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THE EFFECT OF ANNEALING ON THE MORPHOLOGY OF COPPER DENDRITE STRUCTURE

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Copper structures have been synthesized by chemical method and annealed at 200, 400 and 600ºC. X-ray diffraction pattern shows the formation of Cu with cubic structure. SEM image shows the formation of dendrite, cactus, honey comb and tubular like Cu structures. The annealing temperature is found to affect the structure of the prepared Cu particles. The compositional analysis result shows that Cu is present in the sample.

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1. Introduction

The morphology of materials is of great interest in materials science due to their importance in basic scientific research and potential technological applications [1]. Copper crystals with different structures, such as nanoflowers [2], dendrites [3], nanofibers [4] and nanorods [5] have been reported by researchers in the past few decades. Understanding the shape-guiding process and their growth mechanism of dendrites and hierarchical structures will lead to progress the system to yield the building blocks with a desired structure, which have many applications due to their novel physiochemical properties [6]. Copper has attracted much interest because of its wide role in biomedical, electronics, catalysts, resins and thermal conducting applications [7]. In biomedical field, the dietary supplementation of copper in nano and microsize improves the growth performance in mammals [8]. Nanostructure copper has been prepared by different methods such as, chemical reduction in aqueous solutions [9, 10], colloidal synthesis with reduction and extraction steps [11], evaporation and condensation of metal vapor on a cold surface [12], electrochemical methods [13], hydrothermal process [14] and laser ablation [15]. Among these methods chemical method has many advantages such as mild reaction conditions, less energy consumption, eco friendly, simple equipment and offers a large number of variable factors to control the various structures of the particle. In the present work dendrite like structured copper particles have been synthesized, then it was annealed at different temperatures where by cactus, honey comb and tubular like structured copper particles were obtained and their morphology has been studied in detail.

2. Experimental

Copper dendrite like structures has been prepared by chemical method. Copper nitrate [$Cu(NO_3)_2$] has been used as a copper precursor and sodium borohydride as a reducing agent and poly vinly pyrrolidone (PVP) as a capping reagent. 50 mg of copper nitrate was added to 10 ml of PVP and the mixer was stirred for about 20 minutes at room temperature. Freshly prepared sodium borohydride (50mg) was dissolved in 10ml water. Then the solution was added drop-wise to the copper nitrate and PVP mixer solution. Now the blue coloured mixture turns into brick red, the

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stirring is continued until the reddish colour changes into black. The change in colour indicates the formation of metal particles in the solution and then the solution is stirred for 6 hours at room temperature. After 6 hours, the suspension was centrifuged and washed with water and ethanol several times. The samples were then suspended in ethanol and then allowed to age for 2 hours without stirring. After this, the samples were dried at room temperature and also annealed at 200°C, 400°C and 600°C for one hour.

X-ray diffraction studies have been carried out on the copper particles using PANalytical x-ray diffractometer and surface morphology of the samples has been studied using scanning electron microscope (JEOL JSMS 800-V). Transmission electron microscope (TEM) and energy dispersive x-ray analysis (EDAX) of the samples has been carried out using a JEOL JEM2100 microscope.

3. Results and discussion

Fig. 1 shows the XRD pattern of the as prepared, 200°C, 400°C and 600°C annealed copper dendrites. The diffraction peaks at 2θ (degrees) values 43.49°, 50.64° and 73.32° are respectively indexed as the peaks corresponding to the (111), (200) and (220) planes of copper. All the diffraction peaks in the 2θ range measured corresponds to the face-centered cubic structure of copper with lattice constant a = 3.62Å and is in good agreement with the standard data card (JCPDS Card No. 85-1326) value. The diffraction peak of oxide phase has not been detected, indicating that pure Cuhas been obtained. The sharpness of the diffraction peaks suggests that the product is well crystallized. But when the prepared copper particles are annealed at a temperature of 600°C it exhibits one extra peak at 38.49° and this corresponds to the (311) planes of Cu.

