Journal of Alloys and Compounds 509 (2011) 2933–2935

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Synthesis of nanosized $CuCrO_2$ porous powders via a self-combustion glycine nitrate process

Te-Wei Chiu*, Bing-Sheng Yu, Yuh-Ruey Wang, Kun-Te Chen, Yu-Te Lin

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

ARTICLE INFO

Article history:
Received 27 October 2010
Received in revised form
21 November 2010
Accepted 23 November 2010
Available online 30 November 2010

Keywords:
Oxide materials
Delafossite
$CuCrO_2$
Glycine nitrate process

ABSTRACT

The glycine nitrate process has been successfully employed to prepare nanosized, porous, stoichiometric, homogeneous $CuCrO_2$ powders without ambient control. In this method, a precursor solution was prepared by mixing glycine with an aqueous solution of blended (Cu–Cr) metal–nitrates in their stoichiometric ratios. The glycine-mixed precursor solution was first heated in a beaker to evaporate excess water for forming a viscous bluish semi-transparent gel. The beaker was then covered with a metallic mesh, and the temperature increased slowly to 170 °C to auto-ignite the material. The combustion was self-sustaining and very rapid, producing gray colored powders. The as-prepared powders were nanosized (~20 nm) into a spherical shape and crystallized in a delafossite structure. The powders showed a very large surface area of 30.92 m^2/g, as determined by BET surface area measurements. The SEM/TEM studies on these powders confirmed their nanosized nature and porous structure.

1. Introduction

Delafossite $CuCrO_2$ 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]. Related studies on delafossite oxides are interested not only in examining the TCOs properties but also in exploring their applications as photo catalysts for hydrogen evolution [4] and NO_2 removal [5], catalysts for steam reforming process [6] and exhaust gas purification [7], room temperature ozone sensors [8], magnetics [9], and thermoelectric devices [10].

One way to improve the catalysis efficiency is to decrease the size of the catalyst in order to increase the surface area and adsorption ability. Synthesizing nanosized $CuCrO_2$ powder can therefore be expected to improve the performance of catalytic applications, and controlling the valence state of Cu to 1^+ is the key to successful synthesis of $CuCrO_2$. According to the isobaric phase diagram of the bulk Cu_2O–Cr_2O_3–CuO ternary system reported by Jacob et al. [11], when CuO and Cr_2O_3 react in air, CuO and Cr_2O_3 favorably react to form spinel-type $CuCr_2O_4$ at 700 °C. Pure delafossite-type $CuCrO_2$ is converted from spinel-type $CuCr_2O_4$ with residual CuO above 1000 °C. The chemical formulae are shown in (1) and (2):

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

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

According to formula (2), the reducing atmosphere helps obtain the $CuCrO_2$ phase thermodynamically. Thus, to synthesize $CuCrO_2$ under a relatively low temperature, an oxygen-free atmosphere, such as argon gas, is required [3,12].

Nanoparticles of $CuCrO_2$ have been synthesized by hydrothermal [13] and citric acid methods [14]. Although the glycine nitrate process (GNP) is very widely applied to synthesize homogeneous single, binary, and multicomponent oxide systems, it has not been employed to synthesize copper–chromite solid solutions. Therefore, the goal of the present investigation is to determine the utility and usefulness of GNP in producing $CuCrO_2$ nanopowders with a high surface area. $CuCrO_2$ with a typical composition and a delafossite structure was used in the present investigation. The results of the synthesis and characterization of $CuCrO_2$ nanopowders are reported and discussed in this paper.

2. Experimental

2.1. Synthesis of $CuCrO_2$ powders

2.1.1. Solid state reaction

In order to compare the characteristics of $CuCrO_2$ powder prepared by the GNP method to those of traditional $CuCrO_2$ powder, $CuCrO_2$ powder was also prepared by traditional solid state reaction method. The Cu_2O and Cr_2O_3 powders were used as starting materials. These powders were mixed with ethanol in a plastic jar with zirconia balls and milled for 24 h. The resulting slurries were dried at 70 °C in an oven. The dried powders were calcined in a crucible at 1200 °C for 6 h in air.

