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# Morphology of CuO through precipitation process under 2.45 GHz microwave irradiation

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**Abstract**

The morphology of CuO powders formed by a homogeneous precipitation process from aqueous copper precursor complex was investigated. The effect of 2.45 GHz microwave irradiation appeared in the characteristic morphology of the CuO microcrystal with comparison of an ordinal synthesis process. The crystallographic orientation of CuO microcrystals in the particle was examined by HRTEM. Using microwave irradiation, it was demonstrated that the morphology of the particles was kept through the decomposition of the precursor. Also the rapid transformation of a precursor to CuO in aqueous solution under microwave irradiation condition was discussed.


*Keywords:* Microwave processing; Powders-chemical preparation; Electron microscopy; Microstructure-final; Structural applications

## 1. Introduction

Microwave energy is an important source that able to heat materials in a very short period as compared with conventional heat process. If some components in a chemical reaction system strongly could absorb microwaves, the resultant heat would be used to drive a reaction. The feature is expected to develop a new material processing, and lead to unique properties of materials.

Optimum morphology and size of powders are required for raw materials of ceramics, catalysis and thin films. Recently, CuO particles such as fiber, rod and nano-size particles have been prepared by using an aqueous solution technique that is commercially low-cost method. Yang and Gao[1] reported a possibility of synthesizing various morphologies of CuO particles. Zhang et al.[2] and Chen et al.[3] reported a shuttle-shape and leaf-shape of CuO particles were synthesized in an aqueous solution with surfactant. Leung et al.[4] demonstrated to prepare CuO particles by a homogeneous precipitation method using hexamethylenetetramine (HMT). Linag et al.,[5] Wang et al.,[6] Xia et al.[7] reported a synthesizing process of nano-size CuO particles using a microwave irradiation. Keyson et al.[8,9] showed the synthesizing of flower-shape CuO nano-structure by domestic hydrothermal microwave method. There are various kind of solvents are used to synthesize CuO particles, but the effect of microwave irradiation is less well understood.

In this paper, the formation and characterization of CuO particles under microwave irradiation at atmosphere pressure are investigated. The reaction system of CuO synthesis was chosen aqueous system that is convenient to compare the effect the condition with and without microwave on the morphology of particles. Also, we discuss a unique microstructure and crystallographic orientation of CuO crystallites by TEM, and estimate the effects of microwave irradiation on crystal growth and agglomeration.

## 2. Experimental procedure

The copper nitrate $Cu(NO_3)_2{\cdot}3H_2O$ and hexamethylenetetramine HMT ($C_6H_{12}N_4$) were dissolved in distilled water with a concentration of 0.05 mol/l and 0.3 mol/l, respectively. An emerald color precipitate occurred immediately when the two solutions mixed each other. The synthesizing of precursor was carried out with the mixing ratio of 1:6 (molar ratio) of $Cu(NO_3)_2{\cdot}3H_2O$ to HMT. The copper precursor complex solution was directly treated with a microwave irradiation. In the conventional heat process, a mantle heater was used to heat up for synthesizing a CuO microcrystal. The temperature of the copper precursor solution was kept at 95 °C and in the duration time of the heat treatment period to 60 min. The microwave

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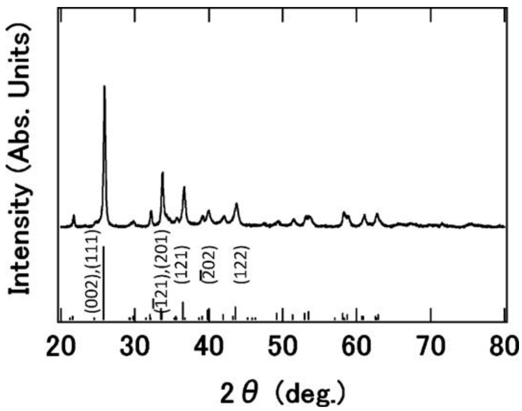


Fig. 1. XRD pattern of the copper precursor synthesized by a homogeneous precipitation.

