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Special fractal growth of dendrite copper using a hydrothermal method

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ABSTRACT

Special fractal dendrite Cu nanostructures have been synthesized through a simple hydrothermal method, and the effects of the volume ratio between glycerol and water and the concentration of H_3PO_3 on the morphologies of dendrite Cu have been studied in detail. The Field emission scanning electron microscopy (FESEM), Transmission electron microscopy (TEM) and X-ray diffraction (XRD) have been used to characterize these Cu products. The results indicate that rhombic diamond and different morphologies of fractal dendrite were prepared because of the accumulation of Cu nuclei based on the diffusion-limited aggregation (DLA) and the nucleation-limited aggregation (NLA) model. Fortunately, symmetrical leaf-like dendrite Cu nanostructures different from Cu dendrites reported before have been obtained. Additionally, an explanation for the growth of fractal dendrite Cu has been discussed carefully.

1. Introduction

Recently, the synthesis of metal nanostructures has been an issue due to their important role in optoelectronics, paste, catalyst, and biological and chemical sensors [1–5]. In general, shape-, size-, composition-, crystalline-, and structure-dependent [6–8] properties of metal nanostructures determine their application, thus metal nanostructures with well-defined morphologies have become the focus of considerable research. In particular, the study of dendrite metal nanostructures with stem and branches has attracted great interests because of their novel properties and the relation to fractal growth [17], which has been reported by several research groups [9–12].

Among all metals, dendrite Cu has been focused in experimental and theory aspects [13–16] due to its excellent properties of high electric and thermal conductivity and an important role in electrochemical, chemical and biological sensor [15,16]. Until now, the widely used approaches for the synthesis of dendrite Cu include electroless deposition, electrochemical and electrodeposition [18–21]. However, these methods are complicated and expensive. In this paper, high yield dendrite Cu are obtained at a relatively low temperature of 120 °C using a simple hydrothermal method without the immersion of metal foil. Moreover, the influences of the ratio of glycerol and water and the concentration of H_3PO_3 on the morphologies of dendrite Cu are carefully discussed.

2. Experimental

2.1. Materials and methods

The chemical reagents used are of analytical grade without further purification. In a typical synthesis experimental procedure, 20 ml glycerol was dissolved in 45 ml distilled water, followed by the addition of 0.5 g of $CuSO_4 \cdot 5H_2O$, 0.047 g of Sodium dodecyl benzene sulfonate (SDBS) and 16.2 g of NaOH to form a dark-blue solution. Subsequently, 0.7 g of H_3PO_3 was introduced into the above mixed solution with a rapid stirring. Then, the resultant mixture solution was transferred into a 100 mL Teflon reaction kettle and heated at 120 °C for 18 h. After being cooled down the room temperature naturally, the products were washed with deionized water and dried in traditional vacuum drying oven. To investigate the influence of the amount of reagent on the morphology of Cu products, a series of experiments were conducted on the volume ratio of glycerol and water of 0.1, 0.3, 0.6 and 1.2 and the corresponding concentration of H_3PO_3 of 0.015, 0.030, 0.060 and 0.300 M, respectively.

2.2. Characterization

After 5-Cycle purification by alcohol and oven dry, the average weight of serial as-obtained Cu was up to 200 mg, and the output rate of Cu was above 60%. The images of series of samples were taken from a Hatachi S-4700 field emission scanning electron microscopy (FESEM) at an accelerating voltage of 10 kV. Small droplets of the diluted (by ethanol) suspension of samples were

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placed on copper grids coated with amorphous carbon film, and they were observed by transmission electron microscopy (TEM, JEOL-2010EX). The selected area electron diffraction (SAED) was used for the structural analysis. To understand the structure, XRD patterns were recorded with an X-ray diffractometer (D8, ADVANCE) using Cu $K\alpha$ radiation at 40 kV and 40 mA.

