RESEARCH ARTICLE

Pechini Sol-Gel Synthesis and Characterization of $NiWO_4/W_5O_{14}/WO_3$ Nanocomposite for Photocatalytic Desulfurization of Thiophene

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ABSTRACT

One of the most important challenges today is the sweetening of petroleum compounds. The presence of sulfur in these compounds can have detrimental effects on the environment, equipment, catalysts, and final products. The aim of this study was to use $NiWO_4/W_5O_{14}/WO_3$ composite nanostructure to solve this problem using photocatalytic oxidative desulfurization method. This composite nanostructure was synthesized by Pechini sol-gel method and analyzed by XRD, EDS, FESEM, FT-IR, and DRS. W_5O_{14} and WO_3, which are types of tungsten oxides, increase the photocatalytic efficiency by reducing the bandgap in the nanocomposite. As a result, the nanostructure can decompose more than 73% of the sulfur in thiophene after 180 minutes under visible light. Efficiency can be increased by optimizing the amount of photocatalyst and irradiation time.

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INTRODUCTION

Due to the increasing progress of science and the development of urbanization, human life has taken a step towards mechanization. In this regard, many destructive pollutants are produced and endanger the lives of humans and other organisms. These pollutants include biological pollutants, oil pollutants, and, most importantly, pollutants from the combustion of fossil fuels, which cause excess compounds in these fuels to enter the air and endanger human health [1-3]. About 10% of crude oil contains additives and impurities such as organic nitrogenous compounds (NCCs), oxygenated compounds (OCCs), and sulfur compounds (SCCs). The most important sulfur compounds in crude oil are sulfides, disulfides, mercaptans, and thiophenes (Ths) [4-6]. Thiophene is an aromatic heterocyclic structure consisting of a sulfur atom attached to four carbon atoms [7]. The presence of sulfur atoms in this structure causes destructive effects such as erosion, acid rain, corrosion, and other environmental problems on human health and the environment [8-9]. One of the most important goals of researchers in recent years is the sweetening of petroleum products derived from these compounds [9-11]. Various methods are used for desulfurization, the most important of which are desulfurization with hydrogen gas, physical adsorption of sulfur compounds on the adsorbent, desulfurization extracted with polar solvents, and oxidation of sulfur compounds [12-13]. 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. Desulfurization products are superior sulfur compounds [14-17]. One of the concerns of this process is a photocatalytic fabrication, which is very efficient in absorbing visible light [18]. To address this

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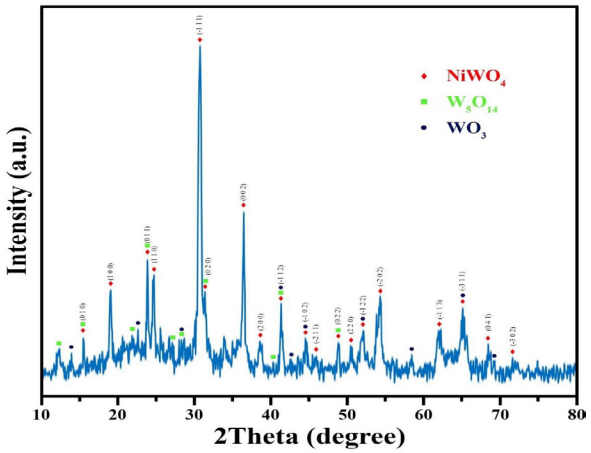

Fig. 1. XRD pattern of the as-synthesized $NiWO_4/W_5O_{14}/WO_3$ composite nanostructures.

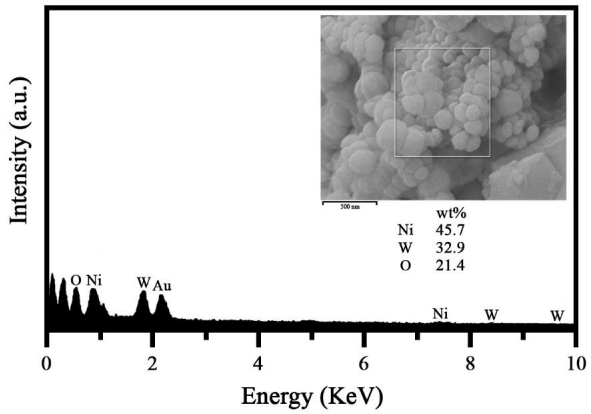

Fig. 2. EDS spectrum of the as-synthesized $NiWO_4/W_5O_{14}/WO_3$ composite nanostructures.