2.1.2. GNP method

For the synthesis of $CuCrO_2$ powders by GNP route, copper nitrate $[Cu(NO_3)_2{\cdot}3H_2O]$, chromium nitrate $[Cr(NO_3)_3{\cdot}9H_2O]$, and glycine were used as starting reagents. Copper nitrate, chromium nitrate, and glycine of required amounts

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

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.11.162

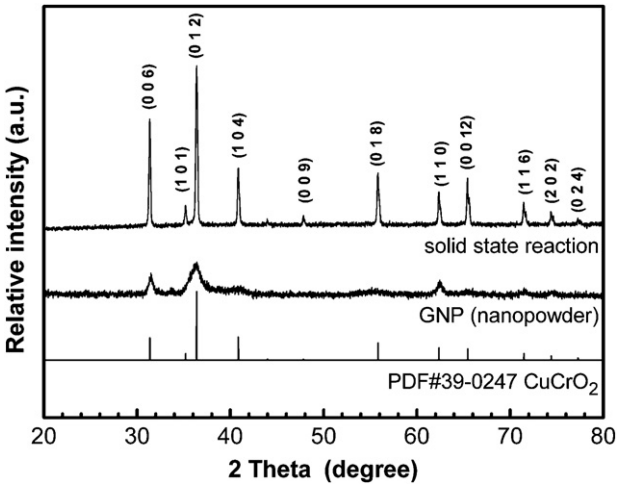

Fig. 1. XRD patterns of $CuCrO_2$ prepared by solid state reaction and GNP route.

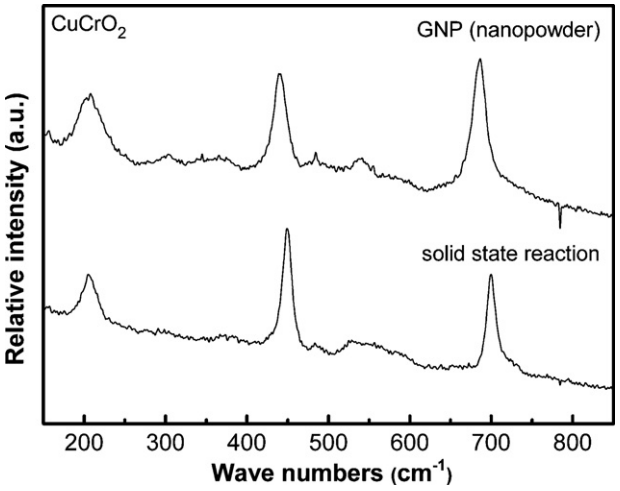

Fig. 2. Raman spectra of $CuCrO_2$ prepared by solid state reaction and GNP route.

(24.16 g, 40.01 g, and 5.63 g respectively) were dissolved in the minimum amount of distilled water to obtain clear solutions. All the solutions were mixed together and aged in a 500 mL beaker at 100 °C for 24 h, after which a transparent moisture-sensitive glassy material was obtained. This glassy material was then heated in the beaker on a hot plate to raise the temperature to around 175 °C. The material ignited spontaneously, resulting in a gray-colored mass. During ignition, the beaker was covered with a fine-mesh sieve to prevent the powder from flying out of the beaker.

2.2. Physico-chemical characterization

The $CuCrO_2$ powders were characterized by various techniques: X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and BET surface area measurement. The crystalline phase analysis of the as-dried powders was performed by XRD (Rigaku DMAX2200) with Cu Kα radiation. The crystalline phase was determined by Raman spectroscopy (Dong Woo 500i). The SEM (HITACHI S-4700) technique was used to determine particle size, morphology, and the nature of agglomerates in the as-dried powders. The morphology and particle size were also determined by TEM (JEOL FE2100, 200 kV). The standard BET (Micromeritics Gemini V) method was applied for measurement of the surface area.

3. Results and discussion

Although it has been reported in the literature that the GNP method is capable of producing single, binary, and multicomponent oxides with better homogeneity, the route has not previously been used to synthesize $CuCrO_2$ powders. Therefore, the aim of the present investigation is to determine the utility of this method in synthesizing solid solution $CuCrO_2$ powders and to study the characteristics of the powders obtained by this route. $CuCrO_2$ with a typical composition was used due to its many applications, as described earlier in Section 1. However, Cu ion and Cr ion tend to easily form spinel type $CuCr_2O_4$, whose stability is up to about 1050 °C. This makes it difficult to obtain delafossite type $CuCrO_2$, thereby posing a barrier against the synthesis of delafossite phase compound under air by the GNP method. Thus, the fuel/cation ratio is a very important factor in synthesizing $CuCrO_2$ by GNP.