3. Results and discussion

The influence of the volume ratio of glycerol and water on the morphology of the products is surveyed. Fig. 1 shows the FESEM images of Cu products prepared from different volume ratios between glycerol and water. When the ratio is 0.1 and 0.3,

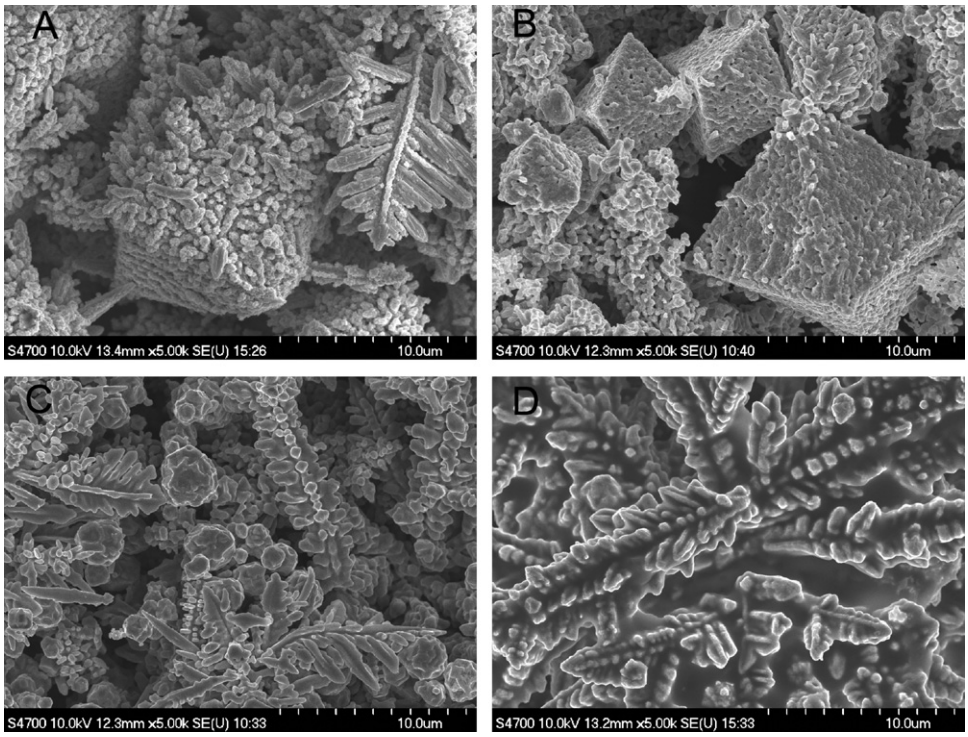

Fig. 1. SEM images of the morphology of products prepared at different volume ratios of glycerol and water: (A) 0.1, (B) 0.3, (C) 0.6 AND (D) 1.2.