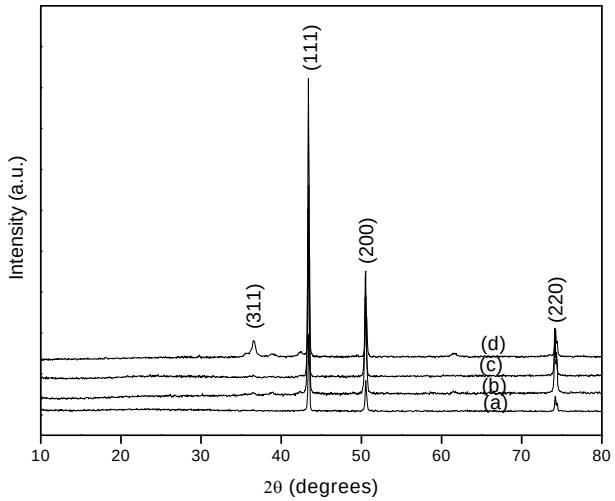

Fig. 2. X-ray diffraction pattern of Copper dendrite like structure (a) as prepared, (b) 200°C, (c) 400°C and (d) 600°C annealed samples.

Fig. 2 (a, b) shows the SEM image of the as-synthesized copper particles. It is clearly seen from the image that the obtained sample at room temperature has a dendrite like structure. The overall morphology observed with low magnification (Fig. 2a) clearly shows that the copper particles having many multi-armed petal like structures arranged along an axis called trunk. The length of the petal is about 5 μm. The structure shows that the many short separated petals are grown from a central trunk and are arranged in a parallel manner on opposite sides. Where the growths occurs in the central axis, meanwhile the lower petal also gets developed and forms an inverted cone shape. The magnified image (Fig. 2b) shows that the trunks are less porous and have a width of about 4 μm. The structure shows that the petals with non porous and central trunk are swelled with a sponge structure as reported by Hu et al [16].

