Materials Letters 136 (2014) 258–261

Contents lists available at ScienceDirect

Materials Letters

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

Synthesis of a novel N–H–TiO_2 photocatalyst by annealing in NH_3 and H_2 for complete decomposition of high concentration benzene under visible light irradiation

Minghui Li, Wulin Song*, Lei Zeng, Dawen Zeng, Changsheng Xie

State Key Laboratory of Materials Processing and Die and Mould Technology, Huazhong University of Science and Technology, Wuhan 430074, China

ARTICLE INFO

Article history:
Received 4 June 2014
Accepted 9 August 2014
Available online 20 August 2014

Keywords:
TiO_2
Photocatalysis
Nanoparticles
Nitrogen doping
Hydrogenation
Defects

ABSTRACT

A novel N–H–TiO_2 photocatalyst was prepared via hydrothermal synthesis followed by a thermal treatment in NH_3 and H_2 atmospheres. The results showed that benzene with the initial concentration of 150 ppm ($\pm$5 ppm) could be thoroughly removed by N–H–TiO_2 under visible light irradiation. The influences of doping and hydrogenation on properties of TiO_2 samples were investigated. It is suggested that the disordered surface layer introduced by hydrogenation contributes to the excellent photocatalytic activity of N–H–TiO_2. The synergistic effect of N doping and surface oxygen vacancies was also confirmed by ultraviolet–visible diffuse reflectance spectra and photoluminescence. Moreover, the diverse role of oxygen vacancies in different positions of TiO_2 has been focused on.

1. Introduction

Benzene, as one of the confirmed carcinogenic substances, is difficult to degrade due to its conjugated π-bond [1]. Hence, there is absolutely a need to develop an effective approach to remove it. It is widely accepted that TiO_2 has many advantages, such as abundance, chemical stability and high activity under ultraviolet (UV) irradiation, providing an efficient way to solve the environment problems [2]. However, the wide band gap and rapid recombination of photogenerated electrons and holes hinder visible light absorption and photocatalytic activity of TiO_2 photocatalyst. Hence various approaches have been developed to engineer band structure and introduce defects, which will improve optical absorption and photocatalytic performance of TiO_2. Among the efforts to modify TiO_2, nitrogen doping and hydrogenation have been extensively investigated [3,4]. Unfortunately, the efficiency of current TiO_2 photocatalyst in decomposing pollutants under visible light remains low so far [5]. Furthermore methods for preparing highly active TiO_2 usually required complicated procedure or rigorous conditions, which definitely became the obstacles for practical application [6].

Here, we present a highly efficient N–H–TiO_2 photocatalyst prepared by a simple hydrothermal method. Surprisingly N–H–TiO_2 exhibites amazing photocatalytic activity in quickly and thoroughly degrading high concentration benzene under visible light irradiation, which is timesaving, economical and efficient with simple preparation technology for large-scale application in removing indoor pollutants.

2. Experiments

TiO_2 was synthesized by a hydrothermal method. Typically, 2 mL tetra-n-butyl titanate was added dropwise to 75 mL distilled water under vigorous magnetic stirring and then the hydrolysate transferred into a 100 mL Teflon-lined autoclave to react at 160 °C for 12 h. Afterwards, the obtained precipitate was separated by a centrifuge and washed several times, and then dried in an oven at 80 °C overnight to acquire TiO_2 nanoparticles. TiO_2 was further modified by annealing at 600 °C in H_2 for 2 h as well as in NH_3 and H_2 for 4 h, denoted as H–TiO_2 and N–H–TiO_2 respectively.

The structures and morphologies of samples were observed by X-ray diffraction (XRD, X'Pert PRO diffractometer with Cu Kα radiation) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F30 field-emission TEM). Ultraviolet–visible diffuse reflectance spectra (UV–vis DRS) were obtained on a Shimadzu U-3010 spectrometer using $BaSO_4$ as a reference. Photoluminescence (PL) emission spectra were acquired under excitation at 325 nm using an Edinburgh Instruments PLSP920 spectrometer.

Photocatalytic activities of the samples were tested by degrading benzene under visible light irradiation for 3 h. A 300 W Xe-arc

* Corresponding author. Tel./fax: +86 27 87557453.
E-mail address: wulins@126.com (W. Song).

http://dx.doi.org/10.1016/j.matlet.2014.08.061
0167-577X/

lamp (CEL-HXF300) with a UV-cutoff filter ($\lambda < 400$ nm) was used as the light source. Generally, 100 mg TiO_2 was dispersed on the loading plate. Afterwards, 150 ppm (± 5 ppm) benzene was injected into the reaction chamber of a gas chromatograph (GC) to measure the concentration of benzene and CO_2. Then the samples H–TiO_2, N–H–TiO_2 and N–H–TiO_2-s (N–H–TiO_2 stored over 6 months) were tested successively. The degradation efficiency is calculated by the functions C/C_0 and $C-C_0$, where C_0 is initial concentration of benzene or CO_2, and C is concentration during the photodegradation process. A blank control test without photocatalyst was conducted for reference.