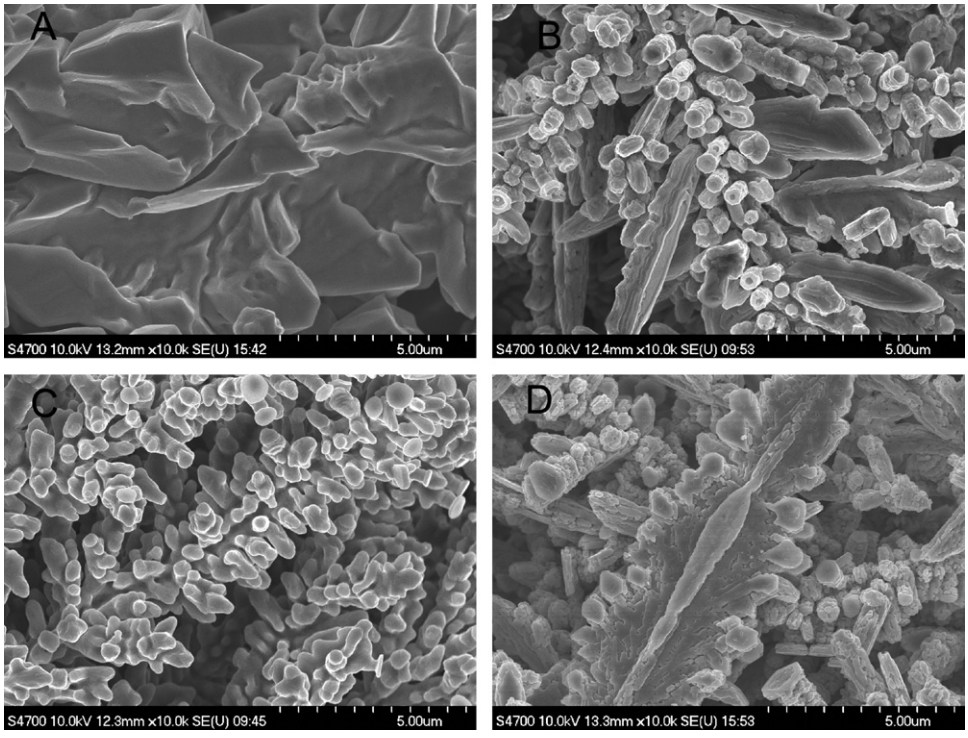

Fig. 2. SEM images of the morphology of products prepared from different concentrations of H_3PO_3: (A) 0.015 M, (B) 0.030 M, (C) 0.060 M and (D) 0.300 M.

rhombic-like clusters are produced due to the piling of irregular Cu nanoparticles, and rarely fractal Cu dendrites are observed. (Fig. 1A and B). Increasing the ratio to 0.6, spherical Cu and fractal dendrite Cu are the main products, as shown in Fig. 1C. When the ratio is further increased to 1.2, the products are dominated by uniform fractal dendrite Cu (Fig. 1D).

Fig. 2 shows the FESEM images of as-prepared products when the concentrations of H_3PO_3 increase from 0.015 to 0.3 M. At the low concentration of H_3PO_3, fractal dendrite is unobvious. The products exhibit folding plate-like structure with smooth surface as shown in Fig. 2A. As the concentration increases to 0.030 M, the morphology of the products becomes typical fractal dendrite with a straight stem and vertical branches because of the aggregation of leaves-like Cu and rod-like Cu (Fig. 2B). Further increasing the concentration to 0.06 M, some changes occur to the fractal dendrite, which comprises the curve stem and branches because of the aggregation of ununiform nanoparticles (Fig. 2C). While the concentration is up to 0.3 M, the complex dendrite Cu has developed into the big leaf (Fig. 2D).

The FESEM image in Fig. 3A demonstrates that the special products are composed of uniform and symmetrical dendrite structures assembled from rod-like stem with the mean length of $\sim$10 μm and branches with the diameter in the range of 0.5–1.5 μm. The rod-like branches parallel to each other, sloping on both sides of the stem at a fixed angle of 60°. The typical TEM image in Fig. 3B illustrates the symmetrical leaf-like dendrite Cu. The width of leaf-like Cu shrinks gradually along the stem, which indicates that the growth of leaf-like Cu starts with the blade. Inset of Fig. 3B is the SAED image presenting the single-crystal nature of dendrite Cu. The corresponding HRTEM images shown in Fig. 3C confirm the face-centered cubic structure of dendrite Cu based on the calculated fringe spacing of 0.207 nm matching with (1 1 1) planes.

The crystal structure of the products can be measured by X-ray diffraction (XRD). Fig. 4 gives the XRD image of as-generated dendrite Cu. Three diffraction peaks at 2θ=43.4°, 50.5° and 74.2° can be indexed to face-centered cubic Cu crystals, and 0.3605 nm of the lattice constant is in good accordance with reported data (JCPDS 04-0836, a=0.3615 nm [22]). Since there is no detection of apparent impurity peaks arising from CuO and Cu_2O, the dendrite Cu obtained is believed to be in high purity.

