DETERMINATION OF THE OPTIMAL CONDITIONS OF THE SYNTHESIS OF MANGANESE TUNGESTATE NANO-PATES

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ABSTRACT

In this study, an orthogonal array design (OAD), OA9, was employed as a statistical experimental method for the controllable, simple and fast synthesis of manganese tungestate nano-plates in flower-like clusters. Ultrafine manganese tungestate clusters were synthesized by a precipitation method involving the addition of manganese ion solution to the tungestate reagent. The effects of reaction conditions, i.e., manganese and tungestate concentrations, flow rate of reagent addition and temperature, on the diameter of the synthesized manganese tungestate nano-plates were investigated. The effects of these factors on the width of the manganese tungestate nano-plates were quantitatively evaluated by the analysis of variance (ANOVA). The results showed that manganese tungestate nano-plates can be synthesized by controlling the manganese and tungestate concentration and flow rate. Finally, the optimum conditions for the synthesis of manganese tungestate nano-plates by this simple and fast method were proposed. The results of ANOVA showed that 0.005 mol/L manganese ion concentration, 0.01 mol/L tungestate ion concentration, 10 mL/min flow rate for the addition of the manganese reagent to the tungestate solution and 30 °C temperature are the optimum conditions for producing manganese tungestate nano-plates with 50 ± 6 nm width.

INTRODUCTION

There has been an increasing amount of interest in the synthesis of inorganic structures with nanoscale dimensions MnWO4 is a complex compound which has bulk electrical conductivity, relatively low melting point and novel magnetic property [1]. $MnWO_4$ is highly sensitive to change in humidity [2] and having great potential to be used as high sensitivity humidity sensors [3,4], which are important for many industrial applications such as meteorology, medicine, food production, agriculture and the domestic environment [2]. It displays photoluminescence with two main bands at 421 and 438nm [5]. In addition, it has been reported that MnWO4 showed attractive

Various methods have been used to synthesis MnWO4, including hydrothermal [6], solvothermal route [2], spray pyrolysis [1], cyclic microwave-assisted spray synthesis [1], precipitation synthesis [7,8], template synthesis [9] and solid state metathetic [10]. The purpose of this work was to produce

MnWO4 nanoplates with flower-like clusters, using precipitation method, which is fast, simple and cost effective method.

EXPERIMENTAL

Analytical-grade Mn chloride and sodium tungstate were used as received from Merk. The $MnWO_4$ particles were prepared by adding Mn^{2+} solution, at various concentrations and different flow rates, to the tungstate solution under vigorous stirring and various temperatures. After precipitation, the formed $MnWO_4$ was filtered and washed with distilled water three times. The product was then washed with ethanol and dried at 70ºC for 2 h. To optimize experimental parameters for the synthesis $MnWO_4$ particles, an experimental design approach was followed. The variables (Mn concentration, tungstate concentration, flow rate of addition of Manganese reagent to the tungstate solution, and temperature) were as shown in *Table 1*. All samples were characterized by scanning electron microscopic (SEM) and energy-dispersive analysis by x-rays (EDAX). SEMs were recorded using on a Philips XL30 series instrument using a gold film for loading the dried particles on the instrument. Gold films were prepared by a Sputter Coater model SCD005 made by BAL-TEC (Switzerland).

Table 1 – Assignment of the factors and levels of the experiments by using an OA_9 (3^4) matrix and mean width of manganese tungestate produced

Experiment Number	Mn^{2+} Concentration (M)	WO_4^{2-} Concentration (M)	Mn^{2+} Feed flow rate (ml/min)	Temperature (°C)	Diameter of $MnWO_4$ particles (nm)
1	0.005	0.005	2.5	0	78
2	0.01	0.005	10.0	30	58
3	0.1	0.005	40.0	60	64
4	0.005	0.01	10.0	60	78
5	0.01	0.01	40.0	0	80
6	0.1	0.01	2.5	30	91
7	0.005	0.1	40.0	30	60
8	0.01	0.1	2.5	60	83
9	0.1	0.1	10.0	0	66

