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Synthesis of MoO_3 nanoparticles for azo dye degradation by catalytic ozonation

Arumugam Manivel [a], Gang-Juan Lee [a], Chin-Yi Chen [b], Jing-Heng Chen [c], Shih-Hsin Ma [c], Tzzy-Leng Horng [d], Jerry J. Wu [a,*]

[a] Department of Environmental Engineering and Science, Feng Chia University, Taiwan
[b] Department of Material Science and Engineering, Feng Chia University, Taiwan
[c] Department of Photonics, Feng Chia University, Taiwan
[d] Department of Applied Mathematics, Taiwan

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ABSTRACT

One-dimensional molybdenum trioxide nanostructures were prepared in three different approaches, including thermal, microwave, and sonochemical methods. The physicochemical properties of the obtained MoO_3 nanoparticles were investigated by diffused reflectance spectroscopy, X-ray diffraction analysis, field emission scanning electron microscopy, high resolution transmission electron microscopy, and Brunauer–Emmett–Teller surface area analysis. Among the methods as investigated, sonochemical synthesis gave well-dispersed fine MoO_3 nanoparticles compared with the other approaches. All the synthesized MoO_3 nanostructures were examined for the catalytic ozonation to degrade azo dye in aqueous environment. Different performances were obtained for the catalyst prepared in different methods and the catalytic efficiencies were found to be the order of sonochemical, microwave, and then thermal methods. The sonochemical MoO_3 catalyst allowed the total dye removal within 20 min and its good performance was justified according to their higher surface area with higher number of active sites that provide effective dye interaction for better degradation.

1. Introduction

In recent years, numerous inspired schemes and pathways have been developed for the synthesis of transition metal oxide nanomaterials. These materials have been the focus of passionate research because of their potential applications in diverse fields of technology [1–3]. Among the intriguing transition-metal oxides, molybdenum oxides and its derivatives are extensively attractive due to their unique structural and optical properties [4–7]. Although molybdenum has oxidation states ranging from +2 to +6, oxides exist mainly in two forms, such as molybdenum (IV) and molybdenum (VI) oxide [8]. The existence of metal-like electronic conductivity of molybdenum (IV) oxide has formulated them as promising materials in energy related applications [8–10]. Molybdenum (VI) oxide (MoO_3), a wide band gap *n*-type semiconductor with distinctive electrochromic, thermochromic, and photochromic properties, has been widely investigated as smart materials for catalysis [11,12], sensors [13–15], lubricants [5], lithium battery [16–18], organic solar cells [19,20], and display materials [21]. Generally molybdenum (VI) oxide exhibits in three forms, including orthorhombic (α-MoO_3), monoclinic (β-MoO_3), and hexagonal (h-MoO_3) [22–24]. The meta-stable β-MoO_3 and h-MoO_3 were intensively investigated than the thermodynamically stable α-MoO_3 due to their excellent physicochemical properties [25,26]. It is literally known that phase purity of MoO_3 relied on the adopted synthetic procedure and experimental conditions [26,27]. Considerable progresses have been accomplished recently for the size and phase controlled synthesis of MoO_3 with optimized catalytic properties [13,28]. Methods, such as flame synthesis [29], thermal evaporation [30], sputtering process [31], chemical vapor deposition [32], hydrothermal [13,21,27,33,34], infrared irradiation [35], microwave methodology [36], electrochemical process [37] and sonochemical approach [7,38], have been noted for the successful synthesis of MoO_3 nanostructures. However, the study on the synthesis of MoO_3 nanostructures in different approaches and their comparison for a catalytic process is still limited and there remains much interest. Therefore, we attempted to prepare MoO_3 nanostructures in this study by using three different methods, including hydrothermal, microwave, and sonochemical methods. This approach offers an opportunity to compare the

* Corresponding author. Tel.: +886 4 24517250x5206; fax: +886 4 24517686.
E-mail address: jjwu@fcu.edu.tw (J.J. Wu).

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influence of experimental methods on physicochemical properties. In addition, their catalytic properties were examined for the heterogeneous catalytic ozonation of orange II dye. To the best of our knowledge, there is no report available for the degradation of orange II dye under MoO_3 assisted catalytic ozonation processes.

2. Methodology

2.1. Materials

Ammonium heptamolybdate tetrahydrate $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, nitric acid, and ethanol were purchased from Merck chemicals. Orange II was purchased from Acros chemicals. All the reagents and chemicals used in this study were used as received without further purification.