A possible explanation for the growth of fractal dendrite Cu is stated as follows: the formation of fractal dendrite nanostructures is controlled by the diffusion and nucleation process in none-quilibrium reactions based on the diffusion-limited aggregation (DLA) and the nucleation-limited aggregation (NLA) model [23–25]. The slow nucleation and diffusion rate caused by low concentration of H_3PO_3 leads to the shortage of Cu crystallite, which is unfavorable to the formation of fractal dendrite Cu. Additionally, the slow nucleation rate relative to the diffusion of Cu nuclei may not catch up with the growth speed of crystal, resulting in the fabrication of bulk crystal. As the concentration of H_3PO_3 increases, accelerating the nucleation and diffusion rates, Cu crystallites could join together to fabricate symmetrical dendrite structures through oriented attachment based on the diffusion-limited and nucleation-limited growth. However, while the nucleation and diffusion rates of Cu nuclei are too high, the aggregation of Cu crystallites could be mainly controlled by random diffusion instead of oriented attachment, which leads to the alterations of the detailed morphology of dendrite Cu. Simultaneously, glycerol in the reaction system exerts its action by coordinating with Cu^{2+} in $CuSO_4$ solution to form Cu^{2+}-glycerol complex, which is prior to its reduction. The effect of glycerol makes the controllable release of free Cu^{2+} in solution, and then manipulates the nucleation and diffusion rate of Cu nuclei.

4. Conclusion

In summary, symmetrical dendrite Cu with straight trunk and side branches paralleling with each other were achieved using a simple hydrothermal process. Based on the result of a series of experiments, it is concluded that by controlling $V_{glycerol/water}$ in the range of 0.6–1.2 and the concentration of H_3PO_3 in the range of 0.06–0.3 M, uniform dendrite Cu can be synthesized.

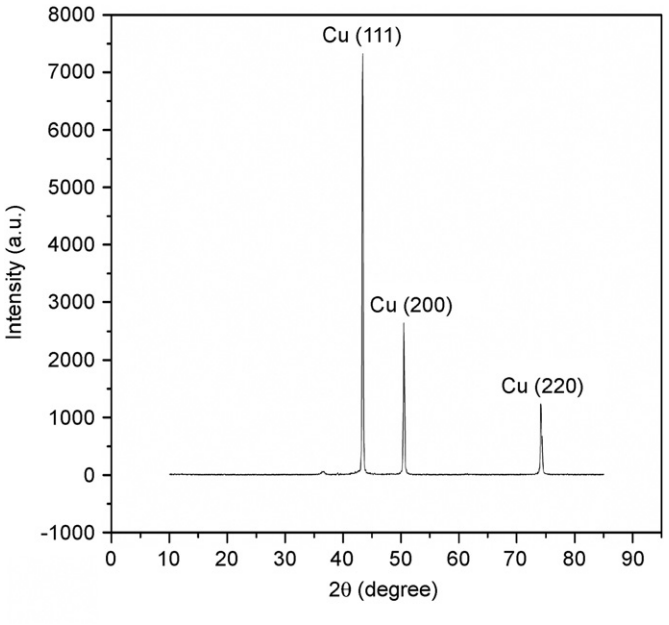

Fig. 4. XRD of dentritic Cu prepared at 0.2 M H_3PO_3, 0.8 of ratio of glycerol and water.

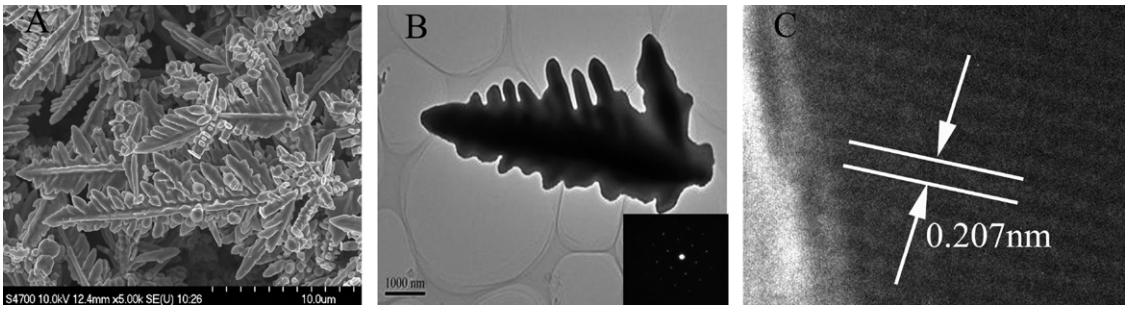

Fig. 3. (A, B) FESEM, (C) TEM (inset is SAED pattern of dendrite Cu), (D) HRTEM images of products prepared from the solution containing 0.2 M H_3PO_3, 0.8 of ratio of glycerol and water.

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