Chinese Journal of Catalysis 36 (2015) 389–399

available at www.sciencedirect.com

ScienceDirect

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

Article

Preparation of Ti^{3+} self-doped TiO_2 nanoparticles and their visible light photocatalytic activity

Xiaotong Wang [a], Yanmin Li [b,*], Xin Liu [a], Shanmin Gao [a,c,#], Baibiao Huang [c], Ying Dai [c]

[a] *College of Chemistry and Materials Science, Ludong University, Yantai 264025, Shandong, China*
[b] *School of Life Science, Ludong University, Yantai 264025, Shandong, China*
[c] *State Key Lab of Crystal Materials, Shandong University, Jinan 250100, Shandong, China*

A R T I C L E I N F O

Article history:
Received 1 September 2014
Accepted 29 September 2014
Published 20 March 2015

Keywords:
Ti^{3+} self-doped
Titanium oxide
Gel
Hydrothermal method
Visible light photocatalysis

A B S T R A C T

Ti^{3+} self-doped TiO_2 nanoparticles were synthesized by hydrothermal treatment of a gel precursor obtained using TiH_2 as the Ti source and H_2O_2 as oxidant. The effects of different states of gel and hydrothermal treatment time on the properties of the samples were studied. The structure, crystallinity, morphology, and optical properties of the nanoparticles were characterized by X-ray diffraction, transmission electron microscopy, high-resolution transmission electron microcopy, and UV-visible diffuse reflectance spectroscopy. The chemical states of Ti and O were confirmed by X-ray photoelectron spectroscopy and electron spin resonance spectroscopy. Methylene blue (MB) solutions were used as simulated wastewater to evaluate the visible-light photocatalytic activity of the samples. The samples exhibited strong absorption in the visible light region compared with pure TiO_2 and an excellent performance in the photocatalytic degradation of MB. When yellow gel was used as the precursor, the sample obtained after hydrothermal treatment at 160 °C for 24 h exhibited the best visible light photocatalytic activity with a reaction rate constant of 0.0439 min^{-1}, 18.3 times that of pure TiO_2. The samples also showed excellent cyclic stability of the photocatalytic activity.

1. Introduction

TiO_2 is one of the most promising semiconductor photoelectric conversion materials due to its excellent chemical stability and nontoxicity [1]. However, the band gap of anatase phase TiO_2 is 3.2 eV, which limits it to the absorption of ultraviolet light, which makes up less than 5% of sunlight. Hence, it is crucial to enhance the light harvesting of TiO_2 in the visible region, which accounts for more than 43% of total solar energy. Although many methods, such as ion doping, noble metal modification, surface plasmon enhanced absorption, organic dye sensitization, and semiconductor compositing, have been used to solve this problem, they do not fundamentally solve the low photoelectric conversion efficiency of TiO_2 [2–7]. The electron transfer rate of pure TiO_2 is low (0.1^{-4} $cm^2·V·s^{-1}$), and lattice defects and doping impurity defects tend to reduce the thermal stability of TiO_2 and increase the number of carrier recombination centers, which may decrease the overall photoelectric conversion efficiency [8,9]. Therefore, the design of TiO_2 having both visible light excitation and rapid photoinduced electron

---

* Corresponding author. Tel/Fax: +86-535-6642910; E-mail: wg-g@163.com
# Corresponding author. Tel: +86-535-6672176; Fax: +86-535-6693096; E-mail: gaosm@ustc.edu

This work was supported by the National Basic Research Program of China (973 Program, 2013CB632401), the Key Project of Natural Science Foundation of Shandong Province (ZR2013EMZ001), and the Project of Shandong Province Higher Educational Science and Technology Program (J12LA01).
DOI: 10.1016/S1872-2067(14)60234-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 3, March 2015

transfer has always been of great interest.

Previous studies have shown that Ti^{3+} self-doped TiO_2 can be excited by visible light [10]. Meanwhile, Ti^{3+} ions give the TiO_2 good electronic conductivity, which is very important for improving its photoelectric conversion efficiency [11,12]. However, based on the electrode potential, the reduction of Ti^{4+} to Ti^{3+} is difficult under normal conditions, and the resulting Ti^{3+} is very easily re-oxidized to Ti^{4+} [13,14]. At present, most methods of preparing Ti^{3+} self-doped TiO_2 are based on "reduction", by heating the TiO_2 in vacuum or a strong reducing atmosphere such as H_2, CO, or by bombarding the TiO_2 with high-energy particles (electrons, argon ions) [15–17]. These methods have some limitations to their practical application, such as multiple reaction steps, harsh conditions, long reaction time and expensive equipment, etc. Moreover, because reduction reactions usually occur on the surface of TiO_2 particles, the obtained Ti^{3+} can easily be oxidized by O_2 in air or dissolved oxygen in water, reducing the stability of Ti^{3+} self-doped TiO_2 [14]. Although the preparation of Ti^{3+} self-doped TiO_2 by reducing Ti^{4+} in mild liquid phase has been reported, the generation of by-products during the reaction process meant that subsequent treatments were needed to obtain pure Ti^{3+} self-doped TiO_2 [18,19]. Thus, it is still a great challenge to develop a simple and economic strategy to synthesize stable Ti^{3+} self-doped TiO_2 nanoparticles.

