Research Article

Synthesis of Fe₃O₄/C/TiO₂ Magnetic Photocatalyst via Vapor Phase Hydrolysis

Fuzhi Shi, Yaogang Li, Qinghong Zhang, and Hongzhi Wang

1 State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China
2 Engineering Research Center of Advanced Glasses Manufacturing Technology, MOE, Donghua University, Shanghai 201620, China

Correspondence should be addressed to Qinghong Zhang, zhangqh@dhu.edu.cn and Hongzhi Wang, wanghz@dhu.edu.cn

Received 14 September 2011; Revised 15 November 2011; Accepted 15 November 2011

Academic Editor: Jiaguo Yu

Copyright © 2012 Fuzhi Shi et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A core/multi-shell-structured Fe₃O₄/C/TiO₂ magnetic photocatalyst is prepared via vapor phase hydrolysis process. The as-synthesized core/multi-shell-structured composite is characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), high-resolution electron microscopy (HRTEM), N₂ adsorption-desorption isotherm analyses, vibrating sample magnetometer (VSM), and ultraviolet-visible (UV-Vis) absorption spectroscopy. TEM and HRTEM show that well-crystallized anatase TiO₂ nanocrystals are immobilized on the surface of as-prepared Fe₃O₄/C microspheres with dimensions around 200 nm. N₂ adsorption-desorption isotherm analysis shows that the obtained photocatalyst exists disorderedly mesoporous structure. The photocatalytic efficiency of the catalyst in degradation of methylene blue is evaluated, and the Fe₃O₄/C/TiO₂ photocatalyst with low TiO₂ content (37%) has a relatively higher activity than commercial anatase TiO₂. The intermediate carbon layer avoids the photodissolution of Fe₃O₄ effectively, and the recycling property is largely improved due to the existence of magnetic Fe₃O₄ core.

1. Introduction

Titanium dioxide (TiO₂) nanoparticles have inspired scientists for their potential application in treatment of environmental pollutants in wastewater [1–9]. However, there have been two obvious deficiencies in their practical application. One is the wide bandgap of TiO₂ (≈3.2 eV), so only a small ultraviolet fraction of solar light can be used. The other is the separation of nanosized photocatalyst from wastewater, which is too difficult and energy consumptive [10]. Both deficiencies result in the low treatment efficiency and increase the loss of photocatalyst. Doping TiO₂ with foreign element [11, 12] and mixing TiO₂ with sensitizer [13, 14] are two most important ways to enhance the utilizing of sunlight. And the related researches on catalyst immobilization have also attracted wide attention in order to solve the separation and recycle of the suspended TiO₂ nanoparticles [15, 16]. Some researchers have coated TiO₂ over glass, zeolite, and other substrates to avoid the catalyst-recovering step [17–19].

Recently, magnetic photocatalysts have been addressed to resolve the separation of TiO₂ nanoparticles [20–23]. Cheng et al. [22] obtained a core/shell-structured bactericidal photocatalyst with Fe₃O₄ core and TiO₂ shell for bactericidal application. Xuan et al. [23] fabricated Fe₃O₄/TiO₂ hollow spheres through poly(styrene-acrylic acid) (PSA) template method and carried out the photodegradation of RhB as a model reaction to investigate the photocatalytic activity of the hollow photocatalyst. Nevertheless, Beydoun et al. [24] indicated that the photodissolution of Fe₃O₄ would occur during the light irradiation. So the barrier layer between magnetic Fe₃O₄ and TiO₂ was prepared to reduce the negative effects [25–28]. Song and Gao [8] synthesized the bi-functional titania-/silica-coated magnetic spheres and used MB to evaluate their photocatalytic properties. Ye et al. [28] obtained the core/shell-structured Fe₃O₄/SiO₂/TiO₂ magnetic nanocomposites with enhanced photocatalytic activity by combining sol-gel process with calcinations. Presence of silica coating is essential to reduce the negative effect to magnetite during the photocatalytic process [8, 28]. However, Wang et al. [29] indicated that the carbon shell coated on Fe₃O₄ microspheres was more compact than others, so the direct contact can be avoided effectively. Its benefit to protect
the magnetic carriers enhance the photocatalytic activity and extend the lifetime of magnetic photocatalyst.