The XRD patterns of the $CuCrO_2$ powders prepared by solid state reaction and GNP route are presented in Fig. 1. The XRD patterns of the $CuCrO_2$ powders prepared by GNP route show three main reflections of a typical delafossite structure of $CuCrO_2$, corresponding respectively to the [0 0 6], [0 1 2], and [1 1 0] planes and indicating that the main compound of the powder prepared by GNP route is indeed delafossite $CuCrO_2$. However, since the entire procedure was performed in air, CuO, Cr_2O_3 and spinel type $CuCr_2O_4$ were probably present, even though they remained undetected in XRD. The broad XRD peaks are attributed to the nanocrystalline form.

The structure of the as-self combusted $CuCrO_2$ powder was further confirmed by Raman spectroscopy. The Raman spectra of both $CuCrO_2$ micro and nanopowders, as shown in Fig. 2, show three main peaks of a delafossite structure of $CuCrO_2$, corresponding to 207 cm^{-1}, 444 cm^{-1}, and 691 cm^{-1}, respectively. The Raman spectroscopy results are consistent with the literature [15]. The Raman peaks shown in Fig. 2, attributed to delafossite, dominate the spectra. In this self-combustion reaction, though the Cu ions started off in the oxidation state II^+ and were combusted in air, Cu^{2+} was reduced by the combustion of the glycine. When glycine and the nitrate group combusted, the results were a partial reduction atmosphere and high temperature, which reduced the Cu^{2+} ions and formed crystallized $CuCrO_2$ with Cr^{3+} ions. At the same time, volume expansion of the generated gas caused a porous structure. In this work, the optimized fuel/ion ratio is found to be 1.5.

A SEM photograph of the as-self combusted $CuCrO_2$ powder is shown in Fig. 3. The as-prepared powder exhibited a porous structure with nanoparticles. TEM was used to further verify this observation. The microstructure features observed in SEM can also be seen in the TEM photo-micrograph shown in Fig. 4. Thus, both the SEM and TEM examinations of the as-prepared GNP material showed a macroporous nature/microstructure of the material. The crystalline size of the $CuCrO_2$ nanoparticles was around 20 nm.

The adsorption curves of the $CuCrO_2$ prepared by solid state reaction and GNP route are given in Fig. 5. BET surface area measurements revealed a surface area of 30.92 m^2/g for the as-self combusted $CuCrO_2$ powder. This is nearly 2 orders larger than that

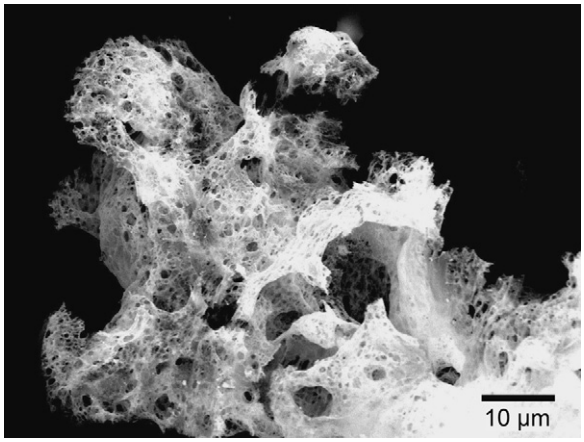

Fig. 3. SEM image of as-self combusted $CuCrO_2$ powder.

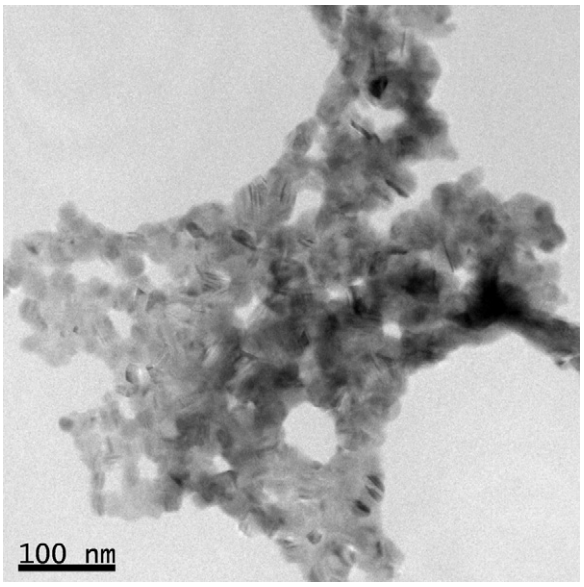

Fig. 4. TEM image of as-self combusted $CuCrO_2$ powder.

