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Microwave-assisted synthesis of molybdenum oxide nanoparticles

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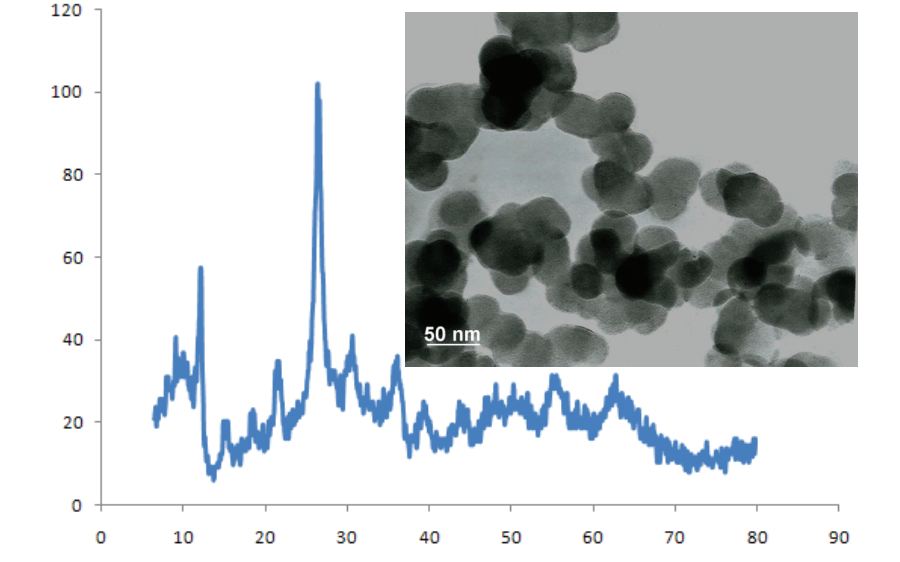
HIGHLIGHTS

- Molybdenum oxide (MoO_3) nanoparticles were synthesized via microwave-assisted method.
- The synthesized nanoparticles were spherical with an average size of about 50 nm.
- Conventional heating and microwave irradiation were compared for MoO_3 synthesis.
- The particles synthesized via microwave heating were smaller and more stable.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper focused on a simple approach for synthesis of molybdenum oxide (MoO_3) nanoparticles and reports a facile route for synthesis of such nanoparticles, using microwave irradiation as a homogenous and powerful source of heating, using ethylene glycol as the solvent and heating medium. For more investigations, besides microwave heating, the obtained solutions were also treated by conventional heating. Finally, product particles were characterized and compared using scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDX). According to the results, microwave irradiated particles showed a good dispersion and stability in relation to the other sample. So, the obtained product was subjected to X-ray diffraction (XRD) analysis to survey the formation of MoO_3 nanoparticles. The transmission electron microscope (TEM) micrographs were also recorded to study the size and morphology of the nanoparticles. According to the results, nanoparticles were spherical with an average size of about 50 nm. The absorbance spectrum of MoO_3 nanoparticles was further studied using the UV-vis spectroscopy and the absorbance peak was observed at 257 nm.

