



RAPID MICROWAVE-ASSISTED SYNTHESIS OF MOLYBDENUM TRIOXIDE NANOPARTICLES

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ABSTRACT

In this paper, molybdenum trioxide (MoO_3) nanoparticles were synthesized by rapid-microwave method using ammonium heptamolybdate (AHM) as a precursor in ethylene glycol (EG) solution with concentrated HNO_3 . This reaction was carried out in a short period of 30 min and the nanoparticles were then heat treated at 600°C . The structures of the products were analyzed by X-ray diffraction (XRD). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to record the morphology and nanoparticle size of MoO_3 . The Raman spectrum of MoO_3 displays three well-defined peaks located at 989.2, 816.0 and 665.3 cm^{-1} which are the fingerprints of the orthorhombic $\alpha\text{-MoO}_3$ crystalline phase.

Keywords: ethylene glycol, molybdenum trioxide, nanosize, microwave.

1. Introduction

Since molybdenum oxide (MoO_3) has revealed its promising applications in electronics and energy storage (Lunk et al., 2010; Hashem et al, 2012; de Castro et al., 2017; Miao et al., 2017; Ren, 2018). Recently, several synthetic methods have applied to control size and morphologies of MoO_3 (de Castro et al., 2017), such as sol-gel (Parviz et al., 2009), hydrothermal/solvothermal (Chithambararaj & Bose, 2011; Hashem et al., 2012; Zhou et al., 2015), template assistance (Yan et al., 2009), chemical vapor deposition (CVD) (Wang et al., 2016), microwave assistance method (Wu et al., 2011; Manteghain, Tari & Bozorgi, 2015; Mirzaei & Neri, 2016; Sun, 2016). Microwave-assisted method showed advantages to produce high purity nanomaterials, to accelerate and reproduce reaction, and to control uniform heat of reaction with low energy (Hayes, 2002, pp. 163-166; Manteghain, Tari & Bozorgi, 2015; Sun, 2016; Anwar et al., 2015).

Purpose of this study is to synthesize molybdenum oxide by reaction of ammonium molybdate salt in ethylene glycol with the presence of acid at elevated temperature. Comparing with traditional convectional heating, microwave heating provides fast chemical reactions with high yields and fewer by-products.

2. Experimental

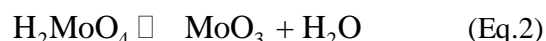
2.1. Materials

All reagents and solvents were purchased from commercial suppliers. Ammonium molybdate tetrahydrate (AHM) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was purchased from Fisher Scientific. Ethylene glycol (EG) and nitric acid HNO_3 were purchased from Merck.

2.2. Synthesis of MoO_3 nanoparticles

Nanoparticles were prepared using ammonium molybdate tetrahydrate (AHM) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$. AHM was dissolved in ethylene glycol (EG) and HNO_3 mixture. Afterwards, the colorless solution was reacted in a microwave oven for 30 min at 240 W to produce a brown mixture. Next, the resultant was separated by centrifugation, dried at 80°C , a light-blue sample was obtained. In the next step, obtained products were calcined at 600°C for 2 h. The given synthetic process was performed again without HNO_3 present to reveal the influence of HNO_3 to MoO_3 nanoparticles.

Reaction periods is described by the following equilibrium:



In the mixture, the initial combination of $\text{Mo}_7\text{O}_{24}^{6-}$ anion and proton feed by HNO_3 to produce H_2MoO_4 . Under microwave radiation, H_2MoO_4 is dehydrated immediately to create MoO_3 nanoparticles. The equilibriums shift toward the products due to high concentration of reactants and MoO_3 precipitation out of reaction mixture. Thus, MoO_3 nanostructure is formed following heterogeneous nucleation and grown subsequently. However, the detailed influence of acidity precursor on the nanostructured growth requires further investigation.

2.3. Characterization

The morphologies of as-prepared sample were studied using scanning electron microscope (SEM) JEOL-JSM-7401F (Saigon Hi-Tech Park – SHTP) at an operating voltage of 15–20 kV and transmission electron microscope (TEM) at 100 kV (National Key Lab for Polymer and Composite Materials – PCKLAB). The structures of MoO_3 were investigated using X-ray diffractometer D8 ADVANCE (General Department of Vietnam Customs) with $\text{Cu-K}\alpha$ radiation and the voltage of 40 kV. Raman spectroscopy was performed using Labram HR VIS (VNU University of Science - Hanoi) with an excitation wavelength of 632.8 nm.

