



Enhanced sunlight photocatalytic performance over Nb₂O₅/ZnO nanorod composites and the mechanism study



Sze-Mun Lam^a, Jin-Chung Sin^a, Ichikawa Satoshi^b, Ahmad Zuhairi Abdullah^a, Abdul Rahman Mohamed^{a,*}

^a School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Pulau Pinang, Malaysia

^b Institute for NanoScience Design, Osaka University, 1-3 Machikaneyama, Toyonaka Osaka, Japan

ARTICLE INFO

Article history:

Received 29 July 2013

Received in revised form

21 November 2013

Accepted 1 December 2013

Available online 8 December 2013

Keywords:

Nb₂O₅

ZnO nanorod

Composite

Sunlight photocatalysis

Phenol

ABSTRACT

Highly effective Nb₂O₅/ZnO nanorods (NRs) were synthesized via a hydrothermal–precipitation method and characterized by X-ray diffraction (XRD), field emission-scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), Brunauer–Emmett–Teller (BET) surface area analysis and photoluminescence (PL) spectroscopy. Under natural sunlight irradiation, Nb₂O₅/ZnO NR composites degraded phenol efficiently and displayed much higher photocatalytic activity than those of pure ZnO, commercial Nb₂O₅ and Degussa P25. Mineralization and intermediates detection upon phenol degradation under natural sunlight, fluorescent light and UV irradiation were systematically studied. The results showed that phenol was almost completely mineralized under sunlight irradiation over the Nb₂O₅/ZnO NRs, while 26.1 and 40.7% of organic carbons were removed under fluorescent light and UV irradiation, respectively that could be associated with the formation of muconic acids and others resulting aromatic ring products. PL analysis suggested that 2 at% Nb₂O₅/ZnO NRs had the lowest electrons and holes recombination rate and revealed good degradation and mineralization efficiencies after 4 times of cycle experiments. Terephthalic acid-photoluminescence (TA-PL) probing test and radical scavenger experiments revealed that hydroxyl radicals were the predominant oxidative species while the hole and superoxide anion radical could be negligible. It was worth nothing that the possible transfer process of photogenerated charge carriers based on the band structures of Nb₂O₅ and ZnO NRs was also proposed.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

In modern society, the applications on conversion of solar energy and degradation of pollutants by semiconductor photocatalysts have been gained much consideration. ZnO as one of the most extensively investigated photocatalysts have been shown relatively high catalytic efficiency, low cost, non-toxicity and environmental stability [1–3]. Nevertheless, owing to its large band gap (~3.3 eV), ZnO is mostly responsive to ultraviolet irradiation, which greatly impedes its practical applications. Additionally, the lack of effective surface area and low transfer rate of charge carriers also limit the photocatalyst developments. Given the conditions above, it is desirable to develop novel photocatalysts with high photocatalytic activity under visible light or natural sunlight.

It is well-known that coupling of different semiconductor materials can reduce the band gap, extending the absorbance range

to visible-light region leading to electron–hole pair separation under irradiation and consequently, achieving a higher photocatalytic activity [4]. These systems also exhibit higher degradation of organic pollutants. The TiO₂/ZnO, WO₃/ZnO, CeO₂/ZnO, SnO₂/ZnO and CdS/ZnO are the different coupled semiconductors that have been successfully fabricated [5–9]. Further, niobium pentoxide (Nb₂O₅) is an important semiconductor with band gap of ~3.1 eV [10]. It has been revealed to potentially serve several applications such as photocatalysis, catalysis, bioelectrochemistry and sensors [11,12]. In literature, successful preparation of TiO₂ coupled with Nb₂O₅ by colloidal preparation method and its application in photocatalytic degradation under UV light has been reported [13]. However, there was no report on the coupling of ZnO with Nb₂O₅. Thus, constructing a photocatalytic system composed of ZnO and Nb₂O₅ may be a good strategy to solve the low quantum yield of ZnO, resulting in enhanced visible light or natural sunlight photocatalytic performance.