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1. Introduction

In recent years, transition metal nanoparticles have been paid remarkable attention because of their potential applications in various fields such as catalysis [1], magnetic [2], optic [3] and etc. Many techniques have been developed for the synthesis of catalytic metallic materials using different reducers and stabilizers including thermal decomposition of organometallic compounds [4], metal evaporation [5] and sonochemical decomposition of metal compounds [6] and so on. It is well-known that molybdenum oxide nanoparticles are remarkable catalysts possessing various applications [7]. In this way, different structures of molybdenum oxide nanoparticles have been synthesized via various methods. For example Li and Ell-Shall [8] prepared MoO_3 nanoparticles by a vaporization-controlled condensation (LVCC) technique. Jia et al. [9] also reported on the mechanism of molybdenum and molybdenum oxide nanoparticles formation from molybdenum oxide microparticles using the electron beam irradiation technique. Bilecka et al. [10] reported on synthesis of MoO_x nanoparticle using microwave-assisted sol-gel synthesis procedure. Lee et al. [11] examined on the synthesis of low-temperature solution-processed molybdenum oxide nanoparticle layers for organic photovoltaic devices. Kanneganti et al. [12] reported on a sustainable approach for synthesis of MoO_3 nanoparticles using citrus limetta. Jadhav et al [13] reported on a microwave-assisted method for synthesis of octahydroquinazolinone derivatives using molybdenum oxide nanoparticles as effective catalyst. So, reviewing on literature, we found that application of microwave heating in combination with an appropriate polyol as the heating medium is nowadays so widespread for preparation of nano-sized catalysts [14, 15]. In this method, some alcohols such as ethylene glycol are used for either reduction or stabilization of metal submicrometer particles. But, because of the slow rate of reaction there is a need to apply specific situations like high temperature and pressure. Scholars have proposed that the use of microwave radiation can effectively facilitate the use of polyol method for preparation of metal nanoparticles. This approach was firstly applied by Komarneni et al. [16]. In this study we tried to improve the rate of the reaction by adding appropriate amount of hydrazinium hydroxide to molybdenum salt solution (in ethylene glycol), and applied microwave irradiation for homogenous nucleation and growth of nanoparticles in desired time.

2. Experimental

2.1. Materials

All the reagents were obtained from Merck (Darmstadt). Ethylene glycol (EG), Hydrazinium hydroxide ($N_2H_4.H_2O$, 100%) and Molybdatophosphoric acid hydrate ($H_3PMo_{12}O_{40}$). All the reagents were of the highest commercially available purity.

2.2. Apparatus

The XRD patterns of the products were recorded with a Philips X'Pert MPD X-ray Diffractometer (using Cu Kα λ=1.78897Å radiation). The transmission electron micrographs (TEM) were imaged on a Ziess W. Germany 900 EM microscope, using an 80 kV accelerating voltage. Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid coated with a carbon film. The grid was then air-dried. SEM images were recorded by an AL30 Philips instrument using a 17 kV accelerating voltage. For EDX, the attached function was linked to the scanning electron microscope (SEM). The samples for SEM and EDX analysis were prepared by placing a little amount of precipitated nanoparticles on a glass plate. It is to be noted that placing the sample on a glass plate has resulted in appearance of peaks corresponding to glass components the spectrum. The UV-vis spectra were recorded with samples in 1 cm^3 quartz cells using a Varian Carry 100 (UV-vis) Spectrophotometer in the spectral range of 190–1100 nm. The microwave-assisted reactions were carried out in a Panasonic MX21WF Spectra-900 W domestic microwave oven, with a 2.45 GHz working frequency.

2.3. Synthesis of molybdenum oxide nanoparticles

For synthesis of molybdenum oxide nanoparticles and investigation on effects of synthesis condition, two separated samples (here mentioned S1 and S2) were prepared simultaneously by dissolving calculated amount of $H_3PMo_{12}O_{40}$ in 50 ml EG under stirring and gradual addition of some droplets of PVP solution and hydrazinum hydroxide. Then, S1 was irradiated at 100˚C for about 50 seconds while S2 was treated by conventional heating at 100˚C for about one hour. In this way, formation of brownish colloidal solution in both samples was considered as the end point of the reaction. In the next step, obtained products were calcinied in the furnace at 500˚C for about 2 hours.

3. Results and discussion

As mentioned above, formation of brownish colloidal particles was considered as the end of the reaction in this work. This phenomenon was also reported by Lee et al. [11] and Kanneganti et al [12]. Also, obtained products were subjected to SEM and EDX analysis for comparison of structures and selected sample was also characterized by XRD, UV-vis spectroscopy and TEM micrographs. As shown in Figs. 1 and 2, sample prepared under microwave irradiation (S1) showed more homogeneity and narrower size distribution in comparison with the sample prepared by conventional heating (S2).

Also, obviously the average particle size of S1 (about 53 nm) was so sharper than S2 (about 300 nm), while EDX analysis shown in Figs. 3 and 4, confirmed the existence of molybdenum element in both samples. In addition, it should be mentioned that it was directly observed that stability of S1 was superior to S2, so that S1 was stable for weeks, while stability of S2 was less than one day. This fact can represent the positive effect of microwave heating (a homogenous and powerful heating during a short period of time) in the synthesis of homogenous nanoparticles with a narrower size distribution compared to conventional methods as reported in literature [14].