3. Results and discussions

3.1. X-ray diffraction

Figure 1 shows the XRD spectra of products from HNO_3 added and HNO_3 free reaction. Comparing with reference pattern supplied by Crystal Impact Match!, spectrum of products from HNO_3 added reaction (Fig.1a) shows the most intense peaks at positions

$2\theta = 12.8, 23.4, 25.7, 27.3, 33.8$ and 39.0° (marked by “●” symbol) which respectively corresponds to (020), (110), (040), (021), (111) and (060) planes of orthorhombic α - MoO_3 (Sen & Mitra, 2014; Wang et al., 2014; Sharma & Reddy, 2014; Nadimicherla et al., 2016). Besides the obvious presence of main phase α - MoO_3 , the pattern shows low intensity peaks at $2\theta = 24.8, 31.4^\circ$ (marked by “#” symbol) corresponding to (450), (180) planes of Mo_5O_{14} and at $2\theta = 22.2, 22.6, 23.6, 25.7^\circ$ (marked by “*” symbol) corresponding to (211), (501), (311), (601) planes of Mo_4O_{11} . A Limited amount of by-products (Mo_5O_{14} and Mo_4O_{11}) were formed at the end of reaction when HNO_3 had totally vaporized by microwave heating.

XRD spectrum of product from HNO_3 -free reaction (Fig. 1b) does not show significant peaks, thus the product has amorphous structure. Different obtuse peaks index two material groups: amorphous ammonium molybdate is indexed by the most intense obtuse peak with foot slope ranged from 6° to 18° and amorphous MoO_{3-x} is indexed by the less intense one with foot slope ranged from 18° to 38° . The obtuse peak of ammonium molybdate shifts toward pattern of $(\text{NH}_4)_6\text{Mo}_8\text{O}_{27} \cdot (\text{H}_2\text{O})_4$ and $(\text{NH}_4)_6\text{Mo}_9\text{O}_{30} \cdot (\text{H}_2\text{O})_5$ stronger than $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot (\text{H}_2\text{O})_4$. This means MoO_3 decomposed from molybdic acid H_2MoO_4 was immediately combined with unreacted $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot (\text{H}_2\text{O})_4$ to produce extra MoO_3 -contained molybdate salt. That procedure is described by the following equilibrium:



Formation of these molybdate polyanions reduced the concentration of $\text{Mo}_7\text{O}_{24}^{6-}$ anion, hence, equilibrium of Eq.1 and Eq.2 shifted toward reactants and quickly stopped reaction chain. Furthermore, the obtuse peaks of MoO_{3-x} (with foot slope ranged from 18° to 38°), which shifts toward the pattern of Mo_4O_{11} , shows that a large amount of by-products formed during reaction. The Growth of molybdate polyanions and by-products depends on balanced situation of all equilibrium given above. The immediate disequilibrium can actuate or inhibit the growth of all products in reaction chains to produce amorphous products.

XRD results of two synthetic processes show that high concentration acid environment accelerated the growth of MoO_3 nanoparticles, which easily combined with a precursor or converted to by-products. While MoO_3 nucleus was growing, it selectively adsorbed NO_3^- anion c-axis paralleled planes. Thus, it induced anisotropic growth and accumulation, resulting in MoO_3 nanoparticles (Ren et al., 2018).