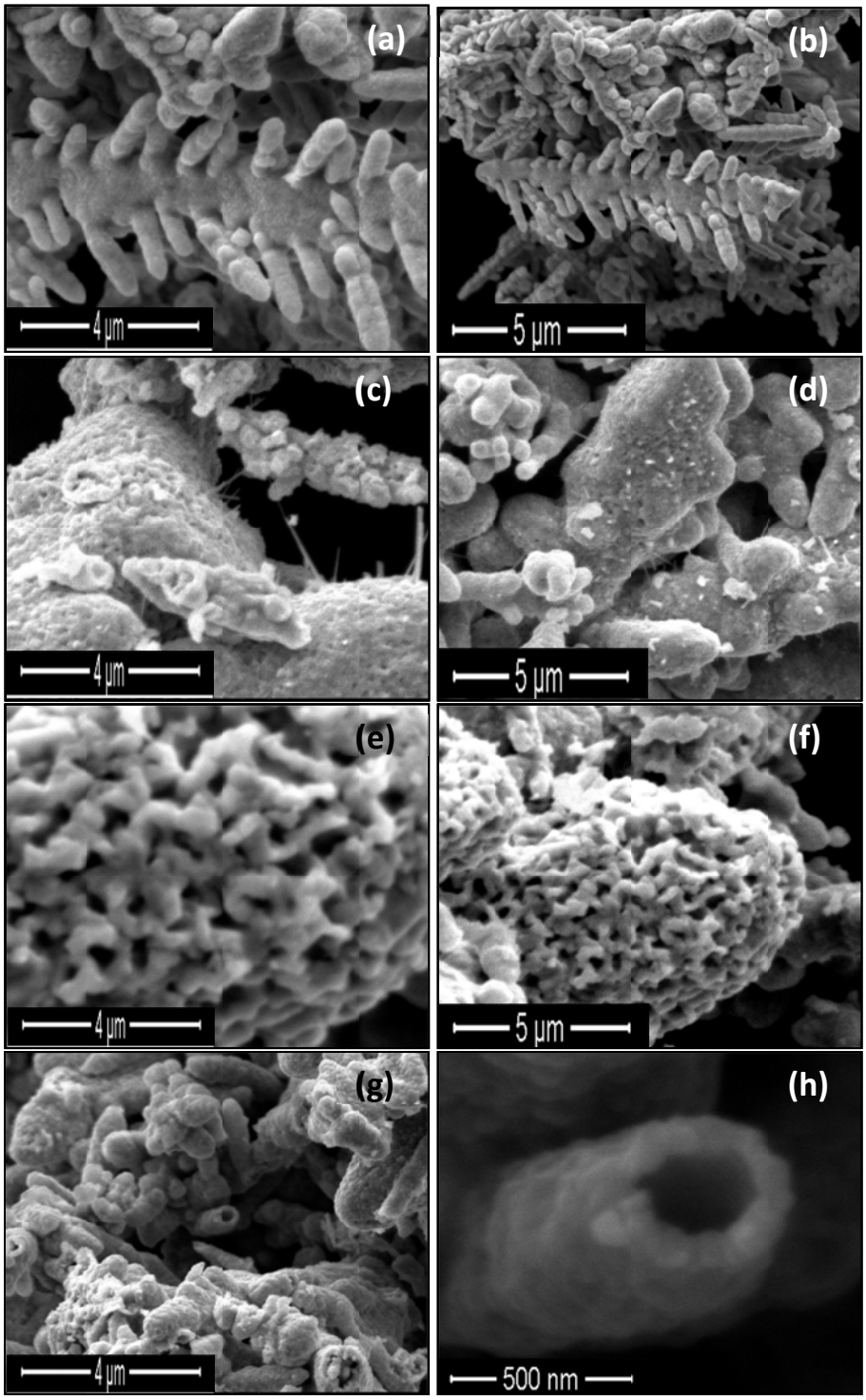

Fig. 2. SEM images of copper (a, b) as prepared and annealed at (c, d) 200°C, (e, f) 400°C, (g, h) 600°C

The as prepared copper has been annealed at different temperatures 200°C, 400°C and 600°C for 1 h to get different structures of copper. Due to rise in temperature the crystalline nature of particles gets changed such that the structure enlarges and results in the formation of different structures [17]. Figure 2 (c, d) shows the SEM image of Cu annealed at 200°C. The SEM image reveals that the copper dendrite like structure transforms to a randomly oriented copper cactus like structure with less multi-armed needle like structures arranged along a sponge structure with high porosity. The length of the petal is about 4µm to 5µm. The structure shows that the central trunk

present in the dendrite has transformed into sponge like structure with increase in size and has swelled. When the temperature is increased, it is clear that a great number of pores appear along the trunk with enlargement of the trunk and also there is reduction in the size of the petals leading to the formation of needles without pores.

Figure 2 (e, f) shows the SEM image of Cu annealed at 400°C. The SEM image reveals that the randomly oriented copper cactus like structure has transformed to copper honey comb structure having many pores. The length of the petal is about 3.8μm to 4.7μm. When there is increase in the temperature, there is an increase in the diameter of the pores present on the enlarged trunk and also there is disappearance of the needle like petals. Figure 2 (g, h) shows the SEM image of Cu annealed at 600°C. It shows that the copper honey comb like structure has transformed into a tubular structure. The length of the tubular part is about 1 μm. Figure 3 shows the EDX spectra of copper. The EDX analysis clearly indicates that the obtained copper sample is quite pure.