concern, researchers have synthesized and used many semiconductors, including WO_3 [19], CdS [20], TiO_2 [21], CeO_2 [22], and ZnO [23]. Tungsten oxides have photocatalytic activity that has been well proven in desulfurization [24, 25]. In our previous work, we synthesized ZnO/WO_3 nanocomposites using the Pechini sol-gel method and used for photocatalytic desulfurization of thiophene [26]. In the present paper, desulfurization of thiophene as a standard sulfur source was followed by $NiWO_4/W_5O_{14}/WO_3$ nanocatalyst in the presence of visible light. The sol-gel method was considered for the production of products with high purity, very high production efficiency, and uniform synthesis of compounds. The obtained product was analyzed by XRD, EDS, FESEM, DRS, and FT-IR techniques.

EXPERIMENTAL

Materials and instruments

Sodium tungstate dihydrate ($Na_2WO_4.2H_2O$), nickel nitrate tetrahydrate ($Ni(NO_3)_2.4H_2O$), citric acid ($C_6H_8O_7$), nitric acid (HNO_3) and ethylenediamine ($C_2H_8N_2$) were purchased from a Merck company and used without any purification. XRD (X-ray diffraction) pattern was studied by Philips-X PertPro device using Nifiltered Cu Kα radiation. FESEM (field emission scanning electron microscopy) images were prepared by MIRA3 FEG-SEM. EDS (energy dispersive spectrum) analysis was performed by the use of Philips XL30 microscope. FT-IR (Fourier transform infrared) spectrum was performed with Magna-IR spectrometer 550 Nicolet with 0.125 cm^{-1} resolution in KBr pellets in the range of 400–4000 cm^{-1}. JASCO V-670 spectrophotometer was used to obtain UV-visible spectrum (DRS).

Synthesis of $NiWO_4/W_5O_{14}/WO_3$ composite nanostructures

First, 0.4 g (2 mmol) of nickel nitrate salt was dissolved in 10 ml of water, and then 5 ml of aqueous citric acid solution was added to the above

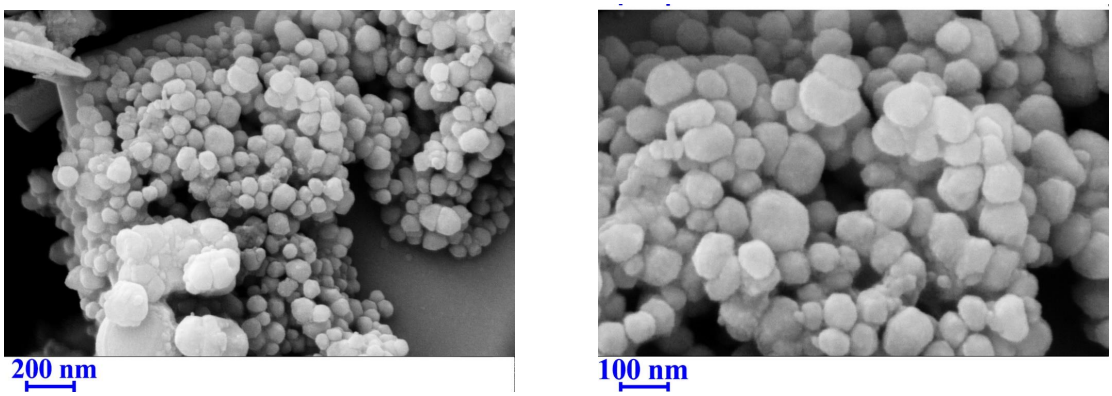

Fig. 3. FE-SEM images of the as-synthesized $NiWO_4/W_5O_{14}/WO_3$ composite nanostructures.

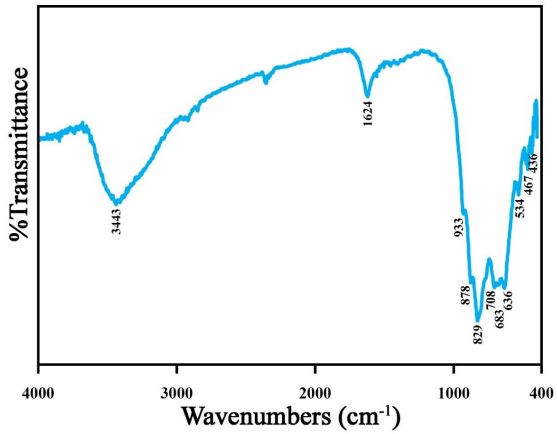

Fig. 4. FT-IR images of the as-synthesized $NiWO_4/W_5O_{14}/WO_3$ composite nanostructures.

solution with a molar ratio of 0.5: 1 to nickel salt. Separately, an aqueous solution of 2 mmol sodium tungstate with citric acid was prepared as above. A few drops of concentrated nitric acid were added until the salts were completely dissolved.

