

A simplified microwave-assisted synthesis of NiMoO₄ nanoparticles by using organic driving agent and study of photocatalytic activity

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Abstract

Organic reagents can be used as a driving agent to synthesize a wide spectrum of nanomaterials. In this work, nickel molybdate (NiMoO₄) nanoparticles with a pure monoclinic crystalline phase were synthesized by using a facile one step microwave heating technique in solid state within a few minutes. Ammonium hepta molybdate tetrahydrate and nickel nitrate hexahydrate as initial materials were mixed to each other without any solvent and put into a domestic microwave oven with one step scheduled run. We introduced an alternative route of power input into chemical reactions in solid state by using microwave radiation. In fact, the obtained results can draw an outlook of the effectiveness and feasibility of this technique for the synthesis of various nanoparticles. Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersion of x-ray spectrometry (EDX) were used to characterize the prepared product. The study of photocatalytic behaviour of the resulting product indicated a high capability on the removal of Methylene Blue (MB) from aqueous solution.

Keywords: Nanoparticles, Microwave, Green, Methylene Blue, NiMoO₄

Introduction

In recent decades, binary metal oxides have attracted a great interest of researches as potential materials for different performances compared with the unary metal oxide systems. The family of metal molybdates is one of the most promising examples of the mixed metal oxides, which have extensively studied in recent years. Nickel molybdate (NiMoO_4) possesses the various applications in catalyses such as oxidative dehydrogenation of light alkanes [1, 2], hydrodesulfurization, hydrodenitrogenation and *etc.*, [3, 4]. Several methods have been taken to synthesize this metal oxide such as sonochemical, hydrothermal, sol–gel, chemical precipitation methods [5-7]. Microwave assisted methods possess many advantages such as high reaction selectivity and rate, high product yield, and energy saving. Microwave assisted combustion method is defined as a beneficial way with the different heating mechanism in comparison with the conventional combustion technique. Combustion technique can be described as a facile, low cost and useful route for the preparation of the powders with a high purity in nanometric scale. The theory of this technique is based on the concept of driving chemistry, where the volatile molecules i.e. CO_2 , H_2O and N_2 are released due to combustion reaction and a stable product remains. In fact, the initial materials are heated by microwave energy, prompted by burning of the fuel and nitrate groups in throughout mixture. In this work, we report for the first time a facile one pot microwave assisted combustion procedure to produce nickel molybdate nanoparticles by utilizing urea as an organic driving agent and fuel. The resulting product was characterized and then, employed to study the removal efficiency of organic azo dye, MB, from aqueous solution.

2. Experimental

2.1. Materials and Synthesis procedure

All of the reagents were purchased from Merck Company and used without further purification. A stoichiometrical amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were mixed, put into a domestic microwave oven and reacted to each other in the presence of urea as a fuel. The program of instrument was adjusted on the power of 900 W for a few minutes. The obtained product was collected and analyzed.

2.2. Characterization

Scanning electron microscopy (SEM) images were taken by VEGA/TESCAN microscope at accelerating voltage of 30 kV to study the morphology of sample. Energy-dispersive X-ray spectroscopy analysis (EDX) to discover the elements present in the products were taken on a Philips XL-30 SEM with gold coating. The powder XRD measurements were performed using STOE diffractometer with monochromatized $\text{Cu K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). FTIR spectra were recorded on a Shimadzu-8400S spectrometer in the range of $400\text{--}4000 \text{ cm}^{-1}$ using KBr pellets. The UV-Vis absorption study was carried out in the wavelength range of $190\text{--}800 \text{ nm}$ at room temperature on a UV-Vis spectrophotometer (Shimadzu UV-1700).

2.3. Photocatalytic test

The photocatalytic experiments were designed under the following conditions: 0.05 g of as prepared catalyst was added to 100 mL of MB aqueous solution with the initial concentrations of 20 mg L^{-1} at room temperature and neutral pH. The concentrations of the residual dye were measured by using UV-Vis spectrophotometer at proper wavelength corresponding to the maximum absorption of MB (665 nm). The light irradiation was supplied using a source of 500 W high-pressure mercury-vapor lamp ($\lambda = 546.8 \text{ nm}$). At specific time intervals of irradiation,

the portions of suspension were taken away from the reaction vessel, centrifuged and analyzed by UV-Vis spectrophotometer.

3. Results and discussion

FT-IR spectrum, XRD pattern and energy-dispersive X-ray analysis (EDX) energy-dispersive X-ray analysis (EDX) were used to investigate the structural characteristics of the synthesized NiMoO₄ nanoparticles. To study the bonding nature of the resulting product was recorded the FT-IR spectrum as shown in Fig. 1. The strong peaks at 946 cm⁻¹ with a weak shoulder at 858 and also, the bands at 586 and 414 cm⁻¹ are characteristics of α -NiMoO₄ structure. These bands can be attributed to the vibrational modes of Mo–O–Mo and Ni–O–Mo in building block of NiMoO₄, respectively.

