

Facile fabrication of novel ZnO/CoMoO₄ nanocomposites: Highly efficient visible-light-responsive photocatalysts in degradations of different contaminants



Mahsa Pirhashemi, Aziz Habibi-Yangjeh*

Department of Chemistry, Faculty of Science, University of Mohaghegh Ardabili, P.O. Box 179, Ardabil, Iran

ARTICLE INFO

Keywords:

ZnO/CoMoO₄
p-n Heterojunction
Visible-light photocatalysis
Organic contaminants

ABSTRACT

A facile route was adopted to fabricate p-n heterojunction ZnO/CoMoO₄ photocatalysts through a refluxing method followed by calcination process. The resulting ZnO/CoMoO₄ nanocomposites were characterized by means of XRD, EDX, FESEM, HRTEM, XPS, UV-vis DRS, FT-IR, BET, and PL techniques. The photocatalytic degradation of rhodamine B was chosen to investigate photocatalytic performances. Compared to the reference materials of ZnO and CoMoO₄, the ZnO/CoMoO₄ nanocomposites showed much higher photocatalytic activity and the ZnO/CoMoO₄ (30%) sample possessed the highest efficiency, which is 19.6 and 6.26 folds greater relative to the ZnO and CoMoO₄, respectively. The results demonstrated that the p-n heterojunction between ZnO and CoMoO₄ could significantly boost the photocatalytic efficiency through highly promoted separation of electron/hole pairs as well as extended absorption to visible light. Finally, the highly enhanced performances of the ZnO/CoMoO₄ (30%) nanocomposite in removal of three more organic pollutants including methylene blue, methyl orange, and fuchsine were confirmed, which indicates the potential of this nanocomposite for practical applications.

1. Introduction

Now a days, our earth is under growing pressure of industrialization and population growth. Hence, water pollution and wastewater treatment have become the most important crisis, which faces human being; because large quantities of synthetic pollutants are continually discharged into our environment [1–4]. These toxic materials are highly persisting in the environment. Hence, it is necessary to remove these chemicals from wastewaters before their discharges to water sources. Among different strategies applied to address environmental pollution, heterogeneous photocatalysis is an efficient route for the abatement of organic pollutants [5–7]. Among various semiconductors, ZnO is the second most popular photocatalyst with high stability, nontoxicity, and cheap price. However, this n-type semiconductor suffers from some limitations including poor visible-light response and fast recombination rate of the produced electron/hole (e⁻/h⁺) pairs [8,9]. To overcome these issues, fabrication of heterojunction between this wide band gap semiconductor and other semiconductors possessing high photosensitivity to visible/solar light has been proposed to improve visible-light-driven (VLD) photocatalytic performance of ZnO [10–21]. In recent years, it was found that suppression of the charge carriers from

recombination in large extent can be done through p-n/n-n heterojunction formations between ZnO (as n-type semiconductor) and small band gap semiconductors with p-type/n-type characteristics [22–32].

In this light, we focused on cobalt molybdate (CoMoO₄), as a p-type semiconductor with narrow band gap of ~1.8 eV [33,34]. This semiconductor has attracted more research interests since its excellent catalytic and electrochemical characteristics, large specific capacitance, natural abundance, and environmentally green [35–37]. For example, Yu et al. [38] and Fang et al. [39] synthesized hierarchical CoMoO₄ porous micro-flowers and nanoneedles, respectively though a facile one-pot hydrothermal method, which exhibited superior electrocatalytic oxygen evolution performance, as well as great stability. Also CoMoO₄ has attracted significant attention due to its excellent electrochemical performances in flexible asymmetric supercapacitors. For examples, Wang et al. [36] reported the flower-like CoMoO₄/MnO₂ heterostructures, which exhibited a high capacitance with good cycle performance. Zhou et al. [40] presented CoMoO₄/Co₃O₄ hierarchical nanohybrid with ultrahigh areal capacitances, which exhibited higher specific capacitance. In addition, CoMoO₄ as photocatalyst can also be applied in photocatalytic reactions, due to its high surface area and good electrical/optical properties. For instance, Umopathy and his

* Corresponding author.

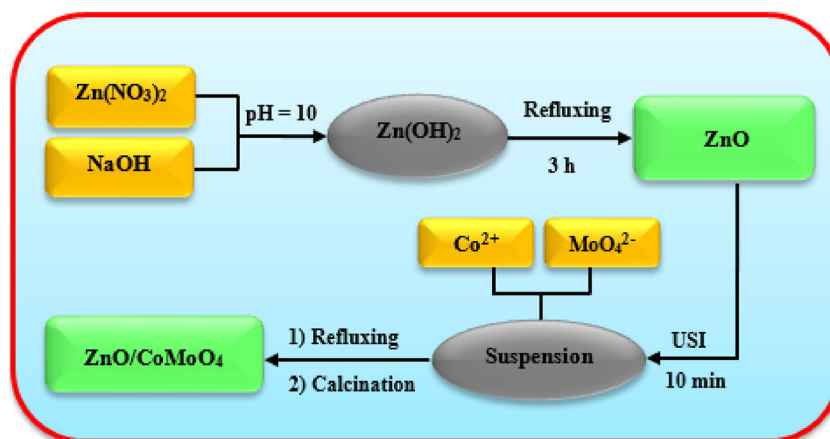
E-mail address: ahabibi@uma.ac.ir (A. Habibi-Yangjeh).

<https://doi.org/10.1016/j.jphotochem.2018.05.027>

Received 9 January 2018; Received in revised form 27 April 2018; Accepted 19 May 2018

Available online 20 May 2018

1010-6030/ © 2018 Elsevier B.V. All rights reserved.



