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Preparation of delafossite $CuFeO_2$ coral-like powder using a self-combustion glycine nitrate process

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Abstract

This study employed a glycine nitrate process to prepare porous, stoichiometric, homogeneous $CuFeO_2$ powders without post-annealing treatment or ambient control. In this method, a precursor solution was prepared by mixing glycine with an aqueous solution of blended (Cu–Fe) metal–nitrates in their stoichiometric ratios. The glycine-mixed precursor solution was first heated in a beaker to evaporate excess water and form a viscous, bluish, and semi-transparent gel. The beaker was then covered with a metallic mesh, and the temperature increased slowly to 250 °C to auto-ignite the material. The combustion was self-sustaining and extremely rapid, producing gray powders. The powders showed a large surface area of 11.38 m^2/g, as determined according to BET surface area measurements. SEM observations of these powders confirmed their coral-like traits and porous structures.

Keywords: A. Powders: Chemical preparation; B. Porosity; C. Chemical properties; D. Transition metal oxides

1. Introduction

$CuFeO_2$ is a delafossite-type compound that has attracted much attention as a p-type transparent conductive oxide (TCO) used for several applications such as transparent diodes and solar cells [1–3]. Related studies on delafossite oxides are interested not only in examining the TCO properties but also in exploring their applications as photo catalysts for hydrogen evolution [4], removal of divalent metal ions [5], reduction of cadmium [6], magnetics [7], and thermoelectric devices [8].

One method for improving the catalysis efficiency is to decrease the size of the catalyst to increase the surface area and adsorption ability. Synthesizing $CuFeO_2$ powder can therefore be expected to improve the performance of catalytic applications, and controlling the valence state of Cu to 1+ and Fe to 3+ is the key to synthesize $CuFeO_2$ successfully. According to the phase diagram of the bulk Fe–Cu–O ternary system reported by Eatkov et al. [9], when CuO and Fe_2O_3 react in air, CuO and Fe_2O_3 favorably react to form spinel-type $CuFe_2O_4$ at 700 °C. Pure delafossite-type $CuFeO_2$ is converted from spinel-type $CuFe_2O_4$ with residual CuO above 900 °C. The chemical formulae are shown in (1) and (2):

$$2CuO + Fe_2O_3 \rightarrow CuFe_2O_4 + CuO \quad (1)$$

$$CuFe_2O_4 + CuO \rightarrow CuFeO_2 + 1/2O_2 \quad (2)$$

$CuFeO_2$ powder with a high surface area is difficult to prepare using solid state reactions and the traditional Pechini method. Using these methods to synthesize $CuFeO_2$ powder requires not only high-temperature heat treatment (as high as 900 °C) but also a noble-gas ambient. During high-temperature treatment, the spinel-type $CuFe_2O_4$ forms at approximately 700 °C and sinters into large-grain material before the $CuFe_2O_4$ reacts with residual CuO and releases O_2 to form $CuFeO_2$ at higher than 900 °C under an N_2 gas ambient. Synthesizing $CuFeO_2$ powder requires intermediate regrinding during calcination in an oxygen-free atmosphere, such as nitrogen gas [10].

Although the glycine nitrate process (GNP) is widely applied in synthesizing homogeneous, single, binary, and multicomponent oxide systems, it has not been employed to synthesize copper–iron solid solutions. Therefore, the goal of this investigation is to determine the utility and

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usefulness of GNP in producing $CuFeO_2$ powders with a high surface area. $CuFeO_2$, with a typical composition and a delafossite structure, was used in this study. This paper presents a discussion on the synthesis results and characterization of $CuFeO_2$ powders.

2. Experimental

2.1. Synthesis of $CuFeO_2$ powders

To compare the characteristics of $CuFeO_2$ powder prepared using a GNP method to those of traditionally prepared $CuFeO_2$ powder, $CuFeO_2$ powder was also prepared using a traditional solid state reaction method, in which Cu_2O and Fe_2O_3 commercial powders are mixed in stoichiometric quantities with ethanol in a plastic jar containing zirconia balls and milled for 24 h. In this study, the resulting slurries were dried at 70 °C in an oven, and the dried powders were treated in a N_2 atmosphere at 900 °C for 12 h.

2.2. GNP method

To synthesize $CuFeO_2$ powders using the GNP method, copper nitrate [$Cu(NO_3)_2 \cdot 3H_2O$], iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$], and glycine were used as starting reagents. The molar ratio of copper nitrate to chromium nitrate was fixed at 1:1, whereas various glycine to nitrate molar ratios of 1:1.4 and 1:1.9 were used. After stirring at 80 °C for 2 h, the precursor solution was heated to 100 °C to evaporate the water, causing the solution to become dry 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 approximately 200 °C. The material ignited spontaneously, resulting in a gray mass. During ignition, the beaker was covered with a fine-mesh sieve to prevent the powder from discharging from the beaker.