Herein, we develop a novel and controllable strategy to prepare the unique Fe₃O₄/C/TiO₂ core/multi-shell-structured photocatalyst via vapor phase hydrolysis (VPH) process. It is crucial that TiO₂ in the shell is perfectly crystallized without calcination. In VPH method, the water molecules are gently contacting with alkoxide in vapor phase with the advantage of hydrothermal treatment to obtain highly crystallized TiO₂. The size and crystallinity of anatase TiO₂ crystallite in the shell could be tuned by reaction temperature, duration, and the thickness of anatase shell could also be tuned by varying tetrabutyl titanate (TBOT) content. Finally, the photocatalytic degradation of MB was selected as a model reaction to demonstrate the unique advantage in their photocatalytic activity and recycle facet.

2. Experimental Procedure

2.1. Materials. Commercial anatase TiO₂, FeCl₃·6H₂O, ethylene glycol (EG), sodium acetate (NaAc), polyethylene glycol (PEG), oleic acid, cetyltrimethylammonium bromide (CTAB), glucose, TBOT, and absolute ethanol were analytical grade and purchased from Shanghai Chemical Reagent Co., China. All chemicals were used as received without any purification. The distilled water for all processes was purified by ion exchange and then followed by distillation. The specific surface area of commercial anatase TiO₂ is 19 m²/g and the crystallite size is about 80 nm.

2.2. Synthesis of Fe₃O₄ Microspheres. The ferrite core was first fabricated by solvothermal method, as described by others [30–32]. Typically, 1.35 g FeCl₃·6H₂O was dissolved in 50 mL EG to form a clear solution, followed by addition of 3.6 g NaAc and 1.0 g PEG. The mixture was stirred vigorously for 30 min at room temperature and then sealed in a 70 mL Teflon-lined autoclave. The autoclave was heated to 200°C for 12 h. After it was cooled to room temperature, the black products were collected by magnet and rinsed with distilled water and ethanol. The final product was dried under vacuum at 60°C for 8 h.

2.3. Fabrication of Fe₃O₄/C Nanocomposites. The magnetic Fe₃O₄/C nanocomposite was fabricated according to the route of Wang et al. [29]. The reactant mixtures were prepared by dissolving glucose in the aqueous solution containing oleic-acid-stabilized Fe₃O₄ nanoparticles. Typically, 4 g glucose was dissolved in 40 mL oleic-acid-stabilized Fe₃O₄ suspension (2.5 g/L). After that, the mixture was sealed in a 50 mL Teflon-sealed autoclave and heated to 170°C for 3 h. Finally, the product isolated from the mixture by external magnetic field was rinsed with distilled water and ethanol. The final product was dried under vacuum at 60°C for 8 h.

2.4. Preparation of Magnetic Fe₃O₄/C/TiO₂ Microspheres. 0.1 g Fe₃O₄/C powders and TBOT were added into 8 mL ethanolic solution and stirred for 2 min to obtain a colloidal solution which was then transferred into the vapor phase hydrolysis device (VPHD, as shown in Figure 1) quickly. 3 mL deionized water was located at the bottom of VPHD as liquid phase to produce vapor at elevated temperature, thus the liquid water did not contact with TBOT directly and the fierce hydrolysis was avoided. The sealed VPHD was heated to different temperature for varying duration. The VPHD content, the reaction temperature, and duration were varied as shown in Table 1. The as-synthesized powder was collected by magnet, rinsed with distilled water and ethanol for several times, and subsequently dried under vacuum at 60°C for 8 h.

2.5. Characterizations. The powder phase composition was identified by X-ray diffraction (XRD) equipment (D/max 2550 PC, Rigaku Co., Japan), using Cu Kα radiation at 40 kV and 200 mA. The crystallite sizes of Fe₃O₄ and anatase are estimated from the corresponding XRD peak at 2θ = 35.4° and 2θ = 25.3° by Scherrer formula (D = kλ/βcosθ), where D is the crystallite size, λ is the wavelength of the X-ray radiation (Cu Kα = 0.15406 nm), k is usually taken as 0.89, β is the line width at half-maximum height of the (311) peak of Fe₃O₄ and the (101) peak of anatase after subtracting the instrumental line broadening, and θ is the diffraction angle. The morphology and size of the particles were observed by transmission electron microscopy (JEM-2100F, JEOL, Japan) equipped with an energy-dispersive X-ray and field emission scanning electron microscope (S-4800, Hatachi, Japan). The nitrogen adsorption-desorption isotherm was obtained at 77 K using a Autosorb-1 MP (Quantachrome, USA) utilizing Barrett-Emmett-Teller (BET) calculations of specific surface area and Barrett-Joyner-Halenda (BJH) calculations of pore volume and pore size (diameter) distributions from the desorption branch of the isotherm. Magnetic characterization was conducted on vibrating sample magnetometer (6000, PPMS, USA). The carbon content in the Fe₃O₄/C nanocomposites and Sample B is quantitatively measured by Elemental Analyzer (Vario EL III, Elementar, Germany).
2.6. Photocatalytic Reaction. Ultraviolet (UV) light photocatalytic reactions were carried out to characterize the degradation rate of methylene blue (MB). The suspension was irradiated with a 300 W medium-pressure mercury lamp. First, 0.4 g catalyst (Sample B or commercial anatase TiO\textsubscript{2}) was suspended in 500 mL 5.35 × 10\textsuperscript{-5} M methylene blue (MB) solution. Oxygen was also bubbled into suspension at a flow rate of 100 mL/min during the whole experiment. Prior to photobleaching, the MB-solution-containing catalyst was stirred and stored in dark for 30 min to obtain the saturated absorption of MB. The MB concentration was determined using Lambda 35 UV-Vis spectrophotometer (Perkin-Elmer, Waltham, USA) by collecting the absorbance of MB at wavelength of 665 nm.

