J Nanostruct 12(2): 446-454, Spring 2022

RESEARCH PAPER

$ZnMoO_4$ Nanoparticles: Novel and Facile Synthesis, Characterization, and Photocatalytic Performance

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ARTICLE INFO

Article History:
Received 29 December 2021
Accepted 28 March 2022
Published 01 April 2022

Keywords:
Nanocomposites
Organic pollutant
Photocatalysis
Ultrasonic
$ZnMoO_4$

ABSTRACT

In this research, $ZnMoO_4$ nanoparticles was synthesized through novel and fast chemical method. The products were prepared under different irradiation time and power. The shape, size, and crystalline structure have been investigated through Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and X-ray diffraction (XRD) analysis respectively. The optical properties of samples were prepared via UV-Vis analysis. Results confirmed that shape and size of $ZnMoO_4$ nanoparticles could be changed under different synthesis condition. The obtained results from optical properties of prepared $ZnMoO_4$ nanoparticles approved that the prepared nanoparticles have high potential for the photodegradation of organic pollutants. Methylene blue and rhodamine B were applied for investigation phtocatalytic properties of $ZnMoO_4$ nanoparticles. Results showed that methylene blue and rhodamine B were photodegraded under UV irradiation after 90 minutes 92.6% and 82.4% respectively. This excellent performance was due to the suitable band structure of synthesized $ZnMoO_4$ nanoparticles which led to prevention recombination of photo-generated electrons and holes. This work introduces $ZnMoO_4$ nanoparticles as an attractive photocatalyst for removal of organic pollutants from water.

How to cite this article
Raya I , Mansoor Al Sarraf A A , Widjaja G et al. $ZnMoO_4$ Nanoparticles: Novel and Facile Synthesis, Characterization, and Photocatalytic Performance. J Nanostruct, 2022; 12(2):446-454. DOI: 10.22052/JNS.2022.02.019

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INTRODUCTION

Renewable energies has found more attention in recent decades [1, 2]. The main environmental challenges lead to find way to overcome these problems [3, 4]. Photocatalyst process can play an effective role in reducing environmental problems. Photocatalysts are considered as agent which degrade organic pollutants under the sun lights containing UV rays [5, 6]. This process has many inherent benefits. The most important of which is the use of free solar energy to reduce environmental problems. The main challenge in applying photocatalytic process is the providing of a suitable photocatalyst so that it can degrade pollutants with high efficiency [7, 8]. In recent years, nanomaterials have been widely applied in photocatalytic process [9-12]. Nanomaterials are a attractive option in the field of photocatalyst due to their excellent optical properties which lead to the sufficient band gap [13, 14]. The other advantage of nanomaterials is that their optical properties can be controlled under the synthesis process [15].

Molybdenum-based nanostructures are found more and more attention for their fascinating narrow band gap and excellent structural properties [16-18]. When the size of these nanostructures decreased to the nanoscale, the optical and structural properties are greatly improved. It is well known that the higher specific surface and the possibility of quantum effects at the nanoscale are responsible for different material properties in the nanostuctures. Because of the scientific and industrial significance of size-dependent properties, the study of size and shape effects on material properties has gotten a lot of attention [19-21].

Min Wang et al. prepared europium and iron ions doped bismuth molybdate via chemical route. The prepared samples were characterized via SEM, XRD, TEM, FT-IR, XPS, UV-vis and PL. they reported that prepared nanomaterial degraded 94.1% of rhodamine B after 50 minutes irradiation. They also confirmed that reusability and stability of provided photocatalyst [22]. Nicholas F.Dummer et al. prepared copper molybdate nanoparticles via surfactant-assisted route. They found that surfactant cease agglomeration and give monodisperse platelet morphology. The XRD pattern and SEM images were applied for structural properties of prepared sample. The band gap of prepared sample was calculated 2 eV. They showed that indigo carmine was successfully degraded by synthesized copper molybdate [23].

