Applied Surface Science 459 (2018) 363–375

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Facile synthesis of Pt assisted Bi-Bi_2WO_{6-x} with oxygen vacancies for the improved photocatalytic activity under visible light

Shuoshuo Zhang[1], Wenhong Pu[1], Hao Du, Yunyang Wang, Changzhu Yang*, Jianyu Gong*

School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

ARTICLE INFO

Keywords:
Pt/Bi-Bi_2WO_{6-x}
Oxygen vacancies
Bisphenol A
Platinum
Photocatalytic activity

ABSTRACT

Pt assisted self-modified microflower like Bi_2WO_6 composites (Pt/Bi-Bi_2WO_{6-x}) were prepared using a simple in-situ $NaBH_4$ reduction method. The characterization of these samples was systematically studied and the photocatalytic activity of as-prepared samples was evaluated through the degradation of bisphenol A (BPA) under visible light illumination. The results indicated that the self-modified Bi-Bi_2WO_{6-x} presented the high separation efficiency of photo-generated carriers due to the introduction of the oxygen vacancies and metallic Bi. Furthermore, because of the presence of Pt on Bi-Bi_2WO_{6-x}, a higher concentration of generated oxygen vacancies was also obtained, resulting in the excellent photocatalytic performance. The 2%Pt/0.2Bi-Bi_2WO_{6-x} sample exhibited the highest degradation efficiency of BPA under visible light illumination, which was approximately 2.88 times and 1.52 times as high as that of Bi_2WO_6 and 0.2Bi-Bi_2WO_{6-x}, respectively. In addition, the degradation efficiency clearly improved at high pH value. The highest degradation efficiency was obtained at alkaline solution (pH = 9). According to the mechanism study, the enhanced photocatalytic property on 2%Pt/0.2Bi-Bi_2WO_{6-x} should be attributed to the presence of oxygen vacancies on the material surface, since oxygen vacancies states were partly overlapping of with the valence band (VB), and increased the width of VB, reducing the band gap of Bi_2WO_6. The possible photocatalytic mechanism was also simulated by chemical calculations, which was proposed to guide further related studies.

1. Introduction

Bisphenol A (BPA) acts as a synthetic phenol, and has been extensively used as a precursor for the production of phenol resins, polyacrylates, polyesters, epoxy resins, and polycarbonate plastics with excellent physicochemical properties [1,2]. BPA is defined as an endocrine disruptor that can induce carcinogenesis, reproductive toxicity, abnormal inflammatory or immune response, and disorders of brain or nervous system through various cell signaling pathways [3]. Nowadays, BPA is widely present in surface water, and causes serious and terrible problems for ecosystem. Many methods have been reported to treat BPA, such as adsorption [4], biological process [5] and advanced oxidation processes (AOPs) [6], including electrochemical oxidation [7], ozone technology [8], Fenton system [9]. However, these continue to suffer from high cost and incomplete mineralization, producing secondary pollution and so on.

Photocatalytic technique has already become one of the hot topics on the degradation of environmental pollutants due to its completely degradable, clean and renewable features [10,11]. Generally, TiO_2 has been most studied and widely used in wastewater treatment and air purification [12]. However, TiO_2 has a weakest point. That is, its band gap is too wide to be excited by visible light, thereby limiting its practical applications to a large extent [13]. In order to make use of solar energy efficiently, plenty of visible light activated photocatalysts were studied. Bismuth tungstate (Bi_2WO_6), one of the simplest Aurivillius oxides, has attracted extensive attention because of its suitable band gaps, non-toxicity and low cost [14]. Nevertheless, due to the low efficiency of photo-absorption and weak photo electron-hole pairs separation efficiency of Bi_2WO_6, the photocatalytic performance of Bi_2WO_6 remains relatively poor [15]. Up to now, many strategies have been employed in order to acquire Bi_2WO_6 materials with high photocatalytic activity, such as controllable syntheses [16,17], surface modification [18,19], and coupling with other semiconductors [20–22].

