Journal of Molecular Structure 1083 (2015) 229–235

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Facile chemical synthesis and structure characterization of copper molybdate nanoparticles

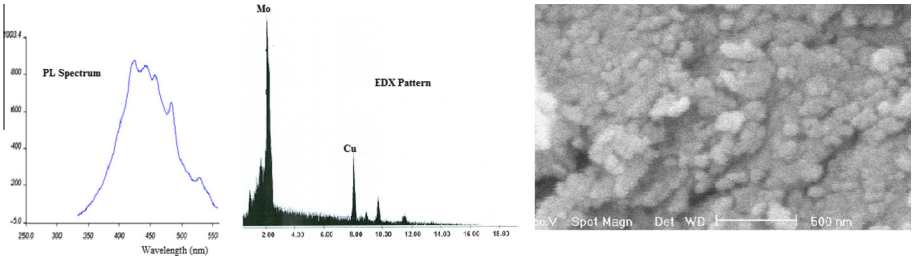
Mehdi Rahimi-Nasrabadi [a,*], Seied Mahdi Pourmortazavi [b,*], Morteza Khalilian-Shalamzari [a]

[a] Faculty of Material and Manufacturing Technologies, Malek Ashtar University of Technology, Tehran, Iran
[b] Nano Science Center, Imam Hossein University, Tehran, Iran

HIGHLIGHTS

- $CuMoO_4$ nanoparticles were synthesized via a facile chemical route.
- Taguchi robust design was applied to optimize synthesis reaction conditions.
- Composition and structural properties of $CuMoO_4$ nanoparticles were characterized.
- $CuMoO_4$ was examined by XRD, SEM, EDX, TEM, FT-IR, UV–Vis and PL techniques.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 October 2014
Received in revised form 3 December 2014
Accepted 3 December 2014
Available online 9 December 2014

Keywords:
Inorganic compounds
Nanostructures
Chemical synthesis
Copper molybdate

ABSTRACT

Experimental parameters of a synthesis route were optimized by Taguchi robust design for the facile and controllable synthesis of copper molybdate nanoparticles. $CuMoO_4$ nanoparticles were synthesized by chemical precipitation followed by hydrothermal process. Effects of different parameters of synthesis procedure, i.e. concentrations of both reagents, copper feeding flow rate and temperature of reactor on the particle size of prepared copper molybdate nanoparticles were investigated. The results of statistical optimization revealed that the size of copper molybdate particles is dependent on the procedure variables involving copper concentrations, flow rate and temperature of the reactor; while, molybdate concentration has a no considerable role in determining the size of $CuMoO_4$ particles. Based on the results obtained by statistical optimization process, the nanoparticles of copper molybdate were prepared and then their structure and chemical composition were characterized by various techniques, i.e. SEM, TEM, XRD, EDX, FT-IR, UV–Vis and photoluminescence spectroscopy.

Introduction

Inorganic nanomaterials have been obtained a great interest and attention in various areas of technology and science. This attraction of nano-structured materials originates from their low density and high specific surface features which makes them suitable candidates for specific usages. Today, the application domain of nano-structured materials is developed for biology, medicine, chemical industries, electronics, and many other areas [1–3].

Molybdate compounds as a group of inorganic materials are involving numerous bivalent cations ($MMoO_4$ with an ionic radius bigger than 0.99 Å, i.e. Ca, Ba, Pb, and Sr molybdate salts) with a scheelite structure which in their structure the molybdenum atom adopts a tetrahedral coordination. Meanwhile, molybdate salts for bivalent cations with a smaller radius ($MMoO_4$ with an ionic radius less than 0.77 Å, i.e. of Fe, Mn, Ni, and Mg molybdate salts) have a

* Corresponding authors at: P.O. Box 16765-3454, Tehran, Iran. Fax: +98 2122936578 (S.M. Pourmortazavi).
E-mail addresses: rahiminasrabadi@gmail.com (M. Rahimi-Nasrabadi), pourmortazavi@yahoo.com (S.M. Pourmortazavi).

http://dx.doi.org/10.1016/j.molstruc.2014.12.017
0022-2860/

wolframite structure, while in their crystal structure the molybdenum atom possesses a six-fold coordination [4,5].

Some of transition metal molybdates ($AMoO_4$, which A = Cu, Zn, Co, Ni, and Ca) are very interesting because of their specific structural, electronic, and catalytic properties [4,5]. The decisive microstructure-based properties of some molybdate salts are probably impacted by dimensional manipulation of their grain-size and grain boundary effect in the polycrystalline structure. These metal molybdate materials, with particle dimension less than 100 nm, are expected to have a great potential for application in many areas of science and technology [4]. Molybdenum compounds are interested as catalysts and their catalytic activities are well-known in different processes, i.e. oxidative dehydrogenation (for simple alkanes [6]), hydro-desulfurization (in petroleum [7]) and selective oxidation (such as epoxidation of alkenes [8] or alkyl olefins [9] or for the selective oxidation of alcohols [10]). Among the widespread family of molybdate salts, $CuMoO_4$ is a piezochromic material which its pD^1 phase diagrams recently has been confirmed [11].