Molybdenum-based nano photocatalyst has been faced with major different challenges including morphology engineering and high-cost. In this study, the $ZnMoO_4$ nanoparticles were prepared via a facile ultrasonic route for the first time. The structural properties and size of obtained products were examined via FTIR, XRD, UV-Vis, FE-SEM, and TEMTEM analysis. Then, the photocatalytic activity of prepared nanoparticles were studied against methylene blue and rhodamine B.

MATERIALS AND METHODS

X-ray diffraction (XRD) patterns analysis was done by a Philips-X'pertpro, X-ray diffractometer employing Ni-filtered Cu Kα radiation. Nicolet Magna-550 spectrometer in KBr pellets was applied for recording Fourier transform infrared (FT-IR) spectra. Morphological properties of products were investigated via scanning electron microscopy (SEM) that obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. For in-depth investigation of morphological structure, Philips EM208S transmission electron microscope was used.

Synthesis of $ZnMoO_4$

First, zinc chloride was dissolved in distilled water under stirring. Second, $Na_2MoO_4.2H_2O$ were separately dissolved in distilled water under a stirrer. The molar ratio of Zn:Mo was kept at 1:1. The Mo-containing solution was added to the Cu-containing solution under ultrasonic irradiation with frequency and power of 60 kHz and 180 W respectively. The prepared solid was centrifuged and washed with distilled water. After drying of sample, the solid was calcined for 3h at 600 °C.

Photocatalytic test

The photocatalytic performance of as-obtained $ZnMoO_4$ nanoparticles was examined toward of methylene blue and rhodamine B. 20 ppm dosage of mentioned dyes were provided separately. 0.05 g of provided $ZnMoO_4$ was dispersed in 50 mL dye solutions under stirrer. The mixture was then stirred in the dark for 30 minutes to complete the adsorption equilibrium of dyes on the surface of the photocatalyst. After that, the xenon arc lamp was applied for providing ultraviolet light to irradiate the as-prepared mixture. In certain