RESULTS AND DISCUSSION

Mixing the solutions of the anion and cation of an insoluble inorganic salt such as $MnWO_4$ is a commonly used technology for synthesis many of water insoluble inorganic materials [11]. The control of particle size and shape is a complex process requiring a fundamental comprehensation of the interactions of reagents. The purpose of this study was to determine how the various parameters affect the diameter of $MnWO_4$ nano-plates in flower-like clusters. The factors included in this study were Mn^{2+} and WO_4^{2-} solution concentrations, flow rate for addition of Mn^{2+} solution to the WO_4^{2-} solution, and the temperature of the solution. Factors and levels tested are reported in *Table 1*.

The generated nano-plates clusters were characterized by X-ray powder diffraction and EDAX spectrum for the evaluation of their composition and purity. *Figure 1* shows the XRD pattern of the obtained manganese tungestate nano-plates. All the diffraction peaks in the figure can be indexed to be in agreement with the hydrated structure of manganese tungestate (Moolooite) from PC-APD, Diffraction software.

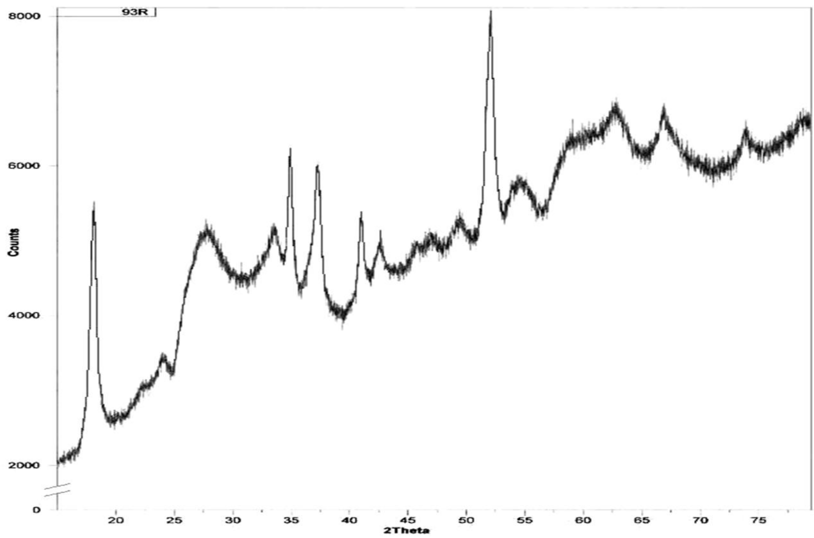

Fig. 1 – XRD pattern of the $MnWO_4$ nano-plates clusters prepared by precipitation method

Figure 2 shows the SEM images for four samples of $MnWO_4$ obtained by this method. Also, data obtained by results of the experiments are given in Table 1.The FTIR spectra (Fig. 3) of $MnWO_4$ with huebnerite structure show the inorganic modes in the range 556–983 cm−1 of the low wavenumber side at 912.30, 874.27, 810.16, 749.26, 652.15, 576.22 and 504.34 cm^{-1}. The vibrations are in accordance with those of other researchers [5, 12]. These bands are assigned to be the internal stretching modes of $v3(Au)$ and $v3(Eu)$ transitions [5].

Fig. 3 shows the photoluminescence (PL) spectra of the present research. By using a 290 nm excitation wavelength, PL spectra show electronic transition within $(WO4)^{2-}$ anion molecular complex, associated with the intrinsic emission. It can be excited either in the excitonic absorption band or in the recombination process [15], resulting from the huebnerite-structured products.

