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Original Article

Preparation of CuO Nanorods by Thermal Oxidation in Ozone Ambient

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Abstract: CuO nanorods were prepared by thermal oxidation method in ozone ambient. The effect of annealing temprature in the range from 400 to 600 °C on morphology and structure of nanorods was studied thouroughly by scanning electron microscopy (SEM) and X-ray diffraction, combining with energy dispersive spectroscopy (EDS) and Raman spectroscopy. The results showed that annealing temprature strongly affected the structure and morphology of the produced CuO nanorods. The most uniform nanorods with highest crystal quality were obtained when annealing temperature is from 450 to 500 °C and annealing time was 2 h as suggested by SEM images together with Raman results.

Keywords: Copper oxide, thermal oxidation, ozone ambient, nanorods.

1. Introduction

The characteristics of nanocrystalline semiconductor particles have drawn considerable interest in recent years because of their special properties such as a large surface-to-volume ratio, increased activity, special electronic properties and unique optical properties compared to those of the bulk materials [1-3]. Copper oxide is a p-type multifunctional semiconductor with a narrow band gap (E_g ~ 1.2 eV in bulk), and has been recognized as an industrially important and exotic material for a variety

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of practical applications [4-6]. For practical applications based on CuO nanomaterials, the good alignment and uniformity of the materials are required.

Various physical and chemical methods have been proposed to synthesize CuO nanomaterials such as quick-precipitation [4], chemical reduction [7], electrochemical [8], microwave-irradiation [6], sonochemical [3], thermal oxidation of copper [9]. Even though a wide range of morphologies have been achieved by these methods such as nanocubes [10], nanospheres [11], nanoneedles [12], nanobelts [13], nanodisks [14], only few chemcial methods are available for construction of CuO nanowires or nanorods [15-17]. In comparison to complex chemical methods, thermal oxidation of copper substrates shows outstanding advantages in term of cost effective, facile process, time saving, etc. Moreover, preferred orientation can also be achieved conveniently by this method. To improve the density and morphology of the nanowires prepared by thermal oxidation method, researchers mostly focused on the effect of copper substrate, i.e roughness, grain size, substrate fabrication process [18, 19]. Meanwhile, the effecct of ozone as an oxidation ambient, which is critical in the oxidation process, has not been mentioned in the previous studies.

In this work, we report the fabrication and characterization of CuO nanorods synthesized by facile thermal oxidation method in ozone, which is much active oxidation ambient compared to the air. The effect of annealing in ozone on morphology and structure of the nanoproducts was investigated thoroughly by scanning electron microscopy (SEM) and X-ray diffraction, combining with Raman spectroscopy and energy dispersive spectroscopy (EDS).

2. Experiment

High-purity Cu substrate (99%) has been used as raw material. Firstly, Cu substrates were immersed in diluted acid (HCl 10%) in 1 hour to remove any possible oxides layer on the surface. Then they were cleaned by distilled water. CuO nanostructures were synthesized by directly heating Cu substrates in ozone. The substrates were placed at the center of a tube furnace XD 1600. Annealing temperature was varied in the range from 400 ^{o}C to 600 ^{o}C while annealing time was fixed at 2 h to study the effect of annealing temperature. Annealing process was performed in ozone ambient, where ozone was produced by a mini ozone generator.

The morphology of the products was investigated by using Nova Nano SEM Fei 450. Raman spectra of samples were collected on Lab Ram 800 from Horiba with excitation wavelength of 632.8 nm. Integration time was kept constant at 120s and power at surface sample was fixed at 0.2 mW. X-ray diffraction measurement was done on Bruker D5005 diffractometer, using the monochromatic wavelength of 1.54056 Å of Cu K_α radiation.

3. Results and Discussion

Figure 1 shows SEM images of CuO nanostructures annealed in 2h in ozone at different temperatures. The crystallization of CuO nanostructures likely starts at the lowest annealing temperature of 400 ^{o}C (Figure 1a). The density of rods is quite low at low annealing temperature. When increasing oxidation temperature, the nanorods grow larger and longer, and at higher density. While annealing temperature increases from 550 ^{o}C to 600 ^{o}C, the morphology of the obtained nanostructures undergoes notable changes. SEM images indicates that some kinds of short nanorods were formed, with the length and the width of around 2-6 μm, and 0.5-1.5 μm, respectively (Figure 1e). One of the most commonly accepted mechanism for the growth of CuO nanorods in thermal oxidation process is the diffusion of Cu atoms via grain boundary. In such mechanism, Cu_2O, CuO layers are formed at the first stage of oxidation. Then Cu atoms will diffuse via grain boundary and oxidized to form CuO nanorods on top of the CuO polycrystalline layer. As oxidation process is prolonged both CuO nanorods and CuO polycrystalline layer grow simultaneously. Depending on the growth condition, if the growth rate of CuO layer is higher than that of CuO nanorods. The final nanorods will becomes shorter at long annealing time because the roots of these nanorods will be merged into CuO polycrystalline layer as it grows thicker. The shorter nanorods obtained at higher annealing temperature in ozone ambient can be understood as reaction in ozone ambient lead to higher crystallization rate of polycrystalline layer beneath as discussed above. This argument of higher oxidation rate induced by ozone ambient is supported by the following Raman data.

