RESEARCH ARTICLE

ZnO/WO_3 nanocomposites: Pechini sol-gel synthesis, characterization, and photocatalytic performance for desulfurization of thiophene

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ABSTRACT

The aim of this study was to investigate and overcome thiophene sulfur contaminants using high purity synthesized ZnO/WO_3 nanocomposite and homogeneous composition by Pechini sol-gel method at low temperature. Zinc oxide is one of the most dynamic elements known in this field, its presence together with tungsten oxide prevents the crystallization of tungsten nanoparticles. Fuzzy structure, percentage of elements, surface morphology, penetration reflection spectrum, and photocatalytic degradation of thiophene were determined by XRD, EDS, SEM, and DRS analyzes, respectively. DRS results indicate high light absorption, reduced bandgap due to the presence of WO_3 after combination with ZnO, and increased efficiency. Finally, the nanocomposite with more than 84% efficiency resulted in the degradation of oxidative desulfurization of thiophene after 150 min under visible light.

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INTRODUCTION

Approximately 10% of crude oil is composed of harmful compounds and impurities, of which impurities include sulfur compounds and their derivatives [1-3]. The presence of sulfur in crude oil can have devastating effects on human health and the environment. These problems include corrosion, erosion, and inactivation of the catalyst, global warming, acid rain, and other environmental problems [3-6]. Due to the importance of this issue in recent years, the extraction of these derivatives from oil and the sweetening process has become the most important goals of researchers. Among the processes used in this field are desulfurization by hydrogen gas, physical adsorption of sulfur compounds on the adsorbent, desulfurization extracted by polar solvents and desulfurization by oxidation of sulfur compounds [7, 8]. For example, desulfurization by hydrogen gas is a common, complex, and costly method in the industry [1, 4]. On the other hand, removing sulfur with this method requires working conditions with high temperature (300-400 °C) and high pressure and consumption (30-130 atmospheres) of hydrogen [9, 10]. Therefore, researchers are looking for a simple method, high efficiency, and low cost. Photocatalytic oxidative desulfurization represents a new and advanced technology of the oxidation process of sulfur compounds. Features of this method include high catalytic activity, safety, non-toxicity, easy recycling, and no need for hydrogen gas compared to other methods [6, 11, 12]. One concern with this process is that the absorption of visible light photocatalytic efficiency is high [13]. Nowadays, metal oxides with nanostructures have attracted the attention of many researchers due to their unique properties, various sizes and morphologies [14]. Researchers have synthesized and used many semiconductors, including SnO_2 [15], $BiVO_4$ [16], $NiCr_2O_4$ [17], CeO_2–CuO [18], Cu-Cu_2O [19], and ZnO [20]. For example, TiO_2 nanoparticles are effective

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photocatalysts with high resistance to light. In other words, its bandgap size (3.2 eV) indicates that this photocatalyst cannot absorb visible light well [16, 21]. Therefore, the fabrication of other photocatalytic materials with the ability to absorb visible light, for example, nanocomposites, was proposed as one of the solutions [22, 23]. ZnO/WO_3 is known as a strong photocatalytic nanocomposite and can be as-synthesized by exothermic, sonochemical, chemical precipitation, sol-gel, microwave irradiation, and electrochemical methods [24-27]. Zinc oxide (ZnO) are widely used in photodegradation process, due to their high stability, low cost, efficiency and environment friendly characteristics [20]. Tungsten oxides have shown significant photocatalytic activity in desulfurization [28, 29]. Herein, we synthesized ZnO/WO_3 nanocomposites for the first time in a new and cost-effective Pechini sol-gel method. By absorbing powerful light in the visible area, this nanocomposite can be used as one of the most promising photocatalysts to remove harmful petroleum compounds. The presence of ZnO, along with tungsten oxide with unique properties, as a stable semiconductor with a narrow bandgap of about 2.2-2.8 eV and high chemical stability, is very effective in removing contaminants [30-32]. This research is considering a helpful point due to the difference in the synthesis method of Pechini sol-gel type with high reaction speed and low temperature, economic superiority compared to previous activities, and differences in the ratio and type of elements.

