

Thermally induced oxidative growth of copper oxide nanowire on dendritic micropowder and reductive conversion to copper nanowire

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Copper nanowires (NWs) were constructed on a dendritic copper powder precursor by a facile thermal oxidation–reduction method. First, copper oxide NWs were grown from high purity dendritic copper powder by thermal oxidation at 500°C. Next, these oxide NWs were reduced to copper NWs under a hydrogen flow at two different temperatures of 220 and 500°C. Oxide NW diameters distribution was in the range of 50–105 nm with length ranging from 1 to 5 µm while copper NWs were shorter and wider. A time-dependent study of oxide NWs growth was carried out. The morphology, composition and crystal structure of the resulting products were characterised by X-ray diffraction and scanning electron microscope. The results indicated that the final product of oxidation process was dispersed cupric oxide (CuO) NW whose density and length increased with time. Furthermore, it was observed that as the reduction temperature increased, the copper NW melted and adhered to the powder surface.

1. Introduction: Nanowires (NWs) are considerably attractive to nanoscience studies as well as to nanotechnology applications. Copper oxide/copper NWs has attracted much attention due to their unique properties and potential technical applications. Two natural oxides of copper; cuprous oxide (Cu₂O) and cupric oxide (CuO) as a semiconductor with a narrow bandgap of 2.0 eV and 1.2 eV, respectively, have potential applications for sensors, energy conversion, catalysts, lithium batteries, supercapacitors, solar cells and field emission [1]. Several methods have been developed for synthesising CuO NWs, such as wet chemical route, electrochemical deposition, electrospinning, direct resistive heating and thermal oxidation [1]. Economic feasibility, mass production, simplicity and excellent crystallinity of the grown NWs make thermal oxidation one of the most attractive methods among all synthesis methods [2]. On the other hand, copper NW, because of high electrical and thermal conductivities, high aspect ratio, corrosion resistibility, quantised conductance and localisation effect may be used as building blocks in constructing micro and nanoelectronics, opto-electronics and chemical/biological sensors [3]. Many of the previous NW synthesis techniques require expensive chemicals, complicated procedures and complex fabrication equipment, which may preclude them from implementation for mass production [4]. Therefore, facile synthesis of copper NWs with large aspect ratio and controllable diameter are of significant importance in both nanotechnologies and material sciences.

Different substrate morphologies such as foil, grid and film [5] have been examined for growing copper oxide NW by oxidations process. Powder structure has many practical application. However, there has been very little research reported on their oxidation. Love *et al.* [6] prepared CuO NWs by heating the spherical copper powders with average particle sizes of 1, 10 and 50 µm in a box furnace and found that NW coverage depends on the particle size. Li *et al.* [7] described synthesis of CuO NWs on spherical surface by thermal oxidation method and reported that the diameter and density of NWs can be controlled by the heating temperature and time. Yang *et al.* [8] thermally treated electrolytic copper powders in the air for 1 h at a temperature range of 200–700°C and found that thin CuO NWs were grown at 300°C and thick CuO NWs were grown at 500°C. On the other hand, oxidation–reduction reaction is a newly proposed method for producing

stable NW on a surface. Lee *et al.* [9] proposed this method for producing superhydrophobic surface with copper NW on a copper foil.

In this Letter, thermal treatment by oxidation–reduction reaction as a simple and inexpensive synthesis approach is used for the direct growth of copper oxide–copper NWs. Oxidation takes places in air at an optimised temperature of 500°C for 4 h on a dendritic copper powder while reduction to metallic copper NWs occurs in hydrogen atmosphere at the temperatures of 220 and 500°C for 2 h. The growth mechanism of copper oxide NW is predicted using images taken in different growth time intervals. The resulting products were examined by X-ray diffraction (XRD) and scanning electron microscope (SEM).