The photocatalytic process is initiated when a ZnO semiconductor absorb photons with an energy equal or superior to its band gap, following by the initiation step of electron–hole formation.

* Corresponding author. Tel.: +60 45996410; fax: +60 45941013.

E-mail address: chrahman@eng.usm.my (A.R. Mohamed).

The photogenerated valence band positively hole (h^+) could react with adsorbed water or hydroxyl group to produce hydroxyl ($\bullet\text{OH}$) radical. In the presence of dissolved oxygen, the conduction band electron (e^-) could be transferred to oxygen, leading to the generation of superoxide anion ($\text{O}_2^{\bullet-}$) radical in the subsequent reaction [14,15]. Depending upon the experimental conditions, the h^+ and the derived reactive species can all play pivotal roles in photocatalytic reactions [16]. It has been reported that some oxidative species generated on coupled metal oxide under visible light irradiation was powerful enough to completely oxidize some organic substrates [17]. Therefore, it is essential to understand the roles of oxidative species in the visible light or natural sunlight induced photocatalytic reactions.

In this regard, the synthesis of Nb_2O_5 nanoparticles loaded on ZnO nanorods (NRs) was reported for the first time by a facile chemical-precipitation method to produce $\text{Nb}_2\text{O}_5/\text{ZnO}$ composite. The one-dimensional ZnO NR was selected as the investigation material because of its advantages over nanoparticle including high surface-to-volume ratio, enhancement of light scattering and absorption and rapid diffusion of reactive species transport along the long direction. The photocatalytic mineralization of phenol by the $\text{Nb}_2\text{O}_5/\text{ZnO}$ composite was examined under natural sunlight, fluorescent light and UV irradiation. To gain further insights into the phenol degradation mechanism under natural sunlight, the intermediate products were identified. The formation and the roles of various oxidative species such as h^+ , $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$ radicals in the photocatalytic degradation of phenol were finally studied with the use of appropriate scavengers.

2. Experimental

2.1. Materials

Hydrogen peroxide (H_2O_2 , Assay 30 vol%), Niobium chloride (NbCl_5 , Assay 99%), phenol (Assay $\geq 99.5\%$), terephthalic acid (TA, Assay 99%), sodium hydroxide (NaOH, Assay 98%) and commercial ZnO and Nb_2O_5 powders were purchased from ACROS Organics. All other reagents were of analytical purity and were used without further purification. Chemical standards include isopropanol (IPA, Assay $\geq 99.5\%$) and benzoquinone (BQ, Assay 98%) from Fisher Chemicals and sodium iodide (NaI, Assay 99%) from Hayashi Pure Chemicals. Deionized water was used throughout this study.

2.2. Preparation of $\text{Nb}_2\text{O}_5/\text{ZnO}$ composite

Pure ZnO NRs were fabricated by hydrothermal route from commercial ZnO powder and H_2O_2 at 180°C for 24 h. The detailed synthesis process was reported in our previous study [6]. $\text{Nb}_2\text{O}_5/\text{ZnO}$ composites were prepared by a chemical-precipitation method. The typical procedure for the preparation of $\text{Nb}_2\text{O}_5/\text{ZnO}$ composites was as follows: 1.0 g of pure ZnO NRs was dispersed in 50 mL deionized water and the suspensions were ultrasonicated for 30 min. The pH of the mixture was adjusted to about 6.5 using NaOH solution. After that, a stoichiometric amount of NbCl_5 was added into above mixture, followed by stirring for 12 h. Subsequently, the as-formed precipitates were filtrated, washed with deionized water and ethanol and dried in air at 60°C for 12 h. The prepared samples were finally calcined at 400°C for 2 h with a heating rate of 2°C min^{-1} .

