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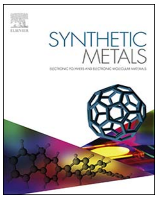

Direct, one-step synthesis of molybdenum blue using an electrochemical method, and characterization studies

Ozge Koyun, Semih Gorduk, Melih Besir Arvas, Yucel Sahin*

Department of Chemistry, Faculty of Arts & Science, Yildiz Technical University, TR34210 Istanbul, Turkey

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ABSTRACT

This article is the first to report the direct, one-step synthesis of molybdenum blue (MB) in solid state, via application of cyclic voltammetry. Electrochemical synthesis of MB was carried out in a three-electrode cell in 1.0 M sulfuric acid and at the appropriate amount of sodium molybdate dihydrate. Both a pencil graphite electrode and a platinum plate electrode were used as working electrodes. The structure of electrochemically synthesized MB was characterized using such techniques as Ultraviolet-visible spectroscopy, Fourier Transform Infrared Spectroscopy, Resonance Raman Spectroscopy, Scanning Electron Microscopy, Energy-Dispersive X-Ray Spectroscopy, X-Ray Powder Diffraction, X-ray Fluorescence Spectroscopy, and X-Ray Photoelectron Spectroscopy. In addition, the electrochemical behavior of the synthesized MB was examined via cyclic voltammetry. Finally, the determination of phosphate was conducted using a UV–vis spectrometer with electrochemically synthesized MB.

1. Introduction

Polyoxometalates (POMs), are molecules formed by oxygen atoms with early transition metals such as V, Mo, and W in high oxidation values [1]. In addition, they may also contain various heteroatoms such as Si, Ge, and P, As. POMs are a group of molecular metal oxides which are definable from the majority of the metal oxides and may include a large number of metal atoms that achieve nuclearities as high as 368 in one single cluster structure creating nanoparticles [2]. POMs have unmatched structural variety and are derived from the assembly of great “virtual combinatorial libraries” of building blocks [3]. POMs that reflect this structural diversity exhibit a wide variety of features, derived from naturally redox-active and rigid anionic architectures, with numerous potential applications, from catalysis to medicine and materials science [3]. Berzelius reported the first synthesized POM in the early 19th century [1,4], after which Marignac victoriously synthesized 1:12 silicotungstic acid in 1864 [5]. A systematic review of the properties of POMs and their structural characterization began with Rosenheim in the early 20th century [6].

Many methods are used to characterize POMs, including ultraviolet visible spectroscopy, infrared spectroscopy, Raman spectroscopy, nuclear magnetic resonance, and electrochemical methods [7]. With regard to electrochemistry, Souchay [8] was the first person to apply polarography in the research solutions of POMs, which have recently received great attention, as a result of their versatile structure, their simple, synthesis, magnetic, and material features, and, especially, their catalytic activities [1,9]. One of the first structurally characterized POMs, the phosphomolybdate Keggin [10], has been the most comprehensive examined, primarily because of its impressive catalytic properties, for example, oxidation of aldehydes, CO, oxidative dehydrogenation, etc. [9]. Examples of other polyoxomolybdates include the molecular big spheres of the Mo_{132} type, the molecular big wheels of the Mo_{154}/Mo_{176} type, and the structurally well-characterized, lemon-shaped Mo_{368} cluster, which is the largest by far. There are several reasons for such versatile behavior, as follows: the simple change of coordination numbers on the side exchange of H_2O ligands at Mo sites; the moderate strength of Mo-O-Mo type bonds, allowing “split and link”-type processes; the simple change, and particularly the increase, of electron densities without the strong propensity to form metal-metal bonds; and the existence of terminal Mo=O groups, which prevent, in principle, limitless growth to an extended structure [11].