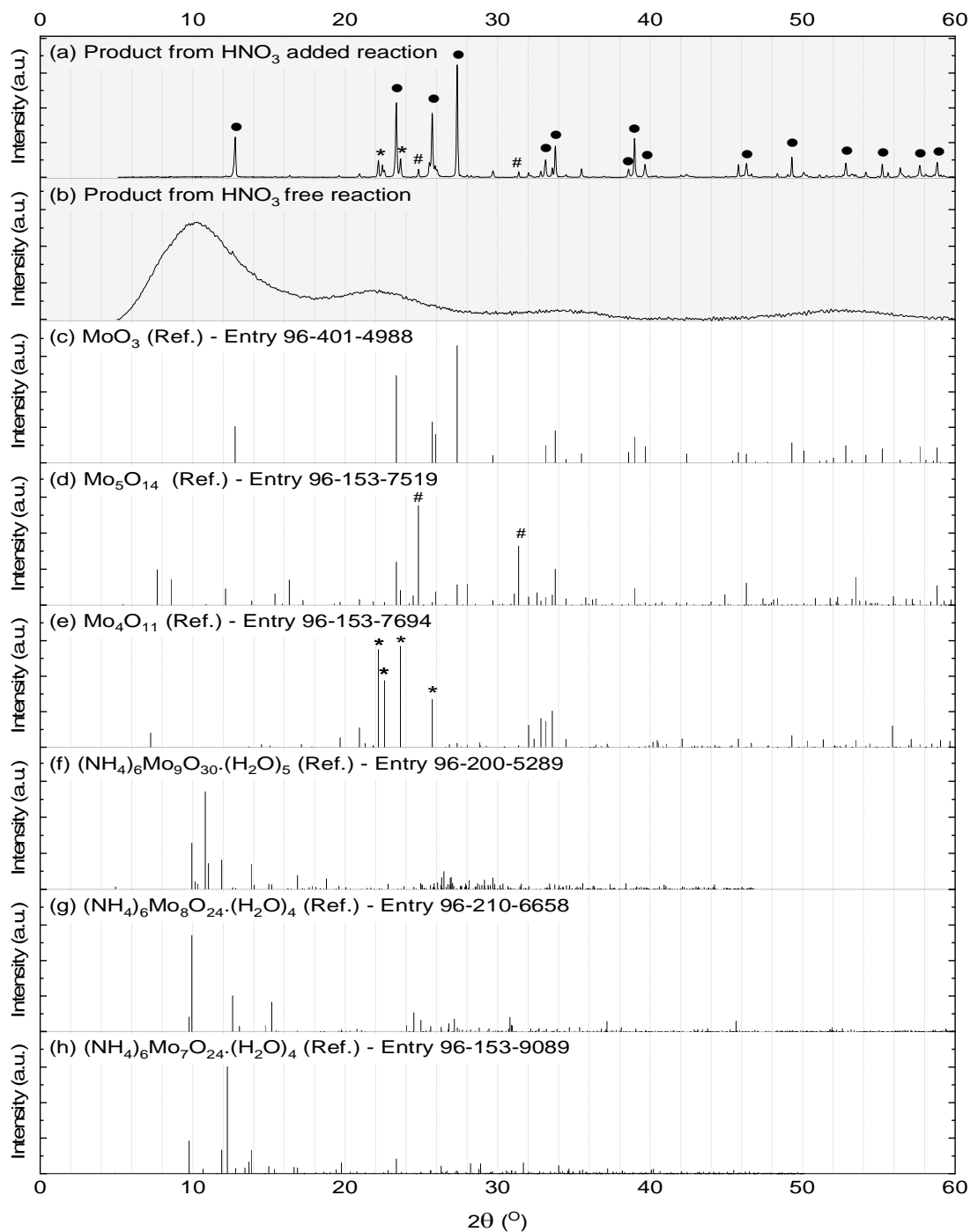


Figure 1. XRD pattern of the as-prepared MoO_3 from HNO_3 added and HNO_3 free reactions

3.2. Raman spectroscopy

Raman spectrum of $\alpha\text{-MoO}_3$ nanoparticles is showed in Figure 2. The vibrational modes found around $200\text{-}400\text{ cm}^{-1}$ and $600\text{-}1000\text{ cm}^{-1}$ correspond to stretching and

bending vibrations of MoO_6 octahedra, respectively, while the modes below 200 cm^{-1} delegates to the deformation and lattice modes. The original $\alpha\text{-MoO}_3$ is demonstrated by a narrow and intense peak at 989 cm^{-1} , which is attributed to stretching mode of terminal oxygen ($\text{Mo}=\text{O}$) along a- and b-axis. The peaks at 816 cm^{-1} and 656 cm^{-1} are respectively indicated the stretching modes of the doubly and triply coordinated oxygen ($\text{Mo}_2\text{-O}$ and $\text{Mo}_3\text{-O}$), which are attributed to bending vibrations of MoO_6 octahedra. The referred modes of $\alpha\text{-MoO}_3$ are acknowledged in literatures (Yan et al., 2009; Wang et al., 2014; Zhang, Gao & Gong, 2015; Ren et al., 2018).