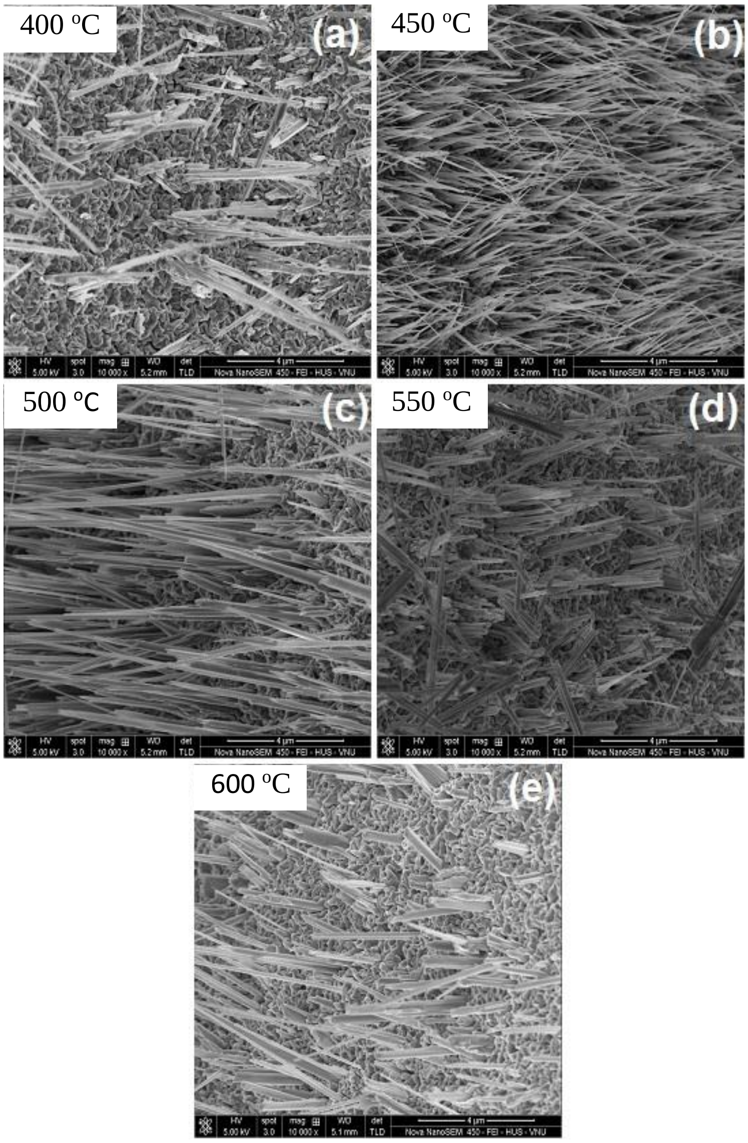

Figure 1. SEM images of CuO nanostructures annealed for 2 h in ozone at difference temperatures: (a): 400 °C, (b): 450 °C, (c): 500 °C, (d): 550 °C and (e): 600 °C

The composition of samples prepared at 500 ^{o}C is verified by EDS. Figure 2 shows that the sample composed of only Cu and O elements. The EDS result implies that the sample has a high purity, no other impurity was introduced during fabrication process.

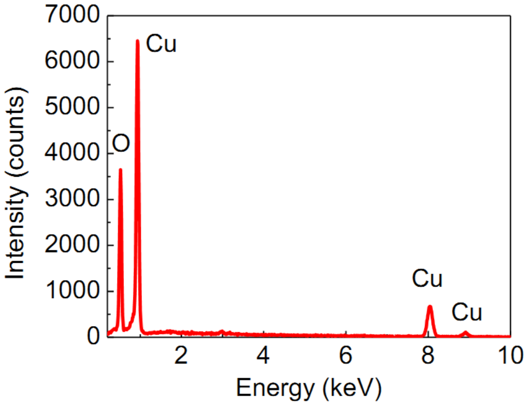

Figure 2. EDS spectrum of the CuO sample annealed at 500 ^{o}C for 2 h.

Raman spectra of the CuO samples synthesized in ozone ambient are shown in Figure 3. The spectra show characteristic peaks of CuO at around 290 cm^{-1} and 340 cm^{-1}. Samples of smaller width of the rods show stronger and sharper Raman peaks which also shift to smaller wave numbers.

