Catalysis Today 274 (2016) 2–7

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Photocatalyst of organic pollutants decomposition: TiO_2/glass fiber cloth composites

Peng Sun [a], Ruiyang Xue [a], Wang Zhang [a,*], Imran Zada [a], Qinglei Liu [a], Jiajun Gu [a], Huilan Su [a], Zhijian Zhang [b], Jianzhong Zhang [b], Di Zhang [a,*]

[a] State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China
[b] Jushi Fiberglass Research Institute, Jushi Group Co., Ltd. 669 Wenhua Road (South), Tongxiang Economic Development Zone, Tongxiang City, Zhejiang Province 314500, PR China

ARTICLE INFO

Article history:
Received 11 January 2016
Received in revised form 19 April 2016
Accepted 20 April 2016
Available online 17 May 2016

Keywords:
Titanium dioxide
Glass fiber cloth
Photocatalyst
Organic pollutants
UV–vis light

ABSTRACT

Herein TiO_2 coated on glass fiber cloth (TiO_2/glass fiber cloth, TGFC) was synthesised by *sol-gel* method. We demonstrated the property about TGFC of photocatalytic decomposition of organic pollutants under ultraviolet-visible (UV–vis) light and sunlight. Glass fiber cloth (GFC) was chosen as the support of TiO_2 in order to improve the practical applications for water purification. TGFC-1–6 were characterized by ERSEM, XRD and XPS. Photocatalytic decomposition of crystal violet (CV) was carried out to investigate the photocatalytic activity of TGFC. The efficiency of TGFC-3 was the best. And its photocatalytic decomposition rate of the second to fifth cycle was higher than the first cycle. The photocatalytic decomposition rate of TGFC-3 was 85% under sunlight from 8:00–14:00. We could design and regulate the shape of TGFC and estimate the area, weight and thickness of TiO_2, more easily than glass fibers. TGFC is suitable for photocatalytic decomposition of organic pollutants in the water, especially to be fixed in sewage treatment pool and reused.

1. Introduction

Photocatalysis has attracted extensive attention in the area of chemistry and material, due to the application of catalysts in decomposition of organic pollutants [1,2], photo energy conversion [3] and water splitting [4], etc. It plays an important role in energy conservation and environment protection. TiO_2 shows the advantages including high efficiency, non-toxicity, chemical stability and low-cost, when used as a photocatalyst to purify water. That's why TiO_2 has already become one of the most popular photocatalysts [5,6].

When TiO_2 is illuminated with light, if energy of light is equal to or greater than the band gap of 388 nm for anatase, the electrons of the valence band(VB) are excited and promoted to the conduction band(CB), leaving positive holes [7,8]. The photo-induced electrons and positive holes can cause a range of reduction and oxidation reactions, respectively [9]. Superoxide anions are produced during the reaction of electrons and oxygen molecules, and hydroxyl radicals are generated during the reaction of positive holes with water molecules at the same time. These two active species cause oxidation of organic pollutants consequently to carbon dioxide and water molecules. The photocatalytic efficiency can be improved by modifying the structure of TiO_2, such as microsphere [1], TiO_2 nanotube arrays [10], porous TiO_2 thin film [11], TiO_2 with the structure of biomaterials [12], and so forth.

Sometimes, researches have been carried out using suspensions of TiO_2 powders in the polluted water, leading to separation process quite difficult, which inevitably causes secondary pollution. However, from the practical point of view, it might not be proper to use photocatalyst suspensions in slurry reactors. It will take us extra time and energy to separate the liquid and solid after purifying. That' s why researchers have explored many solid substrates to immobilize TiO_2, for example composites of Cu-TiO_2/glass fibers [13], TiO_2/glass beads [14], TiO_2 on perlite granules [15], graphene-TiO_2 [16], polymer/TiO_2 [17], zeolite [18], etc.

It was found that degradation percentage of methylene blue under UV irradiation for 6 h using TiO_2 thin films doped with 5mol% Fe and sterilization efficiency of *Escherichia coli* for 60 min were 75.08% and 98%, respectively [19]. Furthermore, it's reported that one kind of titanium dioxide photocatalyst was supported by glass fibers(GF), and more than 99% of initial pollutant concentration of bisphenol A and its analogs was degraded after 3.5 h of exposure

* Corresponding authors.
E-mail addresses: wangzhang@sjtu.edu.cn (W. Zhang), zhangdi@sjtu.edu.cn (D. Zhang).

http://dx.doi.org/10.1016/j.cattod.2016.04.036
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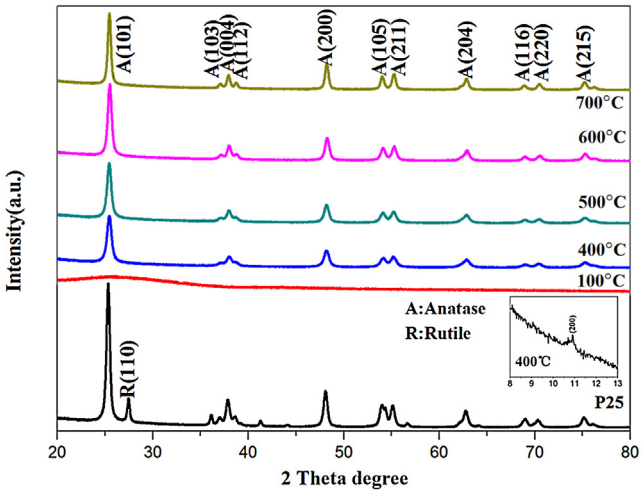

Fig. 1. XRD patterns of TiO_2 active ingredient and P25.

to UV light [20]. Many progresses about photocatalytic activity of TiO_2/GF have been made. However, GF is hard to shape and fix as a practical photocatalyst.

