



Synthesis and magnetic properties of copper cobaltite (CuCo_2O_4) fibers by electrospinning



Ronariddh Nakhowong^{a, c, *}, Romteera Chueachot^{b, c}

^a Program of Physics, Faculty of Science, Ubon Ratchathani Rajabhat University, Ubon Ratchathani 34000, Thailand

^b Program of Chemistry, Faculty of Science, Ubon Ratchathani Rajabhat University, Ubon Ratchathani 34000, Thailand

^c Functional Nanomaterials and Electrospinning Research Laboratory, Faculty of Science, Ubon Ratchathani Rajabhat University, Ubon Ratchathani 34000, Thailand

ARTICLE INFO

Article history:

Received 12 September 2016

Received in revised form

11 April 2017

Accepted 29 April 2017

Available online 30 April 2017

Keywords:

Copper cobaltite

Magnetic properties

Fiber technology

Electrospinning

ABSTRACT

Copper cobaltite (CuCo_2O_4) fibers with diameters of 500–800 nm were successfully synthesized by the combination of the electrospinning process followed by calcination at 600–800 °C for 2 h. Thermogravimetric and differential thermal analysis results showed that weight loss was stable at around 600 °C. The X-ray diffraction and Fourier transform infrared spectroscopy results confirmed the formation of spinel CuCo_2O_4 , with the impurity phase of CuO also detected. Scanning electron microscopy and transmission electron microscopy results revealed that the CuCo_2O_4 fibers had a rough surface of combined nanograins after calcination. Vibrating sample magnetometer measurements determined that the samples exhibited ferrimagnetic and antiferromagnetic behavior at 600–800 °C. The saturation magnetization, remnant magnetization, coercivity, and the anisotropy constant decreased with increasing calcination.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The cobalt-containing spinel oxides MCo_2O_4 ($\text{M} = \text{Zn}, \text{Ni}, \text{Mn}, \text{Cu}, \text{Fe}, \text{etc.}$) are interesting materials due to their superior physicochemical properties with applications in various fields including anode material for lithium-ion batteries, supercapacitors, chemical sensors, pigments and catalysts [1–4]. Among the spinel-type oxides, cobalt oxides have attracted due their high catalytic activity, low cost, ease of preparation, and good chemical stability [5]. However, the toxicity and high cost of cobalt has necessitated partial replacement or substitution of the metal ions in Co_3O_4 with eco-friendly alternatives [5]. Transition metal substituted cobalt oxides including NiCo_2O_4 , ZnCo_2O_4 , MnCo_2O_4 , MgCo_2O_4 , and CuCo_2O_4 have been prepared using different methods for use in lithium-ion batteries and supercapacitors [6–10]. Among the varieties, the spinel CuCo_2O_4 exhibited superior conductivity, electrochemical activity, and high specific capacitance, with better rate capacities compared to transition metal oxides (MnO_2 , V_2O_5 and Co_3O_4) [4]. The spinel CuCo_2O_4 exhibits both normal and inverse

spinel structure depend on the Cu ion distribution in the spinel structure [11]. The spinel structure has two different crystallographic sublattices based on formulae $\text{A[B]}_2\text{O}_4$ (normal spinel) and $\text{B[AB]}_2\text{O}_4$ (inverse spinel), where atoms A (divalent cations) and B (trivalent cations) occupy between the tetrahedral and octahedral sites, respectively [12]. In case of $\text{Cu}_x\text{Cu}_{3-x}\text{O}_4$, transition occurred from a normal to an inverse spinel when $x > 0.2$ [12]. In inverse spinel $\text{Co}^{3+}[\text{Co}^{3+}\text{Cu}^{2+}]\text{O}_4^{2-}$, the Cu^{2+} represents cations in octahedral sites, and the $[\text{Co}^{3+}\text{Cu}^{2+}]$ represents cations equally distributed between tetrahedral and octahedral sites corresponding to typical Jahn-Teller ion [12]. Spinel CuCo_2O_4 has applications in Li–O₂ batteries [5], Li-ion batteries [10], supercapacitors [13], catalysts [14], electrochemical sensors [15], and oxygen reduction reactions [16]. Spinel CuCo_2O_4 has been synthesized in several ways including the porous alumina-template method [1], hydrothermal method [4], microwave assisted reflux method [11], solvothermal method [17], and chemical spray pyrolysis [18]. One-dimensional nanostructured materials such as nanofibers, nanowires, and nanotubes have recently attracted attention due to their unique properties and wide range of potential applications [19,20]. One-dimensional nanostructures have similar advantages of high aspect ratio, high interfacial area, porosity and the shortest pathways for ion diffusion compared to other nanostructures [4].