Scheme 1. Schematic illustration for synthesis of the ZnO/CoMoO₄ nanocomposites.

worker [41] synthesized CoMoO₄ nanoparticles and CoMoO₄/TiO₂ nanocomposites by a sol-gel method, which showed photocatalytic efficiency of 88.0% and 97.5% respectively for the degradation of 4-chlorophenol under UV-vis irradiation. In addition, Li et al. [42] reported p-n heterostructured CoMoO₄/MoO₃ nanocomposites, which exhibited enhanced trimethylamine gas sensing properties including extremely strong response and good selectivity, due to formation of potential barrier at the p-n junction between p-type CoMoO₄ and n-type MoO₃, stronger oxygen adsorption of p-type CoMoO₄, and the form of crystallographic defects. Therefore, incorporation of p-type CoMoO₄ with n-type ZnO to form p-n heterojunction is expected to have substantially enhanced VLD photocatalytic activity, due to broaden the light absorption to visible region and considerable retardation of the e⁻/h⁺ pairs from the undesired recombination. Based on our knowledge, there is no existing report about the fabrication and investigation photocatalytic performance of the ZnO/CoMoO₄ nanocomposites. Herein, a series of ZnO/CoMoO₄ nanocomposites were fabricated by a simple refluxing-calcination method. To date, amongst all the processes used for synthesizing various photocatalysts, wet chemical methods including co-precipitation [43,44] and sol-gel methods [45] have been widely accepted, nevertheless these preparation methods mainly have high temperatures or long reaction times and suffering from using organic solvents and additives and multiple-step procedures. Based on the above considerations, refluxing method is a facile method, which allows to produce required samples with precise controlling the reaction parameters and high productivity at generally lower temperatures. Besides, among the wet-chemical methods, it needs simple procedure, cheap price, and short time. Therefore, the facile and template-free method was applied for preparation of ZnO/CoMoO₄ nanocomposites in water by refluxing for 120 min at about 96 °C. However, post heat-treatment processing at 450 °C was necessary in order to obtain fully crystalline CoMoO₄ counterpart.

2. Experimental

2.1. Preparation section

Firstly, ZnO powder was synthesized using a facile refluxing method reported in our previous work [46]. For synthesis of the ZnO/CoMoO₄ (30%) nanocomposite, where 30% is weight percentage of CoMoO₄, 0.350 g of the synthesized ZnO was ultrasonically irradiated for 10 min to disperse it into 150 mL water. Thereafter, 0.199 g of cobalt nitrate (Loba Chemie, 98%) was put into the suspension and kept for 60 min under magnetic stirring. Afterwards, 0.166 g of sodium molybdate (Merck, 98%) was also dissolved into 50 mL water and slowly dropped to the suspension. The obtained suspension refluxed at 96 °C for 120 min. The final product was collected, washed with water and

ethanol, finally dried in an oven at 60 °C for 24 h and it was calcined at 450 °C for 2 h to provide the target nanocomposite. The procedure for fabrication of the ZnO/CoMoO₄ nanocomposites is presented in Scheme 1.

2.2. Characterization techniques

The XRD patterns were recorded by Philips Xpert X-ray diffractometer using Cu-Kα radiation. The FESEM images, EDX spectra, and element mapping images were provided by a MIRA3 TESCAN-XMU scanning electron microscopy equipped with an energy dispersive spectroscope. Besides, HRTEM image was collected on the JEOL JEM-2100F, operating at 200 kV. Also, the XPS data were recorded by a Thermo Scientific ESCALAB 250Xi instrument (Mg X-ray resource). The FT-IR spectra were logged using a Perkin Elmer Spectrum RX I instrument. The DRS analysis was conducted by a Scinco 4100 instrument. Subsequently, PL spectra were taken using a Perkin Elmer (LS 55) fluorescence spectrophotometer. The BET isotherms were collected using a Micromeritics TriStar II Plus N₂ adsorption apparatus. The UV-vis spectra were plotted by a Cecil 9000 spectrophotometer. The pH of solutions was adjusted with a Metrohm model 744 pH meter. The ultrasound radiation was conducted with a Bandelin ultrasound generator HD 3100 (12 mm diameter Ti horn, 75 W, 20 kHz).

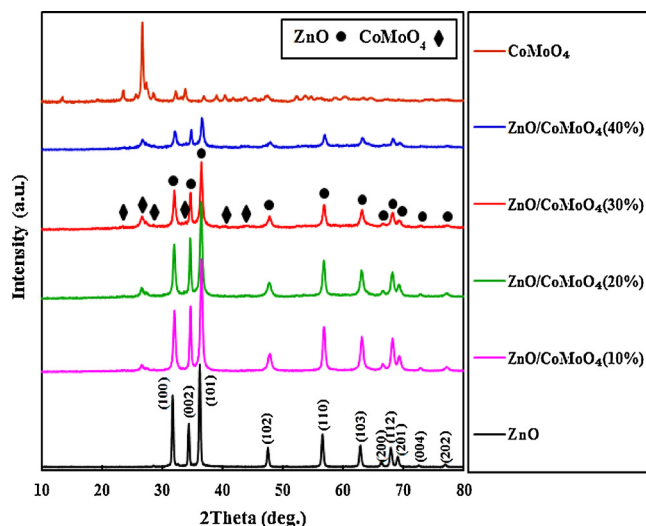


Fig. 1. XRD patterns for the ZnO, CoMoO₄, and ZnO/CoMoO₄ with different weight percentages of cobalt molybdate.

Download English Version:

<https://daneshyari.com/en/article/6492459>

Download Persian Version:

<https://daneshyari.com/article/6492459>

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