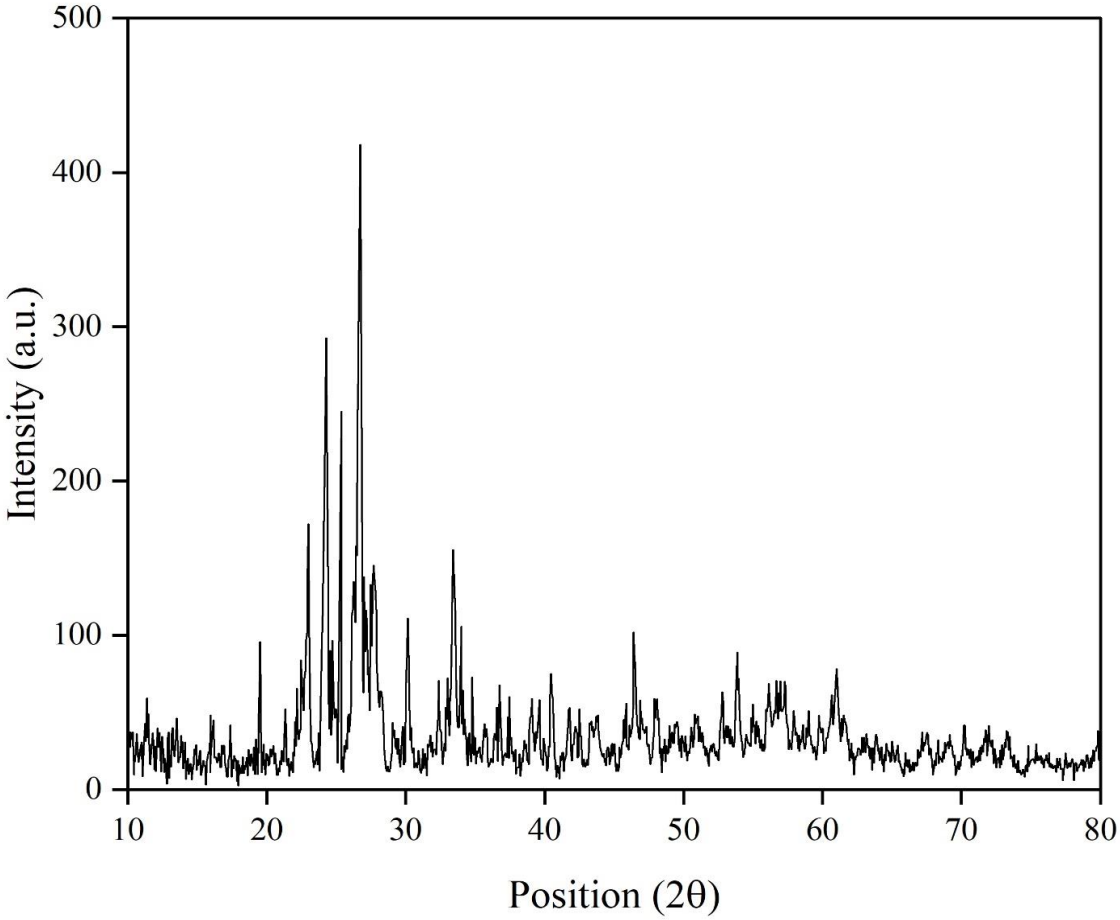

Fig. 1. XRD pattern of prepared $ZnMoO_4$ nanoparticles.

and constant periods, 5 mL of the solution was taken out and centrifuged. The light absorbance of the dyes solution was determined via an UV spectrophotometer and the amount of the dyes within the each solution was measured according to the absorbance of light at the maximum wavelength of dyes.

RESULTS AND DISCUSSION

Characterization of $ZnMoO_4$ Nanoparticles

Fig. 1 represents XRD pattern of synthesized $ZnMoO_4$ nanoparticles. As can be seen in XRD pattern of $ZnMoO_4$ nanoparticles, the pattern is in good agreement with the hexagonal structure of reference code 01-072-1486. The rsults also confirms the formation of $ZnMoO_4$ with any impurity. The XRD pattern of $ZnMoO_4$ nanoparticles have been reported in previously studies. The obtained XRD pattern in present study is completely in agreement with previous studies. Scherer equation was applied for calculation of grain size. The grain size was determined 28 nm. The presence of broad peaks in XRD pattern confirms the small grain size of $ZnMoO_4$ nanoparticles.

FT-IR spectra was used for the surface functional group study. Fig. 2 shows FT-IR spectrum of $ZnMoO_4$ nanoparticles. From the FTIR spectra for $ZnMoO_4$, as can be seen in the Fig. 2, the infrared bands at 3150 and 1612 cm^{-1} relates to OH stretching vibration and bending vibrations of water molecules. Presence of adsorption bands in the range of 750–1050 cm^{-1} confirms formation of of $[MoO_y]^{n-}$. The band at 532 cm^{-1} can be attributed to the stretching mode of zinc-oxygen in $ZnMoO_4$.

Fig. 3a and Fig. 3b shows SEM images of $ZnMoO_4$ nanoparticles at different magnifications. It can be observed that $ZnMoO_4$ nanoparticles were uniformly prepared with 60 nm particle size. For

morphological studying of prepared products TEM images was applied. As well as shown in Fig. 4, small size $ZnMoO_4$ nanoparticles were uniformly. The particle size was measured 48 nm from TEM