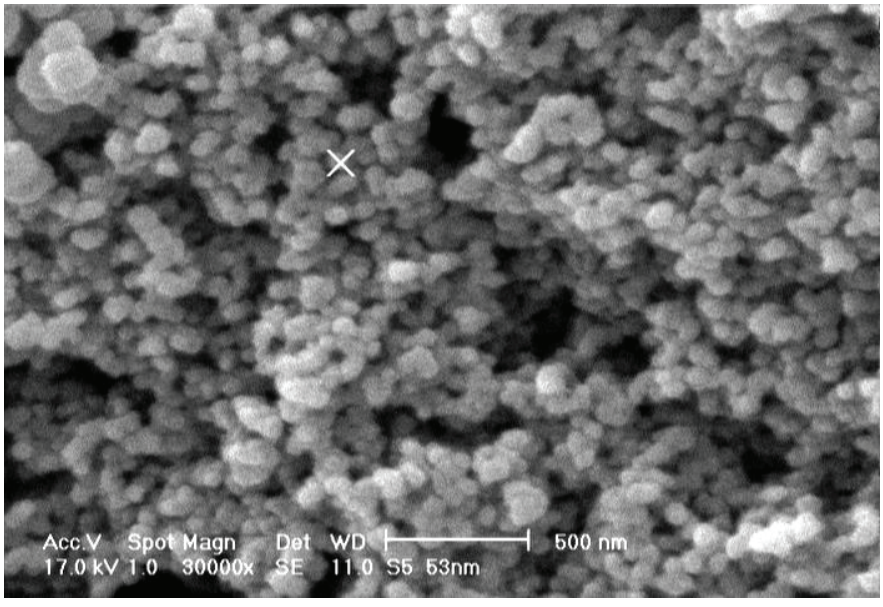


Fig. 1. SEM image of sample S1, prepared under microwave irradiation.

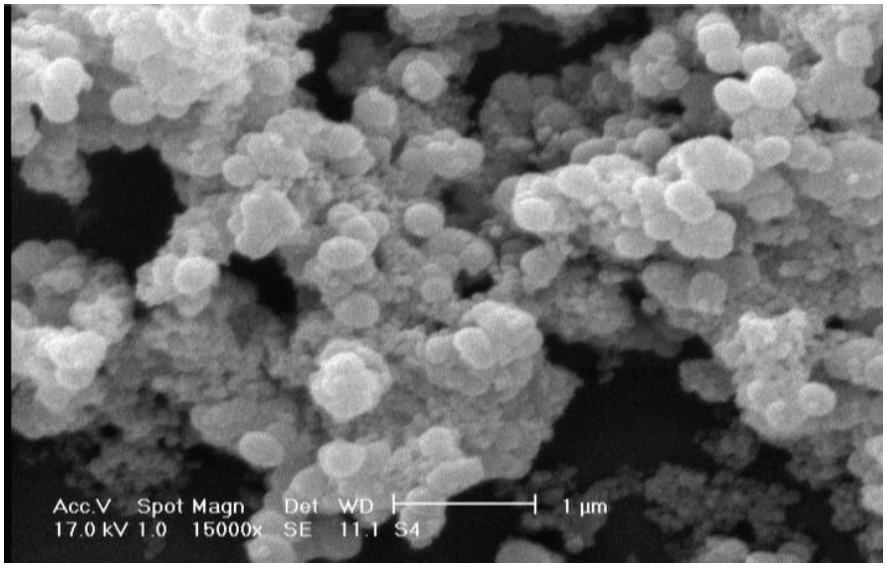
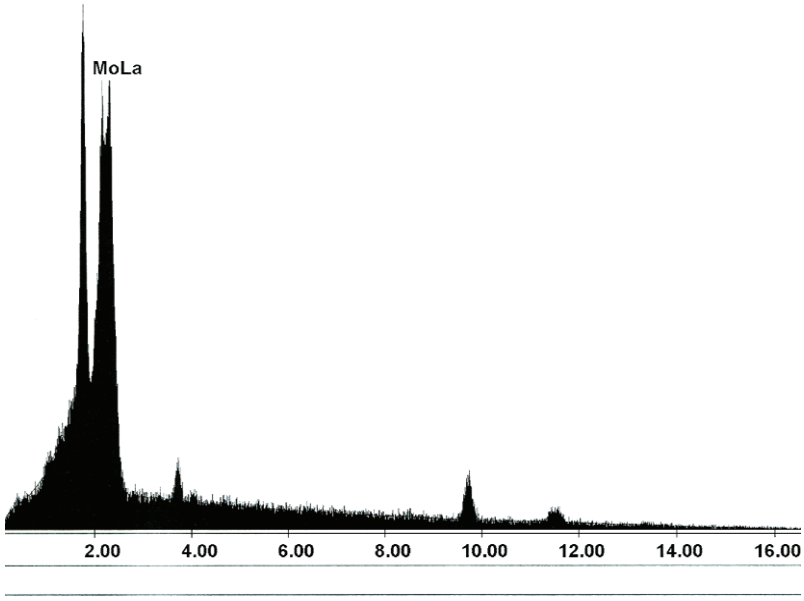


