Materials Science in Semiconductor Processing 33 (2015) 36–41

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Solar photocatalytic activity of chemical solution-prepared barium tungstate nanostructures

Zahra Barzgari *, Seyede Zahra Askari, Ali Ghazizadeh

Department of Chemistry, Payame Noor University, Birjand, Iran

ARTICLE INFO

Available online 11 February 2015

Keywords:
Photocatalytic activity
Nanostructured
$BaWO_4$
Sunlight
Methylene blue

ABSTRACT

Nanostructured barium tungstate ($BaWO_4$) as a solar photocatalyst has been successfully synthesized by a chemical solution method. The sample was characterized using X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and UV–vis diffuse reflectance spectroscopy. Then, the photocatalytic degradation of methylene blue (MB) in an aqueous medium was evaluated with nanostructured $BaWO_4$ under direct sunlight irradiation. The effects of the initial pH, and the catalyst dosage on the dye degradation were studied in order to achieve maximum degradation efficiency. The nanostructured $BaWO_4$ exhibited good photocatalytic activity for degradation of MB under sunlight irradiation at pH 10 after 3 h of irradiation. Also, the optimal catalyst loading of 25 mg/L obtained throughout the present study. The degradation of the dye followed the first-order reaction and the adsorption obeyed the Langmuir model.

1. Introduction

Today, organic dyes commonly used in many industries are important environmental contaminants due to their non-biodegradability, high toxicity to aquatic creatures and carcinogenic effects on humans [1,2]. Thus, simple and economical techniques for the removal of the hazardous dyes are an urgent need. To date, various methods such as physical methods, biological treatment, chemical oxidation, electrochemical oxidation, and photocatalytic degradation have been developed to remove dyes from waste water [3–7]. Among these techniques, the photocatalytic process has attracted considerable attention in recent years due to its advantages such as unlimited resources, low cost, and environmental friendliness [7–9]. Abundant solar energy from renewable resources can be used efficiently in the photocatalytic processes for the degradation of organic pollutants instead of artificial light sources that are expensive and hazardous [10]. So, photodegradation of dyes using solar light is an economical process.

Among various semiconductor oxides, the tungsten compounds are the most studied photocatalysts for environmental decontamination purposes because of their unique combination of physical and chemical properties [11–14]. Alfaro and de la Cruz investigated the photocatalytic activity of bismuth tungstates for degradation of Rhodamine B under visible light irradiation [14]. According to their results, the sample prepared by co-precipitation showed a better degradation of the dye than the sample of solid state reaction. $ZnWO_4$ has been utilized for photocatalytic production of hydrogen from water and mineralization of organic pollutants under UV light irradiation [15–17].

Recently, $BaWO_4$ has potential for use in various fields such as stimulated Raman scattering, scintillators, nuclear spin optical hole burning hosts, and photocatalysts [18–24]. Up to now, several methods have been developed to synthesize $BaWO_4$, including Czochralski technique [25–27], solid-state reaction [28,29], polymeric precursor method [30,31], hydrothermal [32], and precipitation method [33]. The photocatalytic activities of the isostructural photocatalysts

* Corresponding author. Tel.: +98 5632502022; fax: +98 5632502507.
E-mail address: zbarzgari@hotmail.com (Z. Barzgari).

http://dx.doi.org/10.1016/j.mssp.2015.01.028
1369-8001/

MWO_4 (M=Ca, Sr, Ba) for decomposing methyl orange, which were synthesized by a solid state reaction, were investigated by Shan et al. [29]. Their results showed that the photocatalytic activity was in the increasing order of $CaWO_4 < SrWO_4 < BaWO_4$ under both neutral and acidic conditions.

In the present study, we report the synthesis of the nanostructured $BaWO_4$ using a chemical solution method. The photocatalytic activity of nanostructured $BaWO_4$ was evaluated under irradiation of natural sunlight by employing methylene blue (MB) as a model target molecule. The effects of several operating parameters, such as amount of catalyst, and pH of the solution were studied in detail. To the best of our knowledge, this is the first report on solar light photoactivity of $BaWO_4$.

