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Taguchi method assisted optimization of electrochemical synthesis and structural characterization of copper tungstate nanoparticles

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ABSTRACT

Electrochemical process was utilized as a facile method for the preparation of copper tungstate nanoparticles by oxidation of copper anode in a sodium tungstate solution. Some of the factors of the synthesis procedure were optimized by the Taguchi robust design. The optimization results showed that the size of copper tungstate particles could be controlled via tuning the electrodeposition factors, including voltage of electrolysis, concentration of tungstate ion, stirring rate of electrolyte solution and also temperature. Characterization of the copper tungstate particle morphology was carried out by different techniques, i. e., SEM, XRD, EDX, and FT-IR spectroscopy. The characterization results showed that the particle size of $CuWO_4$ is influenced by the electrolysis voltage and increasing the voltage from 4 to 8 V leads to falling the size of copper tungstate particles, while further voltage increasing from 8 to 12 V resulted in larger particles. Further, the size of copper tungstate particles was dependent on the stirring rate and temperature of the electrolyte. The photoluminescence behavior of the nanomaterial prepared at optimum conditions was studied.

1. Introduction

Copper tungstate ($CuWO_4$) as a renowned n-type semiconductor is a member of the wolframite series. Copper tungstate has attracted substantial interest during recent years, because this material could be used in various important areas of science and technology such as scintillation detectors, optical fibers, photoanodes, laser host, sensors, photoelectrolysis electrodes, and positive electrode preparation for lithium based rechargeable batteries [1–8]. Up to now several researches about the crystal growth [9,10], photoelectrochemical performance [10], electrochemical, optical, electrical, magnetic, and ferroelectric behaviors [1,5,11–15] of the copper tungstate have been published.

The structure of copper tungstate crystals could be distinguished as a triclinic distorted wolframite [16], while their unit-cell parameters could be presented as follows: $a = 4.703$ Å, $b = 5.839$ Å, $c = 4.878$ Å, $\alpha = 91.677$ Å, $\beta = 92.469$ Å, and $\gamma = 82.805$ Å [17]. Meanwhile, the wolframite structure is including a framework of the oxygen atoms in a hexagonal close-packing, while the cations are occupying half of the octahedral sites. In the structure of $CuWO_4$, each copper atom is surrounded by six atoms of oxygen. Furthermore, it has been explained [17] that the atoms of copper and tungsten in the $CuWO_4$ crystal create the sequential layers located between the oxygen sheets. Thus, the infinite zigzag chains are formed by edge-sharing WO_6 and CuO_6 octahedra alternatively.

Several physical or chemical synthesis routes, i.e., deposition by spray [18], deposition via pulsed laser [19], radio-frequency assisted sputtering deposition [20], sol–gel method [21], fabrication in solid-phase [22], surfactant aided precipitation [23] and fabrication in polyol-media [24] have been utilized for the preparation of different morphologies of copper tungstate nanoparticles, i.e., nanofilm, nanosphere, and porous film. These methods have own advantages; however, each of them suffers from some restrictions such as requiring for the strictly controlled synthesis media, high synthesis costs, and complexities in the synthesis reaction. Therefore, further investigations directed toward finding easy to handle and economical methods for the synthesis of $CuWO_4$ nanoparticles are interesting. These methods will be more attractive when the proposed methods also have the potential for scaling-up and industrial application. On the other hand, optimizing a synthesis procedure for the production of nanoparticles is an essential step in the development of the proposed method. The principle, theory, and applications of Taguchi robust design as a well-known chemometric method for optimization of a chemical process have been discussed with all the specifics previously [25–28].

Tuning the size of particles during their formation is a complex subject and requires a deep understanding of the interactions between the reagents and other affecting factors [29,30]. The aim of this study was

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the investigation on the effect of some electrochemical process parameters on the size of copper tungstate particles and determination of optimum experimental conditions for electrosynthesis of $CuWO_4$ nanoparticles. In this order, Taguchi robust design as a statistical experiment optimization was used to investigate effects of four parameters on the particle size of copper tungsten, including the concentration of the tungstate solution as electrolyte, the voltage of the electrolysis, the rate of electrolyte stirring and temperature of the reaction. Also, the chemical structure of the copper tungstate nanoparticles, prepared at optimum conditions of the electrosynthesis procedure, was characterized by XRD, FT-IR and EDX techniques. Based on the best of our knowledge, until today there is no report on the fabrication of copper tungstate nanoparticles via electrodeposition route.

2. Experimental

2.1. Materials and instruments

The required chemical reagents were prepared by the Merck Company (Germany). The electrolyte solutions were prepared by dissolving appropriate amount of sodium tungstate in deionized water. The copper tungstate was synthesized electrochemically in a one-compartment cell utilizing a programmable power supply system, psp-603/405/2010, in the potentiostatic electrolysis mode. A copper plate (2.5 cm^2) was utilized as the working electrode and a platinum gauze electrode was used as the cathode.