2.3. Physico-chemical characterization

The $CuFeO_2$ powders were characterized using various techniques: X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal gravity analysis (TGA), and BET surface area measurement. The crystalline phase analysis of the as-dried powders was performed using XRD (Rigaku DMAX2200) with Cu Kα radiation. The crystalline phase was determined using Raman spectroscopy (Dong Woo 500i). The SEM (HITACHI S-4700) technique was used to determine the morphology and characteristics of the agglomerates in the as-dried powders. The thermal behaviors of $CuFeO_2$ powder in air and nitrogen (3 N) flow were investigated using TGA. The standard BET (Micromeritics Gemini V) method was applied to measure the surface area.

3. Results and discussion

Although previous studies have reported that the GNP method is capable of producing single, binary, and multicomponent oxides with more favorable homogeneity, the method has not previously been used to synthesize $CuFeO_2$ powders. Therefore, the aim of this investigation was to determine the utility of this method in synthesizing solid-solution $CuFeO_2$ powders and to study the characteristics of the powders obtained by using this method. $CuFeO_2$ with a typical composition was used because of its many applications, as described in Section 1. However, Cu ions and Fe ions tend to easily form spinel-type $CuFe_2O_4$, whose stability is up to 1200 °C. Normally, for the synthesis of $CuFeO_2$ the reduced ambient such as nitrogen atmosphere was required. This makes it difficult to obtain delafossite-type $CuFeO_2$, thus hindering the synthesis of delafossite-phase compounds in air using the GNP method. Therefore, the fuel/cation ratio is a critical factor in synthesizing $CuFeO_2$ using the GNP method.

Fig. 1 presents the XRD patterns of the $CuFeO_2$ powders prepared using solid state reaction and the GNP method with various GN ratios. The XRD patterns of the Cu–Fe–O powders prepared using the GNP method with GN = 1.4–1.9 show main reflections of a typical delafossite structure of $CuFeO_2$, corresponding respectively to the [006] and [110] planes and indicating that the main compound of the powder prepared using the GNP method

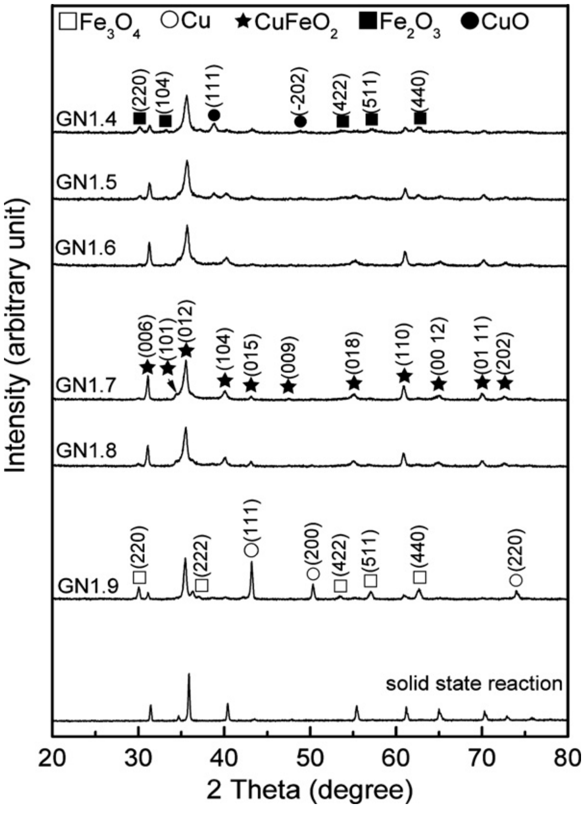

Fig. 1. XRD patterns of $CuFeO_2$ powder prepared using GNP method with various GN ratio and solid state reaction.

is delafossite $CuFeO_2$. However, the GN ratio is less than 1.5 the second phases of CuO and Fe_2O_3 were observed. When the GN ratio was larger than 1.8, the second phases of Cu and Fe_3O_4 were observed. As mentioned in Section 1, the most crucial step in synthesizing delafossite-type $CuFeO_2$ powder is controlling the valence state of Cu to 1+ and Fe to 3+ and the amount of glycine controlled the partially reduction atmosphere at its combustion. When the GN ratio was less than 1.6, the Cu 2+ to 1+ could not com be reduced completely due to lack of glycine and obtain the second phase of CuO. Conversely, too much glycine made the reduction atmosphere too strong and made Cu ions and Fe ions were over reduced to Cu 0 and Fe 2+, respectively. As shown in the XRD chart, even the process window is extremely narrow. The pure-phase $CuFeO_2$ powder was successfully synthesized using the GNP method (GN = 1.7) without additional heat treatment or ambient control.

