Optik 153 (2018) 16–30

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Full length article

Fabrication of highly efficient mesoporous $NaBiO_3/ZnO$ nanocomposites for recyclable photocatalytic degradation of organic pollutants

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ARTICLE INFO

Article history:
Received 7 June 2017
Accepted 22 September 2017

Keywords:
UV–vis light
$NaBiO_3/ZnO$
Nanocomposites
Acetophenone
Nitrobenzene

ABSTRACT

A novel nanocomposite photocatalyst $NaBiO_3/ZnO$ with three different molar ratios (0.5%, 1%, 1.5% of $NaBiO_3$) were synthesized successfully by hydrothermal precipitation-deposition method and characterized by UV–vis diffuse reflectance spectroscopy (DRS), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), high resolution transmission electron microscopy (HR-TEM) with SAED pattern, Brunauer-Emmett-Teller surface analysis (BET) and photoluminescence spectroscopy (PL) techniques. The λ_{max} of the prepared nanocomposite was highly red shifted from wavelength 390 nm to 520 nm compared to bare metal oxides. The degradation of organic pollutants such as Nitrobenzene (NB) and Acetophenone (AP) were studied by using the prepared nanocomposite. The nanocomposite with molar ratio of 1% $NaBiO_3/ZnO$ photocatalyst possess excellent photocatalytic activity than the nanocomposite with molar ratio 0.5% $NaBiO_3/ZnO$, 1.5% $NaBiO_3/ZnO$, and the individual components $NaBiO_3$, ZnO. The band edges of materials have been theoretically calculated on the basis of Mulliken electronegativity of atoms. The effect of operational parameters such as pollutant concentration, pH, catalyst dosage, $OH^{\bullet}$ radical trapping and COD have been investigated in details. The kinetics of photodegradation reactions were correlated with the pseudo-first-order model. The stability of nanocomposite was examined by recycling experiments.

1. Introduction

Photocatalysis has been a hot research area for the utilization of solar energy [1,2]. In recent years, much attention has been paid to H_2 generation from water and degradation of organic contaminants [3–8]. Many conventional methods such as catalytic reduction, osmosis and adsorption techniques have been used to deal with these pollutants in environmental surroundings. There are many drawbacks still existed in these methods because of their expensiveness and the increasing many of refractory pollutants. Besides the semiconductor photocatalysts, composite photocatalysts have been studied as well [9,10]. Due to the formation of heterojunctions that can significantly reduce the recombination and speed up the separation rate of photogenerated charge carriers, the composites are photocatalytically more active than the individual components.

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https://doi.org/10.1016/j.ijleo.2017.09.082
0030-4026/

A lot of composites have been synthesized, such as Bi@Bi_2O_3 [11] microspheres, three dimensional Bi_2WO_6/TiO_2 [12], $BiOI/TiO_2$ [13], AgI/BiOI [14], $BiOCl/Bi_2O_3$ [15], $NaBiO_3$/BiOCl [16], BiOCl/BiOI [17], $BiVO_4/WO_3$ [18] and $Bi_2O_3/NaBiO_3$ [19]. Nonetheless, the structures of heterojunctions are complex, and the fabrication of composite photocatalysts with band gap specificity remains as a big challenge.

On the basis of the results of extensive investigations, it is generally agreed that the coupling of two semiconductor photocatalysts would result in better photocatalytic activities. Among the reported photocatalysts, the bismuth-containing ones such as $NaBiO_3$ [20,21], $BaBiO_3$ [22], $KBiO_3$ [23], and $LiBiO_3$ [24] are used much interest because they respond to visible light. To avoid the drawback, many attempts focused on exploiting and utilizing some new materials with high photocatalytic activity. $NaBiO_3$ showed a relatively high activity for degradation of malachite green and rhodamine B due to its strong dispersion in the hybridized orbital which was firstly reported [25,26]. However, there are still some questions that have not been answered. The photocatalytic kinetics and the water stability of $NaBiO_3$ photocatalyst are still unknown and relevant results have not been published, both of which are essential in the application of waste water treatment. To our best knowledge, two different kinds of AP and NB were done for the first time. Most papers about the photodegradation of dyes just focused on one kind of dye or a class of organic pollutants.

In this paper, $NaBiO_3$/ZnO heterojunctions were fabricated by a hydrothermal precipitation deposition method and successfully characterized by UV-vis-DRS, FT-IR, XRD, PL, SEM with EDX, HR –TEM with SAED pattern and BET surface area analysis. The as-synthesized composites were examined for the photocatalytic degradation of NB and AP under UV–vis-light irradiation. The correlation between the catalytic performance and structure of the photocatalyst was also investigated.

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade and used as received without further purification.

2.2. Synthesis of $NaBiO_3$

$NaBiO_3$ powder was synthesized by hydrothermal technique. The measured amount of commercial $NaBiO_3 \cdot 2H_2O$ was added to 60 ml of 0.2 M NaOH solutions and then vigorously stirred for 2 h. The above reaction mixture kept at 100 ml of Teflon-lined stainless steel autoclave for 120 °C for 12 h and subsequently cooled to room temperature naturally, the obtained precipitate was dried at 120 °C for 2 h and further calcined for 2 h.

2.3. Synthesis of $NaBiO_3$–ZnO nanocomposites

The $NaBiO_3$–ZnO nanocomposites were synthesized by a precipitation-deposition method. To the clear solution of $Zn(NO_3)_4 \cdot 2H_2O$, the $NaBiO_3$ solution of molar ratio of 0.5%, 1.0%, and 1.5% were added respectively. The resulting mixed solution was added in ammonia solution and pH was maintained at 9. The obtained precipitate was stirred for 2 h. The resulting yellow precipitate was filtered, washed thoroughly with distilled water and dried at 110 °C and calcined at 500 °C for 2 h in air.

2.4. Characterization

The optical properties were investigated using UV-vis-diffuse reflectance spectroscopy (UV-vis-DRS) in a JASCO V-150 double beam spectrometer with PMT detector equipped with an integrating sphere assembly. The crystalline structure of the nanoparticles was studied by an X-ray diffraction (XRD; XPERT PRO X-RAY) with Cu Kα radiation at 25 °C and the structural assignments were made with reference to the JCPDS power diffraction files. Photoluminescence was recorded on fluorescence spectrometer (Perkin- Elmer LS 55). The morphology of all samples was examined using SEM and HR-TEM. SEM measurements were carried at VEGA3 TESCAN, USA. HR-TEM experiments were performed using a FEI TECNAI T20 G2 instrument and the sample was prepared by casting on a copper grid. The measurements of low-temperature N_2 adsorption were carried out by using a Micromeritics ASAP 2020 apparatus at −196°C, all the samples were degassed at 100 °C for 6 h prior to the measurement. Photocatalytic experiments were performed in a HEBER immersion type photoreactor (HIPR-Compact – p-8/125/250/400) and pH was monitored using EUTECH instrument pH meter. The absorptions spectra were recorded using a JASCO V-530 UV–vis spectrophotometer.

2.5. Measurement of photocatalytic activity

All the photocatalytic experiments were performed in hallow cylindrical immersion type photoreactor equipped with a glass water jacket. A 150 W high pressure mercury lamp was positioned in the inner part of the photo reactor and cooling water was circulated through the water jacket surrounding the lamp. Bare $NaBiO_3$ and ZnO nanoparticles and $NaBiO_3$/ZnO heterojunctions are used as a photocatalyst to degrade the organic contaminants NB and AP. In typical reaction, NB and AP solutions and photo catalyst were poured into a reactor in which air was bubbling continuously from the bottom of the