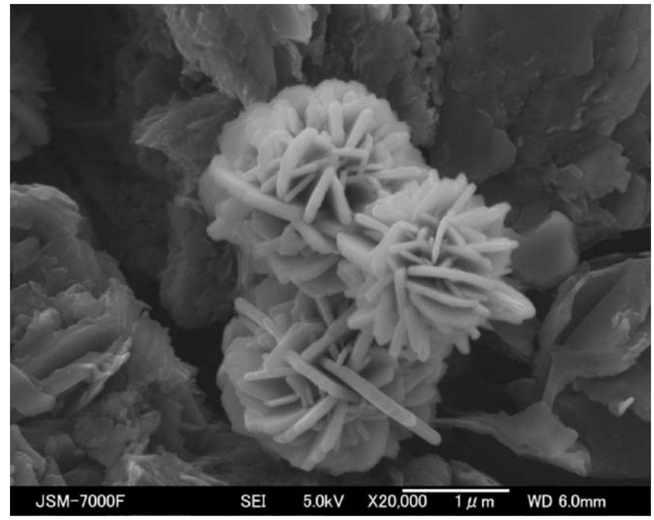


Fig. 2. SEM images of copper precursor particles synthesized by a homogeneous precipitation.

irradiation was carried out in a multimode cavity microwave oven with thermocouple located on the center point of the oven and magnetic stirrer. The maximum power of the magnetron generator was 700 W and the output power was controlled to keep the temperature of the solution. The obtained samples were washed with distilled water, and corrected by the filtration and finally dried at room temperature for 24 h.

The identification of crystal phase of the samples was using an X-ray diffractometer (XRD: Rigaku Rint 2000, Japan) with Cu Kα, and the morphology of the microcrystal was observed by a scanning electron microscope (SEM: JEOL JSM-7000F, Japan) and a high-resolution transmission electron microscope (HRTEM: Hitachi HF-2000, Japan).

## 3. Results and discussion

### 3.1. Synthesis of copper precursor

The XRD pattern of the obtained copper precursor is identical to the single-phase monoclinic copper hydronitrate $Cu_2(OH)_3(NO_3)$ and the diffraction data showed good agreement to the intensities in JSPDS 75-1779 as in Fig. 1. A crystal structure of the copper hydronitrate is analogous to the layered double hydroxide family, and their details have been examined by Guillou et al.[10] The morphology of copper hydronitrate precursor synthesized at room temperature is shown in Fig. 2. The tabular plates are aggregating and resulted in forming a secondary particle with flower-shape. The thickness of tabular plates is 50–100 nm and the mean particle size is approximately 1.5 μm. This morphology is different from another precipitation method using sodium hydroxide, instead of HMT, as reported by Henrist et al.[11]

### 3.2. Synthesis of CuO from precursor by heat treatment

Fig. 3 shows the XRD patterns of the CuO microcrystals under different heat treatment using (a) mantle heater at 95 °C for 60 min and (b) microwave irradiation at 95 °C for 60 min. Both of the patterns can be indexed using the single-phase monoclinic CuO (JSPDS 80-1917). No other peak corresponding to copper

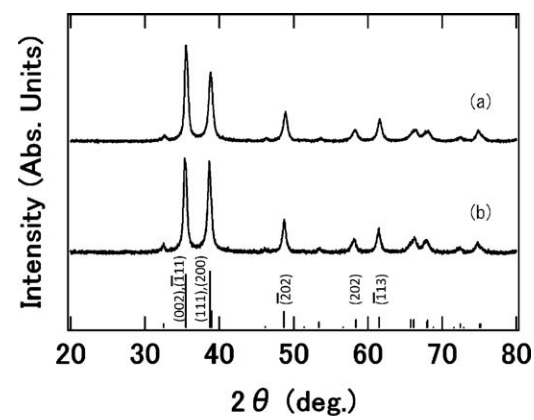


Fig. 3. XRD patterns of the synthesized CuO microcrystals using (a) mantle heater and (b) microwave irradiation.

precursor is recognized in Fig. 3. Fig. 4 shows the XRD patterns of the microwave irradiated specimen for (a) 0 min, (b) 10 min, (c) 30 min and (d) 60 min. Fig. 4(b) shows the co-existence both

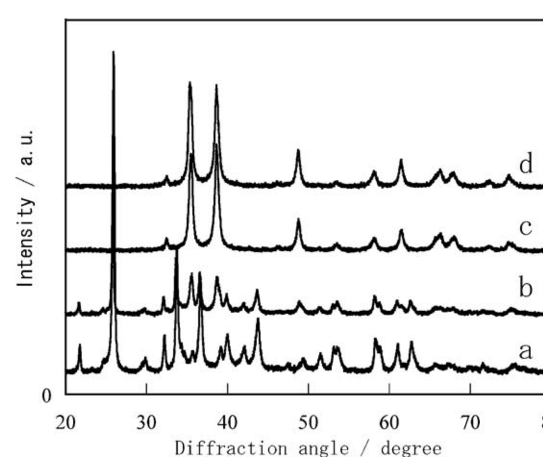


Fig. 4. XRD patterns of microwave irradiated specimen for (a) 0 min, (b) 10 min, (c) 30 min and (d) 60 min at 95 °C.

of the copper precursor and the monoclinic CuO phase clearly. On the other hands, it was not clearly confirmed the co-existence the two kind phases. These results show the difference of the mechanism of the monoclinic CuO microcrystals.

