Journal of Alloys and Compounds 754 (2018) 153–162

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Enhanced photodegradation of sulfamethoxazole by a novel WO_3-CNT composite under visible light irradiation

Wenyu Zhu [a, b], Zhong Li [c], Chao He [d], Sun Faqian [a], Yan Zhou [a, b, *]

[a] School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798, Republic of Singapore
[b] Nanyang Environment and Water Research Institute (NEWRI), 1 Cleantech Loop, CleanTech One, Singapore, 637141, Republic of Singapore
[c] School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798, Republic of Singapore
[d] School of Chemical and Biomedical Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798, Republic of Singapore

ARTICLE INFO

Article history:
Received 21 December 2017
Received in revised form
15 April 2018
Accepted 26 April 2018
Available online 27 April 2018

Keywords:
Carbon nanotubes
Tungsten trioxide
Antibiotic
Sulfamethoxazole
Photocatalysis

ABSTRACT

As one of the emerging environmental issues, the existence of antibiotics in the water bodies is believed to pose threat to not only the environment but also human health. Recently, semiconductor-based photocatalysis has drawn wide attention since it shows great potential in removal of organic pollutants as well as other emerging organic contaminants from aquatic systems. Therefore, in this study, efforts were devoted to fabrication of novel visible light driven heterogeneous photocatalysts to explore their possible applications in photodegradation of antibiotics. Particularly, multi-walled carbon nanotubes (MWCNTs) was selected as co-catalyst to WO_3, and three WO_3-MWCNTs (WO_3-CNT) composites were prepared as photocatalysts, namely WT-2, WT-4 and WT-8. The physical and chemical properties of these obtained WO_3-CNT composites were thoroughly characterized by different methods. Simultaneously, sulfamethoxazole (SMX), one of the most widely used antibiotics was chosen as the target pollutant to evaluate the photocatalytic performance of the WO_3-CNT composites. The degradation intermediates were analyzed by LC/MS/MS, and subsequently a possible degradation mechanism was proposed. Compared to bare WO_3, all three WO_3-CNT composites showed notably enhanced photocatalytic activity, demonstrating that they have the potential to be used as effective photocatalysts to degrade sulfonamide class of antibiotics.

1. Introduction

With rapid industrialization, many hazardous contaminants have been released to the environment. Among various kinds of contaminants, the emergence of antibiotics and their residues in various aquatic systems has drawn intensive attention due to their potential threat to not only aquatic ecosystems but also human health [1,2]. Nevertheless, many studies have proved that conventional water treatment cannot efficiently remove antibiotics as well as other recalcitrant organics. Consequently, it is still urgent to develop highly efficient, stable, and eco-friendly “green” methods to achieve the elimination of antibiotics and their residues from aquatic systems [3,4].

Semiconductor-based photocatalysis has emerged with inestimable superiority since it is considered as an economic, renewable, clean, and safe technology, which requires only the inexhaustible solar light as driving force, and suitable semiconductors as photocatalysts to conduct catalytic reactions for a variety of applications including decomposition of organic pollutants [4]. However, the challenge lies in its effectively harvesting and conversion of solar energy. In recent years, semiconductors with nanostructures have attracted a lot of attention and they can be applied as photocatalysts driven by solar energy.

Though TiO_2 has been widely studied as photocatalysts, the wide band gap (3.2 eV) of it largely limit its photocatalytic efficiency which could only be photoexcieted by UV light irradiation. It is important to note that UV light only accounts about 3–4% of the whole solar spectrum, while visible light ($\lambda > 400$ nm) takes a proportion of around 44% [5]. Thus, if visible light could be effectively utilized by appropriated designed photocatalysts, the photocatalytic performance can be largely improved [6]. To achieve so, one important way is to search semiconductors with narrower

* Corresponding author. School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798, Republic of Singapore.
E-mail addresses: zhuw0007@e.ntu.edu.sg (W. Zhu), zhouyan@ntu.edu.sg (Y. Zhou).

https://doi.org/10.1016/j.jallcom.2018.04.286
0925-8388/

band gaps that can be powered by visible light, which has now attracted lots of attention. Tungsten trioxide (WO_3) is an n type semiconductor with a band gap of 2.4–2.8 eV, and it is recognized as a promising candidate due to its specific physical and chemical properties [7]. Nevertheless, Pure WO_3 as photocatalyst is found to be not efficient enough due to its low conduction band level which restricts its capability to react with electron acceptors like oxygen while concurrently increases the electron-hole recombination rate [8,9]. Thus, to improve its photocatalytic efficiency, it is crucial to effectively reduce the recombination rate and to tune the energy band structure [10]. Generally, two strategies are widely used, namely nanostructuring the morphology and modifying the surface of WO_3 with co-catalysts [11–16].

Particularly, the use of multi-walled carbon nanotubes (MWCNTs) as co-catalysts in the photocatalytic system has attracted wide attention due to their unique properties. MWCNTs have large specific surface area, specific tubular structure, high mechanical strength, good electron conductivity and chemical stability [17–22]. They are suggested to be capable to work as catalyst supports or catalyst carriers to provide more activity sites, moreover, as a result of their good conductivity they can act as electron sink to improve the electron-hole separation process [18,21–23].