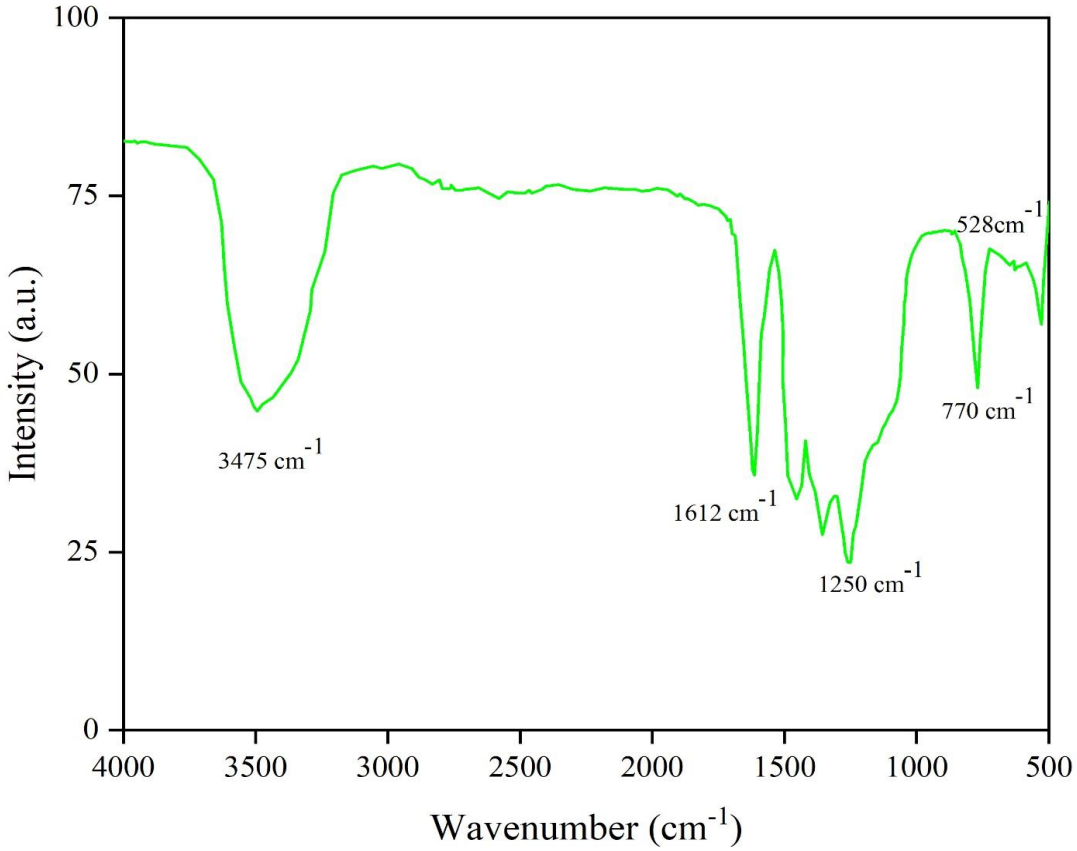

Fig. 2. FTIR spectrum of prepared $ZnMoO_4$ nanoparticles.

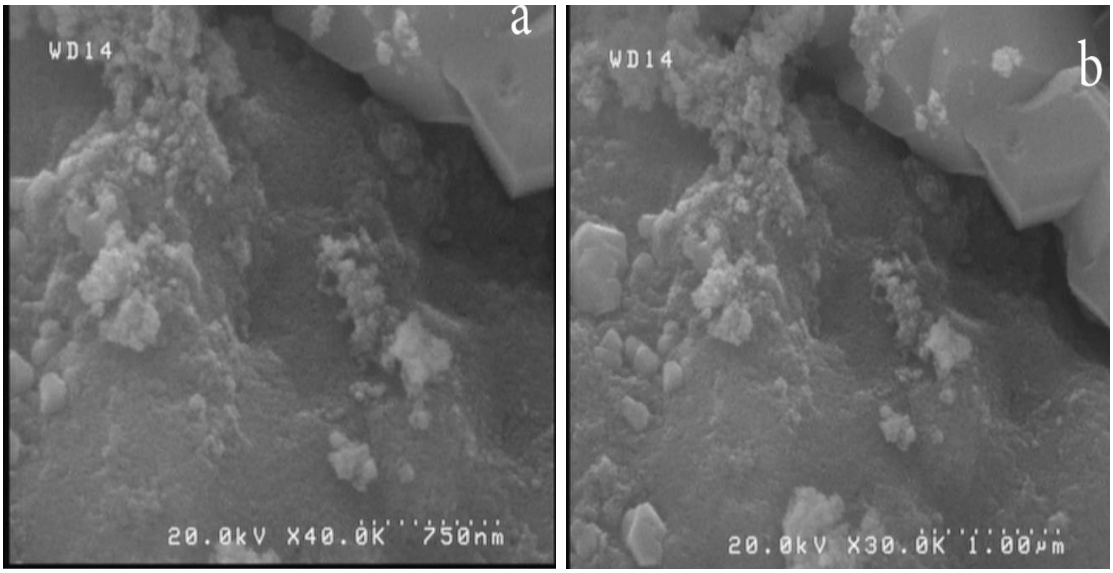

Fig. 3. The SEM images of synthesized $ZnMoO_4$ nanoparticles at different magnifications.