### 3.3. Morphology of CuO microcrystals

The SEM images of the CuO microcrystals synthesized by a mantle heater and a microwave irradiation are shown in Fig. 5(a) and (b), respectively. The leaf-like CuO microcrystals heated by mantle heater have 0.5–2 μm size, and have different morphology from starting powders of plate-aggregated copper precursor. The CuO particles with the star-shape morphology are found in Fig. 5(b), when the precursor is only treated by microwave irradiation. The mean size of the star-shaped particles is 1.2 μm, that is similar to the copper precursors, and CuO microcrystal with the star-shape morphology seems to be reflected by the morphology of starting precursor.

The TEM image and selected area electron diffraction (SAED) of a leaf-like CuO microcrystal synthesized by mantle

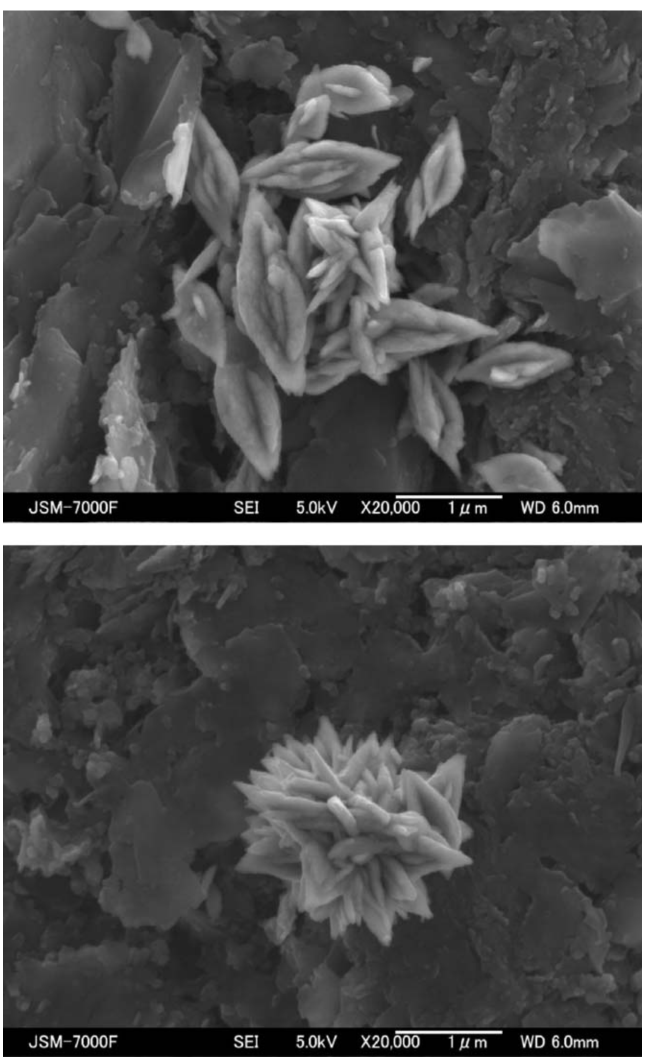


Fig. 5. SEM images of the synthesized CuO microcrystals using (a) mantle heater and (b) microwave irradiation.

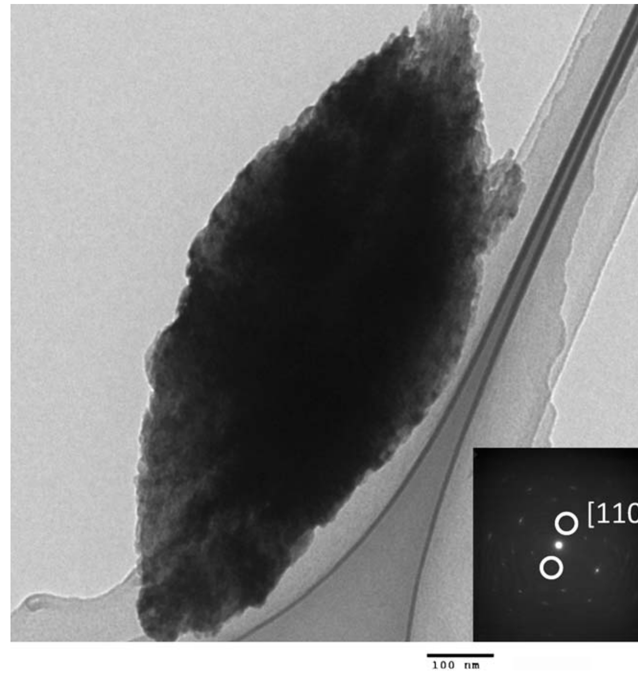


Fig. 6. TEM image and SAED patterns of the leaf-shaped CuO microcrystals synthesized by mantle heater heat treatment.