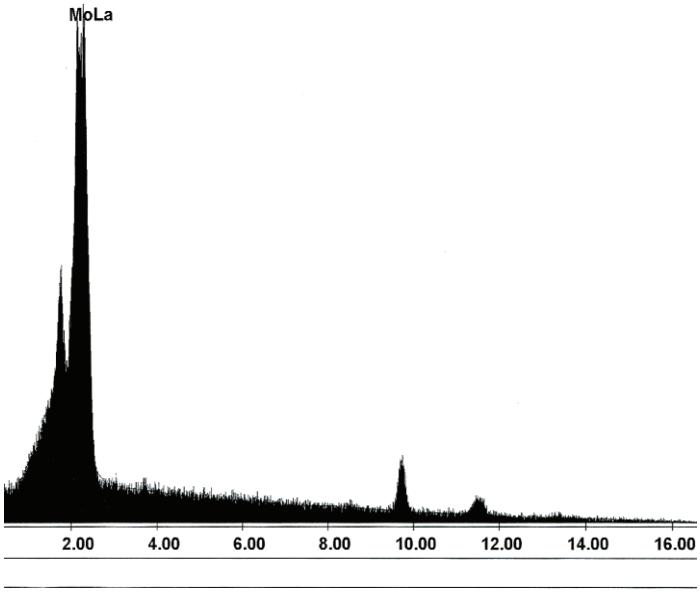
Fig. 2. SEM image of sample S2, prepared by conventional heating.



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %
MoL	100.00	100.00
Total	100.00	100.00

Fig. 3. EDX spectrum of sample S1, prepared under microwave irradiation.



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %
MoL	100.00	100.00
Total	100.00	100.00

Fig. 4. EDX spectrum of sample S2, prepared by conventional heating.

say that microwave homogenous heating was absorbed by ethylene glycol medium (possessing high absorption factor), improved the nucleation and growth process and also controlled the particles growth rate so that particles size was limited in nanometer scale. While in conventional heating, all parts of solution were not heated simultaneously and homogenously.

Fig. 5 shows a typical XRD pattern of the sample prepared under microwave irradiation. Similar to what Chibane et al. [17] have reported, comparison of the prominent peak positions (2θ-values) of the XRD spectra with the ASTM data file for MoO_3 (file no. 00-035-0609) revealed that the product was mainly composed of MoO_3 nanoparticles crystallized in orthorhombic system. Also JCPDS software analysis confirmed that the obtained product was orthorhombic MoO_3 nanoparticles.