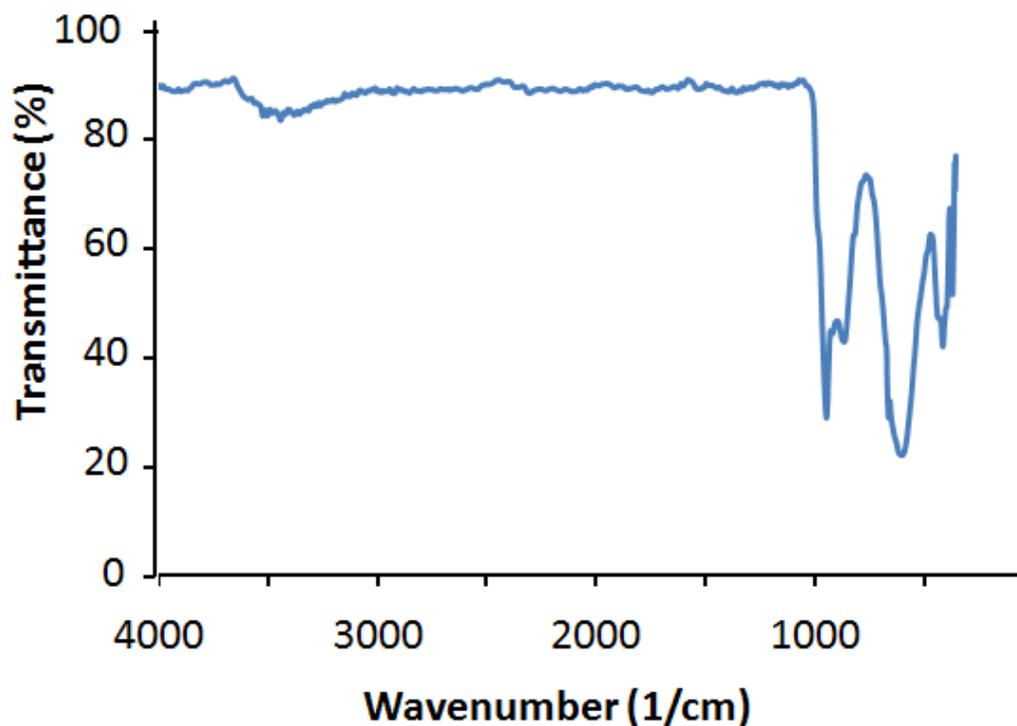


Fig. 1. FT-IR spectrum of the prepared NiMoO₄

XRD pattern shown in Fig. 2 indicated a crystalline monoclinic phase of α -NiMoO₄ with the space group of *I2/m* and lattice parameters of $a=9.509\text{\AA}$, $b=8.759\text{\AA}$, $c=6.667\text{\AA}$ (JCPDS Card No. 33-0948). The sharp diffraction peaks confirmed the formation of a pure crystallinity of monoclinic α -NiMoO₄ phase. EDX analysis (Fig. 3) illustrated the presence of the stoichiometrical amounts of elements in the structure of as-prepared product.