Here, we focus on glass fiber cloth (GFC) as a kind of TiO_2 photocatalyst support, which is a piece of woven glass fibers, as shown in Fig. 3a. GFC is low cost, easy to access, highly stable against activated oxygen, hydroxyl radical species, ultraviolet rays and high calcination temperatures [21]. What's more, it is so flexible a piece of woven GFs that it could be configured to a certain shape and more convenient to fix and recycle than GF. So we propose a design of TiO_2/glass fiber cloth (TGFC) as an efficient photocatalyst, and it is low cost, easy to prepare, use and recycle.

2. Materials and methods

2.1. Chemicals and materials

Titanium oxysulfate ($TiOSO_4$) was purchased from Aladdin chemical reagent Ltd. Ammonia water ($NH_3{\cdot}H_2O$), nitric acid (HNO_3), hydrogen peroxide (H_2O_2) and crystal violet were purchased from Sinopharm Chemical Reagent Co. Ltd. P25 was purchased from Degussa. Glass fiber cloth (GFC, E-glass fiber cloth, alkali free, 200 g/m^2) was purchased from China Jushi Ltd. Distilled water was used throughout all process.

2.2. Catalyst preparation

2.2.1. Preparation of precursor

A titanium oxysulfate ($TiOSO_4$) sol was used as the precursor when fabricating TGFC. 19.6 g $TiOSO_4$ was devolved in 400 ml distilled water and then 200 ml distilled water was added into it to form clear solution. The pH of system was adjusted to 8.0 by 20% immersed water ($NH_3{\cdot}H_2O$) solution under stirring to achieve a white suspension. The system was then left at room temperature for 40 min until it layered. The supernatant liquid was removed and the lower precipitation was washed for three times by suction filtration. Then the white precipitation was diluted into a white suspension (the molar ratio of Ti^{4+} to H_2O was 1:500). Later H_2O_2 was slowly added into the white suspension under stirring to achieve a yellow suspension (the molar ratio of Ti^{4+} to H_2O_2 was 1:6). Let it stand for aging at room temperature for 24 h. Finally a stable yellow transparent sol-precursor of $TiOSO_4$ was achieved.

2.2.2. Pretreatments of GFC

GFC (200 g/m^2) was cut into pieces of 2.5cm × 7.5 cm, and then sintered in muffle furnace at 350 °C for 1 h at the heating rate of 2 °C/ min to remove impurities. The sintered GFC was taken out in preparation for usage.

2.2.3. Preparations of the photocatalyst

To gain multi-layer titanium dioxide glass fiber cloth, several steps should be followed. First, the sintered GFC was immersed into the sol-precursor of $TiOSO_4$ at room temperature for 24 h. These samples named TGFC-1 were taken out and put into dryer at 100 °C for 1 h. Second, TGFC-1 was put into the sol-precursor of $TiOSO_4$ again for another 12 h and then taken out to dry at 100 °C for 1 h. These samples were named TGFC-2. Third, TGFC-2 was repeated the second step and named TGFC-3. This process was repeated until we got TGFC-6. Then TGFC-1–6 were all put into muffle furnace and sintered at 500 °C for 1 h. Finally we got TGFC with 1–6 layers of TiO_2, respectively.

2.3. Characterization techniques

2.3.1. Morphology and composition analysis

The surface structures of sintered GFC and TGFC were studied using an Extreme-Resolution Analytical Field Emission Scanning Electron Microscope (ERSEM, JEOL JSM-7800F Prime). X-ray diffraction (XRD) measurement was carried out by an X-ray diffractometer (Ultima IV) with Ni-filtered Cu-Kα radiation at a power source of 40 kV × 30 mA. X-ray photoelectron spectroscopy (XPS) analysis was performed on an X-ray photoelectron spectrometer (Kratos, AXIS Ultra DLD).

2.3.2. Photocatalytic experiment

The photocatalytic activity of the photocatalysts was examined by way of crystal violet (CV) dye decomposition. In the experiments, TGFC-1, TGFC-2, TGFC-3, TGFC-4, TGFC-5, TGFC-6, P25 and the TiO_2 active ingredient of TGFC were added into 100 ml of CV solution (initial concentration $C_0 = 5 \times 10^{-6}$ mol/L), respectively. The solutions were kept in dark for 30 min, in order to achieve adsorption-desorption equilibrium between dye and catalyst. The photocatalytic experiments of UV–vis light were carried out under Xenon lamp (PLS-SXE 300/300UV, 10A). Furthermore, the sunlight photocatalytic experiments were carried out under sunlight between 8 a.m. and 14 p.m. on 2nd November 2015. Samples were taken out every 30 min from the CV dye solution.

The concentration change of CV, which was determined by the absorbance of the CV solution at wavelength of 590 nm, was evaluated with a UV–vis spectrophotometer (Perkin Elmer, Lambda 750S).

3. Results and discussion

3.1. XRD patterns of TiO_2 of TGFC

The X-ray diffraction patterns of 5 varieties of TiO_2 active ingredient of TGFC and P25 are shown in Fig. 1. Only TiO_2 active ingredient of TGFC was tested, since the amount of TiO_2 coated on the surface of GFC is very small. As a reference object, mixed crystals of anatase and rutile of P25 were observed and the peaks were more intense. The XRD patterns of TiO_2 prepared at 100 °C for 1 h only showed a broad peak corresponding to amorphous or poor crystalline phase. However, the other 4 sorts of TiO_2 active ingredient prepared at 400 °C, 500 °C, 600 °C and 700 °C for 1 h, are all crystalline states. The main diffraction peaks of these 4 samples exhibited in the patterns corresponded to TiO_2 anatase crystalline phase, which is the most active crystal form of TiO_2 in photocatalytic decomposition [22]. TiO_2 was also highly thermal stable and