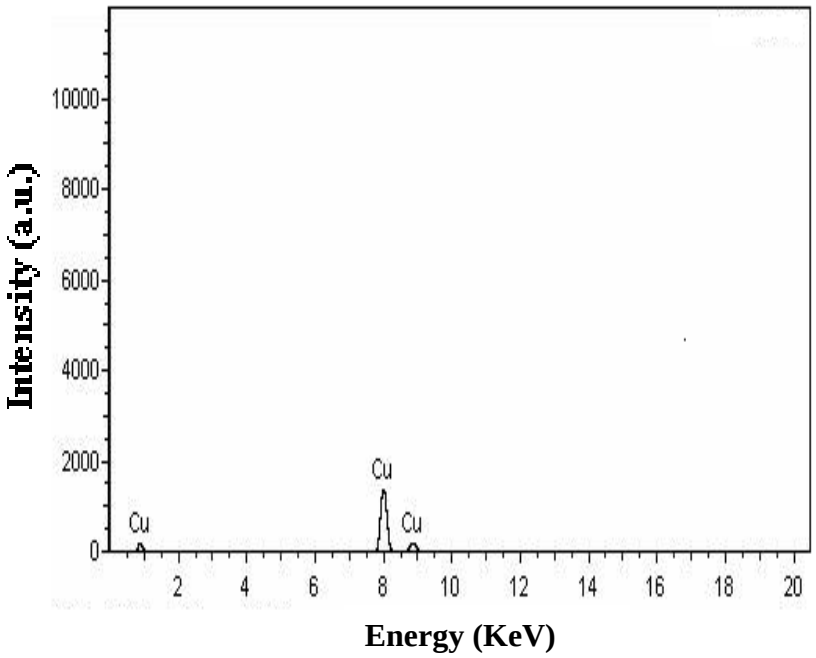

Fig. 3. EDX spectra of copper.

To understand the growth mechanism of the copper dendrite like structure to copper tubular like structure, time-dependent experiments were carried out by annealing the particles at different temperatures 200°C, 400°C and 600°C for 1 h. It shows that the growth process of the porous dendrites, cactus, and honey comb and tubular like structures is similar to that of the nonporous dendrites. Herein, we choose the nonporous dendrites as the model because the reaction rate of it is relatively slower than that of porous dendrites and different stages can be clearly obtained. A series of SEM images in Figure 2 show the morphology at different reaction stages corresponding to the annealing is carried out at different temperatures 200°C, 400°C and 600°C for 1 h. With increasing of the temperature, copper dendrites are transformed into cactus, and honey comb and tubular like structures with various diameter. The possible growth process demonstrating the transformation of copper dendrite like structure to tubular like structure can be described schematically as shown in figure 4.

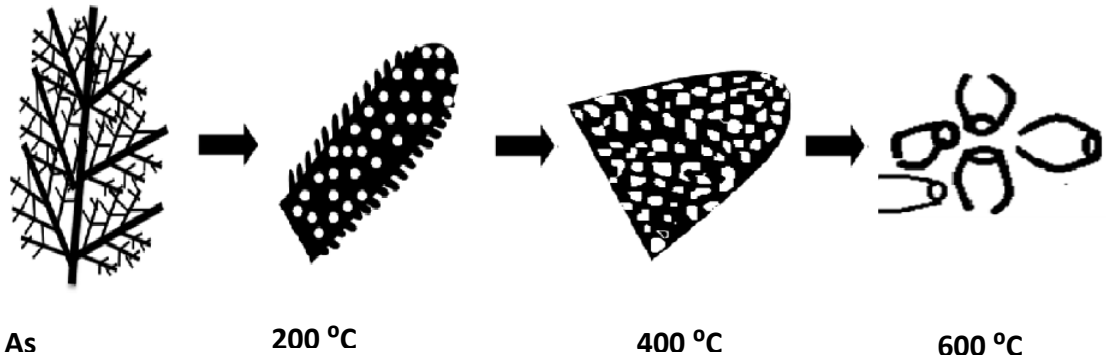

Fig. 4. Schematic description of the growth process of hierarchical copper structures.

4. Conclusions

The different morphology structures of copper particles like dendrites, cactus, honey comb and tubular like has been synthesized by simple chemical method. The prepared copper structures have been characterized using x-ray diffraction method, scanning electron microscopy and energy dispersive x-ray analysis. X-ray diffraction analysis reveals that Cu exhibit cubic structure. The formation of dendrite, cactus, honey comb and tubular like Cu particles has been conformed using scanning electron microscope. This studies carried out indicate that it is possible to prepare copper particles with different structures by the simple chemical method.

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