Later, the aqueous solution of nickel 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.

Photocatalytic desulfurization performance of $NiWO_4/W_5O_{14}/WO_3$ composite nanostructures

First, 50 ml of thiophene solution was prepared with a concentration of 800 ppm in n-hexane. Then, 50 mg of the catalyst and 10 ml of dimethylformamide were added to the above solution. The mixture was first stirred in the dark while aerating with oxygen for 30 minutes to establish an adsorption-desorption equilibrium. The mixture was kept in the dark for 30 minutes while aerated with oxygen to establish an adsorption-desorption equilibrium. Then, the solution was irradiated with a 400 watt Osram lamp. At the specified times, 5 ml of the solution was separated and centrifuged, and the sulfur content was recorded by the Tanaka Scientific RX-360SH sulfatometer. Visible light was irradiated in solution for 180 minutes.

RESULTS AND DISCUSSION

XRD studies

Fig. 1 shows the XRD pattern of the as-synthesized $NiWO_4/W_5O_{14}/WO_3$ composite nanostructure. According to the peaks shown in the pattern, the product is a mixture of $NiWO_4$

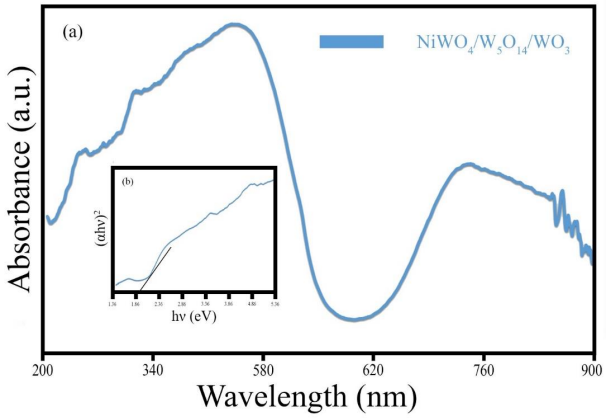

Fig. 5. Diffuse reflectance spectra of the as-synthesized $NiWO_4/W_5O_{14}/WO_3$ composite nanostructures.

nanoparticles with monoclinic crystal structure (JCPDS No. 15-0755 and cell constants a = 4.6000 Å, b = 5.6650 Å, and c = 4.9120 Å) and W_5O_{14} nanoparticles with tetragonal crystal structure (JCPDS No. 41- 0745 and cell constants a = 23.3300 Å, b = 23.3300 Å, and c = 3.7970 Å) and WO_3 nanoparticles with hexagonal crystal structure (JCPDS No. 33-1387 and cell constants a = 7.2980 Å, b = 7.2980 Å, and c = 3.8990 Å).

EDS studies

Fig. 2 shows a qualitative and quantitative analysis of the $NiWO_4/W_5O_{14}/WO_3$ composite nanostructure by EDS spectroscopy. There is a gold peak due to the conductivity of the surface for SEM analysis. According to the given spectrum, there are no impurities in the nanostructure and compatible with XRD analysis.

SEM studies

Fig. 3 shows the SEM images of the $NiWO_4/W_5O_{14}/WO_3$ composite nanostructure at different magnifications. As seen in the images, the as-synthesized nanostructures composite is mostly spherical in structure and has a uniform particle size distribution.

FTIR spectrum

Fig. 4 shows the surface impurities of $NiWO_4/W_5O_{14}/WO_3$ composite nanostructures by FTIR spectrum. As can be seen in Fig. 4, the peaks at 3443 cm^{-1} and 1624 cm^{-1} indicate the stretching and bending vibration of O-H bond, which is due to water adsorption by the product [9]. The peaks at 933, 878, 829, 708, 683, and 636 cm^{-1} belongs to the asymmetric and symmetric stretching vibrations of W-O-W and O-W-O bonds [27]. The peaks at 534 cm^{-1} and 467 cm^{-1} are related to the Ni-O-W and Ni-O stretching vibrations [27, 28].