3. Results and discussion

The visible light photocatalytic activity of TiO_2, H–TiO_2, N–H–TiO_2 and N–H–TiO_2-s samples was evaluated with a blank control test, as shown in Fig. 1. The result shows that N–H–TiO_2 and N–H–TiO_2-s exhibit the best photocatalytic activity, which indicates the unique performance and good stability of N–H–TiO_2. The conversion of benzene over N–H–TiO_2 under visible light irradiation is as high as 100% within 3 h. Meanwhile, the performance of H–TiO_2 is better than that of TiO_2 while the blank test gives almost no activity when decomposing benzene. Obviously, the fundamentally enhanced performance of N–H–TiO_2 can be attributed to the synergistic effect of N doping and hydrogenation.

Fig. 2 displays the crystalline structures of all the samples characterized by XRD. The diffraction peaks of all the samples can be indexed to anatase (JCPDS File no. 21-1272). Moreover, H–TiO_2 and N–H–TiO_2 have increased crystallinity after annealing. The average particle sizes of TiO_2, H–TiO_2 and N–H–TiO_2 are, respectively estimated to be 19.46, 36.72 and 33.55 nm by the Scherrer formula, consistent with TEM images presented in Fig. 3. Furthermore, surface amorphous structure introduced by hydrogenation can be clearly observed in H–TiO_2 depicted in the range 25–35° of XRD and the blurry edge of HRTEM image (e). This result is similar to those of previous investigations for TiO_2 nanoparticles annealed in reducing atmospheres, which show that the disordered phase separates fully crystalline inner part from disordered (amorphous) surface of a nanoparticle [7,8].

Fig. 4 shows the optical absorption properties examined by UV–vis DRS. The onset of optical absorption edge of N–H–TiO_2 has extended to 550 nm compared with TiO_2, which indicates the typical redshift of nitrogen doped TiO_2 [9]. This can be assigned to the significant cause for enhanced visible light absorption and band gap narrowing of N–H–TiO_2. Besides, a new absorption band up to infrared region emerging in H–TiO_2 means that band structure of TiO_2 has been modified by hydrogenation, which has been reported by previous studies [10,11].

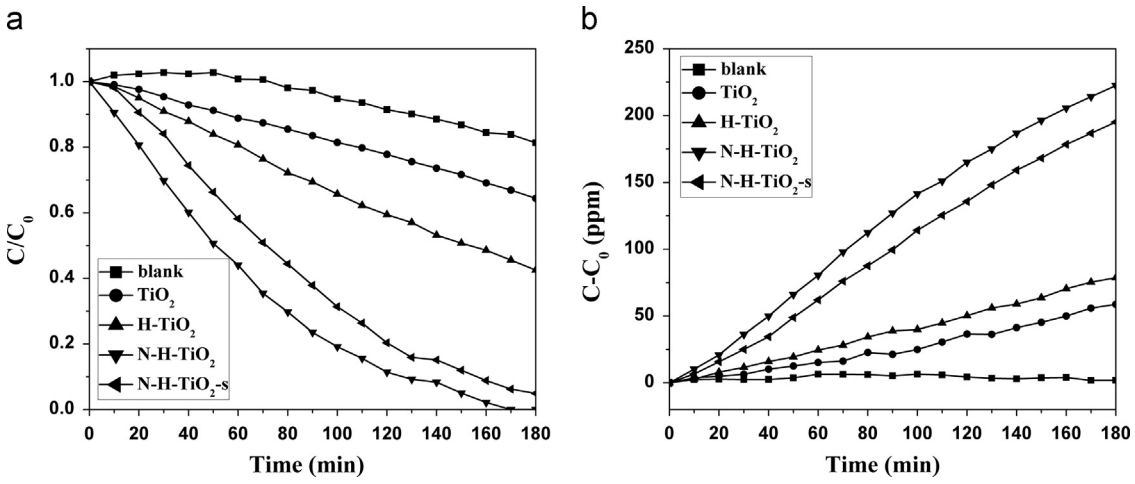

Fig. 1. Photocatlytic decomposition of benzene (a) and CO_2 generation (b) using TiO_2, H–TiO_2, N–H–TiO_2 and N–H–TiO_2-s under visible light irradiation.

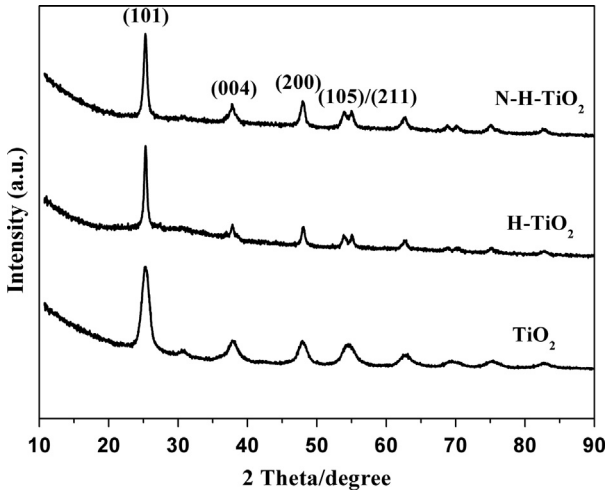

Fig. 2. XRD patterns of TiO_2, H–TiO_2 and N–H–TiO_2.