* Corresponding author. Program of Physics, Faculty of Science, Ubon Ratchathani Rajabhat University, Ubon Ratchathani 34000, Thailand.

E-mail address: ronariddh.n@ubru.ac.th (R. Nakhowong).

Electrospinning is a new, simple, versatile and cost-effective method for fabricating ultrafine fibers with diameters ranging from several micrometers to nanometers [21]. The usefulness of nanofibers has been reported by many researchers, Luo et al. noted that gallium nitride nanofibers exhibited an improved response to ethanol sensing with enhanced selectivity over the gallium nitride nanoparticles [22]. Darbar et al. reported that MgCo_2O_4 fibers showed reversible capacity of 795 mAh g^{-1} after 50 cycles, higher than the bulk material capacity of 227 mAh g^{-1} at a current rate of 60 mA g^{-1} [9]. Huang et al. reported that $\text{NiCo}_2\text{O}_4/\text{C}$ nanofibers prepared by the hydrothermal method, exhibited a high specific capacitance of 1029 F g^{-1} at a current density of 1 A g^{-1} , higher than NiCo_2O_4 nanoparticles with specific capacitance of 866 F g^{-1} [6]. Thus, the electrospinning technique has the potential to generate nanofibers with promising attributes for practical applications in various fields. Here, we report the CuCo_2O_4 fibers were synthesized by a combination of the electrospinning and calcination processes. The crystalline phases, crystallite size, structural parameters, chemical compositions, and magnetic properties of the CuCo_2O_4 fibers were investigated.

2. Experimental procedure

2.1. Preparation of CuCo_2O_4 fibers

Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Carlo Erba) and cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Carlo Erba) at molar ratios of 1:2 were dissolved in 10 mL of *N,N*-dimethylformamide (DMF, Carlo Erba) and subjected to magnetic stirring for 2 h to obtain a homogenous solution. Consequently, 7 g of polyacrylonitrile (PAN, $M_w = 150,000$, Sigma-Aldrich) were then added to copper nitrate/cobalt nitrate mixture and stirred continuously at 60°C for 12 h to achieve a clear solution. The composite was loaded into a 10 mL plastic syringe equipped with a needle of 23-gauge stainless steel. A high voltage power supply (Gamma High Voltage Research, ES30P-5W) was connected to the syringe needle tip and the rotating collector which was covered with aluminum foil. A voltage of 17 kV was applied to the needle tip and the drum collector which were separated at a distance of 15 cm. The solution was controlled by a syringe pump with a constant feed rate of 1.0 mL/h . The synthesized fibers were calcined at 600 , 700 , and 800°C for 2 h to completely decompose the polymer and induced crystallization, consistent with the TG-DTA results. The heating rate was 2°C/min in air.

2.2. Characterization

The thermal behavior of sample was carried out by thermogravimetric and differential thermal analysis (TG-DTA, Thermo plus TG8120, Rigaku, Japan) under nitrogen atmosphere at a heating rate of 10°C/min . The morphology of the fibers was observed by scanning electron microscope (SEM, JOEL JSM-6010LV, Japan) and transmission electron microscopy (TEM, FEI Tecnai G² F20 FE-TEM, Netherlands). The phases structure of the samples were identified using an X-ray diffraction (XRD, Phillips, X pert' MPD, Netherlands) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The functional groups of the samples were confirmed by Fourier transform infrared spectroscopy (FT-IR, PerkinElmer, Spectrum-RX, USA). The magnetic properties of samples were measured at room temperature with a vibrating sample magnetometer (VSM, LakeShore Model 7403, USA). The surface chemical compositions and valence states was carried out using X-ray photoelectron spectroscopy (XPS, AXIS ULTRA^{DL}, Kratos analytical, Manchester, UK) equipped with a monochromatic source (Al $\text{K}\alpha$ X-rays at 1.4 keV).