The structure of the as-self combusted $CuFeO_2$ powder was further confirmed using Raman spectroscopy. The Raman spectra of both $CuFeO_2$ powders, prepared using GNP and solid state reaction, show two main peaks of a delafossite structure of $CuFeO_2$, corresponding to 338 cm^{-1} and 687 cm^{-1} (Fig. 2). The peak at 478 cm^{-1} is attributed to plasma. The Raman spectroscopy results are consistent with those of relevant literature [11].

Fig. 3 shows an SEM photograph of the $CuFeO_2$ powder prepared using the GNP method and solid state reaction. The as-combusted $CuFeO_2$ powder prepared using the GNP method exhibited a porous structure with a coral-like shape. By contrast, the $CuFeO_2$ powder prepared using solid state reaction shows sintered large grain. SEM observations of the as-prepared GNP material showed a macroporous microstructure of the material. The crystalline size of the $CuFeO_2$ nanograin was approximately 32 nm, as calculated using Scherrer's equation.

Table 1 lists the BET surface areas of the $CuFeO_2$ prepared using solid state reaction and the GNP method. BET surface area measurements revealed a surface area of 11.38 m^2/g for the as-self combusted $CuFeO_2$ powder. This is nearly 20 times larger than that of the $CuFeO_2$ powder prepared using solid state reaction with intermittent grindings (0.57 m^2/g).

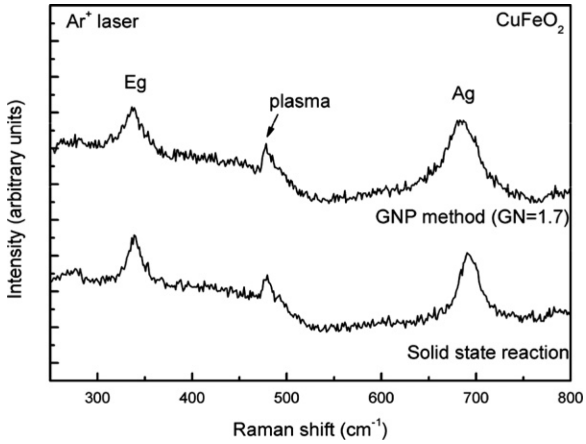

Fig. 2. Raman spectra of $CuFeO_2$ prepared using GNP method and solid state reaction measured at room temperature.

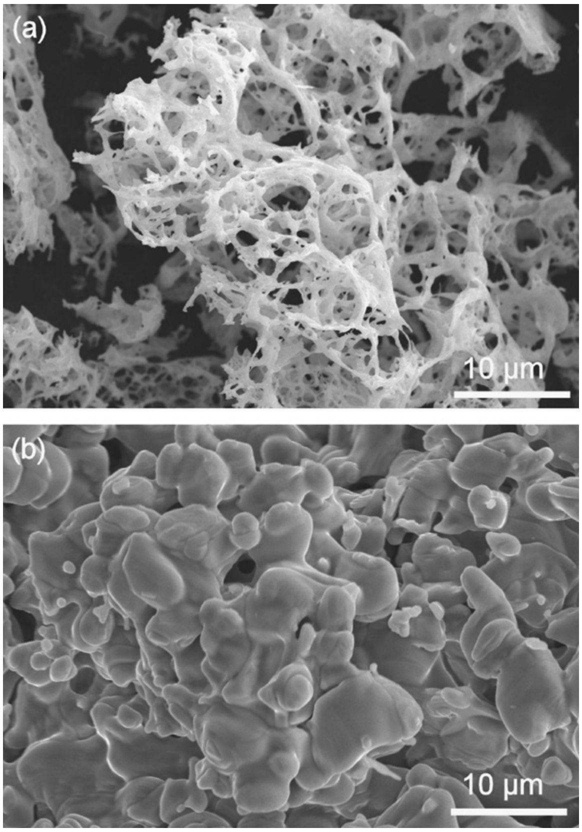

Fig. 3. SEM images of $CuFeO_2$ powder prepared using (a) GNP method (GN = 1.7) and (b) solid state reaction.

Table 1
BET surface area of $CuFeO_2$ powder.