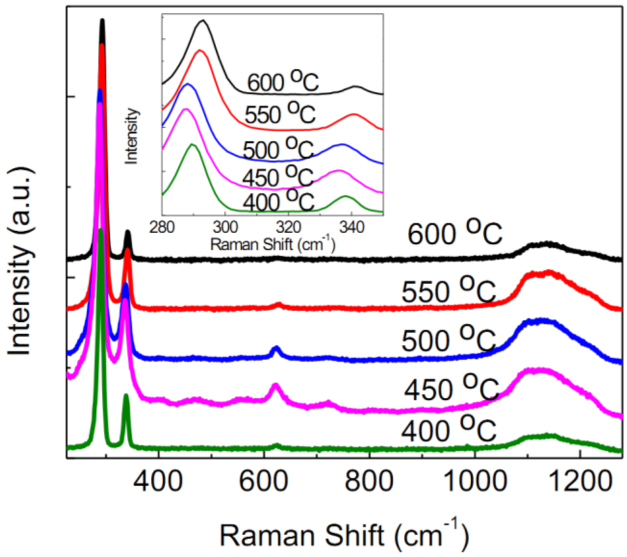

Figure 3. Raman spectra of CuO nanorods annealed for 2 hours in ozone.

From our previous study, it is noted that annealing at low temperature of around 400 and 450 ^{o}C in oxygen results in formation of nanorods of both cupric and cuprous phase with a characteristic peak at around 200 cm^{-1} [6, 9, 20]. However, Raman spectra of nanocrystalline CuO annealed in ozone ambient at all oxidation temperatures show only A_g and $B^1{}_g$ characteristic peak of CuO. Thus, from the Raman data one can suggest that ozone ambient provides a larger reaction rate than the open air condition does.

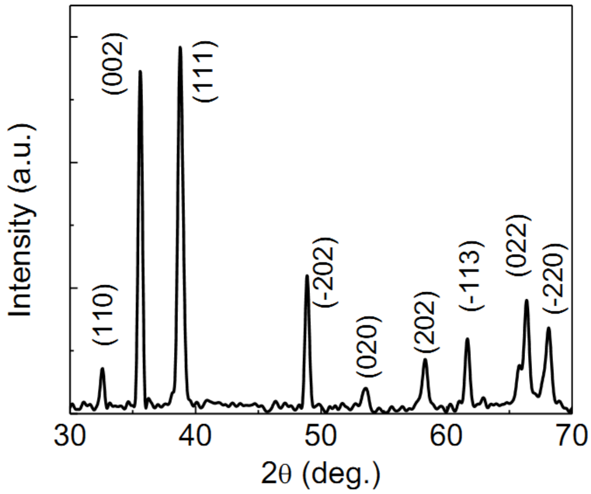

Figure 4. XRD patterns of CuO nanorods annealed at 500 ºC for 2 h in ozone ambient.

The XRD pattern of the sample prepared at 500 °C is shown in Figure 4. The pattern also confirms the pure phase of the products with a monoclinic structure with space group of C2/c. The intensities and positions of the peaks are in good agreement with the data reported in [21]. No peak of impurities appeared in the XRD patterns. The broadening of the peaks indicates that the crystal size is small. The average size of the CuO nanocrystals estimated by using Scherrer formula is of 21 nm. To calculate crystalline lattice constants, one has to calculate the distance between crystal lattice planes by using the Bragg's diffraction condition:

$$2d \sin\theta = \lambda$$

where, d is the distance of neighbor crystal lattice planes, θ is the diffraction angle and λ (= 1.54056 Å) is the wavelength of X-ray used. Lattice constants (a, b and c) of monoclinic the structure can be then determined according to the formula of distance between neighbor planes of monoclinic structure:

$$\frac{1}{d^2} = \frac{1}{sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2 sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\, cos\beta}{ac}\right)$$

The calculated lattice constants are: a = 4.6902 Å, b = 3.4211 Å, c = 5.1209 Å, β = 99.33. These values are similar to the lattice data for CuO materials reported in [3].

4. Conclusion

CuO nanocrystals with a monoclinic structure have been successfully prepared in ozone by thermal annealing for 2 h. The research suggests that ozone is an active environment for thermal oxidation process, which offers a larger oxidation rate. However, growth conditions should be controlled carefully to obtain uniform nanorods of preferred orientation. Annealing temperature in the region from 450 to 500 ºC offers nanorods of the highest quality with a high density. This method is potential for expanding to industrial scale for practical application because it is a safe, simple, environmentally-friendly, and efficient method. The obtained results suggest promising applications in bio sensor; supper hydrophobic and surface enhance Raman scattering, etc.

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