2. Experimental procedures: The commercial electrolytic copper powder of 99.9% purity with high specific area and apparent density of 1.7 g/cm³, processed by electrolysis of raw copper, annealed for oxygen reduction and sieved for particle size smaller than 45 µm; was used as the starting material. The copper substrate was polished with an ultra-fine grade sandpaper #3000. The copper powder was spread on the top of the copper substrate to form a tin disc of about 1 mm thickness and 2 cm diameter to be loaded into a furnace. The copper oxide growth was performed by exposing of Cu powders to air at 500 °C under an ambient pressure of 88 kPa and a relative humidity of 60%. The ramp time to the set temperature was fixed at 30 min, and the isothermal regime lasted for 4 h. Furnace was cooled naturally to room temperature to avoid thermal stress fracturing. The reduction step was done to transform oxide NWs into metal NWs. There was no chemical treatment between the oxidation and reduction steps. The copper oxide NW was heated under a temperature ramp time of 30 min, using 50% of reducing H₂ and 50% of neutral N₂ gas. In order to investigate the temperature effect in the reduction process, this process is done at two different temperatures of 220 and 500°C for 2 h. After cooling the furnace to ambient temperature, to prevent oxidation, the copper sample was removed from the furnace.

The structures of the samples were characterised with a Rigaku RINT-2100 X-ray diffractometer (45 kV, 0.1 mA, Unisantis XMD-300) at a scanning rate of 0.02°/s in 2θ ranging from 20° to 80°. SEM images were obtained using a VEGA TEScan microscope operated at an acceleration voltage of 30 kV.

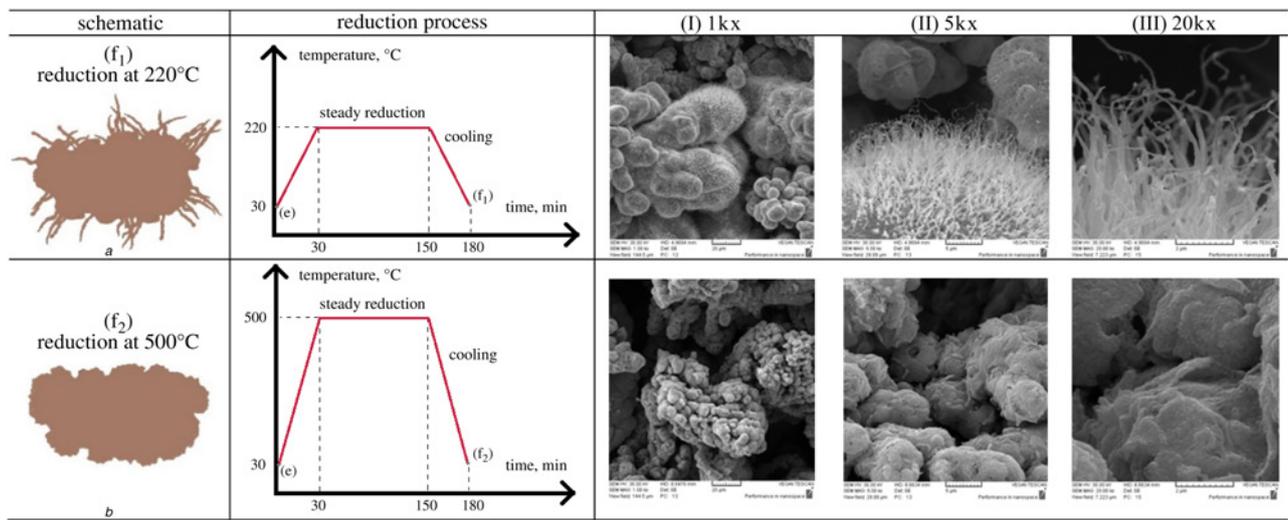


Fig. 3 SEM images and schematic representation of copper oxide NW reduction at f_1 220°C for 2 h in magnification of (I) 1k x, (II) 5k x, (III) 20k x f_2 500°C for 2 h in magnification of (I) 1k x, (II) 5k x, (III) 20k x