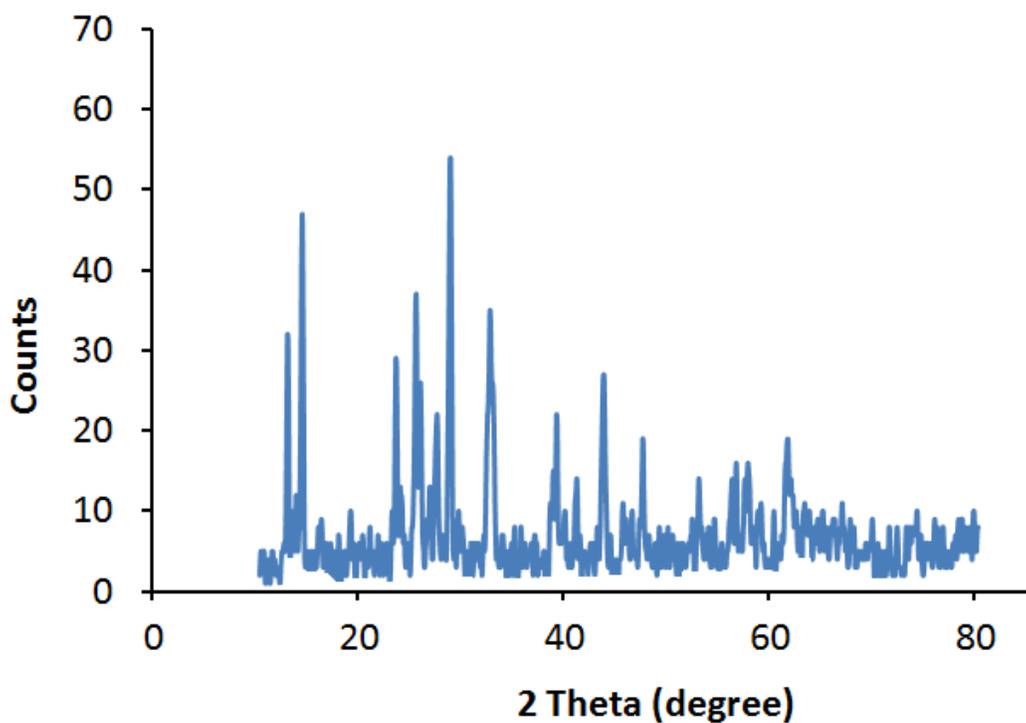


Fig. 2. XRD pattern of α -NiMoO₄ nanoparticles.

SEM images (Fig. 4) indicated the particulate morphology of the resulting specimen with a wide distribution of nanosized particles in the range of 50 to 200 nm.

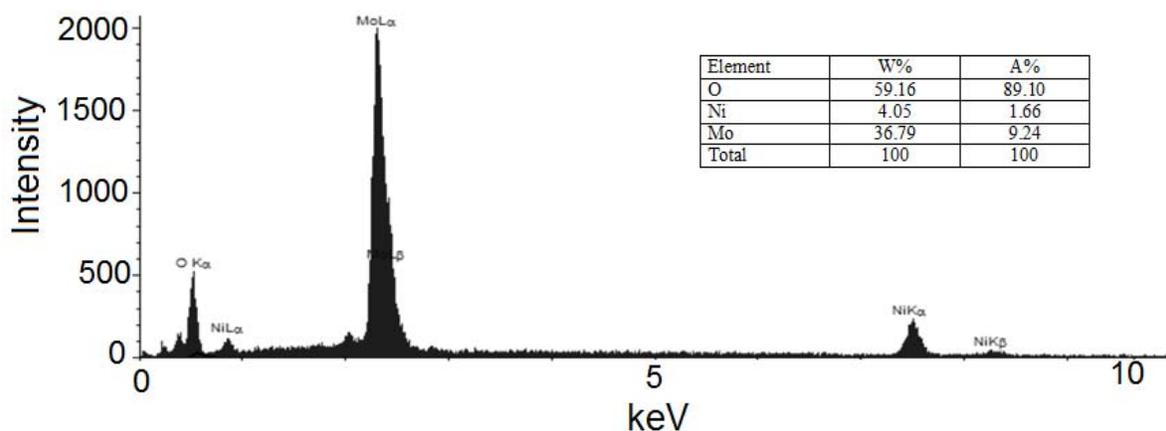


Fig. 3. EDX analysis of NiMoO₄.

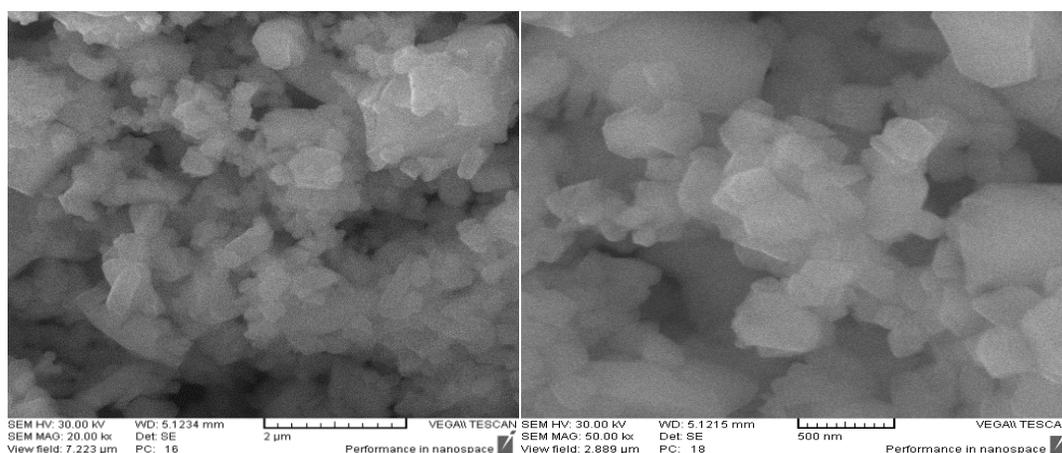


Fig. 4. SEM images of product.

The photocatalytic activity of product was studied by introducing the prepared NiMoO₄ nanoparticles into a 100 mL MB (20 mg.L⁻¹) aqueous solution under UV- Vis light irradiation.