Although there are some studies on application of WO_3-CNT composites in the areas like gas sensors [24,25], supercapacitor [26], acid electrooxidation [27], only very few of them investigated the photocatalytic performance of WO_3-CNT composites [16,28]. Hence, in this study, efforts were given to study the possible photocatalytic performance of WO_3-CNT obtained via a simple hydrothermal method. In particular, sulfamethoxazole (SMX), one of the most extensively used antibiotics [29–32] was applied to evaluated the photocatalytic performance of as prepared WO_3-CNT composites under visible light irradiation.

2. Materials and methods

2.1. Materials

MWCNTs was purchased from Shenzhen Nanotech Port Co. China. Nitric acid (HNO_3, 70%), hydrochloric acid (HCl, 35%), ethanol, dimethylformamide (DMF), sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), *iso*-propanol (IPA), benzoquinone (BQ) and sodium oxalate (SO) and sulfamethoxazole (SMX) were purchased from Sigma-Aldrich. Hydrogen peroxide (H_2O_2, 30%) was supplied by VWR. All chemicals were used as received and no further purification was needed.

2.2. Preparation of WO_3-CNT composites

The Pristine MWCNTs were firstly refluxed in concentrated HNO_3 at 120 °C for 4 h under stirring to remove metallic impurities and introduce oxygen-containing functional groups onto the surface of MWCNTs [33]. The functionalized MWCNTs were washed and prepared following the procedure described by Nassr et al. [34], which were subsequently named as fCNTs. The fCNTs were dispersed into DMF-H_2O (20 vol%) solution with the assistance of ultrasonic, and the final concentration was 0.5 mg mL^{-1}.

For the synthesis of WO_3-CNT composites, a simple hydrothermal method was applied. Three different WO_3-CNT composites were prepared which contained different amount of fCNTs. For each sample, 400 mg $Na_2WO_4 \cdot 2H_2O$ was firstly dissolved in above fCNTs DMF-H_2O mixture, and the amount of fCNTs was set at 2.0 mg, 4.0 mg and 8.0 mg separately. DI water was added to make sure that the total volume of each sample was 16 mL. Under continuous stirring, 5 mL 35% HCl was then slowly added. After that, the suspension was transferred to a 45 mL Teflon-lined stainless steel autoclave to undergo a heating process for 4 h at 140 °C. After cooling down naturally, the sample was collected and washed with ethanol and DI water for several times before being dried by vacuum freeze drier. Pure WO_3 sample was prepared with the same method where $Na_2WO_4 \cdot 2H_2O$ was dissolved in DI water. With different amount of fCNTs, these three samples were named WT-2, WT-4 and WT-8 respectively.

2.3. Materials characterization

The crystal phases of the obtained samples were characterized by X-ray powder diffraction (XRD) using a D8-Advacne Bruker-AXS diffractometer with Cu Kα irradiation operated at 40 kV and 30 mA. The morphologies and structures of the products were observed by a field-emission scanning electron microscope (FESEM, JEOL 6340) and transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) using a JEOL 2010 microscope operated at 200 kV. X-ray photoelectron spectra (XPS) were measured by a Kratos Axis Ultra Spectrometer with a monochromic Al Kα source at 1486.7 eV, a voltage of 15 kV and an emission current of 10 mA. UV–Vis Spectra were obtained with a Scan UV–Vis spectrophotometer (UV–Vis Spectrometer 2501 P C, Shimadzu). Photoluminescence (PL) emission spectra were recorded on a PerkinElmer LS 55 Fluorescence spectrometer at 325 nm. Raman Spectra were conducted by a Renishaw inVia Raman microscope with the excitation wavelength of 532 nm.

2.4. Photocatalytic activity evaluation for SMX degradation

Photocatalytic activity of pure WO_3 nanoplates and its WO_3-CNT composites was evaluated by degradation of SMX (10 mg L^{-1}) using a 1.5 a.m. solar simulator (NEWPORT, USA) with a 300 W Xe arc lamp. Dichroic mirrors were utilized to control wavebands in specific ranges 420–630 nm (visible light). To remove the UV residual, a polycarbonate filter was utilized. In a typical experimental procedure, 50 mg sample was firstly dispersed into 50 mL of DI water in the reaction vessel of 250 mL, and then mixed with 50 mL of 20 mg L^{-1} SMX solution and the final concentration was 10 mg L^{-1}. After that, the vessel was continuously stirred for 1 h in the dark to reach the adsorption equilibrium. The photocatalytic test was initiated by switching on the solar simulator. Sampling was carried out at various time intervals by drawing 3.0 mL of the aliquot from the reaction vessel. The samples were immediately filtered with 0.45 μm cellulose acetate syringe membrane filters. Filtered samples were analyzed by high performance liquid chromatography (HPLC) to determine the SMX concentration. Operating conditions of HPLC can be found in Supplementary Information. The formation of various radicals in the photocatalytic process was investigated using SO, BQ and IPA as scavengers (0.5 mM).

3. Results and discussion

3.1. Morphology and crystal structure characterization

Pure WO_3 powder presented a light yellow color as illustrated in Fig. S2, on the contrary, the sample color turned to grey and the more fCNTs added the darker the color was. In order to investigate the possible composition and crystallinity change caused by the fCNTs introduction, XRD was applied and the result was shown in Fig. 1. Specifically, the XRD pattern of bare WO_3 well matched the standard XRD pattern of monoclinic-WO_3 (m-WO_3, PDF NO: 01-083-0951) [35–37]. No other peak was spotted indicating the high purity of the as prepared WO_3. Moreover, all observed peaks were sharp suggesting the good crystallinity of WO_3. In the case of fCNTs, two typical peaks located at around 25.7° and 42.7° which can be