EXPERIMENTAL

Materials and instruments

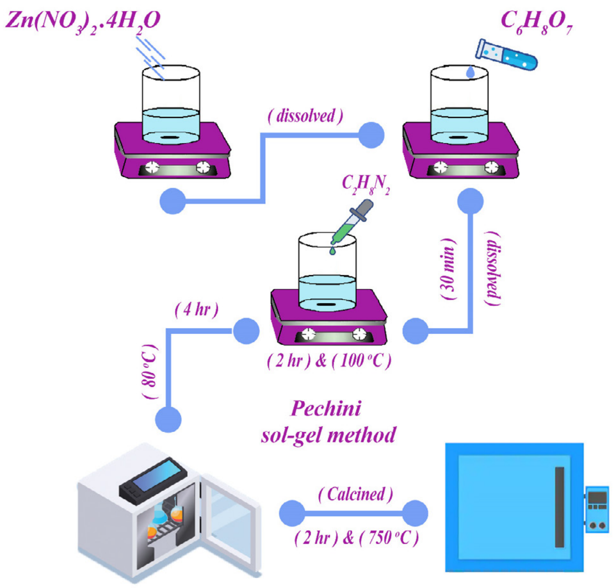
$Zn(NO_3)_2.4H_2O$ (zinc nitrate tetrahydrate), Na_2WO_4 (sodium tungstate), citric acid, nitric acid, benzoquinone (BQ), dimethylformamide (DMF), ethylenediamine (en), isopropanol (IPA), ethylenediaminetetraacetic acid (EDTA), n-hexane, and ethanol were purchased from Merck company. All these chemicals were of analytical grade and used without any purification. X-ray diffraction (XRD) patterns were obtained by Philips-X ʼ PertPro device using Ni-filtered Cu Kα radiation. Energy dispersive spectrum (EDS) analysis was performed by use of a Philips XL30 microscope. Field emission scanning electron microscopy (FESEM) images were prepared by MIRA3 FEG-SEM. The diffused reflectance. JASCO V-670 spectrophotometer was used to obtain the UV-visible spectrum (DRS).

Synthesis of ZnO/WO_3 nanocomposites

First, 0.4 g of Zn salt was dissolved in 10 ml of distilled water, and then 5 ml of aqueous citric acid solution with a molar ratio of 0.5:1 to zinc salt was added to the above solution. Aqueous solution of Na_2WO_4 was prepared separately with citric acid according to the above. A few drops of concentrated nitric acid were added until the Na_2WO_4 was completely dissolved. The aqueous solution of zinc was added to the aqueous solution of tungsten while stirring, and then a few drops of ethylenediamine (equivalent to the total weight of citric acid in these two mixtures) were added to the resulting solution. The final solution was placed on the heater at 100 °C for 2 hours until the solvent evaporated to form a gel-like state. Afterward, the resulting gel was placed in an oven for 4 hours at 80 °C, and finally, the resulting powder was calcined at 750 °C for 2 hours. Schematic diagram of formation of ZnO/WO_3 nanocomposite is presented in Scheme 1. Experiments on photocatalytic desulfurization of thiophene were performed according to the method mentioned in our previous work [6].

RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of the as-synthesized ZnO/WO_3 nanocomposite. According to Fig. 1, the obtained product is a mixture of ZnO nanoparticle with hexagonal phase (JCPDS No. 01-089-1397 and cell constants a = 3.2530 Å, b = 3.2530 Å, and c = 5.2130 Å), and WO_3 nanoparticle with monoclinic phase (JCPDS No. 01-087-2398 and cell constants a = 5.2776 Å, b = 5.1608 Å, and c = 7.6730 Å). Using Scherrer equation [20, 33], the average crystallite size was obtained about 36 and 65 nm for ZnO and WO_3, respectively. The EDS spectrum of ZnO/WO_3 nanocomposites are shown in Fig. 2. The peak of Au is due to its use for sample preparation in FESEM analysis. According to the EDS results, only the elements Zn, W, and O are seen and there are no impurities. This indicates the high purity of the synthesized nanocomposite. Fig. 3 shows the SEM images of ZnO/WO_3 nanocomposite with different magnifications. According to the pictures, the formed nanocomposite mainly contains spherical nanoparticles. It has been found that ZnO nanoparticles roughen the surface of the composite and reduce the size below 100 nm, creating a composite with high capability in photocatalytic processes [24-27]. Fig. 4 shows UV-Vis diffused reflectance spectrum of the as-synthesized ZnO/WO_3 nanocomposite. As shown in Fig. 4, the