DRS spectrum

The absorption spectrum of $NiWO_4/W_5O_{14}/WO_3$ composite nanostructures are shown in Fig. 5. As shown in Fig. 5a, the $NiWO_4/W_5O_{14}/WO_3$ nanocomposite exhibits a very wide light absorption, which can lead to the high ability of the composite in the photocatalytic process. Fig. 5b shows the bandgap calculation, the bandgap for the example according to Fig. 5a shows the value of 1.89 eV.

Photocatalytic desulfurization studies

The degradation of thiophene to measure the photocatalytic efficiency of the as-synthesized $NiWO_4/W_5O_{14}/WO_3$ nanocomposite is shown in Fig. 6a. This nanocomposite has resulted in more than 73% degradation of the thiophene contaminant at 180 min under visible light for photocatalytic desulfurization, while the process was not very efficient without nanocomposite and in the presence of light alone. Also, the lack of light in the process is accompanied by a slight degradation, which means that desulfurization without light is not done well. Moreover, the reusability of the $NiWO_4/W_5O_{14}/WO_3$ nanocomposite was evaluated by four consecutive recycling photocatalytic experiments under the identical condition for thiophene removal. As illustrated in Fig. 6b, the photocatalytic degradation efficiency can still reach 68% after four cycles. The result indicates that $NiWO_4/W_5O_{14}/WO_3$ nanocomposite is a highly stable photocatalyst, which is a fundamental

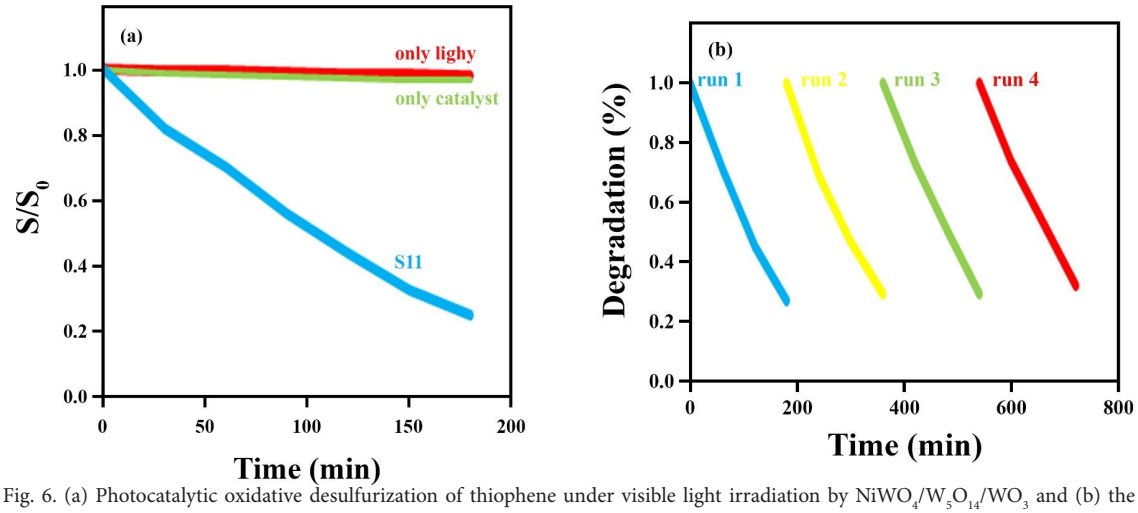

Fig. 6. (a) Photocatalytic oxidative desulfurization of thiophene under visible light irradiation by $NiWO_4/W_5O_{14}/WO_3$ and (b) the photodegradation reusability of $NiWO_4/W_5O_{14}/WO_3$ in recycling reactions under the same condition.

feature in practical applications for the removal of pollutants.

CONCLUSION

In summary, this study was performed to improve the properties and performance of the photocatalytic oxidative desulfurization of thiophene. This method has been used compared to other methods due to its superiority in high efficiency, low cost, and simple mechanism. The $NiWO_4/W_5O_{14}/WO_3$ composite nanostructure was synthesized under controlled conditions, low temperature, and high purity by Pechini sol-gel method. Tungsten oxides (WO_3 and W_5O_{14}) play an important role in reducing the bandgap, which increase the absorption of light in the visible region. As a result, the presence of three nanostructures $NiWO_4$, W_5O_{14}, and WO_3 increases the surface area and increases the light absorption of the nanocomposite. For the same reason, it resulted in 73% photocatalytic degradation after 180 minutes under visible light.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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