Preparation method	Surface area (m^2/g)	[Ref]
Solid state reaction	0.045	This study
GNP	11.38	This study
Solid state reaction with grinding	0.57	[10]

The thermal behavior of the $CuFeO_2$ GNP powders was examined using TGA in air and N_2 flow, and the compound was confirmed using XRD. As shown in Fig. 4. Both TGA curves measured in air and N_2 flow show weight loss before 200 °C, indicating that the desorption of water and weight increased after 400 °C in air and after 500 °C in N_2 flow. Based on the XRD patterns shown in Fig. 5, O_2 was intercalated into $CuFeO_2$ to form $CuFe_2O_4$ and CuO, even at a lower O_2 partial pressure in 3 N N_2 flow. In N_2 flow, the $CuFeO_2$ powder shows reversibility of a delafossite-to-spinel phase transition at 500 °C and a spinel-to-delafossite phase transition at 800 °C. However, in air, the delafossite-to-spinel phase transition did not occur. This phenomenon is consistent

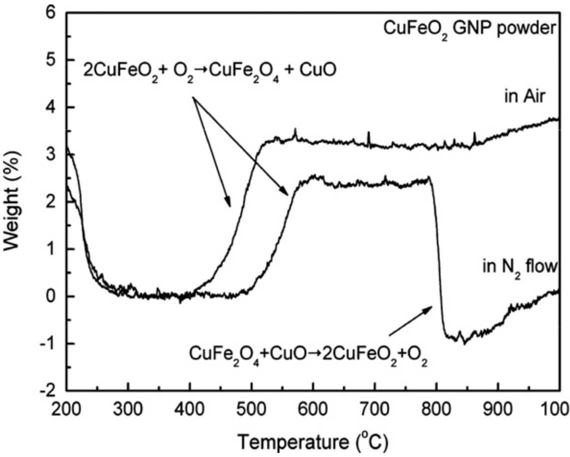

Fig. 4. TGA analysis of $CuFeO_2$ GNP powder in air and N_2 flow.

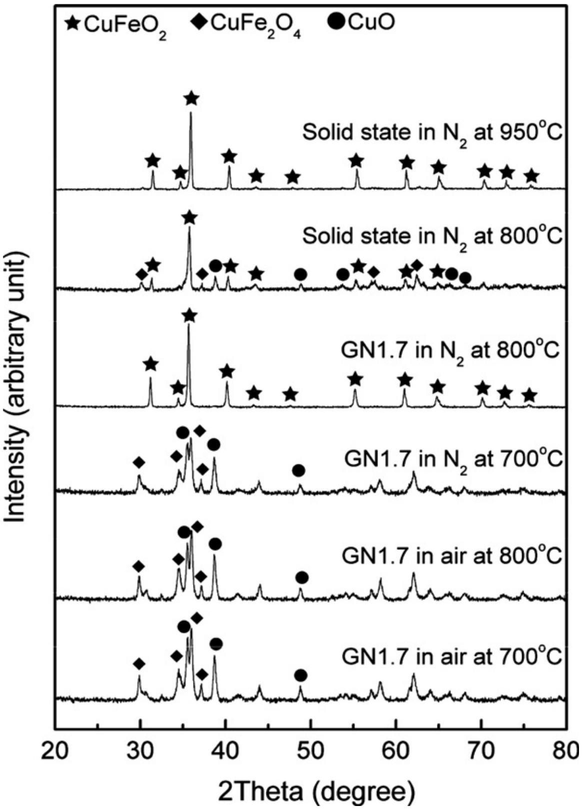

Fig. 5. XRD patterns of $CuFeO_2$ powder prepared using GNP and solid state reaction post-heat treatment at various temperatures in air and N_2 flow.

with Lalanne [10] and shows the reason why $CuFeO_2$ cannot synthesize in air. However, we demonstrated that $CuFeO_2$ power could be prepared in air without further heat treatment using the GNP method.

Therefore, all of these characterization results confirm that the GNP method creates macroporous, stoichiometric, homogeneous $CuFeO_2$ powders. An additional study to control the pore structure by varying the preparation parameters during GNP synthesis, as well as to understand the role of glycine in producing a porous microstructure, is currently underway. Furthermore, the catalytic efficiency of nanosized $CuFeO_2$ powder will also be investigated.

4. Conclusion

This study successfully employed the GNP method to obtain porous, homogeneous, stoichiometric $CuFeO_2$ powders. The powders show a coral-like structure. The crystalline structure was confirmed using an X-ray diffractometer and Raman spectroscopy. BET surface area measurements showed that the pore structure has a surface area of 11.38 m^2/g.

Acknowledgments

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