doi:10.1246/cl.2010.44
Published on the web December 12, 2009

Preparation and Characterization of a New-type Composite Photocatalyst of 3DOM TiO_2/Carbon Materials

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In this paper, a new-type composite photocatalyst of titania/carbon (TiO_2/C) with three-dimensional ordered macroporous (3DOM) structure was successfully prepared by combining the macroporous structure of 3DOM carbon and the catalytic properties of TiO_2. Under ultraviolet light, the obtained 3DOM TiO_2/C materials were used to degrade Methyl Orange solution as simulated organic waste–water and had a high catalytic activity. Furthermore, compared with commercial Degussa p25 catalyst, obtained 3DOM TiO_2/C materials displayed an excellent regenerative ability.

It is well known that TiO_2 is a very promising green photocatalyst, which has been applied in many important fields. Powdery TiO_2 materials like Degussa p25 are widely used as photocatalyst in many fields, such as organic decomposition, water purification, and antibacterial.[1–9] However, the separation and recycling of the TiO_2 powders can be problematic. One of the approaches to solve this problem is to support TiO_2 particles on various supports. Porous carbons including activated carbon[10,11] and carbon fibers[12] and small spheres[13] have been used to support TiO_2. Although the regeneration of TiO_2 powders could be improved to some degree, conglomeration occurs and the connection between TiO_2 and supports is not robust and easily separates in applications to liquid systems.

In this paper, 3DOM carbon was chosen as support and TiO_2 nanoparticles were inserted into the macroporous interior of 3DOM carbon to form a new-type composite photocatalyst, that is, 3DOM TiO_2/carbon (TiO_2/C). This kind of 3DOM TiO_2/C composite combines the photocatalytic properties of TiO_2 powders with the wide macroporous structure of 3DOM carbon. Compared with commercial Degussa p25 catalyst, 3DOM TiO_2/C materials displayed similar catalytic activity but more better regenerative ability.

3DOM carbon materials were first prepared by using sucrose as carbon source and SiO_2 spheres as template, according to procedures reported in the literature.[14,15] The average diameter of SiO_2 spheres obtained by Stöer method was 300 nm, and the macroporous size of 3DOM carbon was 280 nm. Uniform and transparent sol solution of TiO_2 with concentration of 0.8 M was prepared by mixing tetrabutyl titanate ($Ti(OC_4H_9)_4$), ethanol, acetic acid, and water under constant stirring at 30 °C. The prepared sol was aged for ten days at room temperature. After aging, 3DOM carbon materials were soaked in the aged sols for 30 min. The sol solution was infiltrated into the macroporous structures of 3DOM carbon by capillary force, and then the excess sol solution was removed by vacuum filtration. The infiltrated 3DOM carbon materials were preliminary heat-treated at 80 °C for 2 h in an oven. The infiltration processes were repeated three times to ensure sufficient quantity. After infiltration, the composites were heated to 500 °C at a heating rate of 2 °C min^{-1} under nitrogen atmosphere and kept at constant temperature for 2 h. After being cooled on standing, 3DOM TiO_2/C composite materials were obtained successfully. The obtained samples were first studied by SEM, TEM, and XRD.

3DOM carbon materials could be easily obtained by traditional colloidal crystal templating. From Figures 1a and 1c, it can be seen that 3DOM carbon had uniform macropores and integrated structure, which offered broad space for the infiltration of catalyst. After infiltration and calcination, as shown in Figures 1b and 1d, three-dimensional ordered macroporous structure was remained, and significant quantities of nanoparticles were inserted in the surface and interior of 3DOM carbon, which indicated that TiO_2 nanoparticles with average size of 18 nm could be uniformly distributed in the macroporous structures. At the same time, during calcination, the crystal transformation could produce some shrinkage to form interspace between the macroporous wall and TiO_2 catalyst, which possibly favors transportation and contact of target molecules during application.

