Available online at www.sciencedirect.com
ScienceDirect
Materials Letters 62 (2008) 447–450
materials letters
www.elsevier.com/locate/matlet

Preparation and photocatalytic activity of WO_3/TiO_2 nanocomposite particles

Dingning Ke [a], Huajun Liu [a], Tianyou Peng [a,b,*], Xun Liu [a], Ke Dai [a]

[a] Department of Chemistry, Centre of Nanoscience and Nanotechnology Research, Wuhan University, Wuhan 430072, China
[b] Hubei Key Laboratory for Catalysis and Material Science, College of Chemistry and Material Science, South-Central University for Nationalities, Wuhan 430074, China

Received 8 February 2007; accepted 24 May 2007
Available online 2 June 2007

Abstract

A novel photocatalyst WO_3/TiO_2 nanocomposite was prepared through a hydrothermal method by using cetyltrimethylammonium bromide (CTAB) as surfactant. The obtained WO_3/TiO_2 was characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), transmission electron microscope (TEM) and diffused reflectance spectroscopy (DRS). Photocatalytic experiments indicate that the nanocomposites show much higher photoactivity than that of pure TiO_2 in the photodegradation reaction of Rhodamine B (RhB). The increased photoactivity of WO_3/TO_2 may be attributed to the improvement of the light absorption properties and the slow down of the recombination between the photoexcited electrons and holes during the photoreaction.

Keywords: Catalysts; Nanocomposites; Titanium dioxide; Tungsten oxide; Rhodamine B

1. Introduction

Since Frank and Bard conducted photocatalytic degradation of CN^- in an aqueous solution over TiO_2 [1], heterogeneous photocatalysis technique by using the wide optical band gap material (e.g. TiO_2) has received increasing attentions over the past two decades for purifying various environmental pollutants in water and air. However, this technique cannot successfully satisfy the practical water treatment due to the rapid recombination of the photoexcited carriers and the limited efficiency in visible light. Therefore, many strategies have been taken to improve this situation. Among these, WO_3 coupling has been widely studied to improve the photocatalytic performances of TiO_2 since WO_3 can be served as an electron accepting species [2–7]. However, WO_3/TiO_2 or WO_x/TiO_2 were mainly prepared by physical mixing [8], multi-step grafting of ammonium tungstate [9,10], improved sol–gel method and coprecipitation method [11,12], and WO_3 or WO_x only wrapped on the surface of TiO_2 with low amount in the most situations.

In the present paper, WO_3/TiO_2 composite nanoparticles with high amount of WO_3 were prepared through a simplified hydrothermal method by employing cetyltrimethylammonium bromide (CTAB) as surfactant. Its photocatalytic activities were also evaluated by using Rhodamine B as a model organic compound.

2. Experimental section

2.1. Preparation and characterization of nanocomposites

A typical synthesis process for the preparation of WO_3/TiO_2 (molar ratio 1:1) nanocomposite oxides was as follows: 2.67 g Ti $-(SO_4)_2$ was added into 10 mL deionized water. The obtained solution was added into 15 mL of 0.18 M cetyltrimethylammonium bromide (CTAB) aqueous solution under magnetic stirring. Then 15 mL of 0.74 M Na_2WO_4 solution was added dropwise into above mixture under continuous stirring. Then the resulting mixture was transferred into a PTFE-lined autoclave, kept at 100 °C for hydrothermal treatment. After 96 h, the resulting solid was centrifuged, washed, dried and calcined. Pure TiO_2 sample was also prepared via a similar method as described above.

X-ray diffraction patterns were obtained on a XRD-6000 diffractometer using Cu Kα as radiation (λ=0.15418 nm). The morphology and grain size of the WO_3/TiO_2 particles were

* Corresponding author. Department of Chemistry, Centre of Nanoscience and Nanotechnology Research, Wuhan University, Wuhan 430072, China.
E-mail address: typeng@whu.edu.cn (T. Peng).

0167-577X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2007.05.060

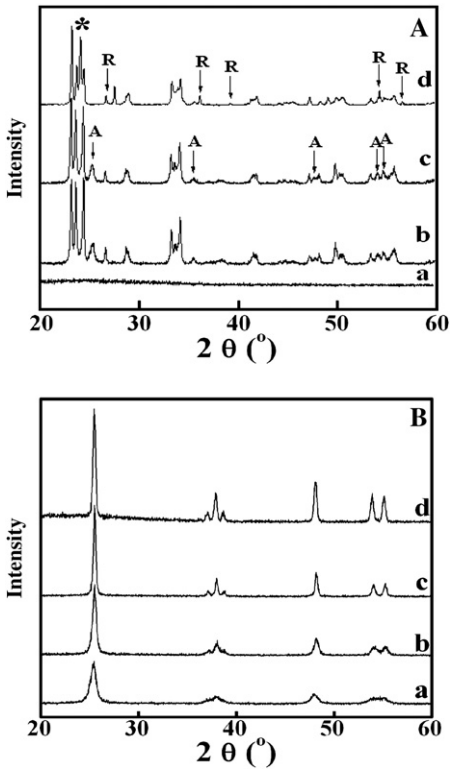

Fig. 1. X-ray diffraction (XRD) patterns of samples. (A) WO_3/TiO_2 (molar ratio 1:1) and (B) TiO_2 calcinations temperature (a): 450 °C, (b): 550 °C, (c): 750 °C, (d): 900 °C. R — rutile TiO_2, A — anatase TiO_2,* — orthorhombic WO_{3-}.

observed by Sirion FEG field emission transmission electron microscope. The transmission electron microscope images and microanalysis were obtained on a LaB6 JEM-2010 (HT)-FEF electron microscope. The diffused reflectance spectra were performed with a Cary 5000 UV–Vis-NIR spectrophotometer equipped with an integrating sphere.