Scheme 1 Schematic diagram of formation of ZnO/WO_3 nanocomposite

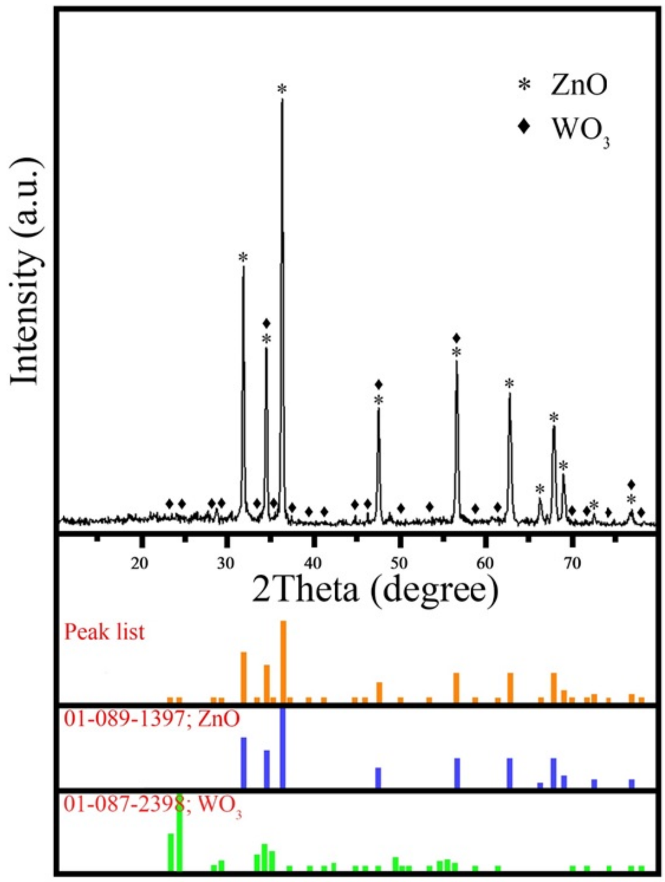


Fig. 1. XRD patterns of the as-synthesized ZnO/WO_3 nanocomposite

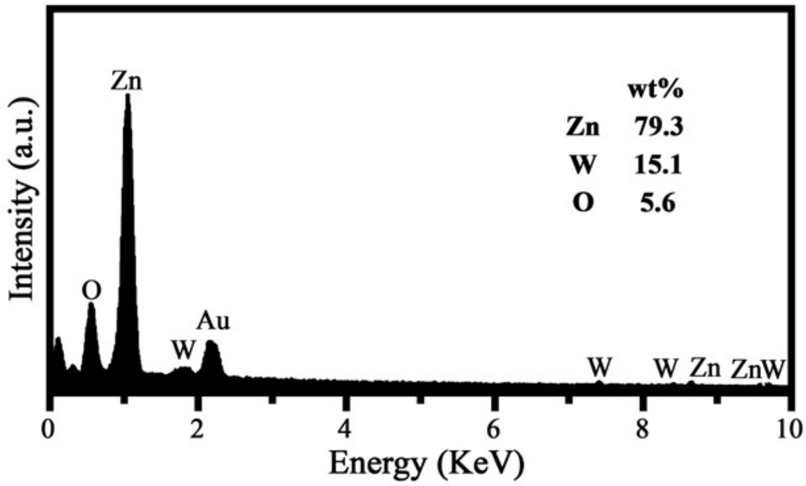


Fig. 2. EDS spectrum of the as-synthesized ZnO/WO_3 nanocomposite

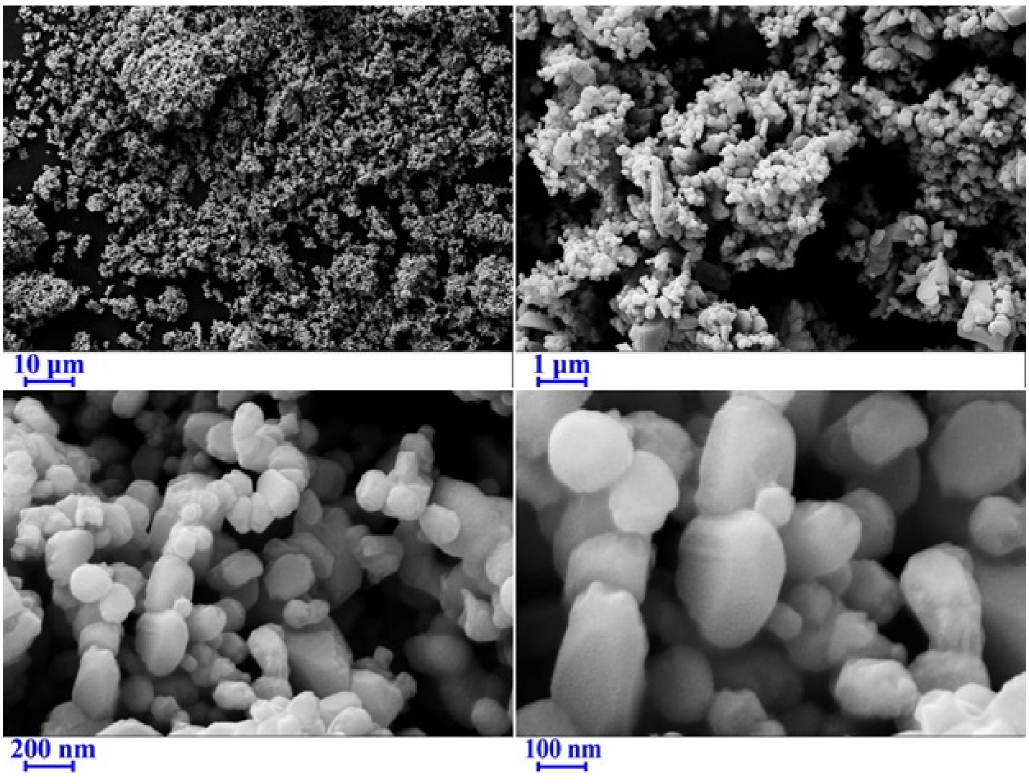


Fig. 3. FESEM images of the as-synthesized ZnO/WO_3 nanocomposite

synthesized nanocomposite has a bandgap of about 2.56 eV, which is smaller than that of pure ZnO (3.2 eV) and pure tungstate (2.78 eV) and therefore more suitable for absorbing visible light. The presence