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Preparation of Well-aligned CuO Nanorods by Thermal Oxidation Method

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Abstract: Well-aligned CuO nanorods were successfully prepared by thermal oxidation method. The effect of annealing time and annealing temperature on the morphology of the nanorods were studied by scanning electron microscopy. The results show that annealing temperature plays a more critical role in affecting the diameter and density of nanorods. Besides SEM images, the effect of annealing time and temperatures on the structure of the product were also studied by X-ray diffraction and Raman spectroscopy. The diameter of CuO nanorods varies from 30 nm to above 100 nm when annealing temperature changes from 400 °C to 600 °C, while the length of the rods is up to several tens of micrometers. The most uniform nanorods with highest crystal quality of CuO were obtained when annealing temperature is 500 °C and annealing time was 2 h as suggested by SEM images together with Raman results.

Keywords: Cupric, Nanorods, Raman, Thermal oxidation.

1. Introduction

The distinctive characteristics of nanostructures of metal oxide semiconductor have drawn considerable interest in recent years because of their special properties such as a large surface-to-volume ratio, enhanced activity, unique electronic and optical properties compared to those of bulk materials [1-3]. The use of metal oxide nanostructures has become promising in solid state chemistry, because of their controllable properties and structures. Among metal oxides, copper oxide is a narrow band gap (~1.2 eV in bulk) p-type multifunctional semiconductor which has been recognized as an industrially important material for various applications [4-7].

The reduction of CuO dimensions to the nanoscale results in significant deviation of some of its physical properties from its bulk counterpart because of the “quantum-size effects”. Therefore, a thorough understanding of the fundamental properties of CuO nanostructures is crucial to their synthesis and applications and a key to the rational design of CuO nanostructure-based functional devices. CuO nanorods can be applied in many different fields, such as gas sensor, magnetic storage media, solar-energy transformation, electronics, high sensitivity glucose sensors, super hydrophobic surfaces [8, 9] or low cost solar cells... The successful preparation of aligned CuO nanorods is

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believed to enrich our understanding of its fundamental properties, which may lead to enhancement of performance in its applications. In this paper, we report the preparation of uniform and well-aligned CuO nanorods by thermal oxidation methods. The effect of oxidation temperature and time on structure and morphology of the nanorods was investigated thoroughly by scanning electron microscopy, Raman spectroscopy and Xray diffraction measurement.

2. Experiment

High purity copper wire (purity higher than 99% and diameter of about 1 mm) was used as raw material. The native oxide layer on copper wire was removed by using chemical corrosive. First, Cu wire was put into diluted acid (HCl 10%) for 1 hour, then rinsed with distilled water. CuO nanorod was prepared from Cu wire by thermal oxidation process in an electrical furnace XD-1600MT.

Two sets of samples were prepared at different temperatures from 400 to 600 °C in 2 hours or 4 hours to study the influence of annealing temperature and time on the morphology and structure of the products. The morphologies of the products were investigated by using Nova Nano SEM 450. Raman spectra of samples were collected on Labram 800 from Horiba with excitation wavelength of 632.8 nm. Acquisition time was fixed at 120s for all samples with power at surface sample of about 0.2 mW. Xray diffraction measurement was done on Bruker D5005 diffractometer, using the wavelength of 1.54056 Å of CuK_α radiation.

3. Results and discussion

SEM images show that at all annealing temperature from 400 to 600°C, we obtained high density and well-oriented nanorods (Fig.1). At 400°C, length and width of the obtained nanowires are 3-5 μm, and 40-60 nm, respectively.