In order to investigate the recycle property and long-term photocatalytic activity, Sample B was used to degrade MB solutions five times. After ultraviolet light irradiation for 3 h, the magnetic photocatalyst was recycled by external magnetic field, washed three times with deionized water and dried at 105 °C for 5 h, the recovered photocatalyst was subsequently used to degrade fresh MB solution under the same irradiation conditions for 3 h. Then 3-cycle, 4-cycle and 5-cycle were also carried out in the same process.

The degradation rate (\(H\)) of MB was calculated using \(H = \frac{C}{C_0} \times 100\%\), where \(C\) and \(C_0\) are the concentration of remaining MB at different intervals and primal MB solution.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis. The crystallinity and structure of as-prepared Fe\textsubscript{3}O\textsubscript{4} particle and Fe\textsubscript{3}O\textsubscript{4}/C/TiO\textsubscript{2} nanocomposite are confirmed by XRD. As showed in Figure 2, the peak position and relative intensity of Fe\textsubscript{3}O\textsubscript{4} (curve a) match well with standard powder diffraction date (JCPDS No. 74-2402), indicating phase purity of Fe\textsubscript{3}O\textsubscript{4}. Well-resolved diffraction peaks reveal good crystallinity of Fe\textsubscript{3}O\textsubscript{4}. The average crystallite size of as-prepared ferrite powder estimated by Scherrer formula is around 14 nm, which is in agreement with the result of Zhang et al. [31]. There is no diffraction peaks of carbon appears in curve b due to its amorphous nature and low content compared with Fe\textsubscript{3}O\textsubscript{4} and anatase TiO\textsubscript{2}. In addition to all diffraction peaks of Fe\textsubscript{3}O\textsubscript{4}, there are other four diffraction peaks appear at \(2\theta = 25.3\degree, 37.8\degree, 48.1\degree,\) and 55.1\degree which correspond to (101), (004), (200), and (211) planes of anatase TiO\textsubscript{2} (JCPDS No. 21-1272), respectively. The crystallite size of anatase TiO\textsubscript{2} calculated by Scherrer formula is to be ca. 11.2 nm. And the intensity of XRD peaks of Fe\textsubscript{3}O\textsubscript{4} has been decreased because there is some carbon and anatase TiO\textsubscript{2} coated on it. XRD results demonstrate that the crystalline anatase TiO\textsubscript{2} and Fe\textsubscript{3}O\textsubscript{4} coexist in Sample B.

3.2. Morphology and EDS Analysis. The morphologies of the selected samples are revealed by TEM (Figure 3) and SEM (Figure 4). The Fe\textsubscript{3}O\textsubscript{4} crystallites are ultrafine as observed in Figure 3(a) and connect tightly to one another to form spheres. And the diameter of the aggregated particles is around 200 nm (Figure 4(a)). Figure 3(b) shows that amorphous carbon and well-crystallized anatase TiO\textsubscript{2} formed on the surface of Fe\textsubscript{3}O\textsubscript{4} microspheres, and the amorphous carbon shell is compact while polycrystalline titania shell is around the carbon shell. The carbon content in the Fe\textsubscript{3}O\textsubscript{4}/C nanocomposites and Sample B is measured to be 4.4 wt.% and 2.8 wt.%. The crystallite sizes of Fe\textsubscript{3}O\textsubscript{4} and anatase TiO\textsubscript{2} are around 15 and 12 nm, which is in agreement with the calculation of XRD. The distances marked in the pattern (Figure 3(c)) between (101) plane of anatase and (311) plane of Fe\textsubscript{3}O\textsubscript{4} are 0.35 nm and 0.25 nm, respectively. A well-defined core/multishell structure with Fe\textsubscript{3}O\textsubscript{4} as core, carbon