2. Experimental sections

2.1. Preparation of $BaWO_4$

All the reagents used in this work were Merck products of analytical grade and used without further purification. Deionized water was used throughout this study. The details are as follows: 0.005 mol of $Na_2WO_4 \cdot 2H_2O$ and 0.005 mol of $Ba(NO_3)_2 \cdot 2H_2O$ were separately dissolved in 25 mL of distilled water with magnetic stirring. Then, the two solutions were mixed and stirred for 30 min to form a homogeneous precipitate, while the temperature was fixed on 85 °C. The solution pH was adjusted to 7 using NaOH and HNO_3. The obtained product was filtered, washed with water and ethanol, and dried at 200 °C for 7 h. It is known that W^{6+} stability is a function of solution's pH and proper modification of experiment media would leads to formation of various tungstate species such as: $WO_3 \cdot xH_2O$ (pH=2), polyanions $W_2O_7^{-2}$ and $W_7O_{24}^{-6}$ (pH=2–7), WO_4^{-2} (pH=7) [34]. Therefore, in this experiment the pH of the solution was fixed in 7.0.

2.2. Sample analysis

X-ray diffraction (XRD) pattern was recorded using a Bruker D8 Advance diffractometer with CuKα radiation in the 2θ range from 10° to 80°. The morphology of the photocatalyst was examined by using SEM (JSM-6301, Japan). UV–visible diffuse reflectance spectrum was measured using Avantes, model Avaspec-2048-TEC spectrophotometer. The UV–vis absorption spectra of MB during the photodegradation process were recorded by a UV–vis spectrophotometer (PC1601, Shimadzu).

2.3. Photocatalytic experiments

Methylene blue (MB) was chosen as the pollutant model molecule to examine the photocatalytic activity of the nanostructured $BaWO_4$ under direct sunlight irradiation. The MB is a cationic dye and releases MB^+ ions on dissolution in water, absorbing the light in the 500–700 nm range. All photocatalytic experiments were conducted under similar conditions on sunny days in summer between 10:00 a.m. and 13:00 p.m. (the reaction time was 3 h). Initial reaction mixture was 25 mL of 5 ppm MB solution containing appropriate quantity of photocatalyst, with different initial pH values. The temperature of the solution was between 28 and 32 °C.

Before sunlight irradiation, the suspensions were magnetically stirred in the dark condition for 1 h to establish an adsorption/desorption equilibrium between MB and photocatalyst surface. During the reaction, 6 mL of the suspension was sampled at specific time intervals and centrifuged to separate the residual catalyst. The concentration of the MB was measured by recording its maximum absorbance (λ_{max}=664 nm) using a UV–vis spectrophotometer. Experiments under different dosage of photocatalyst were also carried out to reveal the role of amount of catalyst on the degradation of MB. The pH of the reaction mixture was adjusted by adding a dilute aqueous solution of NaOH or HCl solutions.

3. Results and discussion

3.1. Sample characterization

Fig. 1 shows the X-ray diffraction (XRD) pattern of nanostructured $BaWO_4$. The results indicated that this sample had a tetragonal unit cell (a=0.5612, c=1.2706 nm). All diffraction peaks are in good agreement with the literature value (JCPDS Card, No. 43-0646) [35]. The strong and sharp peaks indicate the high crystallinity of $BaWO_4$. The particle size was calculated using Scherrer's formula:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where D is the particle diameter, λ is the wavelength of Cu Kα radiation (1.54059 Å), k is a constant and equals 0.89, θ is Bragg's angle of the (112) plane and β is FWHM of the (112) peak in radian. The estimated crystallite size of $BaWO_4$ was 29.9 nm. The particle size and crystallite morphology of $BaWO_4$ were examined using SEM. As shown in Fig. 2, according to SEM studies the tetragonal $BaWO_4$ showed spherical morphology with an average size ranging from 50 nm to 250 nm.

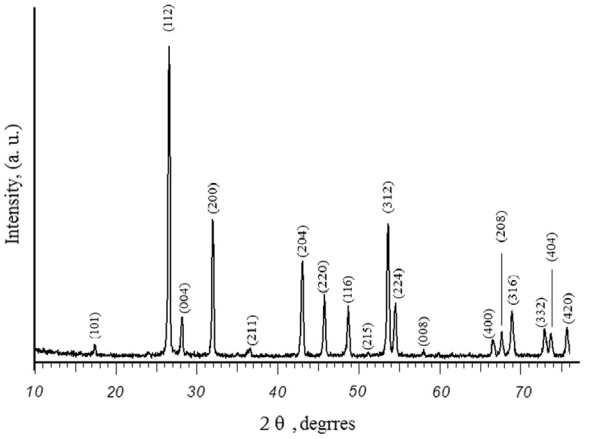

Fig. 1. XRD pattern of the nanostructured $BaWO_4$.