According to the corresponding electrode potential (Ti^{3+}, Ti^{2+}, $A = -0.37$ V), Ti^{2+} is easily oxidized to Ti^{3+}. Therefore, we have adopted an oxidation-based method to prepare Ti^{3+} self-doped TiO_2 nanomaterials in aqueous solution using the water- and air-stable industrial raw material TiH_2 as the Ti source. TiH_2 has a unique advantage as a raw material, namely, Ti^{3+} self-doped TiO_2 is easily obtained by controlling the oxidation of Ti^{2+} to Ti^{3+}, completely avoiding the need for the harsh conditions and long reaction time required when using H_2 or CO to reduce Ti^{4+} to Ti^{3+} [20,21].

In our previous work, we used H_2O_2 to oxidize TiH_2 and obtained a yellow-green precursor gel, after which different treatment methods were used to produce Ti^{3+} self-doped TiO_2 [22]. The amount of H_2O_2, the oxidation time, and other factors were not considered in the gel preparation process. The reaction of Ti^{4+} and H_2O_2 creates complex ions with different compositions, which would affect the types and amounts of oxygenated compounds generated on the TiH_2 surface during the gel preparation process, thereby affecting the final product performance. In this paper, the amount of H_2O_2 and the oxidation time were controlled to obtain two different states of precursor gel, and the gels were hydrothermally treated at 160 °C for different times. The relationship between the structures and photocatalytic performance of the different products obtained from the different precursor gels were studied in detail. The structure, morphology, and other properties of the samples were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR) spectroscopy, and UV-visible diffuse reflectance spectroscopy (UV-Vis DRS). Methylene blue (MB) solutions were used as simulated wastewater to evaluate the visible-light photocatalytic activity of the samples.

2. Experimental

2.1. Photocatalyst preparation

The precursor gel preparation process was similar to that described in our preliminary study [20], except that yellow and green precursor gels were obtained by controlling the amount of H_2O_2 and the oxidation time. The precursor gels were transferred to dry Teflon-lined autoclaves, and then heated to 160 °C for different times. After natural cooling to room temperature, the gray-blue or light-blue mixture was collected and washed with distilled water and ethanol three times, and then dried in an oven at 60 °C for 3 h. The products obtained from the yellow gel are labeled as Y-t, while the products obtained from green gel are labeled as G-t, where t indicates the hydrothermal treatment time (hours). For comparison, pure TiO_2 (denoted p-TiO_2) was obtained by hydrothermal treatment at 160 °C for 24 h using $TiCl_4$ as the Ti source.

2.2. Characterization

The phases of the final products were identified using XRD (Rigaku D/max-2500VPC) with graphite monochromated Cu K_α (λ = 0.15418 nm) radiation at a scanning rate of 0.02°/s. A Hitachi H-800 model TEM and JEOL JEM-2100 model HRTEM were used to determine the size and shape of the particles. TEM sample specimens were prepared by briefly ultrasonicating the sample powders in ethanol, followed by placing a drop of suspension onto a carbon-coated copper grid. The grids were dried before imaging. XPS measurements were carried out on an X-ray photoelectron spectrometer (ESCA 3000) using Al K_α (1486.6 eV) X-rays as the excitation source. C 1*s* (284.6 eV) was chosen as the reference. ESR measurements were carried out using a FA-200 spectrometer/X-bond. UV-vis DRS were recorded on a Shimadzu UV-2550 UV-vis spectrophotometer in the range 200–800 nm at room temperature, with a $BaSO_4$ standard used as the reference.

2.3. Photocatalytic activity measurements

The photocatalytic activities of the as-prepared samples were evaluated using the photodecomposition of MB solution under visible light irradiation at room temperature. The visible light was provided by a 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.) equipped with an ultraviolet cutoff filter (UVCUT 400, Beijing Trusttech Co., Ltd.). The vertical distance between the surface of the sample suspension and the light source was set at 30 cm. In a typical photocatalytic experiment, 0.06 g of sample was dispersed into 100 mL MB solution (2×10^{-5} mol/L) under constant stirring. The suspension was stirred for 30 min in the dark prior to irradiation. Aliquots of about 3 mL were removed from the suspension at 10 min intervals during visible light illumination and centrifuged to remove the remaining particles. The absorbance of the centrifuged solutions was measured at 500–800 nm as a function of