heater are shown in Fig. 6. From the analysis of SAED pattern of Fig. 6(b), the observed diffraction patterns are confirmed as the monoclinic CuO structure as well as the XRD patterns. Also, it suggests that the leaf-shape morphology was formed along the [1 1 0] axis. This structure is similar to that of smaller leaf-like CuO particles reported by Zhang et al.[2] According to their investigation, the nano-size rods, grown in a solution, arrange to aggregate one another, and finally form leaf-like morphology. In our process, Cu species can solve slowly into a solution from the copper precursor, and contribute to the growth of the larger particles by heat treatment using mantle heater.

Star-shaped CuO microcrystal synthesized by microwave irradiation are investigated by HRTEM as shown in Fig. 7. The lattice fringes in this image illustrate the crystallographic orientation of CuO microcrystal. The interplanar distance are estimated to be 0.270, 0.253, and 0.252 nm, which correspond to the (−1 1 0), (−1 1 1), and (0 0 2) planes of monoclinic CuO. The relationship between the crystallographic orientation and morphology reveals that the projection direction of the image is [−1 1 0] and the growth direction of a CuO microcrystal is along the [−1 1 0] and [−1 1 1] directions.

### 3.4. Chemical reaction and crystallographic relation under microwave irradiation

The decomposition of $Cu_2(OH)_3(NO_3)$ in ambient atmosphere has been investigated using thermal analysis. The thermal decomposition and subsequent conversion into copper oxide takes place in single step as following equation[11]:

$$Cu_2(OH)_3(NO_3) \rightarrow 2CuO + HNO_3(g) + H_2O(g). \quad (1)$$

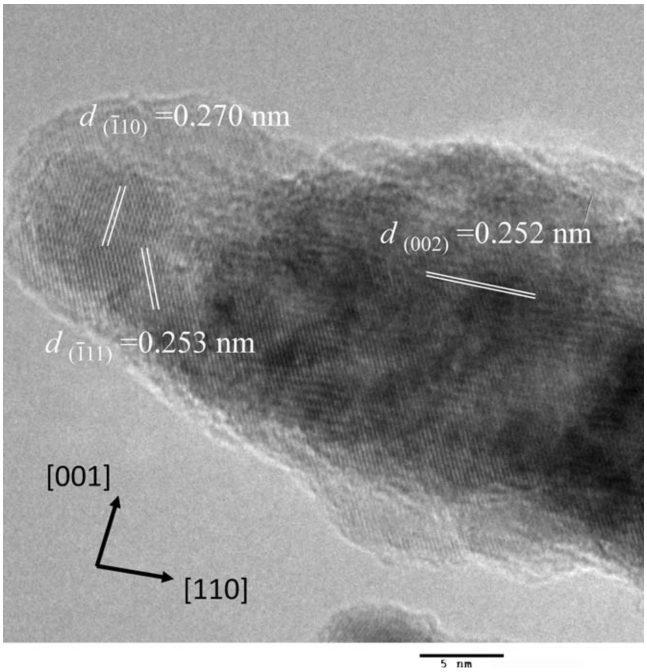


Fig. 7. [−1 1 0] projection of HRTEM image for CuO microcrystal synthesized by microwave irradiation.

The dissociations of $HNO_3$ and $H_2O$ are taken place together at 250 °C. In this work, since the thermal treatments of copper precursor carried out in the solution, the decomposition Eq. (1) will not take place in single step as in air. The leaf-like CuO microcrystal consists of nano-size rods that are grown in the copper solution using a mantle heater. Therefore, once the copper precursors solved into solutions, and then the nano-size CuO rods were grown and aggregated to leaf-shape.