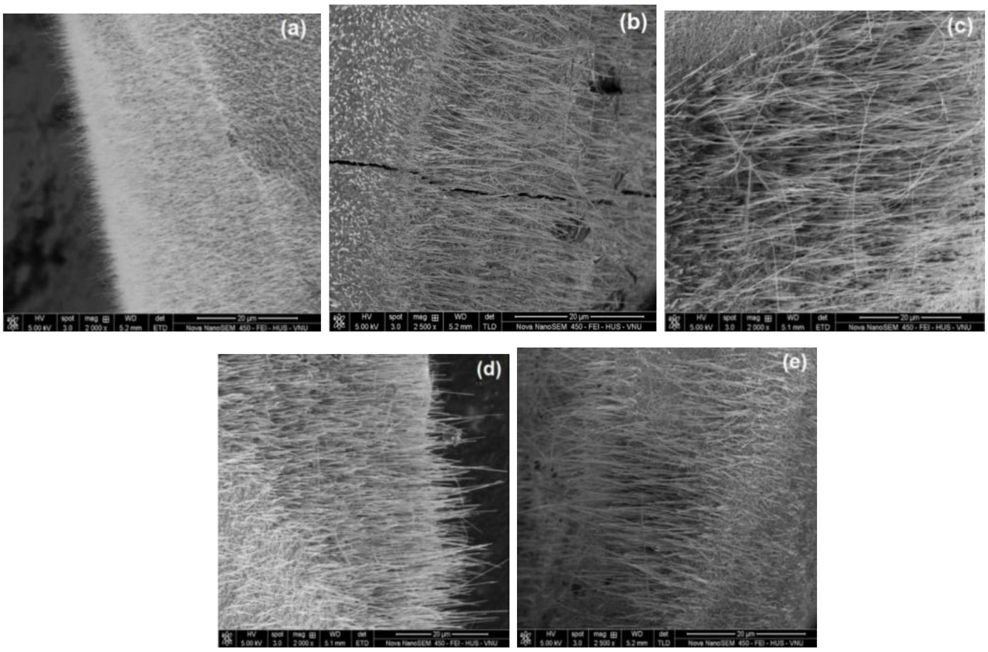

Figure 1. SEM images of CuO nanowires prepared by thermal oxidation in air in 2 h at different temperatures: (a): 400°C, (b): 450°C, (c): 500°C, (d): 550°C and (e): 600 °C.

When annealing time was fixed at 2 h, higher annealing temperature resulted in thicker and shorter rods. As annealing temperature increased from 400 to 600 °C, the diameter of nanorods increased from 30 nm to 200 nm. The maximum length of the nanorods, which was above 20 micrometers, was obtained at 500 °C and the length of nanorods decreased when annealing temperature was higher or lower than 500 °C.

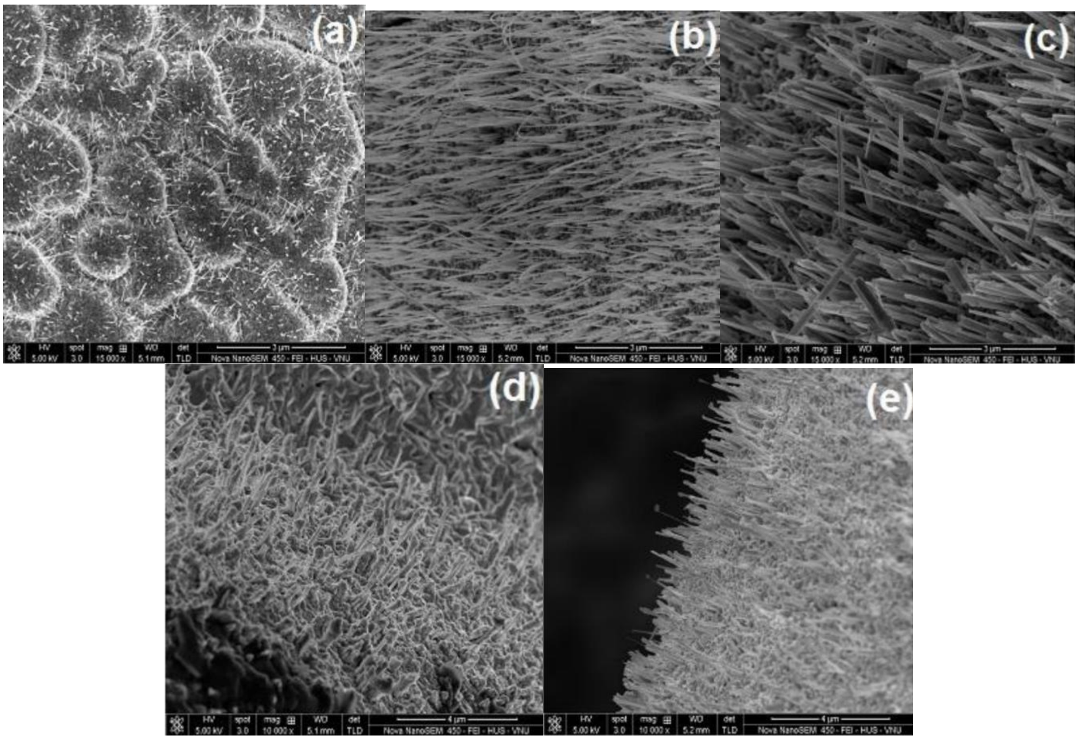

Figure 2. SEM images of CuO nanostructures annealed in 4 h at different temperatures (a): 400 °C, (b): 450 °C, (c): 500 °C, (d): 550 °C and (e): 600 °C