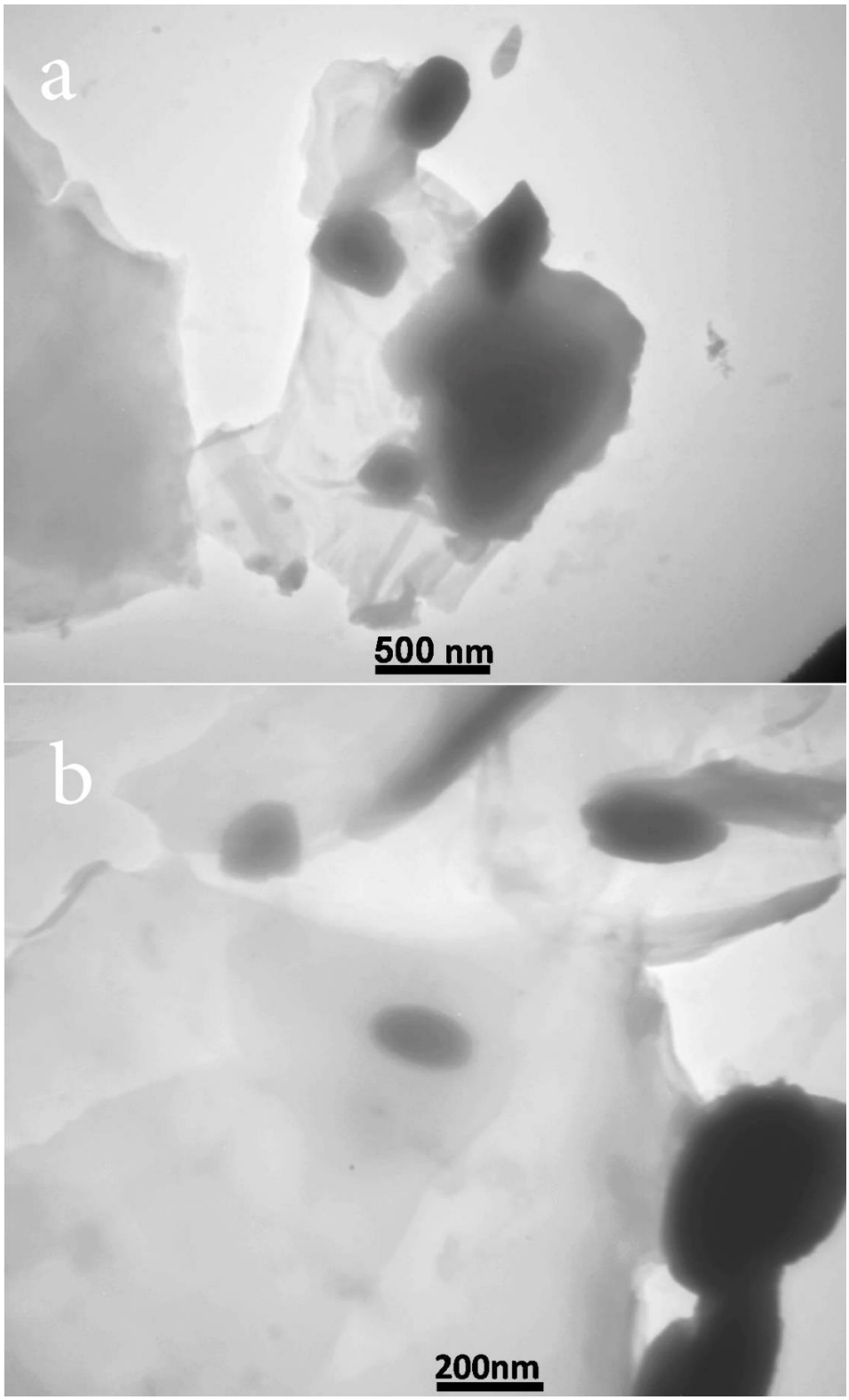

Fig. 4. The TEM images of synthesized $ZnMoO_4$ nanoparticles at different magnifications.