At present, studies have found that this photocatalytic activity could be enhanced by making oxygen vacancies [23,24]. Lv reported the wide–range–visible photoresponse Bi_2WO_{6-x} nanoplates fabricated by introducing surface oxygen vacancies through the controllable hydrogen reduction method exhibited grade degradation efficiency, which

* Corresponding author.
E-mail address: jygong@hust.edu.cn (J. Gong).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.apsusc.2018.07.222
Received 19 June 2018; Received in revised form 25 July 2018; Accepted 30 July 2018
Available online 31 July 2018
0169-4332/

was 2.1 times as high as that of Bi_2WO_6 [25]. The deposition of noble metal nanoparticles (NPs) over semiconductors could also bring a large improvement in photocatalytic performance due to surface plasmonic resonance (SPR) [26,27]. Ag/Bi_2WO_6 [28], Au/Bi_2WO_6 [26] and Pt/Bi_2WO_6 [29,30] plasmonic composites have been reported to enhance visible photocatalytic activity. Yu [29] synthesized a Pt/Bi_2WO_6 composite via the hydrothermal method followed by the combination of Pt using photo-deposition to improve the photocatalytic performance of Bi_2WO_6 under visible light irradiation, and the deposition of the optimal amount of 1%Pt brought an approximately 2.8 times increase in degradation rate of acid orange II. Incorporating additional Bi metal nanostructures into Bi_2WO_6 has also been regarded as an effective method to boost the photocatalytic activity of Bi_2WO_6. According to Huang's research [31], Bi/Bi_2WO_6 fabricated by a simple two-step route obtained high efficiency for the photocatalytic degradation of organic contaminants. Yu [32] produced metallic Bi deposited on Bi_2WO_6 composite photocatalyst via simple in-situ reduction method, using Bi_2WO_6 as self-sacrificing template. When the molar ratio of Bi_2WO_6 and $NaBH_4$ was 5:1, the photocatalyst exhibited the highest efficiency, which was over three times as high as Bi_2WO_6 for the degradation of phenol.

In this work, the Pt/Bi-Bi_2WO_{6-x} sample with great photocatalytic property was fabricated by introducing surface oxygen vacancies. Self-modified Bi-Bi_2WO_{6-x} combined with Pt was synthesized via a simple in-situ $NaBH_4$ reduction method. With a certain trace of $NaBH_4$ as the reducing agent, the oxygen vacancies and metallic Bi could be formed on the surface of materials. Meanwhile, Pt was also produced by the reduction of $H_2PtCl_6{\cdot}6H_2O$. The photocatalytic activity of different Pt content modified Bi_2WO_6 samples was investigated through the degradation of BPA under visible light illumination. These results revealed that Pt/Bi-Bi_2WO_{6-x} exhibited higher photocatalytic performance when compared to Bi_2WO_6. In the present study, Pt/Bi-Bi_2WO_{6-x} performed a high photocatalytic response in the range of visible light, and it was anticipated that this compound could be utilized for broad applications in remediating polluted wastewater.

2. Experimental

2.1. Materials and chemicals

$Bi(NO_3)_3{\cdot}5H_2O$, $Na_2WO_4{\cdot}2H_2O$, bisphenol A, $NaBH_4$, $H_2PtCl_6{\cdot}6H_2O$, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), N,N-diethyl-p-phenylenediamine (DPD), horseradish peroxidase (HRP) and anhydrous ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd., China. All solutions were prepared with deionized water. All the chemicals used in this work were of analytical grade and without further purification.

2.2. Photocatalysts preparation

Bi_2WO_6 was synthesized via a traditional hydrothermal method. Briefly, 0.971 g $Bi(NO_3)_3{\cdot}5H_2O$ and 0.329 g $Na_2WO_4{\cdot}2H_2O$ were added to 20 mL and 10 mL deionized water, respectively. After stirring for 30 min, the $Na_2WO_4{\cdot}2H_2O$ solution was added into $Bi(NO_3)_3{\cdot}5H_2O$ suspension and magnetically stirred for another 60 min. Then the mixture was transferred into a 50 mL Teflon-lined stain-less autoclave and heated at 180 °C for 20 h. When cooled to room temperature naturally, the precipitate was washed with deionized water and anhydrous ethanol for several times followed by dried at 60 °C for 4 h in vacuum.