3. Results and discussion

3.1. TG-DTA analysis

TG-DTA curves of the as-spun fibers are shown in Fig. 1. It could be observed that TG curve at weight loss below 195 and $195\text{--}335^\circ\text{C}$ are attributed to loss of volatile solvents, and the decomposition of nitrile groups, respectively [23]. The weight loss between 335 and 342°C is corresponds to decomposition of PAN main chain [24]. Two exothermic peaks of DTA curves at 350 and 420°C could be attributed to decomposition of PAN, nitrate groups and crystallization of metal oxide [25]. Above the temperature of 350°C , the weight loss almost constant and DTA peaks disappeared after 600°C . TG-DTA results indicated that the calcination temperature should be selected initially at 600°C to ensure that all organic compounds and PAN were completely removed.

3.2. XRD analysis

The X-ray diffraction (XRD) patterns of the as-spun and calcined fibers at 600 , 700 , and 800°C for 2 h are shown in Fig. 2. No diffraction peaks of the as-spun fibers appeared due to their amorphous nature. After the fibers were calcined at 600°C , characteristic diffraction peaks at $2\theta = 19.07^\circ$, 31.31° , 36.89° , 38.87° , 44.87° , 59.41° , and 65.29° could be indexed to the (111) , $(2\ 2\ 0)$, $(3\ 1\ 1)$, $(2\ 2\ 2)$, $(4\ 0\ 0)$, $(5\ 1\ 1)$, and $(4\ 4\ 0)$ planes of the spinel CuCo_2O_4 structure. The diffraction peaks matched well with cubic CuCo_2O_4 spinel (JCDPS no. 01-1155, $a = 8.039 \text{ \AA}$) with an $\text{Fd}3\text{m}$ space group and a small amount of CuO detected as a secondary phase. The diffraction peaks of CuO agreed with $2\theta = 35.61^\circ$ corresponding to the (-110) plane. Shanmugavani et al. reported that synthesis of stoichiometric compositions of CuCo_2O_4 was very difficult and took a long time due to its thermal stability [11]. Consequently, the CuCo_2O_4 decomposed into CuO , oxygen and a cobalt-enriched spinel phase at temperature higher than 400°C in air atmosphere.

Fibers calcined at 700 and 800°C , gave more intense and narrow diffraction peaks, indicating the increasing crystallinity of CuCo_2O_4 with increasing the calcination temperature. The crystallite sizes (D) of samples were calculated based on Scherrer equation [26]:

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of the X-ray radiation, β is the full width

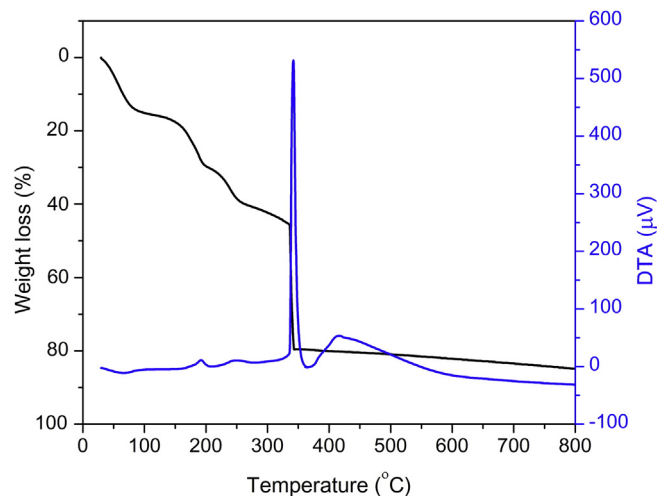


Fig. 1. (a) TG-DTA curves of as-spun fibers.

Download English Version:

<https://daneshyari.com/en/article/5459205>

Download Persian Version:

<https://daneshyari.com/article/5459205>

[Daneshyari.com](https://daneshyari.com)