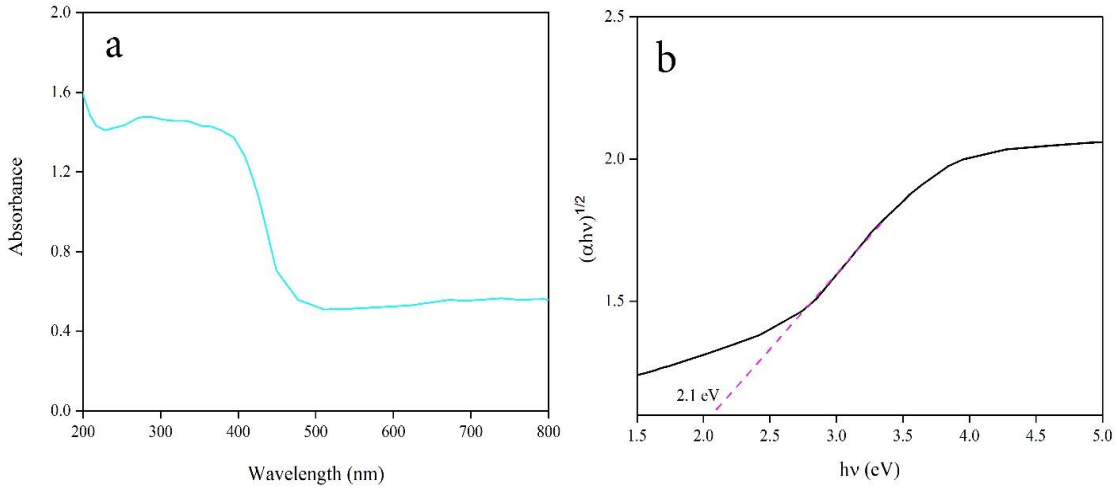

Fig. 5. . a) UV-vis diffuse reflectance spectra and b) band gap energy of prepared $ZnMoO_4$ nanoparticles.

images. The different particle size obtained from TEM and SEM images is considerable. It can be concluded that applied synthesis route was successful to produce pure $ZnMoO_4$ nanoparticles with sufficient shape and size.