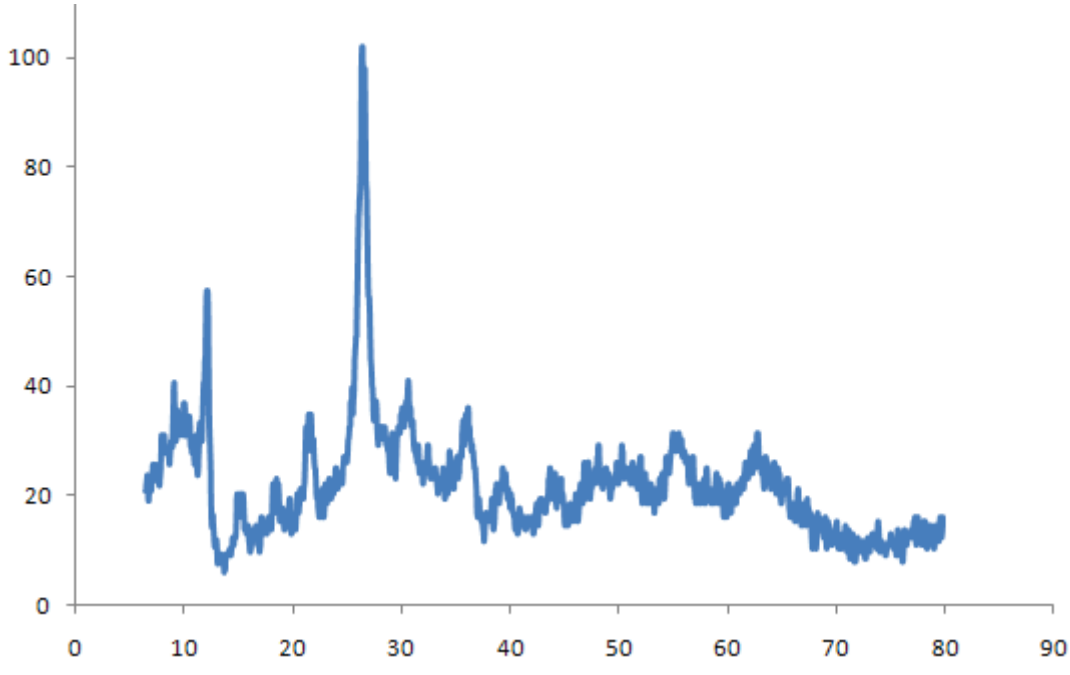


Fig. 5. XRD pattern of molybdenum oxide nanoparticles prepared under microwave irradiation.

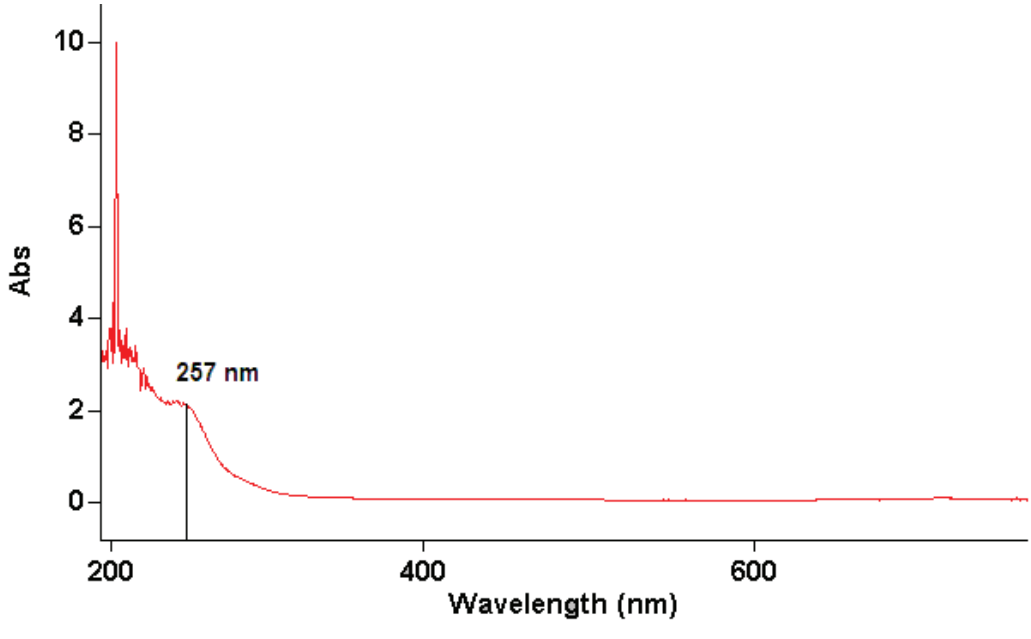


Fig. 6. UV-vis spectrum of molybdenum oxide nanoparticles prepared under microwave irradiation.