The fabricated samples were characterized by scanning electron microscopy (SEM) on a Philips XL30 series instrument, while a golden film was utilized for the loading of the dried particles on the SEM instrument. A gold layer was coated on the samples by a sputter coater, model SCD005, manufactured by BAL-TEC (Switzerland). FT-IR spectrophotometer (Perkin-Elmer Spectrum 100) was utilized to obtain the IR spectra by the aid of KBr pellet technique. The X-ray powder diffraction (XRD) analysis was carried out on a Rigaku D/max 2500 V diffractometer equipped with a Cu target and graphite monochromator. A photoluminescence (PL) spectrometer (Spectro Fluorescence JASCO fp-6200) was utilized to prepare the PL spectrum, while 290 nm was used as the excitation wavelength at room temperature.

2.2. Procedure

Electrochemical synthesis of the copper tungstate nanoparticles was carried out in an electrolyte solution which resulted from dissolving various amounts of sodium tungstate in the de-ionized water. The electrochemical synthesis was carried out in a Pyrex cell ($V = 300\ cm^3$) during 30 min under various stirring rates and temperatures according to Table 1 [31]. The utilized platinum and copper electrodes were sonicated in the de-ionized water and also polished electrochemically before each trial. Further, the platinum electrode was washed with the diluted nitric acid. The type and size of electrodes and also the time of electrolysis were fixed in all trials. Collection of the product was carried out via electrolyte solution filtering and two times washing the resulting precipitate with de-ionized water and then washing with ethanol. The product was then calcined at 600 °C for 2 h.

Table 1
OA_9 (3^4) matrix applied for designing the experiments.

Trial number	Tungstate conc. (mol/L)	Applied voltage (V)	RPM	Temperature (°C)	Average size of $CuWO_4$ particles (nm)
1	0.01	8	250	0	87
2	0.01	12	500	25	72
3	0.01	16	1000	50	70
4	0.05	8	500	50	83
5	0.05	12	1000	0	99
6	0.05	16	250	25	102
7	0.1	8	1000	25	90
8	0.1	12	250	50	77
9	0.1	16	500	0	107

3. Results and discussion

3.1. Optimization of electrodeposition procedure

Table 1 shows the utilized orthogonal array and the resulting average particle size of the $CuWO_4$ at each trial. As seen, four operation parameters, i.e., concentration of the tungstate in the electrolyte solution, the applied voltage during electrolysis, stirring rate of the electrolyte and its temperature were investigated in triple levels. The electrodeposited copper tungstate was characterized by SEM to determine the morphology of the resulting particles at different trials. Four SEM images of the $CuWO_4$ samples prepared at different trials are given in Fig. 1. The figure reveals that the size of $CuWO_4$ particles is depending on the trial conditions of the synthesis procedure.

In this study, design of trials was carried out by the use of orthogonal array and hence pointing out of the individual effect of each parameter at different levels is possible through averaging the corresponded responses. The average particle size of each level of the studied factors was calculated according to the trial results as planned by Taguchi method [32,33] (Table 2). Indeed, the average values for the triple levels of the investigated parameters disclose the presented trend in the adjustment of copper tungstate particle size by changing the level of any parameter. The first studied parameter in this work was the concentration of tungstate electrolyte. The effect of this parameter on the particle size of synthesized copper tungstate at three different levels (0.01, 0.05 and 0.1 mol/L) was also investigated. The presented results in Fig. 2 reveal that 0.01 M of tungstate solution is the optimum concentration for the electrochemical synthesis of the $CuWO_4$ nanoparticles. Different electrolysis voltages (8, 12, 16 V) were applied during optimization of the electrodeposition procedure. It was found that 12 V is best applied voltage for the production of the $CuWO_4$ nanoparticles via the proposed procedure. We further found that 50 °C and 1000 RPM are the optimal temperature and stirring rate in order to the electrochemical synthesis of the copper tungstate nanoparticles.

In the next stage, analysis of variance (ANOVA) was applied on the calculated average particle sizes of the $CuWO_4$ corresponding to each level of the explored factors. The results of ANOVA before and after pooling of the insignificant parameter are given in Table 2. In this table, the *S* symbol characterizes the sum of the squares for any of the studied factors and/or error term, while *V* epitomizes the variance for these terms. In the meantime, the analysis of variance (ANOVA) yields the significance of the investigated parameters. The results of this study exhibit that except for the stirring rate, at the 90% confidence interval, all studied parameters, i.e. concentration of the WO_4^{2-} in the electrolyte, applied voltage, and temperature of the electrolyte have significant effects on the particle size of the resulting $CuWO_4$. Meanwhile, the probable interactions between the investigated parameters were neglected. Accordingly, considering the average size of $CuWO_4$ particles (calculated for various levels of the studied factors presented in Fig. 2) and the outcomes of ANOVA (Table 2), it could be proposed that the optimum conditions for synthesis of $CuWO_4$ nanoparticles via the electrodeposition process are including: 0.01 M concentration of WO_4^{2-} in the electrolyte solution, 12 V as the electrolysis voltage and 50 °C as the temperature of the electrolyte solution.

As suggested in the Taguchi method [31,32], the size of $CuWO_4$ nanoparticles at the optimum conditions of electrodeposition process might be predicted by the succeeding equation:

$$Y_{opt} = \frac{T}{N} + \left(V_{App} - \frac{T}{N}\right) + \left(C_T - \frac{T}{N}\right) + \left(T_{Elec} - \frac{T}{N}\right).$$

Where in the above equation, T/N is the average size of $CuWO_4$ particles which resulted during all trials of Table 1; T is the summation