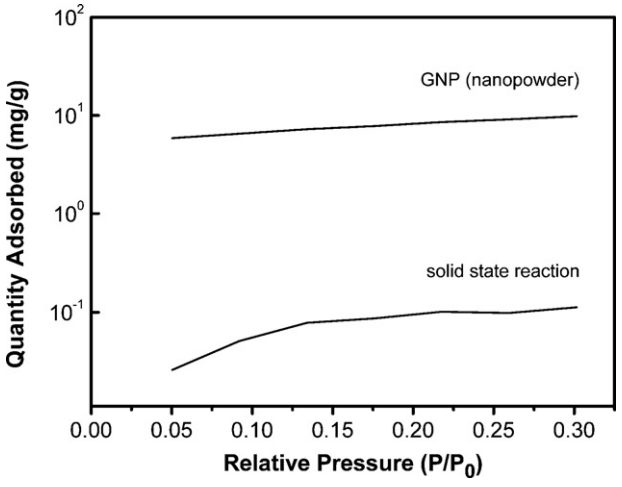

Fig. 5. The BET adsorption curves of $CuCrO_2$ prepared by solid state reaction and GNP route.

of the $CuCrO_2$ powder prepared by solid state reaction (0.47 m^2/g). Therefore, all the above characterization results confirm that the GNP method results in macroporous, stoichiometric, homogeneous $CuCrO_2$ powders. A further study to control the pore structure by varying the preparation parameters during GNP synthesis and to understand the role of glycine in producing a porous microstructure is underway and the catalytic efficiency of nanosized $CuCrO_2$ powder will also be investigated.

4. Conclusion

The GNP method has been successfully employed to obtain porous, homogeneous, stoichiometric $CuCrO_2$ powders. The powders are nanosized in nature and have a spherical shape with a delafossite structure. The crystalline structure has been confirmed by X-ray diffractometer and Raman spectroscopy. BET surface area measurements have shown that the pore structure has a surface area of 30.92 m^2/g.

Acknowledgements

This work was supported by the National Science Council (NSC-98-2218-E-027-004) and Much Fortune Technology Co., Ltd., Taiwan. We would like to express our gratitude to Prof. C. Su for BET measurements.

References

[1] R. Nagarajan, A.D. Draeseke, A.W. Sleight, J. Tate, J. Appl. Phys. 89 (2001) 8022–8025.
[2] T.W. Chiu, K. Tonooka, N. Kikuchi, Vacuum 83 (2009) 614–617.
[3] T.-W. Chiu, S.-W. Tsai, Y.-P. Wang, K.-H. Hsu, Ceram. Int., submitted for publication.
[4] S. Saadi, A. Bouguelia, M. Trari, Sol. Energy 80 (2006) 272–280.
[5] W. Ketir, A. Bouguelia, M. Trari, Water Air Soil Pollut. 199 (2009) 115–122.
[6] S. Kameoka, M. Okada, A.P. Tsai, Catal. Lett. 120 (2008) 252–256.
[7] Delafossite Type Oxide, Method for Manufacturing the Exhaust Gas Purification Catalyst, Japanese Patent No. 2008-156130.
[8] S. Zhou, X. Fang, Z. Deng, D. Li, W. Dong, R. Tao, G. Meng, T. Wang, Sens. Actuators B 143 (2009) 119–123.
[9] T. Okuda, Y. Beppu, Y. Fujii, T. Kishimoto, K. Uto, T. Onoe, N. Jufuku, S. Hidaka, N. Terada, S. Miyasaka, J. Phys.: Conf. Ser. 150 (2009), 042157-4.
[10] K. Hayashi, K. Sato, T. Nozaki, T. Kajitan, Jpn. J. Appl. Phys. 47 (2008) 59–63.
[11] K.T. Jacob, G.M. Kale, G.N.K. Iyengar, J. Mater. Sci. 21 (1986) 2753–2758.
[12] S.H. Lim, S. Desu, A.C. Rastogi, J. Phys. Chem. Solids 69 (2008) 2047–2056.
[13] S. Zhou, X. Fang, Z. Deng, D. Li, W. Dong, R. Tao, G. Meng, T. Wang, X. Zhu, J. Cryst. Growth 310 (2008) 5375–53749.
[14] W. Li, H. Cheng, J. Cent. South Univ. Technol. 14 (2007) 291–295.
[15] J. Shu, X. Zhu, T. Yi, Electrochim. Acta 54 (2009) 2795–2799.