In addition, using Debye–Sherrer method, the crystallite size was determined to be about 55 nm. In addition a weak peak appeared at 2θ = 18.45˚ corresponded to molybdenum dioxide nanoparticles, which was negligible compared to obvious molybdenum oxide particles peaks. For more investigations, spectrum of MoO_3 nanoparticles in sample S1 was studied using UV-vis spectroscopy. Obviously, as shown in Fig. 6, a broad peak at 257 nm represented the spectrum of molybdenum oxide (MoO_3) nanoparticles that was similarly reported by Kanneganti et al. [12]. Furthermore, as shown in Figs.7 and 8, TEM micrographs of S1 revealed that size distribution of the nanoparticles (shown in 50 nm and 100 nm scales) was homogenous and nanoparticles were almost spherical in shape with an average diameter of about 50 nm, comparable with the SEM results shown in Fig. 1.

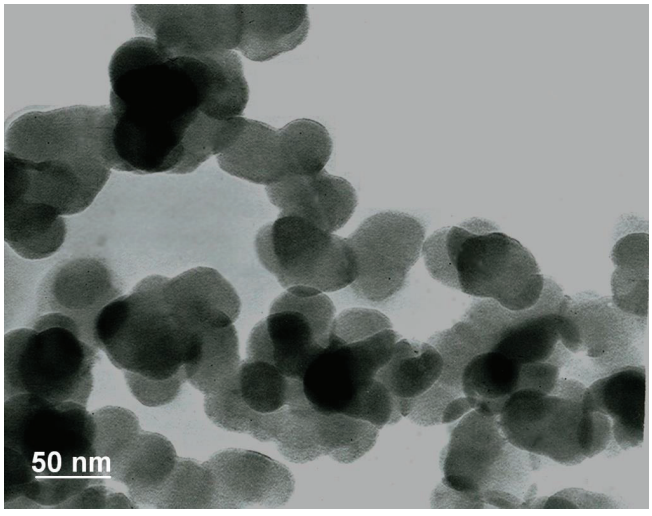


Fig. 7. TEM micrograph of molybdenum oxide nanoparticles prepared under microwave irradiation at 50 nm scale.

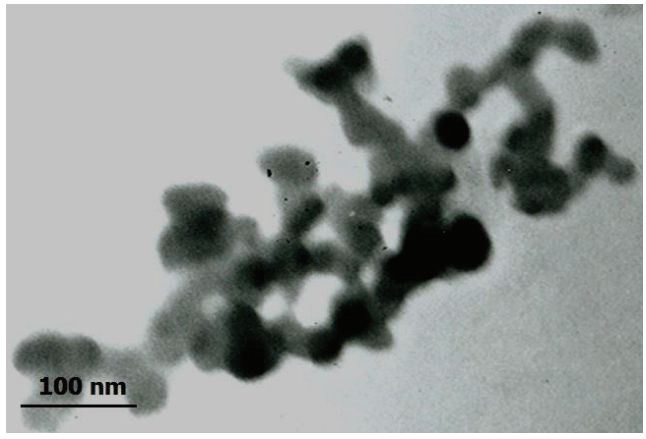


Fig. 8. TEM micrograph of molybdenum oxide nanoparticles prepared under microwave irradiation at 100 nm scale.

4. Conclusions

Molybdenum oxide nanoparticles were prepared in this study using conventional heating and microwave irradiation as heating sources to compare the final product based on particle size and also stability. According to the SEM analysis results particles prepared under microwave irradiation were nano-sized with a good dispersion and stability in colloidal solution, while particles synthesized via conventional heating were unstable with larger diameters. Moreover, the sample prepared under microwave heating (S1) was mostly composed of molybdenum oxide nanoparticles with average size of about 50 nm which was confirmed by SEM, TEM and XRD techniques.

Acknowledgment

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