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe\textsubscript{3}O\textsubscript{4}/C powder (g)</th>
<th>Anatase calculated from TBOT (g)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>(S_{BET}) (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.1</td>
<td>0.125</td>
<td>150</td>
<td>10</td>
<td>57</td>
</tr>
<tr>
<td>B</td>
<td>0.1</td>
<td>0.25</td>
<td>150</td>
<td>10</td>
<td>61</td>
</tr>
<tr>
<td>C</td>
<td>0.1</td>
<td>0.5</td>
<td>150</td>
<td>10</td>
<td>72</td>
</tr>
<tr>
<td>D</td>
<td>0.1</td>
<td>0.25</td>
<td>150</td>
<td>5</td>
<td>58</td>
</tr>
<tr>
<td>E</td>
<td>0.1</td>
<td>0.25</td>
<td>150</td>
<td>20</td>
<td>53</td>
</tr>
<tr>
<td>F</td>
<td>0.1</td>
<td>0.25</td>
<td>100</td>
<td>20</td>
<td>155</td>
</tr>
<tr>
<td>G</td>
<td>0.1</td>
<td>0.25</td>
<td>200</td>
<td>10</td>
<td>39</td>
</tr>
<tr>
<td>H</td>
<td>0.1</td>
<td>—</td>
<td>150</td>
<td>10</td>
<td>38</td>
</tr>
</tbody>
</table>
as intermediate shell, and anatase as outer shell is indeed formed by the evidence of TEM images (Figures 3(b) and 3(c)). The direct contact between Fe$_3$O$_4$ and TiO$_2$ was inhibited. The EDS results of the selected area in Figure 3(b) are given in Figure 3(d). Ti, Fe, and some C elements come from Sample B; Cu and C come from copper grid and carbon film for TEM analysis. Figure 4 gives the SEM images of the selected samples. It provides more structural information about the three-dimensional morphology of the product. A large quantity of as-prepared Fe$_3$O$_4$, carbon-coated Fe$_3$O$_4$, and core/multi-shell-structured Fe$_3$O$_4$/C/TiO$_2$ with narrow distributions has been synthesized. As shown in Figure 4(b), the greater crosslinking degrees and slickness of the Fe$_3$O$_4$/C surface can be seen compared with Figure 4(a) due to the amorphous carbon. Because the small anatase TiO$_2$ crystallite is coated on the surface of Fe$_3$O$_4$/C particles, the result that the surface of Sample B becomes rough can be obtained from Figure 4(c). Up to now, the core/multishell-structured Fe$_3$O$_4$/C/TiO$_2$ composite is confirmed by the evidence of SEM and TEM analysis.

### 3.3. Magnetic Study

The magnetic property of as-prepared Fe$_3$O$_4$, Fe$_3$O$_4$/C and Fe$_3$O$_4$/C/TiO$_2$ is investigated with vibrating sample magnetometer at room temperature. Figure 5 gives the magnetization-hysteresis loops of samples with different composition. It shows that the magnetic saturation value of samples is closely related with the thickness of nonmagnetic shells in given external magnetic field [8]. The magnetic saturation values are 75.1 emu/g for Fe$_3$O$_4$ [30], 65.1 emu/g for Fe$_3$O$_4$/C, and 56.1 emu/g for Fe$_3$O$_4$/C/TiO$_2$ particles. The decrease of saturation magnetization is most likely attributed to the existence of nonmagnetic C and TiO$_2$ shells on the surface of Fe$_3$O$_4$ as shown in curves b and c. Because of the magnetic core, it is notable that these magnetic photocatalysts could be easily recycled from solution.
after treatment by external magnetic field. The inset is the image of Sample B separated from aqueous solution by an external magnetic field (inset). The magnetic photocatalyst (Sample B) is recycled by attracting towards the magnet located in right-hand side of sample vials over a short period, demonstrating the high magnetic sensitivity of as-synthesized magnetic photocatalyst.