of ZnO creates a W-O-Zn bond that increases the absorption wavelength via UV-Vis. So, the use of ZnO/WO_3 nanocomposites is expected to improve the photocatalytic process's efficiency.

Photocatalytic desulfurization studies

The degradation of thiophene to measure the photocatalytic efficiency of the as-synthesized ZnO/WO_3 nanocomposite is shown in Fig. 5. This nanocomposite for photocatalytic desulfurization

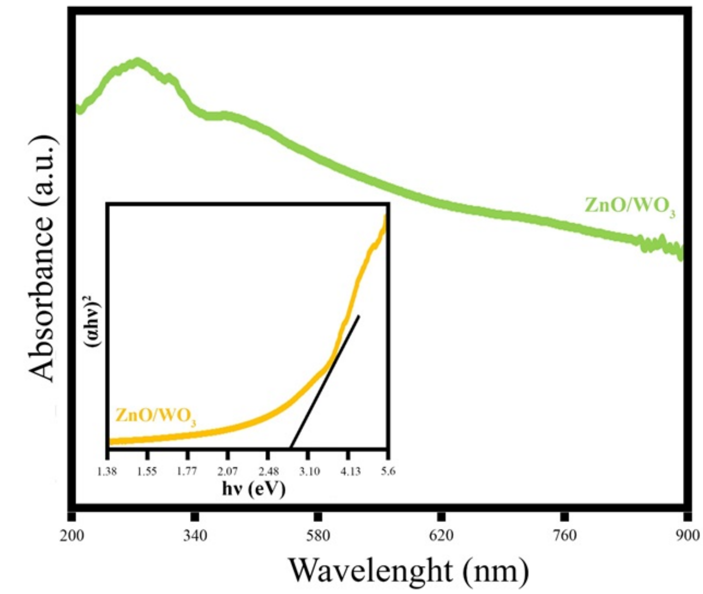


Fig. 4. Diffuse reflectance spectrum and the plots of the $(\alpha h\nu)^{1/2}$ vs $(h\nu)$ of the as-synthesized ZnO/WO_3 nanocomposite