Bi-Bi_2WO_{6-x} samples were prepared using a simple in-situ $NaBH_4$ reduction method. 20 mL of $NaBH_4$ solution with different concentration (4 mM, 8 mM, 12 mM and 16 mM) was added dropwise into 20 mL of Bi_2WO_6 suspension (40 mM) under a nitrogen atmosphere, and stirred for 60 min, respectively. The corresponding molar ratio of $NaBH_4$ and Bi_2WO_6 was 0.1:1, 0.2:1, 0.3:1 and 0.4:1. The precipitates were collected and washed with deionized water for three times, and dried at 60 °C for 4 h in vacuum to obtain the samples. The corresponding samples were marked as 0.1Bi-Bi_2WO_{6-x}, 0.2Bi-Bi_2WO_{6-x}, 0.3Bi-Bi_2WO_{6-x} and 0.4Bi-Bi_2WO_{6-x}. The Pt/Bi-Bi_2WO_{6-x} was synthesized in a similar way with the presence of a certain amount of $H_2PtCl_6{\cdot}6H_2O$ (20 mM) and $NaBH_4$ (8 mM, 20 mL) as the reducing agent. The precipitates were washed and dried in the same manner. The contents of Pt in Pt/Bi-Bi_2WO_{6-x} were 1.0%, 2.0%, 3.0% and 4.0% by mass ratio marked as 1%, 2%, 3%, and 4% Pt/0.2Bi-Bi_2WO_{6-x}, respectively.

2.3. Characterization

A Sirion 200 FSEM (FEI, Netherlands) was employed for nanoparticles morphology characterization. A JEM-2100F STEM/EDS HRTEM (JEOL, Japan) was used to characterize the samples. The phase detection and analysis were accomplished by XRD (2θ ranges from 10 to 90) using a diffractometer at 40 kV and 40 mA (X'Pert PRO, PANalytical B.V., the Netherlands) with radiation of a CuKa target (k = 0.154 nm), and the XRD results were analyzed with Highscore software. Electron paramagnetic resonance (EPR) spectroscopy (Bruker A200, Germany) was used to identify the generation of ROS and presence of oxygen vacancies. Raman spectra was obtained by using Thermo Fischer DXR (Thermo Fisher Scientific, USA) at ambient temperature. X-ray photoelectron spectroscopy (XPS) measurement was performed on a 5300 ESCA instrument (Perkin–Elmer PHI Co., USA). The UV–visible diffuse reflectance spectra was obtained with a UV–visible spectrophotometer equipped with CARY-50 Probe (USA). The reactive oxygen species (ROS) was detected with electron paramagnetic resonance (EPR) spectroscopy (Bruker A200, Germany). The UV–visible diffuse reflectance spectra (DRS) was measured by a UV–visible spectrophotometer equipped with CARY-50 Probe (USA).

2.4. Photocatalytic experiments

The photocatalytic activity of as-prepared samples was evaluated by the photocatalytic degradation of BPA under visible light irradiation provided by a 300 W Xe lamp with a 420 nm cutoff filter. 0.1 g photocatalyst was added to 100 mL BPA (0.2 mM) solution. Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to achieve absorption-desorption equilibrium. At 30 min intervals, 1 mL suspension was taken and filtered through 0.45 μm membrane filter for analysis. The concentration of BPA was analyzed by high performance liquid chromatography (HPLC, Agilent) equipped with a UV detector (SPD-10AV) and C18 column (250 mm × 4.6 mm). The mobile phase was a mixture of 60/40 (v/v) methanol-water mixture. The wavelength for detection was 225 nm and the rate of eluent is 0.8 mL min^{-1}. The concentration of H_2O_2 was measured by using DPD and HRP reported before [33].

2.5. Photochemical electro-catalytic (PEC) testing

VMP2/Z multichannel Potentiostat (Princeton Applied Research) was used to measure the photo-electrochemical responses of Bi_2WO_6, 0.2Bi-Bi_2WO_{6-x}, 2%Pt/0.2Bi-Bi_2WO_{6-x} in a three electrode cell. The doped the prepared nanoparticle electrode and a platinum plate served as the working and counter electrodes, saturated calomel electrode served as reference electrode. 0.1 M Na_2SO_4 aqueous solution was used as electrolyte solution. A 300 W Xe lamp ($\lambda > 420$ nm) was used as a visible light source. The photocurrent responses of the samples as visible light switched on and off were measured at 1.2 V (νs. SCE).

2.6. First-principles calculations

The structure of Bi_2WO_6 crystal was fabricated according to the theoretical atomic coordinates of Bi, W and O in Bi_2WO_6 reported everywhere [34]. All first principle calculations were conducted by using