The changes of MB concentration versus irradiation time in the range of 0-4 h as shown in Fig. 5a were plotted. It was seen that at the first hour of phtocatalytic operation the adsorption-desorption process of pollutant molecules onto catalyst surface lead to increase the absorbance value, although the continuance of process is resulted in a desirable photodegradation of

pollutant. After 4 h of irradiation, the photocatalytic activity increased from 27% (without light) to 66% for 4 (Fig.5 b).

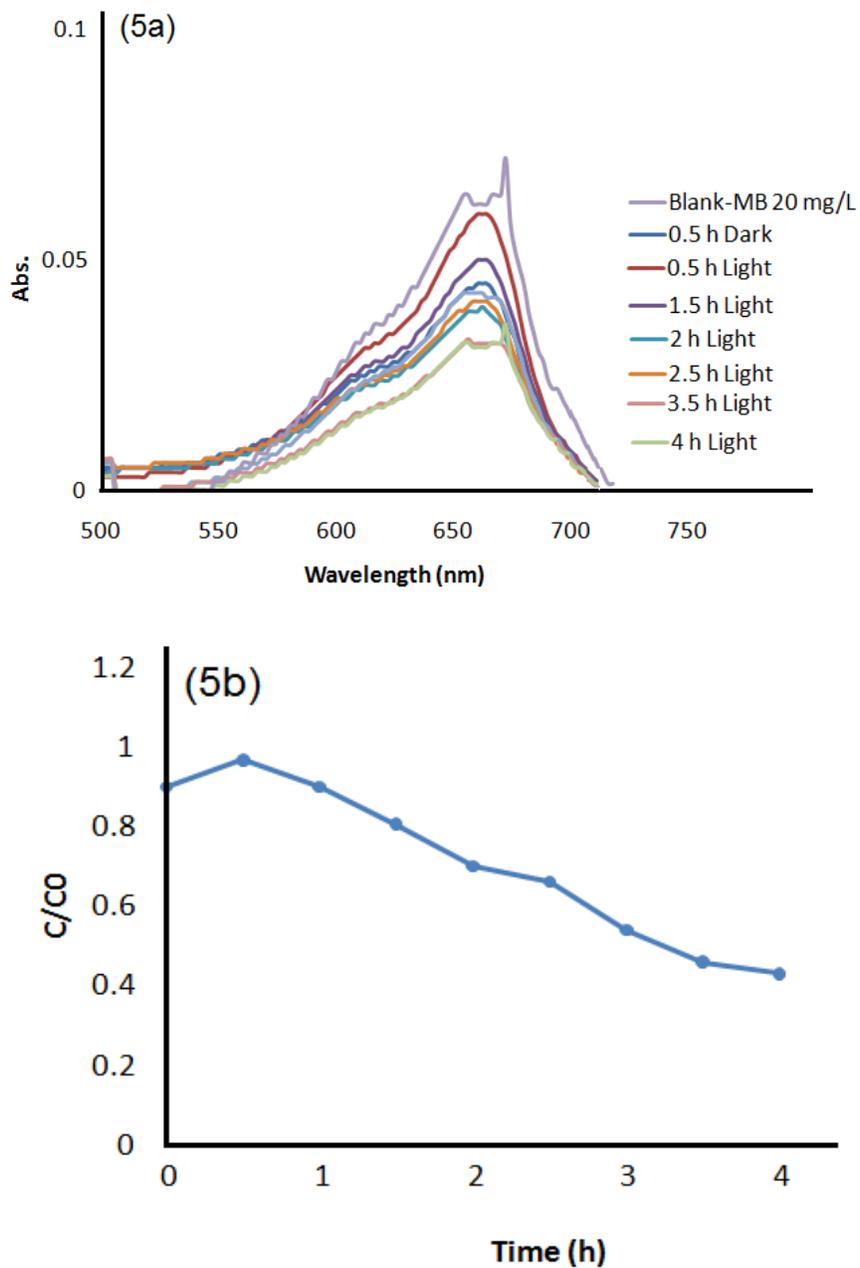


Fig. 5. UV-Vis absorption spectrum for MB solution (a) and plot of MB concentration versus irradiation time during the photodegradation reaction in the presence of as-prepared NiMoO₄ nanoparticles (b).

Conclusion

It has been established that the microwave assisted combustion method by using organic driving agent can be used for the straightforward synthesis of NiMoO₄ nanomaterial with a high purity. In fact, the presence of organic agents and nitrate anions in reaction led to construct and organize structured nickel molybdate in nanoscale by heating treatment *via* microwave irradiation. Meanwhile, the obtained results of the photocatalytic study demonstrated that compound may be a good potential photocatalyst in the photodegradation of some organic dyes.

Acknowledgments

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