“This is a substance or group of substances about which there has been much discussion” is an interpretation referred in an old inorganic chemistry textbook [12]. Refers to the blue material that was first mentioned by C. W. Scheele in 1778 and which is now known as “molybdenum blue” (MB) and is generally amorphous [13,14]. Since that time, this material has been subject to many publications, and generations of chemists and students have used the “MB test” as a rapid, straightforward and precise process in a qualitative determination of molybdenum. However, the structure of the compound has remained

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* Corresponding author.
E-mail addresses: yucelsahin06@gmail.com, yusahin@yildiz.edu.tr (Y. Sahin).

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mysterious, and it is therefore not surprising that most of its extraordinary behaviors have not been explained [13]. The ring structure of Mo_{154} polyoxomolybdate and other polyoxomolybdate nanostructures have the deep-blue MB coloration; therefore, all of the aforementioned polyoxomolybdate clusters are of the MB type [15].

Solutions of MB are almost immediately provided by the reduction of Mo^{VI}-type species in acid solutions (pH ≤ 3). As Reducing agents, metals (Cu, Mo, Pb, Al, Hg, Cd, Zn), B_2H_6, $NaBH_4$, N_2H_4, NH_2OH, H_2S, $S_2O_4{}^{2-}$, $S_2O_3{}^{2-}$, $SO_3{}^{2-}$, SO_2, $SnCl_2$, $MoCl_5$, $MoOCl_5{}^{2-}$, Mohr's salt, ascorbic acid, formic acid, tartaric acid, hydroquinone, D-glucose, sucrose, thiourea, ethanol, gaseous H_2, or CO (under pressure) can be used [14]. Furthermore, spectrophotometric analysis of phosphate, molybdenum, silicon, and other constituents by the formation of MB is generally used in chemical analysis [15]. MB formation by chemical/thermal reduction under acidic conditions has been standardized by some of the working groups mentioned [13,16,17]; another group has used photochemical reduction in the existence of an electron donor [12]. Almost all of the methods for the synthesis of MB that have been proposed in previous studies are time-consuming, require a high temperature, and have relatively low product purity [13,18].

In this work, for the first time, we demonstrated that MB can be synthesized directly in one-step and a solid state using a voltammetric method. The pure product was obtained without the use of a reducing agent, meaning that an additional purification method was not necessary. The structure of the electrochemically synthesized MB was subsequently characterized using such techniques as Ultraviolet-visible Spectroscopy (UV-vis), Fourier Transform Infrared (FTIR) Spectroscopy, Resonance Raman Spectroscopy, Scanning Electron Microscopy (SEM), Energy-Dispersive X-Ray Spectroscopy (EDX), X-Ray Fluorescence Spectroscopy (XRF), X-Ray Powder Diffraction (XRD), and X-Ray Photoelectron Spectroscopy (XPS). Furthermore, the electrochemical behavior of the synthesized MB was investigated using cyclic voltammetry (CV). Finally, the determination of phosphate was carried out using a UV–vis spectrometer with electrochemically synthesized MB.

2. Experimental procedure

2.1. Reagents and apparatus

Sodium molybdate dehydrate (≥99%), potassium phosphate monobasic (ACS reagent) and sulfuric acid (95–97%) were obtained from Sigma-Aldrich (UK), and sodium sulfate was purchased from Merck (DE). All solutions were prepared using ultra-purified water provided by a Milli-Q system (Millipore®).

The electrochemical experiments, including CV, were recorded with an Autolab electrochemical analyzer (PGSTAT302N Potentiostat/Galvanostat), and cyclic voltammetric measurements were carried out in a three-electrode cell, in 1.0 M H_2SO_4. In all electrochemical measurements, both pencil ends (1.0 cm in length and 0.5 mm in diameter, HB, Tombo, geometric area = 0.16 cm^2) and platinum (Pt) plate (geometric area = 3.44 cm^2) were used as working electrodes, Ag/AgCl (sat. KCl) was used as a reference electrode, and Pt wire was used as a counter electrode. All the potentials are given against the Ag/AgCl (sat. KCl) electrode, and all experiments were conducted at an ambient temperature of 25° C. The weighing process was conducted using Shimadzu analytical balances (ATX224, d = 0.1 mg).