3.4. Nitrogen Adsorption-Desorption Analysis. The N\textsubscript{2} adsorption-desorption isotherm (Figure 6(a)) of all four samples presents type-IV-like curve with an H3 hysteresis loop, characteristic of mesopores in the spherical cores and shells. Comparing with Sample H, the hysteresis loop of Sample F is shifted to low \( \frac{P}{P_0} \) direction relatively because small crystallite stacking small intraparticles pores on the surface of Fe\textsubscript{3}O\textsubscript{4}/C spheres. The hysteresis loops of Sample B, G are also shifted to low \( \frac{P}{P_0} \) direction, but it is not obvious in the Figure 6(a). The hysteresis loop of Samples F, B, and G illustrates the fact that the larger crystallite stacking larger intraparticles pores at elevated temperature. The pore size of Sample F is smaller than that of Sample B. It can be explained that the anatase crystallite prepared under 100°C is ultrafine and cumulates small pores. Figure 6(b) gives the pore-size distribution curves of different samples, confirming a preferred porous structure with pore volumes \( (V_p) \) 0.36, 0.32, 0.40, and 0.42 cm\textsuperscript{3}/g and average pore diameters 68.1, 4.7, 9.5, and 81.5 nm corresponding to Samples H, F, B and G, respectively. The high specific surface area of Sample F (155 m\textsuperscript{2}/g) is the result of fine anatase crystalline prepared under this temperature. Such a porous structure can promote more adsorption of pollutants.
3.5. Photocatalytic Activity. Different catalysts are suspended into the MB solution for 30 min in the dark as the adsorption experiment. Figure 7 indicates that the concentration of MB solution is almost no any change (3.33%) in commercial TiO$_2$ suspension. In contrast, the adsorption of Sample B reaches 12.5%. This adsorption property could increase the local concentration of MB near the titania layer and enhance the photocatalysis efficiency [33]. Figure 8(a) shows the photocatalytic activities of Sample B and commercial anatase TiO$_2$ in photocatalytic decomposition of MB under ultraviolet light irradiation. As shown in Figure 8(a), the decolorization ratio of MB (control) was less than 20% [34] after 180 min irradiation due to the photodecomposition. Because of the anatase TiO$_2$ located on the outsurface of Fe$_3$O$_4$/C/TiO$_2$ microspheres, it can utilize the light effectively than solid TiO$_2$ sphere. The TiO$_2$ content in Sample B is 37%, so the photocatalytic activity of Sample B is relatively higher than that of commercial anatase TiO$_2$. If the iron oxide directly contacts with a crystalline titanium dioxide phase, electronic interactions between the titanium dioxide coating and the iron oxide core, when the photogenerated electrons in the titanium dioxide phase are transferred into the lower lying conduction band of the iron oxide phase. It is these injected electrons which lead to the reduction of the iron oxide...
core, with Fe ions are being formed and migrating to the solution through the porous titanium dioxide coating [24, 33]. So the protection role of intermediate carbon layer is to avoid the direct contact between Fe3O4 and titania. Due to the compacted coating with intermediate carbon layer, it can be avoided the electron interaction or photodissolution of Fe3O4 probably occurrence of at the point of contact. The long-term photocatalytic activity of Sample B is showed in Figure 8(b). MB is removed completely from the solution in every cycle and photocatalytic degradation efficiency is not varied. Owning to the regenerative property of magnetic photocatalyst and relatively high photocatalytic activity, the Fe3O4/C/TiO2 hybrid spheres are well likely to be promising catalyst in the near future.

4. Conclusions

In summary, the core/multi-shell-structured Fe3O4/C/TiO2 magnetic photocatalyst has been prepared via a vapor phase hydrolysis process, and the thickness of TiO2 shell can be tuned from monolayer to several hundred nanometers by varying the TBOT content. The size and crystallinity of anatase TiO2 crystallite in the shell could be tuned by temperature and duration. The photocatalytic activity of Fe3O4/C/TiO2 photocatalyst has relatively higher activity than commercial anatase TiO2 in photocatalytic degradation of methylene blue (MB) but its recycling property is improved largely. The intermediate carbon layer can avoid the electron interaction or photodissolution of Fe3O4 probably occurring at the point of contact effectively.

Acknowledgments

This research was supported by the Opening Project of State Key Laboratory of High Performance Ceramics and Superfine Microstructure (no. SKL2010002SIC), the National Natural Science Foundation of China (no. 50772127 and no. 50925312), Shanghai Leading Academic Discipline Project (B603), and the Program of Introducing Talents of Discipline to Universities (no.111-2-04).

References