2.2. Measurement of photocatalytic activity

The photocatalytic experiments were conducted to photodegrade RhB in photocatalyst aqueous suspension system. Reaction suspensions were prepared by adding 0.0080 g photocatalyst into 30 mL RhB (1.0×10^{-5} M) aqueous solution. Prior to irradiation, the suspension was stirred in the dark for the adsorption–desorption equilibrium. The suspension containing RhB and photocatalyst was then irradiated under the UV light (250 W high pressure Hg lamp with a maximal emission at approximately 365 nm). Photodegradated sample was taken out from the reaction suspension and centrifuged RhB was analyzed using a Shimadzu UV-240 spectrophotometer.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction (XRD) patterns for WO_3/TiO_2 (molar ratio 1:1) and the pure TiO_2 sintered at different temperatures are depicted in Fig. 1 (A) and (B), respectively. Enhancing the calcination temperature to 550 °C, the XRD pattern shows obvious diffraction peaks for the monoclinic WO_3 (JCPDS No.83-950) and anatase TiO_2 (JCPDS No. 1-562), indicating a preferable crystallinity of the composite sample after sintering at 550 °C. Previous investigations on bulk WO_3 have reported the following phase transformation sequence: triclinic (−30 °C)→monoclinic (330 °C)→orthorhombic (740 °C)→tetragonal [13]. A new strong diffraction peak of the XRD pattern (WO_3/TiO_2) that correspond with orthorhombic WO_3 (JCPDS No. 20-1324) about 24° emerges when calcination at 900 °C, which gives evidence of WO_3 in the composite undergoing the phase transformation to orthorhombic. This phenomenon suggests that the presence of TiO_2 can prevent the phase transformation from WO_3 monoclinic to orthorhombic.

For the pure TiO_2, the XRD patterns show that it remained an anatase phase after calcinations at 900 °C. But the TiO_2 in the WO_3/TiO_2 composite oxide completely transformed to rutile accompanying at the same calcination condition. From this result, it is easy to know that the WO_3 would promote the phase transformation from anatase to rutile TiO_2.

There is not any new diffraction peak can be ascribed to the crystal phase of $W_xTi_{1-x}O_2$ in the present calcination temperature ranges, which can be concluded that no new solid solution of $W_xTi_{1-x}O_2$ is formed or at least that only trace amount of solid solution like $W_xTi_{1-x}O_2$ is formed in the reaction process, which is consistent with some previous results [8,14]. It is possible that WO_3 can accept electrons from the conduction band of TiO_2 to form W (V) and extra oxygen vacancies due to the lower standard reduction potential (ca.−0.03 V) from W (VI) to W (V) [5]. Whereas the oxygen vacancies can generally accelerate the phase transformation from TiO_2 anatase to rutile [15,16].

3.2. Microstructure analysis

Fig. 2 show the field emission scanning electron microscope and transmission electron microscope images of WO_3/TiO_2 (1:1) calcined at 550 °C. As it can be seen from the FESEM image (Fig. 2A), the

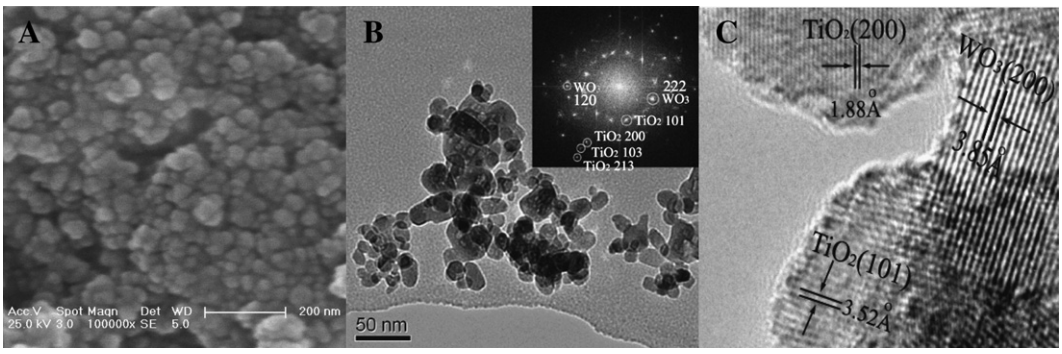

Fig. 2. FESEM image (A), TEM (B) and HRTEM images (C) of WO_3/TiO_2 (molar ratio 1:1) after calcination at 550 °C.