Fig. 8 shows the schematic drawing of the crystal directions of the CuO microcrystal needle observed in Fig. 7 (Fig. 8(a)) and the copper precursor that corresponding to the same position (Fig. 8(b)). The edge of the microcrystal are made by $(1\,0\,0)_{Cu_2(OH)_3(NO_3)}$ and $(2\,1\,0)_{Cu_2(OH)_3(NO_3)}$ plane as shown in Fig. 8(a), and which are also corresponding to $(0\,0\,1)_{CuO}$ and $(1\,1\,4)_{CuO}$ plane as shown in Fig. 8(b), respectively. This orientation was proposed by Auffrédic et al. as the hypothetical crystallographic relation between $Cu_2(OH)_3(NO_3)$ and their decompositions.[12] The supposed relation can be described as:

$$[1\,0\,0]_{Cu_2(OH)_3(NO_3)}//[1\,1\,0]_{CuO}$$

$$(1\,0\,0)_{Cu_2(OH)_3(NO_3)}//(1\,1\,0)_{CuO}$$

If the $NO^{3-}$ and $OH^-$ anions are eliminated from $Cu_2(OH)_3(NO_3)$ without the destruction of the lattice, the flat $CuO_4$ plates that are similar to the monoclinic CuO structure are remained. The schematic in Fig. 8 suggests that the framework of the precursor is kept even in the decomposition and the reformation of copper precursor form planer shape to needle like shape.

Under the microwave irradiation, the precursor particles are heated directly and the temperature of the particles should increase rapidly at its inner part. The decomposition reaction will take place in the core of plate-aggregated particle and the transformation from $Cu_2(OH)_3(NO_3)$ to CuO extend from the inner part to the outside of a particle. Moreover, since CuO has relatively higher microwave absorption ratio compared with other components, the transformation progress goes very rapidly. During this transformation progress, the plate-shaped $Cu_2(OH)_3(NO_3)$ single crystal was split to several direction because of the strain of transformation. This process resulted in forming star-shaped particles from flower-shaped precursors. This unique and rapid process resulted in the formation of star-shaped CuO particle, which is not observed in the conventional heat treatment method.

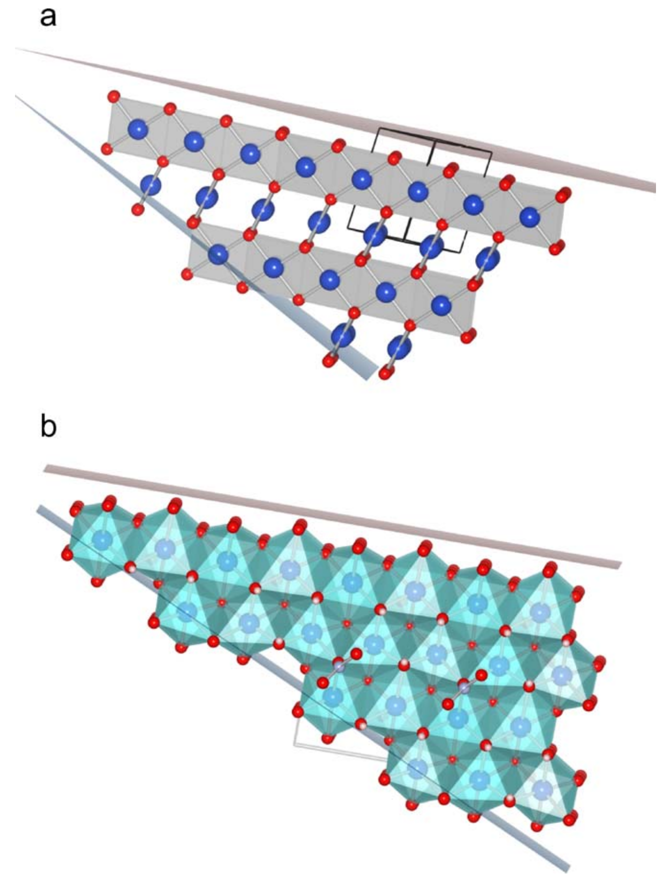


Fig. 8. Schematic drawings of a crystal directions for (a) the monoclinic CuO corresponding to Fig. 7 and (b) the copper precursor that corresponding to the same position.

## 4. Conclusions

CuO particles were synthesized using two heat treatment processes for precursor particles prepared by a homogeneous precipitation method. By SEM observation, the precursors were confirmed to form flower-shaped particles. CuO particles were synthesized at 95 °C using HMT solutions. The morphology of CuO particles was characterized by leaf-shape that was observed for a mantle heater process, and star-shape observed for microwave irradiation process. By analyzing of the crystallographic relationship between copper precursor and CuO, the direct transformation process of the precursor to

CuO was experimentally suggested under microwave irradiation method.

## Acknowledgments

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