2.2. Characterization of materials

Resonance Raman spectra of MB were recorded in the region of 4.000–50 cm^{-1} with a Bruker Senterra Dispersive Raman Microscope using the 1064 nm excitation from a 3 B diode laser with 3 cm^{-1} resolution. Absorption spectra in the UV–vis were obtained with a Shimadzu 2001 UV spectrophotometer. IR spectra were recorded on a Perkin Elmer Spectrum One FTIR (ATR sampling accessory) spectrophotometer, and an X-ray powder diffractometer (BRUKER D8 Advance) was used for XRD measurements. The XRD pattern was scanned in a 2θ range of 20–80°, and the sample was mounted on rotating sample holders (15 rpm). In order to determine the weight percentage of the elements present in the synthesized MB using the electrochemical method, a Rigaku ZSX Primus model XRF instrument was used. For XPS measurements, an Al-Kα micro-focused monochromator and a Thermo Scientific K-Alpha X-ray photoelectron spectrometer, equipped with a hemispherical electron analyzer were used. The morphology of the MB sample was examined by SEM, using an ESEM-FEG/EDAX Philips XL-30 instrument, with dialyzed samples dropped on copper grids. In addition, the surface composition of MB was qualitatively and semi quantitatively determined by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX), using a ZEISS EVO® LS 10/EDAX Element SDD instrument.

2.3. Measurement procedure

A special electrochemical cell with five necks was used in all experiments. Three of these necks belonged to the electrodes that were used as the working, reference, and counter electrodes. The three-electrode system was used for the electrochemical synthesis of MB. The Ag/AgCl electrode was used as the reference electrode, Pt wire was used as the counter electrode, and pencil graphite electrode (PGE) and Pt plate electrodes were used as working electrodes. Stock solutions of 1.0 mol L^{-1} of H_2SO_4 were prepared by dissolving the specified amount in double-distilled water, and the required amount of the stock solution was added to the electrochemical cell. Voltammograms were then recorded using a voltammetric analyzer under parameters that had been optimized for an improved sulfuric acid and sodium molybdate dihydrate concentration. These optimized parameters were used throughout the experiments. The synthesis of MB was realized using the CV method, and all electroanalytical measurements were made at room temperature.

2.4. UV–vis spectroscopy measurement for phosphate determination

Standard phosphate solutions prepared using KH_2PO_4 were used. The relationship between phosphate concentration and absorbance was evaluated using a UV spectrometer with electrochemically synthesized MB. The reaction mixture contained a constant concentration of phosphate. Recording began immediately after MB was added, at 1-min intervals for a total of 75 min. It was observed that the optimum reaction time for the complexation reaction between phosphate and MB was 40 min. Six different solutions were prepared at phosphate concentrations of 5.0, 10.0, 20.0, 30.0, 40.0, and 50.0 mg/L using the standard phosphate solution, and absorbance measurements were made 40 min after the addition of MB solution into all solutions at wavelength of 400–900 nm (using purified water as a blank solution). The absorbance values were recorded on a UV–vis spectrometer.

3. Results and discussion

3.1. Electrochemical synthesis of MB

MB was synthesized by electrochemical reduction of sodium molybdate dehydrate under aqueous acidic conditions by applying an appropriate cathodic potential. A 1.0 mol L^{-1} H_2SO_4 solution was used as a supporting electrolyte. Experiments to optimize pH were conducted, and pH 1 was the most widely used [13,14]. There are a variety of parameters for electrochemical synthesis of MB in the solid state, such as the type of working electrode and size of its surface area, type and amount of supporting electrolyte, the amount of sodium molybdate dihydrate salt, pH level, scan rate and number of cycle. All these parameters are highly effective in increasing the quantity of MB on the surface of the working electrode. Realization of synthesis of MB in the cathodic potential is important because the formation of MB that has