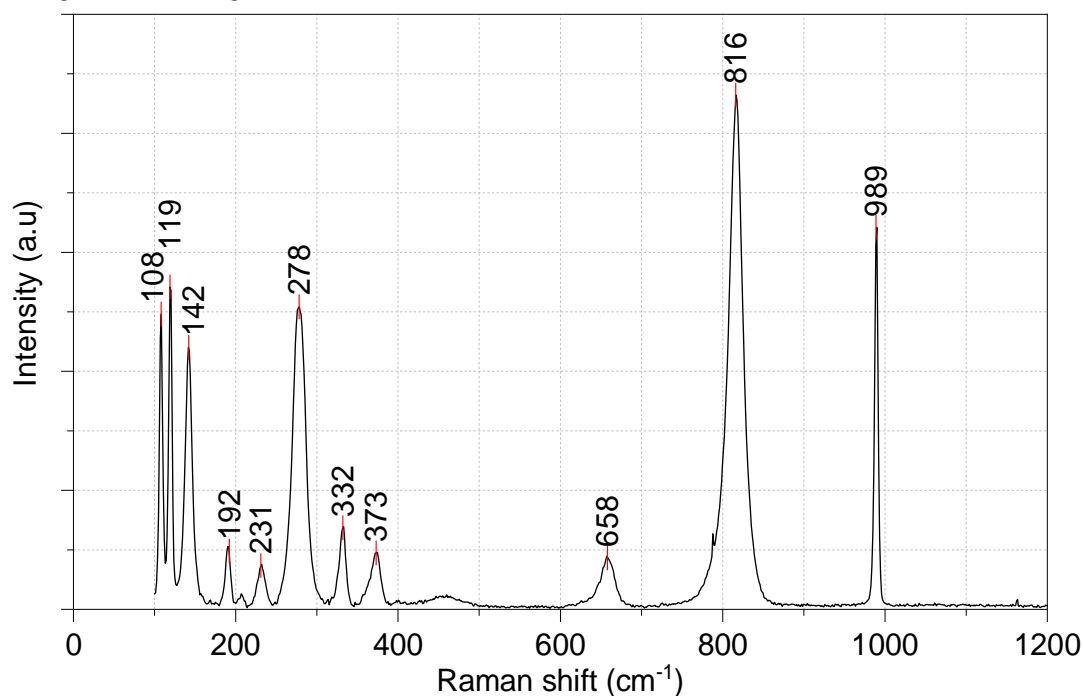


Figure 2. Raman spectra of MoO_3 nanoparticles

3.3. SEM and TEM

Morphology and size of MoO_3 nanoparticles were recorded by SEM, TEM micrographs (Fig.3). In TEM images, MoO_3 nanoparticles are found in hexagonal flake shape and SEM micrographs confirmed that none of the rod particle grown in samples. This record confirmed results of Raman spectrum that MoO_3 nanoparticles were grown in a- and b-axis widthwise. The layered structure of MoO_3 nanoparticles was sized in a range of 50-100 nm.