UV-Vis DRS analysis was applied for

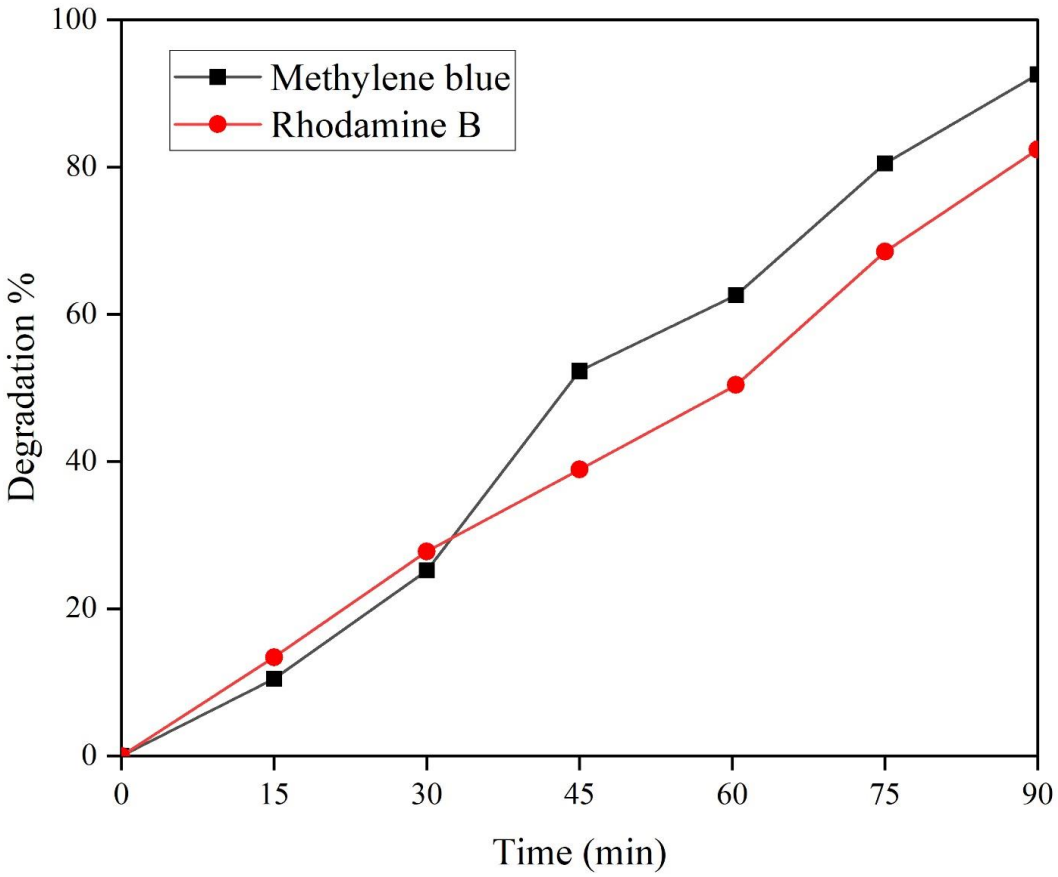

Fig. 6. Photocatalytic activity of $ZnMoO_4$ nanoparticles for removal of methylene blue and rhodamine B.

