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Preparation of $CuCrO_2$ nanowires by electrospinning

Te-Wei Chiu*, Yi-Ting Chen

Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, 1, Sec. 3, Zhongxiao E. Rd., Taipei 106, Taiwan

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Abstract

$CuCrO_2$ nanowires were synthesized by electrospinning method. A mixed solution including cupric nitrate, chromium acetate and ployvinylpyrrolidone gel was used as the precursor for electrospinning. Annealing conditions are investigated to obtain a single phase of $CuCrO_2$. It is found that the reducing atmosphere helps to obtain the $CuCrO_2$ phase. The experimental results revealed that the single-phase of delaffosite-type $CuCrO_2$ wire was obtained when it was annealed at 700 °C for 20 min in vacuum.

Keywords: Eelectrospinning; $CuCrO_2$; Functional ceramics; Catalyst

1. Introduction

Delafossite-structure $CuCrO_2$ has attracted much attention as a p-type transparent conductive oxide (TCO), which is of great interest for several applications such as transparent diodes and solar cells [1–3]. $CuCrO_2$ is also one of the most promising candidates for p-type transparent optoelectronic devices. Currently, researchers have been exploring new properties on delafossite oxides such as photocatalyst for heavy metal reduction [4,5], hydrogen evolution [5,6], NO_2 removal [6], catalysts for steam reforming process [7,8], exhaust gas purification, room temperature ozone sensors [9], and thermoelectric devices [10].

It is well known that a way to boost the catalytic efficiency is to reduce the size of catalyst material for increasing the surface area and adsorption ability. Synthesizing nanosized $CuCrO_2$ powder can therefore be expected to improve the catalytic performance. However, controlling the valence state of Cu to unstable 1^+ is the key to successful synthesis of $CuCrO_2$.

Cu ions in a delafossite structure is Cu(I); however, typically wet chemical-derived Cu ion is Cu(II), which will react with B site ions, such as Al and Cr, to form stable spinel-type AB_2O_4 [11,12].

According to the isobaric phase diagram of the bulk Cu_2O–CrO_3–CuO ternary system [13], if CuO and Cr_2O_3 react in the air atmosphere, it favorably forms a spinel-type $CuCr_2O_4$ at 700 °C. Pure delafossite phase of $CuCrO_2$ can be obtained when spinel-type $CuCr_2O_4$ reacts with residual CuO at temperatures above 1000 °C. The chemical formulae are shown in the following formulas:

$$2CuO + Cr_2O_3 \rightarrow CuCr_2O_4 + CuO \quad (1)$$

$$CuCr_2O_4 + CuO \rightarrow 2CuCrO_2 + 1/2O_2 \quad (2)$$

According to formula (2), the reducing atmosphere could help to obtain sing-phase of $CuCrO_2$ thermodynamically. Thus, to synthesize $CuCrO_2$ under a relatively low temperature, an oxygen-free atmosphere such as argon gas is required [3,10].

Metal oxide with 1D nanowire has received increasing interest since it provides a good material system to investigate the dependence of electrical, optical, thermal and mechanical properties on dimensionality and size reduction [12]. 1D structure of ceramic nanowires or microwires have the potential application in various areas due to high surface area [13]. Recently, ceramic nanowires have been explored as effective

*Corresponding author. Tel.: +886 2771 2171x2742; fax: +886 2 2731 7185.
E-mail address: tewei@ntut.edu.tw (T.-W. Chiu).

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electrode materials for electrochemical energy storage devices [14]. In the past decade, various ceramic nanowires are fabricated by the combination of two conventional techniques: electrospinning and sol–gel. Electrospinning is a simple method that is not only being employed in university laboratories, but also increasingly being applied in industry. The applications are in fields as diverse as optoelectronics [15], sensor technology [16], catalysis [17] and medicine [18].

Electrospinning is a method of making wire structured materials that inducing static electrical charges in the solution at such a density that the self-repulsion of the charges causes the liquid to stretch into a wire in an electric field. When a high voltage is applied to the solution, the ohmic current distributes the charges throughout the molecules [19]. The charges are transported from the electrospinning tip to the target through the deposition of the wire. The electrical charges during electrospinning process can be positive, negative or both (alternating current). Generally, ceramic nanowires require a high temperature calcination step after creating wire-shaped precursors by electrospinning to crystallize [20–22].