In order to indentify the crystal phase, the samples were further studied by XRD patterns. From Figure 2, it was found

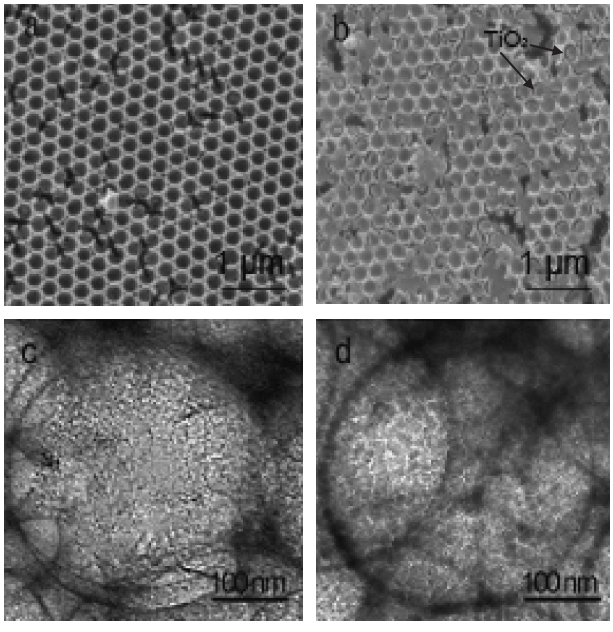

Figure 1. The SEM images of 3DOM C (a), 3DOM TiO_2/C (b), and TEM images of 3DOM C (c), 3DOM TiO_2/C (d).

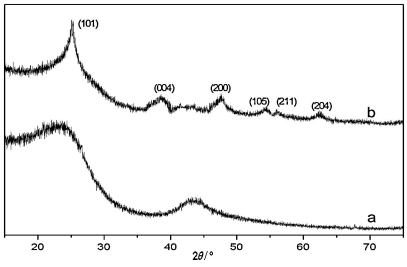

Figure 2. XRD patterns of 3DOM carbon (a) and 3DOM TiO_2/C (b).

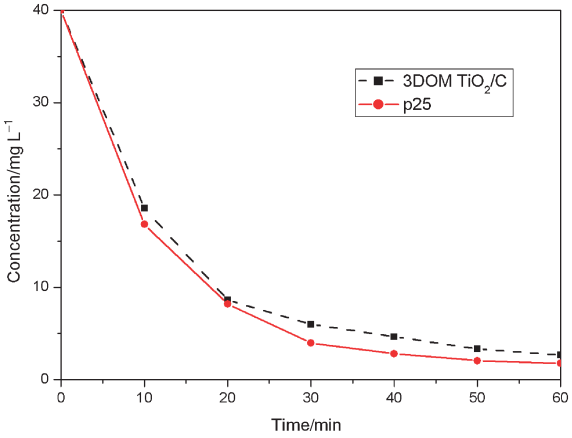

Figure 3. The degradation curves of Methyl Orange solution by 3DOM TiO_2/C and Degussa p25.

that the 3DOM carbon had amorphous structure. After uploading TiO_2, the XRD pattern of 3DOM TiO_2/C composite displayed obvious anatase form.

The obtained 3DOM TiO_2/C materials were used as a new-type photocatalyst to degrade Methyl Orange solution with concentration of 40 mg L^{-1} which was seen as simulated organic waste–water. In order to test the catalytic ability of 3DOM TiO_2/C samples, Degussa p25 was used as a reference. A high-pressure mercury lamp was used as ultraviolet (UV) light source, and the wavelength of major emission was 365 nm. Under the same reaction conditions, 3DOM TiO_2/C and Degussa p25 were used to degrade the Methyl Orange solution, and the added quantity of the solid catalyst was 3.5 g L^{-1}. The catalyst was added into the Methyl Orange solution, and the degradation reaction was continued for 60 min under UV light and constant stirring.

The degradation curves are shown in Figure 3, it can be seen that the degradation efficiency was similar between 3DOM TiO_2/C and Degussa p25, which indicates that the catalytic ability of 3DOM TiO_2/C is very close to the commercial product.

