2\)/g. Therefore, the porous microstructures provide a great chance to pollutant accumulation.

3.3. The composite and morphology when carbon was loaded on TiO\(_2\) ceramics

The morphology of TiO\(_2\) particles which are covered with a layer of carbon was characterized by TEM. As shown in Fig. 5, TEM analysis reflects that TiO\(_2\) particles are decorated with a layer of an approximately 2 nm carbon thick film. The average size of TiO\(_2\) particles was about 20 nm, which was suitable to prepare ceramics using particle-stabilized emulsions. Meanwhile, in Fig. 6, EDS analyses determined the element composition of C/TiO\(_2\) with the solid content of TiO\(_2\) particles was 30 vol\%. The peaks exhibited that the elements in the sample included Ti, C and O. The element composition indicated that a layer of nanoscale carbon film continuously covered on TiO\(_2\) particles surface. More importantly, the carbon covered on the TiO\(_2\) surface would adsorb pollutants from water.

3.4. Photocatalysis performance

In order to evaluate the photocactivity of the as-prepared samples, the results of dark adsorption and photocatalytic degradation of Rh\(_6\) were illustrated in Fig. 7 and Fig. 8, respectively. As shown in Fig. 8, the high adsorption efficiency of porous TiO\(_2\) ceramics indicating that the prepared samples have the high specific surface and abundant pores. The result is consistent with the SEM-microstructure images. Meanwhile, the photocatalytic rate of TiO\(_2\) porous ceramics indicates the existence of the large number of anatase phase. The anatase phase TiO\(_2\) has the higher photocatalytic activity than amorphous TiO\(_2\) and other crystal TiO\(_2\). Moreover, the porous structure of TiO\(_2\) ceramics have as shown in Fig. 4. They have the orderly and homogeneous pores and show two advantages over other photocatalysts. Firstly, the increased surface area can provide more active catalytic sites. Apparently, compared with nonporous structures, a number of pores in TiO\(_2\) were conducive to pollutant adsorption and further reactions. Secondly, UV light absorption efficiency was increased. The higher UV light absorption efficiency enhanced light-harvesting and consequently increased the quantity of photo-generated charge carriers. The enhancement effect could be interpreted as follows: When photons enter the pores, it is difficult for photons to escape from the pores and various reflections occur within the interior pores. Therefore, the opportunities to absorb UV light can be largely increased. As a result, the photocatalytic efficiency was markedly improved [21–23]. However, as shown in Fig. 9 and Fig. 10, due to a layer of carbon covered on TiO\(_2\) particles surface, the roughness and specific surface of TiO\(_2\) particles were enhanced. Thus the adsorption and photocatalytic rate of C/TiO\(_2\) porous ceramic was enhanced as compared with TiO\(_2\) porous ceramics. Meanwhile, they also illustrated that the adsorption process benefits the subsequent photocatalytic reactions.

4. Conclusions

Based on the micro-emulsion method, we successfully developed a novel method for prepared macrostructure TiO\(_2\) and C/TiO\(_2\) porous ceramic catalysts. With the high specific surface area, excellent pore structures, and other outstanding performances, these two kinds of catalysts had the greatly improved photocatalytic rate and the gathering capability of Rhodamine B. Moreover, the particle-stabilized emulsion method is a novel simple route to prepare the porous materials with the higher porosity and uniform pore structures. Therefore, the method proposed here can be used to fabricate several porous materials for environmental protection.

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References