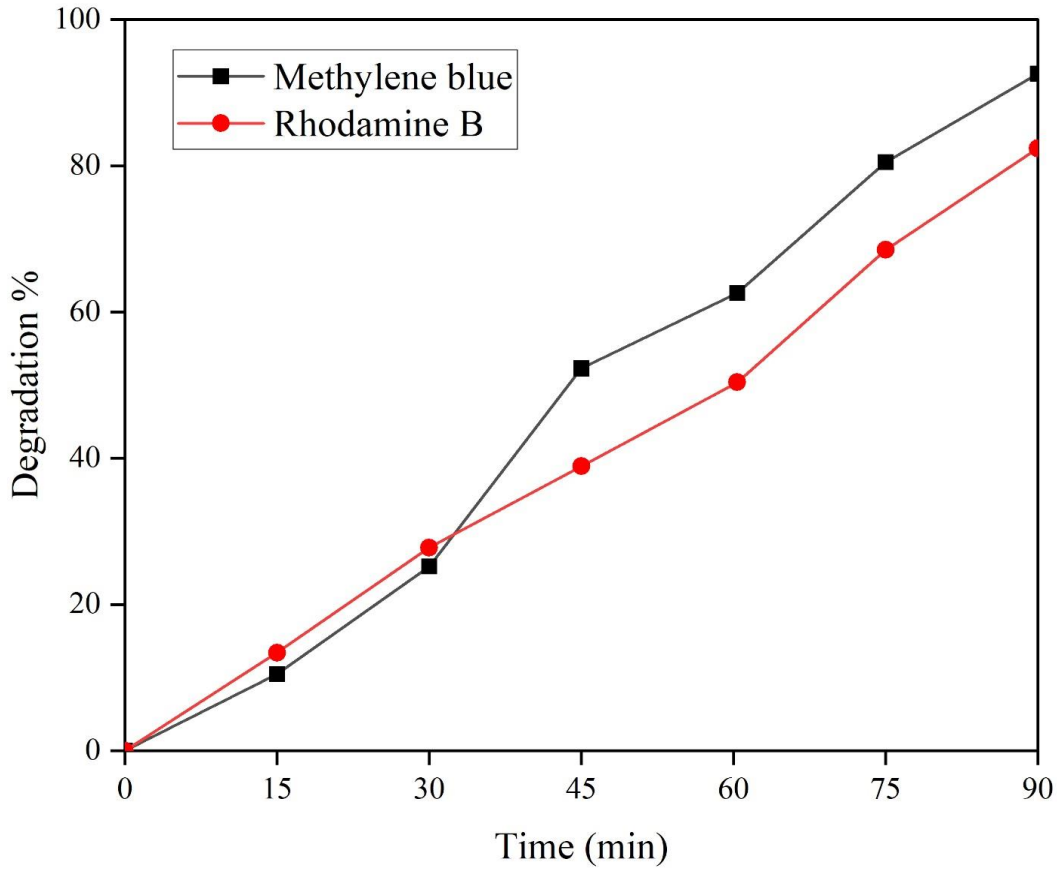

Fig. 7. Photocatalytic activity of $ZnMoO_4$ nanoparticles under different dye concentrations (10, 15, 20, and 25 ppm)

characterization of optical properties of sample. As well as shown in Fig. 5a, synthesized $ZnMoO_4$ nanoparticles displayed broad absorption edge within the visible range, which was owing to the band gap transition absorption [24]. The Tauc plot was drawn using UV-Vis DRS analysis and the Tauc equation. As illustrated in the Fig. 5b, the optical band gap is calculated via plotting $(\alpha h\upsilon)^2$ vs $h\upsilon$, where, h, υ, and α are a constant, the Planck's constant, the light frequency, and the absorption coefficient, respectively. In Fig. 5b, calculated E_g of $ZnMoO_4$ nanoparticles were 2.69 eV, which is in good agreement with previously reported papers. The narrower E_g of the prepared $ZnMoO_4$ nanoparticles is advantage for using visible light more efficiently, making it easier to generate electronic transitions, which was important to lead to better photocatalytic performance. Fig. 6 displays the photocatalytic activity of prepared $ZnMoO_4$ nanoparticles to the degradation of rhodamine B and methylene blue. As well as illustrated, after 90 min the photocatalytic efficiency of $ZnMoO_4$ nanoparticles against methylene blue and rhodamine B were calculated 92.6.% and 82.4 % respectively (Fig 6 a and Fig. 6b). The findings show that $ZnMoO_4$ nanoparticles had the better photocatalytic activity against methylene blue than rhodamine B. Fig. 7 shows the effect of dye concentration on the photocatalytic performance of $ZnMoO_4$ nanoparticles. The photocatalytic activity in the 10 ppm (92.6%) and 15 ppm (89.2%) are higher than 20 ppm (51.6) and 25 ppm (41.1%) of methylene blue. Via increasing dye dosage, the active sites of catalyst decreases and disrupting the process of receiving UV light by the $ZnMoO_4$ nanoparticles and lead to prevention of free hydroxyl radical formation. The possible photodegradation mechanism can be explained as equation:

$$ZnMoO4 \xrightarrow{h\upsilon} ZnMoO4\ (e^-_{CB}) + ZnMoO4\ (h^+_{VB}) \quad (1)$$

$$O_2 + e^- \rightarrow \bullet O_2^- \quad (2)$$

$$\bullet O_2^- + H^+ \rightarrow \bullet HO_2 \quad (3)$$

$$2 \bullet HO_2 \rightarrow O_2 + H_2O_2 \quad (4)$$

$$H_2O_2 + e_{CB}^- \rightarrow 2 \bullet OH \quad (5)$$

$$h_{VB}^+ + H_2O \rightarrow \bullet OH + 2H^+ \quad (6)$$

$$MB + \bullet OH \rightarrow \text{Degradation of MB} \quad (7)$$

CONCLUSION

In conclusion, this work introduced $ZnMoO_4$ nanoparticles as a new photocatalyst. First, the $ZnMoO_4$ nanoparticles was prepared via sonochemical route. Then, the prepared sample was characterized via XRD, FTIR, SEM, TEM, and UV-Vis analysis. The results showed that prepared $ZnMoO_4$ nanoparticles have attractive optical properties. About 92.6% of methylene blue and 82.4% of rhodamine B was photodegraded after 90 min of treatment at optimum conditions (0.05 g of catalyst, 10 ppm of methylene blue). The reason for the formation of active radicals in photocatalytic processes was the electron-hole mechanism.

CONFLICT OF INTEREST

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

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