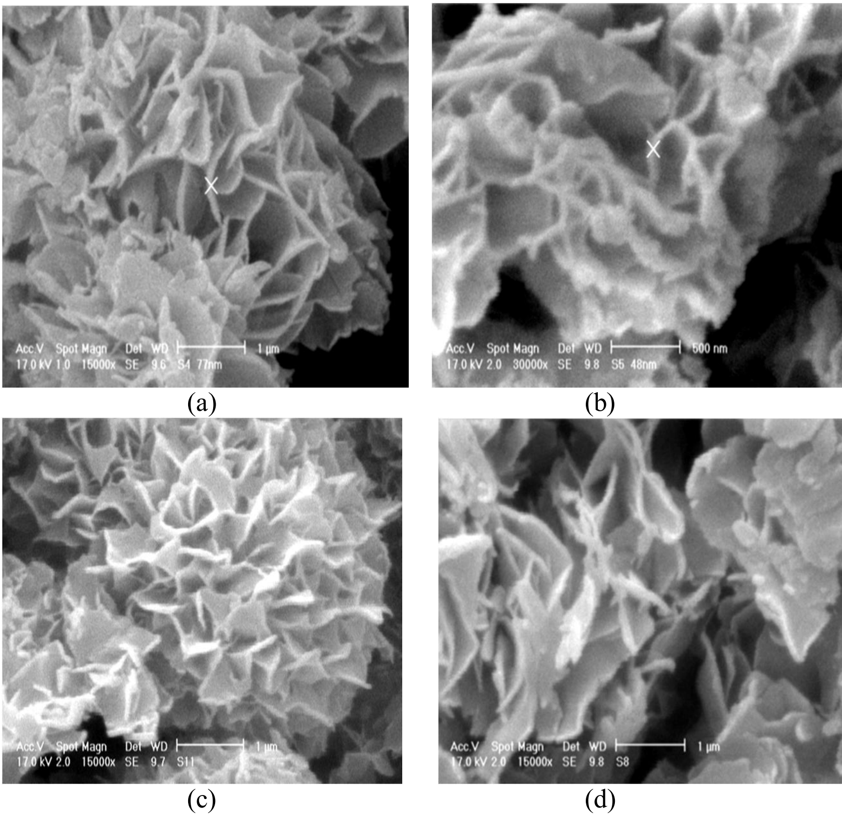

Fig. 2 – SEM images of $MnWO_4$ nano-plates clusters obtained at different runs by precipitation method: (a) run 1, (b) run 2, (c) run 4, and (d) run 7

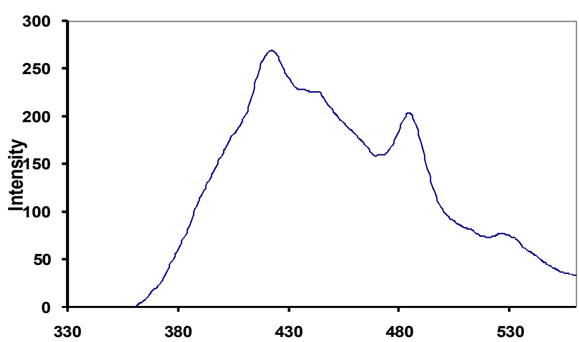

Fig. 3 – PL spectra (292 nm excitation wavelength) of $MnWO_4$ nano-plates clusters prepared with precipitation method

The emissions are blue spectra at 415–423 nm. Although the products were produced using different conditions. The results are in accordance with those detected by other researchers [5, 13].

CONCLUSIONS

In summary, a simple, fast and controllable method for the synthesis of manganese tungestate nano-plates in flower-like clusters in aqueous media was explored. An OAD method was employed for the optimization of the reaction conditions. Some experimental parameters, such as manganese ion concentration, tungestate concentration and flow rate were found to play significant roles in determining the particle size of the manganese tungestate nano-plates. The experiments proved that by using this method, the prediction of the optimum synthesis conditions of manganese tungestate nano-plates can be successfully performed.

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