Due to the small nanosize of Degussa p25, it was very difficult to separate and recycled from solution, which was the main defect in the application to waste water. 3DOM TiO_2/C materials overcame the defect of Degussa p25 because the size of 3DOM TiO_2/C composite was in micrometers, which could be separate easily from the solution through simple filtration. In our experiment, the recycled 3DOM TiO_2/C samples were washed several times using distilled water and then were dried for 6 h at 110 °C in an oven. After drying, regeneration of the samples was completed with nearly no weight loss. In order to

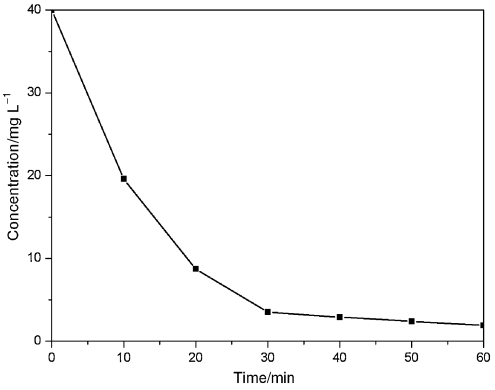

Figure 4. The degradation curves of Methyl Orange solution by regenerated 3DOM TiO_2/C.

test the catalytic ability of regenerated samples, the regenerated 3DOM TiO_2/C samples were used to degrade new Methyl Orange solution under the same conditions. A similar process degradation and regeneration were repeated six times. Before the beginning of the next cycle, fresh Methyl Orange solution was used. After the regenerated 3DOM TiO_2/C simples were used six times, the degradation curve of Methyl Orange solution is shown in Figure 4. The curve is very similar to Figure 3, which indicates that the regenerated 3DOM TiO_2/C samples still had excellent catalytic ability. Consequently, 3DOM TiO_2/C materials could be used as an efficient photocatalyst.

In summary, a new-type photocatalyst of 3DOM TiO_2/C was prepared by combining 3DOM carbon with TiO_2 by a simple sol–gel and soaking method. The catalytic ability of obtained 3DOM TiO_2/C materials was similar to commercial Degussa p25. However, 3DOM TiO_2/C materials had better regenerative ability than Degussa p25. After using six times, 3DOM TiO_2/C materials still had good catalytic ability. Therefore, it can be concluded that 3DOM TiO_2/C itself was an efficient and promising photocatalyst. Moreover, the application of 3DOM carbon is potentially broad and offers new ideas for new uses of macroporous structures.

References

1 M. Abdulla-Al-Mamun, Y. Kusumoto, *Chem. Lett.* **2009**, *38*, 826.
2 S.-Z. Chu, S. Inoue, K. Wada, D. Li, H. Haneda, S. Awatsu, *J. Phys. Chem. B* **2003**, *107*, 6586.
3 H. Li, X. Zhang, Y. Huo, J. Zhu, *Environ. Sci. Technol.* **2007**, *41*, 4410.
4 H. Li, J. Zhu, G. Li, Y. Wan, *Chem. Lett.* **2004**, *33*, 574.
5 T. Paul, P. L. Miller, T. J. Strathmann, *Environ. Sci. Technol.* **2007**, *41*, 4720.
6 B. Tryba, *J. Hazard. Mater.* **2008**, *151*, 623.
7 T. Tachikawa, Y. Takai, S. Tojo, M. Fujitsuka, T. Majima, *Langmuir* **2006**, *22*, 893.
8 G. Wu, T. Nishikawa, B. Ohtani, A. Chen, *Chem. Mater.* **2007**, *19*, 4530.
9 H. Yamashita, K. Maekawa, Y. Nakatani, J.-J. Park, M. Anpo, *Chem. Lett.* **2003**, *32*, 930.
10 X. Wang, Y. Liu, Z. Hu, Y. Chen, W. Liu, G. Zhao, *J. Hazard. Mater.* **2009**, *169*, 1061.
11 C. H. Ao, S. C. Lee, *J. Photochem. Photobiol., A.* **2004**, *161*, 131.
12 R. Yuan, J. Zheng, R. Guan, Y. Zhao, *Colloids Surf., A* **2005**, *254*, 131.
13 G. Li, R. Bai, X. S. Zhao, *Ind. Eng. Chem. Res.* **2008**, *47*, 8228.
14 W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62.
15 G. Gundiah, A. Govindaraj, C. N. R. Rao, *Mater. Res. Bull.* **2001**, *36*, 1751.