In this work, we shaped $CuCrO_2$ nanowires by electrospinning method and developed an annealing condition to form a single phase of $CuCrO_2$ without impurity phase.

2. Experimental

2.1. Preparation of precursor

A sol–gel method was used to prepare the $CuCrO_2$ precursor for the electrospinning. Cupric nitrate and chromium acetate were mixed with molar ratio of 3:1 and the mixture was dissolved in ethanol to obtain 0.2 M of metal source solution. Then, 1.5 g polyvinylpyrrolidone (PVP) powder and 8.5 g ethanol were added into the 10 ml metal source solution to make the target precursor. After vigorous stirring at 80 °C for 12 h, a viscous gel-like solution of $CuCrO_2$/PVP precursor was obtained.

2.2. Electrospinning process

In the electrospinning process, the precursor was placed in a 5 ml syringe. The syringe was then clamped to a ring stand that was 15 cm above a grounded bowl-shape stainless steel mesh. A high-voltage source was connected to a metallic needle, which was attached to a syringe pump. The precursor feeding rate was 0.2 ml/h and the applied voltage was 20 kV.

2.3. Annealing process

In the rapid annealed condition, the wires were annealed by the following method: First, move the tube out from the oven then heat the furnace up to desire temperature. Second, roll the crucible with the as-spun wires into the tube. Third, pump down the tube to vacuum and then refill it with annealing ambient. When the furnace is heated to the desired temperature, directly move the tube into the furnace and rapidly anneal the wires. After annealing them for a short time, move the tube out of the oven, and cool them outside of the furnace.

Table 1
Annealing conditions of $CuCrO_2$ electrospun wires.

Ambient	Time (min)	Temp. (°C)
Air	30	500
		700
		900
N_2	20	700
	30	
$10\%H_2+90\%N_2 \rightarrow N_2$ (T-1)	15–20	400–600
$Air \rightarrow N_2$ (T-2)	15–30	500–700
Vacuum	20	700

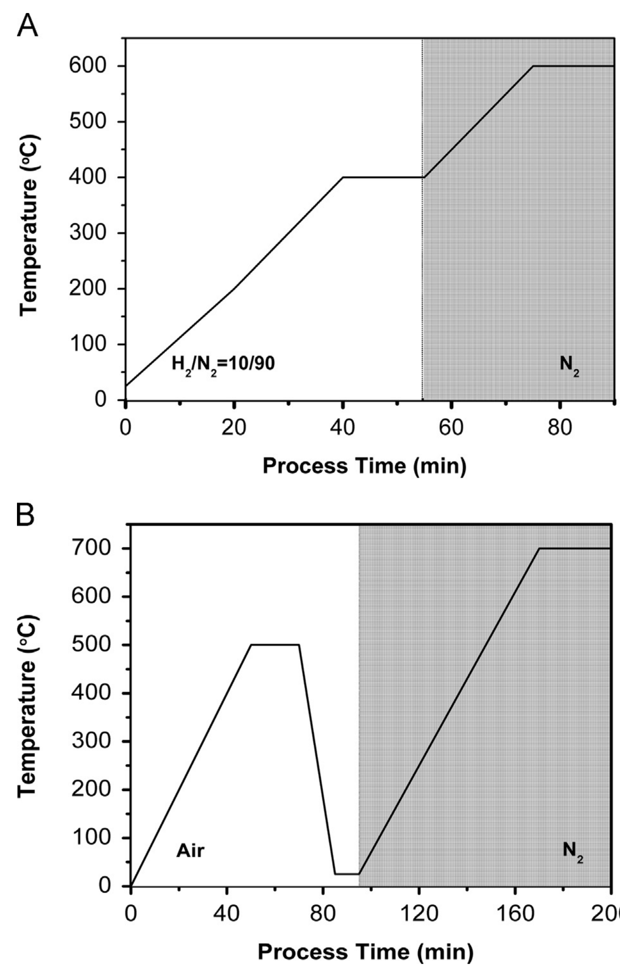

Fig. 1. Schematic of the (A) T-1 and (B) T-2 processes.

2.4. Annealing ambient

The $CuCrO_2$ nanowires were annealed in the air, nitrogen at 1 atm, and vacuum, pumped by rotary pump, to obtain single phase of $CuCrO_2$. Two-step annealing methods were also investigated in this work.