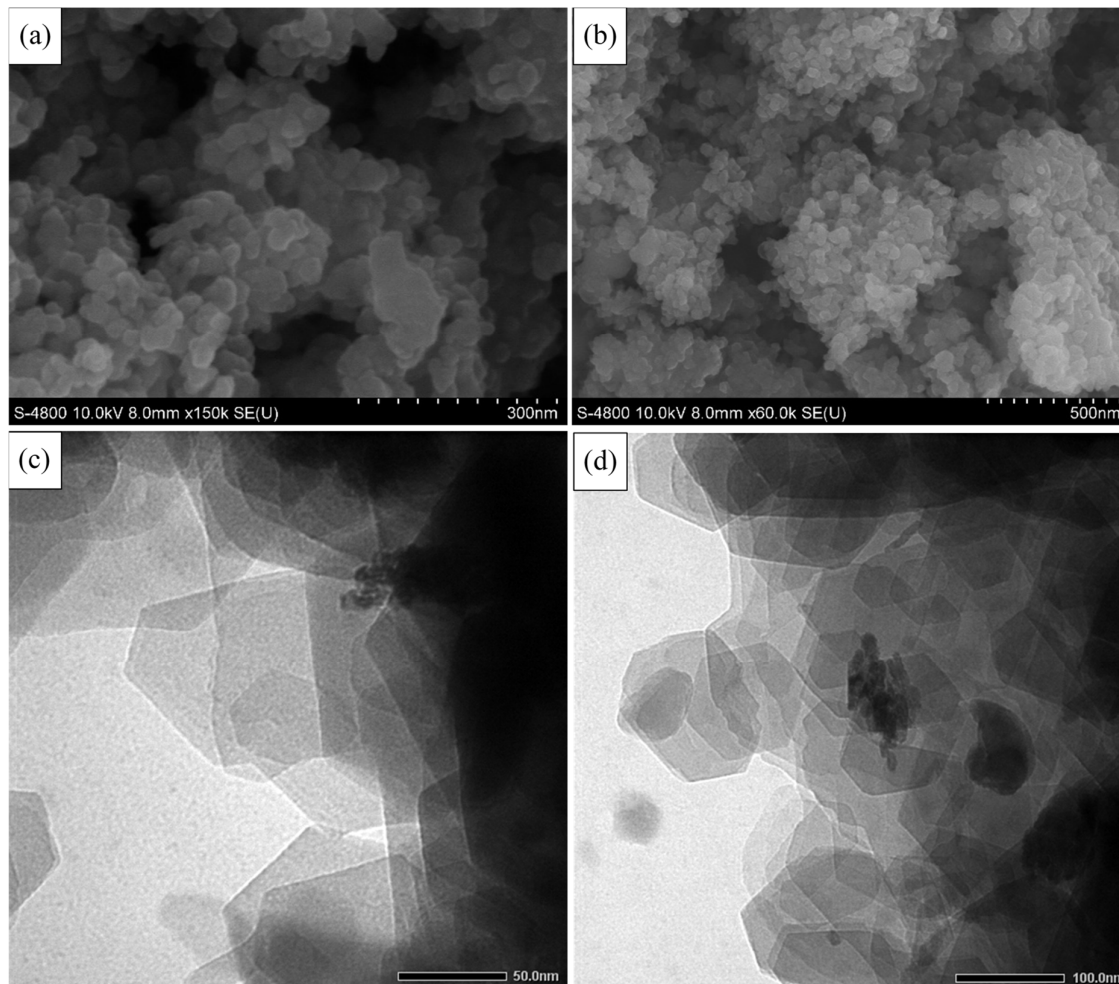


Figure 3. SEM (a,b) and TEM (c,d) micrographs of as-prepared MoO₃

4. Conclusion

MoO₃ nanoparticles are synthesized by the simple and effective microwave assisted reactions. Upon microwave irradiation, HNO₃ rapidly actuates decomposition process of molybdate acid to MoO₃ nanoparticles and orients growth of nanocrystal to layered flake shape. The products were characterized by XRD, Raman spectroscopy, SEM, TEM. The results showed that the hexagonal nanoflake MoO₃ grows directly in a- and b-axis with a size in a range of 50-100 nm. Characterization of MoO₃ nanoparticles indicates that the acidic reaction mixture can inhibit the formation of by-products during the chain reaction.

❖ **Conflict of Interest:** Authors have no conflict of interest to declare.

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PHƯƠNG PHÁP TỔNG HỢP NHANH HẠT NANO MOLYBDENUM TRIOXIDE VỚI SỰ HỖ TRỢ CỦA VI SÓNG

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TÓM TẮT

Nghiên cứu này trình bày phương pháp tổng hợp nhanh hạt nano molybdenum trioxide (MoO₃) từ tiền chất ammonium heptamolybdate (AHM) trong môi trường ethylene glycol (EG) và HNO₃ đậm đặc, với sự hỗ trợ của năng lượng vi sóng. Phản ứng tổng hợp được thực hiện trong 30 phút, sau đó hạt nano MoO₃ được xử lý nhiệt ở 600°C. Phổ XRD sản phẩm chính của phản ứng có cấu trúc orthorhombic của α-MoO₃. Đồng thời, phổ Raman cũng chứng minh sự hình thành α-MoO₃ qua các đỉnh phổ tại các số sóng đặc trưng 989,2, 816 và 665,3 cm⁻¹. Hình thái cũng như kích thước hạt MoO₃ được phân tích bằng ảnh hiển vi điện tử SEM, TEM.

Từ khóa: ethylene glycol, molybdenum trioxide, nanosize, microwave.