In view of widespread application domain of this inorganic material, several physical or chemical techniques such as complete evaporation of a polymer-based metal-complex precursor solution [4], hydrothermal [6], precursor [6], and solid-state reaction [12] have been proposed until today for the synthesis of $CuMoO_4$ nanoparticles with different morphologies including nanoparticle, nanorod, and porous $CuMoO_4$ films. Although, each of these methods possesses some benefits and advantages but all of these techniques suffer from remarkable defects such as high costs for synthesis, requiring the strict control of synthesis medium, and complicating of the synthesis process. Therefore, further investigations directed toward finding other procedures for the synthesis of $CuMoO_4$ nanoparticles, which have a potential to facile handling, scaling-up and economic benefits are interested.

In the light of the above mentioned requirements, the main aim of this investigation was developing a facile procedure for preparation of $CuMoO_4$ nanoparticles. During literature survey several reports were found on the synthesis and preparation of $CuMoO_4$ micro and nanoparticles through different methods [4,6,12], while no such information is available about the preparation of $CuMoO_4$ nanoparticles through chemical precipitation reaction in the absence of templates, surfactants, or catalysts.

Experimental

Materials and procedure

Analytical-grade copper chloride and sodium molybdate were used as received from Merck Company. $CuMoO_4$ particles were prepared via chemical reaction in aqueous molybdate solution by direct addition of Cu^{2+} solution to it. The reaction was carried out under vigorous stirring; while, concentrations of both reagents, flow rates for feeding of copper ion solution and temperature of reactor were varied at each trial according to Table 1. By completing the mixing process, the formed precipitate was introduced to an autoclave and hydrothermal conditions (200 °C temperature during 24 h) were applied. Then, the resulted $CuMoO_4$ particles were filtered and washed several times with distilled water. Thereafter, the filtered powder was washed with ethanol and then dried in oven at temperature of 75 °C for 3 h. The effect of the above mentioned variables on the size of $CuMoO_4$ particles was investigated via experimental design approach in order to optimize these parameters for preparation of $CuMoO_4$ nanoparticles. As seen in Table 1, the variables were studied at three different levels using an OA_9 proposed by Taguchi robust design.

Characterization of prepared copper molybdate particles

$CuMoO_4$ samples obtained at different experiments were characterized by scanning electron microscope (SEM) and energy-dispersive analysis by X-rays (EDX). A Philips XL30 series instrument was used for recording the SEM images. The dried particles were coated by gold film using a sputter coater model SCD005 manufactured by BAL-TEC (Switzerland), before their loading on the instrument. Transmission electron microscopy (TEM) was carried out on a Ziess- EM10C microscope. Prior to the measurement, preparation of the sample was performed by coating on formvar carbon coated grid Cu Mesh 300. A Rigaku D/max 2500V diffractometer equipped with graphite monochromator and Cu target was used for X-ray powder diffraction (XRD) analysis. A FT-IR spectrophotometer (Perkin Elmer Spectrum 100) was used for recording IR spectra of the samples using KBr pellet technique. Photoluminescence (PL) spectrometer (Spectro Fluorescence JASCO fp-6200) was utilized for recording the PL spectrum of the prepared nanoparticles at the room temperature using 290 nm as excitation wavelength.

Results and discussion

Nanoparticles preparation and optimization of procedure

Taguchi robust design as an optimization methodology was applied to optimize synthesis procedure parameters. The experiments designed by fractional factorial techniques, i.e. Taguchi design, utilize the orthogonal arrays to assign several factors during a series of combined experiments [13,14]. The results obtained in such manner could be analyzed by general mathematical methods and at the end of procedure the main effects of studied parameters be extracted independently [15–17]. In the statistical experimental design, after performing the experiments, the effects of different parameters could be separated. Meanwhile, using the orthogonal arrays reduces the required number of experiments [18–20].

Table 1
OA_9 (3^4) matrix for parameter optimization in synthesis of $CuMO_4$ nanoparticles via direct precipitation reaction and mean diameter of produced nickel molybdate as the response.

Experiment number	Cu^{2+} concentration (M)	MoO_4^{2-} concentration (M)	Cu^{2+} feed flow rate (ml/min)	Temperature (°C)	Average diameter of $CuMoO_4$ particles (nm)
1	0.005	0.005	2.5	0	98
2	0.005	0.01	10.0	30	111
3	0.005	0.1	40.0	60	80
4	0.01	0.005	10.0	60	124
5	0.01	0.01	40.0	0	139
6	0.01	0.1	2.5	30	125
7	0.1	0.005	40.0	30	147
8	0.1	0.01	2.5	60	252
9	0.1	0.1	10.0	0	155