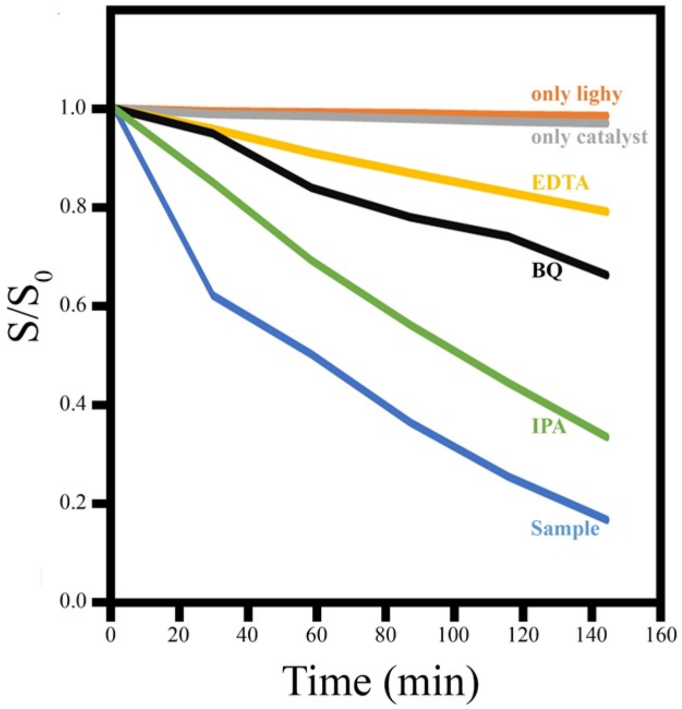


Fig. 5. Photocatalytic oxidative desulfurization of thiophene under visible light irradiation by ZnO/WO_3 under different conditions including: only catalyst, catalyst in the presence of EDTA, BQ, and IPA as the radical trapping species

has resulted in more than 84% degradation of the thiophene contaminant at 150 min under visible light, while the process without nanocomposite and the presence of light alone are not very efficient. Also, the lack of light in the process is accompanied by a slight degradation, which means that desulfurization without light is not done well. According to the figure, the efficiency of photocatalytic desulfurization process in the presence of IPA, BQ, and EDTA with the aim of determining the active hydroxyl radicals ($^{\bullet}OH$), holes (h^+), and superoxide ($^{\bullet}O^{2-}$) was reduced to

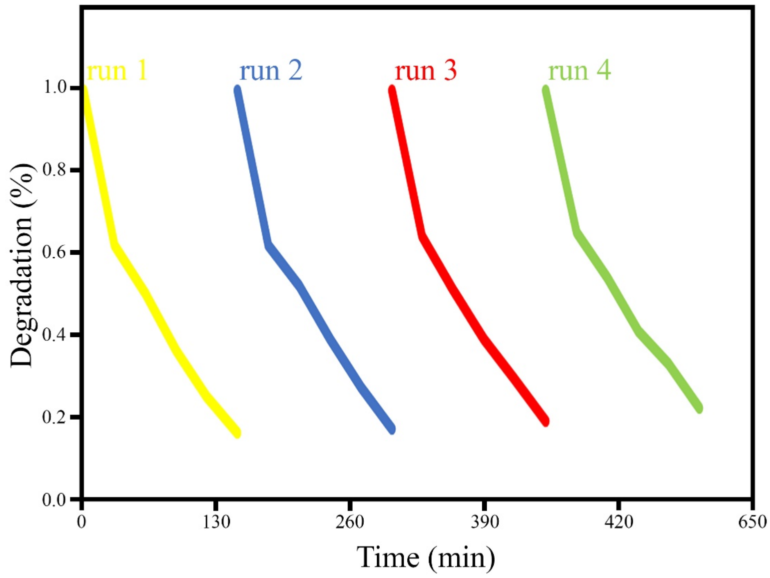


Fig. 6. Photocatalytic desulfurization recyclability of ZnO/WO_3 nanocomposite for 4 cycles

67%, 34%, and 21%, respectively. Given this, it can be said that $^{\bullet}O^{2-}$ and h^+ are more effective and active species. The recyclability of the synthesized nanocomposite was investigated in a photocatalytic process and according to the results presented in Fig. 6, after 4 reuse, only a small decrease in desulfurization efficiency is seen, which reveals the high capability of this nanocomposite.

CONCLUSIONS

In this paper, the effect of ZnO/WO_3 nanocomposite with the aim of photocatalytic desulfurization of thiophene as harmful oil pollutants in the environment was investigated. ZnO/WO_3 nanocomposite was synthesized by Pechini sol-gel method due to its superiority over other methods in terms of good stoichiometric control and high purity and uniformity. The fabricated nanocomposite was analyzed by XRD, EDS, SEM, and DRS techniques. The presence of ZnO creates a W-O-Zn bond that increases the absorption wavelength via UV-Vis. Reducing the bandgap and increasing light absorption, reducing electron-hole recombination as well as increasing the specific surface area after combining ZnO with WO_3 led to an increase in efficiency, and 84% photocatalytic degradation was achieved after 150 min under visible light, while the process without nanocomposite and the presence of light alone are not very efficient.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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