2.3. Analytical methods

The samples were characterized using X-ray diffraction (XRD) pattern recorded on a Philips PW1820 diffractometer with Cu K α radiation at a scanning rate of 2°min^{-1} in the range of 20° – 80° . The morphology of the catalyst was performed on a Quanta FEG

450 field emission-scanning electron microscope (FESEM) with an energy dispersive X-ray spectroscopy (EDX) analysis. Transmission electron microscopy (TEM) image was captured using a Philips CM-12 operated at 120 keV. High resolution transmission electron microscopy (HRTEM) image was taken on a Fei Tecnai 20. The specific surface area of the sample was determined through nitrogen adsorption-desorption at 77 K on the basis of BET equation using a micrometrics ASAP 2020. X-ray photoelectron spectroscopy (XPS) spectra were obtained with Omicron els 5000 spectrophotometer using Al K α at 1480 kV as radiation source. UV–vis diffuse reflectance spectrum (DRS) was recorded on a Perkin Elmer Lambda 35 UV–vis spectrophotometer with BaSO_4 as a reference. The photoluminescence (PL) measurement was carried out using a Perkin Elmer Lambda S55 spectrofluorometer using a Xe lamp with an excitation wavelength of 325 nm at room temperature.

HPLC analysis was performed using HPLC model: Perkin Elmer Series 200, C18 column (150 mm-length \times 4.6 mm-ID \times 5 μm particle size), isocratic pumps from Varian with an UV–vis detector, liquid flow rate of 1 mL min^{-1} , column temperature of 36°C , detector wavelength of 254 nm and solvent mixture of water and acetonitrile ($\varphi_r = 7:3$). The total organic carbon (TOC) remained in the solution were measured using a Shimadzu TOC-V_{CPH} analyzer. To identify the possible intermediate products in the phenol degradation process, pyrogallol, resorcinol, hydroquinone, benzoquinone and muconic acid which have been reported as main intermediates in the studies of phenol degradation by ZnO-based catalysts [18,19] analyzed with HPLC under the same analytical conditions. The assignment of HPLC peaks to the corresponding compounds was based on the retention time. The solution pH of degraded phenol was monitored using a calibrated Mettler Toledo 320 pH meter.

2.4. Photocatalytic activity tests

The photocatalytic activities of the $\text{Nb}_2\text{O}_5/\text{ZnO}$ composites were evaluated by the degradation of phenol aqueous solution. The experiments were carried out as follows: 1.0 g L^{-1} of the sample was dispersed in 100 mL of 20 mg L^{-1} phenol solution in a 150 mL beaker. During all experiments, air was bubbled through the solution at a fixed flow rate of 6 mL min^{-1} . The suspensions were continuously stirred with the aid of a magnetic stirrer. The heterogeneous mixture was equilibrated for 1 h in the dark and subsequently, the solution was irradiated under natural sunlight. The period of the experiment was between 11:00 and 14:00 during the months of January and February. The average intensity of natural sunlight was measured using a digital lux meter and it was found to be $8.90 \times 10^4 \text{ lux}$. At specific time intervals, 2 mL of the sample was withdrawn from the system, centrifuged and then the concentration of the phenol at different time intervals was monitored by HPLC. For comparison, photocatalytic activities of $\text{Nb}_2\text{O}_5/\text{ZnO}$ composites under UV and visible light irradiation were also investigated. The light sources were a 365 nm mercury UV lamp (UVP Pen-Ray, 15 W, light intensity of 1.2 mW cm^{-2}) and a fluorescent lamp (World Lighting Germany, 55 W, light intensity of $1.45 \times 10^4 \text{ lux}$), respectively. Meanwhile, the comparison studies with TiO_2 Degussa P25 were also conducted.

2.5. Detection of reactive oxygen species

The examination experiment process of reactive species is similar to the photodegradation experiment. Different type of scavengers was introduced into the phenol prior to addition of the catalyst. The dosages of these scavengers were evaluated by adding 2 mM of different scavengers in the photodegradation experiment.

Moreover, photoluminescence technique with terephthalic acid (PL-TA) as a probe molecule was used to investigate the formation

Download English Version:

<https://daneshyari.com/en/article/39909>

Download Persian Version:

<https://daneshyari.com/article/39909>

[Daneshyari.com](https://daneshyari.com)