result of such a reaction is the formation of oxide layers. The oxide layers would be in the order of Cu_2O with CuO on top of it as oxygen partial pressure increases from Cu substrate towards the free surface [11]. Oxide layers continue to grow as copper ions are supplied by grain boundary diffusion and their growth is mainly controlled by the difference between the copper oxide nucleation surface pressure and copper powder [14, 15]. CuO and Cu_2O layer have different crystal structures leading to lattice mismatch. On the other hand, molar volume of CuO is greater than that of Cu_2O . The two reasons mentioned above along with the difference in density of CuO and Cu_2O , induces compressive stress on the interface of these two oxide layers. This stress is accumulated as the oxidation process continues. When reaching a critical limit, the compressive stress is released through the growth of NWs from the interface of two copper oxide layers. This accumulating stress gets larger with increase in time, therefore the density of NWs increases with time as it can be seen in Fig. 2. Moreover, no sufficient stress will be accumulated to form protuberances if the growth time has not reached the ample time needed for NW growth [16, 17]. The stress-induced growth mechanism may explain the growth of NWs in the early stages, however it cannot justify the long NWs grown in the later stages [15].

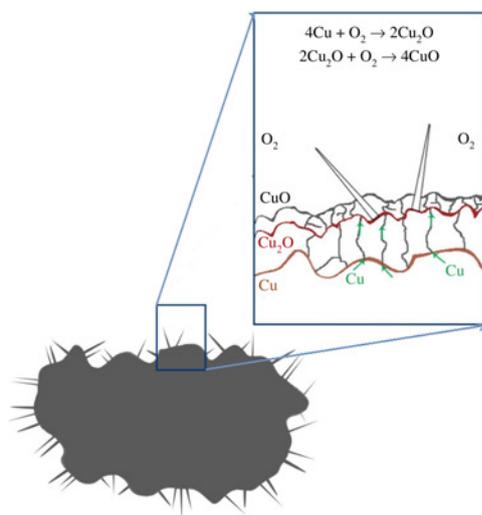


Fig. 4 Schematic illustration of the proposed copper oxide NW growth mechanism

Goncalves *et al.* [18] suggested that grain boundary diffusion governs the growth of CuO NW at the temperature range of 400–600°C. Cu ions diffuse across the Cu_2O layer which is full of pores and defects due to large compressive stress exerted on it from Cu layer. As diffused atoms increase the stress on CuO layer, this layer releases the stress by the growth of NW. Continuous growth is achieved by the diffusion of Cu atoms through grain boundaries in Cu_2O layer. As Goncalves suggests, the rate of the growth is limited by the mass transport by diffusion [15]. A schematic representation of the proposed mechanism is shown in Fig. 4.

Finally, it can be stated that NW growth in this experiment is the result of two simultaneous effects: (i) stress accumulation and release in the CuO layer and (ii) copper powders continuously supply copper atoms by diffusion [16], part of which is due to the stress and the other part due to chemical potential gradient established by the many orders-of-magnitude difference in oxygen partial pressure between the oxide–atmosphere and oxide–metal interfaces [13].

The mechanical adhesion between the NWs and the substrates synthesised by thermal method is very weak. Cracking and flaking of NWs or even exfoliation from the substrates is still a common problem [19–21]. In this study, powder plays as a mechanically stable platform for NW growth. During thermal oxidation process, the discontinuous surface allows stress relief at the edges of dendrites. Consequently, the detachment of CuO/Cu NWs from the precursor is prevented. However, adhesion of oxidised and reduced powder to copper substrate is weak.

4. Conclusion: Copper oxide NWs were grown by thermal oxidation of copper powders and followed by their transformation to copper NWs by thermal reduction in a hydrogen flow. The straight oxide NWs grow normal to the copper powder surface with radial curvature greater than about 3 μm . The average diameter and length of copper oxide NWs are about 80 nm and 3 μm , respectively. The reduction process in 220°C effectively transforms oxide NWs into metallic wavy copper NWs with thicker diameter and shorter length. However, increasing the reducing environment temperature to 500°C causes NW melting and attachment to powder surface. XRD analysis shows the transformation of Cu_2O and CuO phases in oxidation process to Cu in reduction process.

5 References

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