2.2. Instrumental

Microwave reactions were carried out in CEM Discover microwave system (300 W) equipped with in-situ magnetic stirrer and programmable microwave exposure time and temperature. The preset profile (desired time and temperature) was followed by automatically adjusting the applied microwave power. A horn type (20 kHz SONICS sonifier) with a tip diameter of 1 cm was used for carrying out sonochemical synthesis. The X-ray diffraction (XRD) patterns were recorded using Rigaku Ultima III diffractometer (Japan) with Cu-Kα1 radiation in the scan angle range from 10° to 90°. The morphologies of the catalysts were examined by using JEOL JSM-7401F field emission scanning electron microscope (FE-SEM). Prior to FE-SEM measurements, the samples were placed on conductive carbon ink and then gold sputtering was performed. High resolution transmission electron microscopic (HR-TEM) images were recorded using JEOL JEM-2010 model. Samples for HR-TEM were prepared as follows: a small amount of samples were mixed with ethanol and ultrasonically dispersed for 5 min. A drop of this suspension was placed onto the copper grid and then drying in air. The UV–vis diffuse reflectance spectra were recorded using Shimadzu UV-2600 spectrophotometer with integrated sphere attachment and barium sulfate as a reference. The absorbance of the dye was also measured by using the same instrument with universal liquid cell attachment. In addition, the Brunauer–Emmett–Teller (BET) surface area, pore size, and pore volume of the catalysts were measured by nitrogen adsorption method using Micrometrics ASAP-2020 instrument. Prior to analysis, 0.5 g of powder was degassed at 120 °C for 15 h.

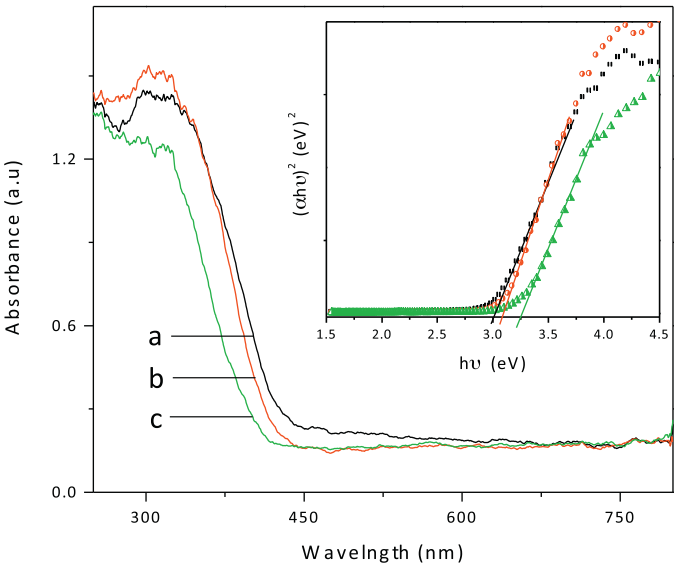

Fig. 1. Solid state UV–vis spectrum of MoO_3 nanoparticles synthesized in (a) thermal, (b) microwave, and (c) sonochemical method. Inset shows the bang gap graph obtained from UV data.

2.3. Synthesis of MoO_3 nanoparticles

MoO_3 nanoparticles were prepared according to the procedure reported in the Ref. [13,34] but with a slight modification in the current study. Briefly, 10 mL 0.2 M of ammonium heptamolybdate tetrahydrate was used in the beaker and stirred for 10 min to obtain a clear solution. Then 5 mL of concentrated HNO_3 was added drop-wise to the above solution and stirred for 10 min. This mixture was served as the common solution for all synthesized methods. For hydrothermal method, the mixture was transferred to the autoclave and heated to 100 °C for 2 h. The heating rate was maintained at 10 °C min^{-1}. After 2 h of heating, the autoclave was allowed to cool down to room temperature. The resultant mixture was centrifuged

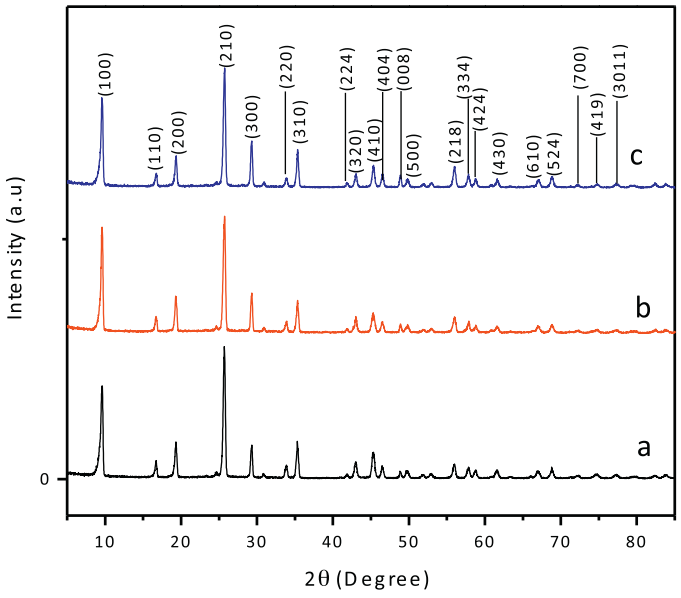

Fig. 2. X-ray diffraction patterns of MoO_3 nanoparticles prepared in (a) thermal, (b) microwave, and (c) sonochemical methods.