The same trend was observed for the samples prepared at different temperatures in 4 h (Fig. 2). At 400 °C, we found only rods of low density. In temperature region from 450 to 500 °C, we obtained well-aligned and uniform rods with diameter of about 100 nm and length of about 3 to 5 μm. At temperature region from 550°C to 600°C, we obtained short and thick nanowires of 150 -300 nm in diameter and length of these wires is shorter than 2 micrometers.

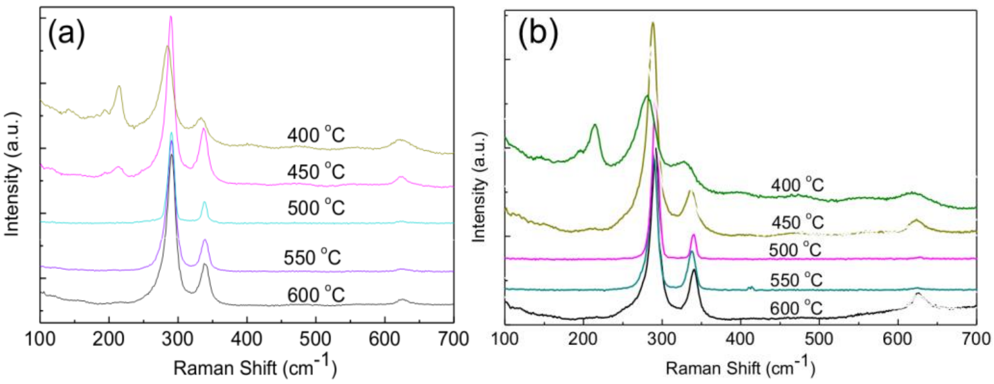

Figure 3. Raman spectra of CuO nanorods prepared in 2 h (a) and in 4 h (b) in air at different temperatures from 400 to 600 °C.

Group theory shows that CuO, with a monoclinic structure and belonging to the space group C^6_{2h}, has three Raman-active modes (Ag + 2Bg). Typical Raman spectra of the as-prepared nanorods consist of three characteristic Raman peaks of CuO. The peak at around 288 cm^{-1} can be assigned to the Ag mode, and the peaks at around 330 and 621 cm^{-1} corresponds to the B^1_g and B^2_g modes, respectively [2].

Raman spectra of the CuO synthesized in 2 h and 4 h in air are shown in Fig. 3a and b, respectively. The evolution of the Raman spectrum with increasing temperature in both cases is quite similar. The high intensity and sharp Raman peaks confirm that CuO material with good crystalinity was formed. The spectra contain characteristic peaks of CuO at 289 cm^{-1}, 332 cm^{-1}, and 630 cm^{-1}. The A_g and B^1_g Raman peaks of CuO nanorods prepared at high temperatures also shift to longer wave number with decreasing temperature.

Quantum confinement due to the reduced size to nanoscale of the samples is not likely the reason for the peak shift because the sample of smallest size, obtained at 500 °C, did not exhibit any shift. The peak shift observed most clearly in samples prepared at 400 °C for both sets of sample prepared in 2 h or 4 h suggested that the reason might be the phonon confinement on defects formed in the samples at low annealing temperature.

At low temperature region, we observed another peak at around 200 cm^{-1}, which might be attributed to vibration of copper sub-oxide ($Cu_{1-x}O$) lattice. This peak grows as temperature decreases from 450 to 400 °C. The decrease in intensity of this peak implies that higher annealing temperature is preferred to get pure CuO nanowires. However, temperature higher than 550 °C results in fast oxidation reaction, which may reduce the crystal quality of the obtained nanowires. This remark is illustrated by the broadening of Raman peak of sample prepared at 600 °C. Then, together with SEM images, Raman spectrum of the samples suggest that product of highest quality could be obtained at around 500°C. The XRD patterns of the samples prepared at 500°C, in 2 and 4 h, shown in Fig. 4 also confirm the pure phase of the products.

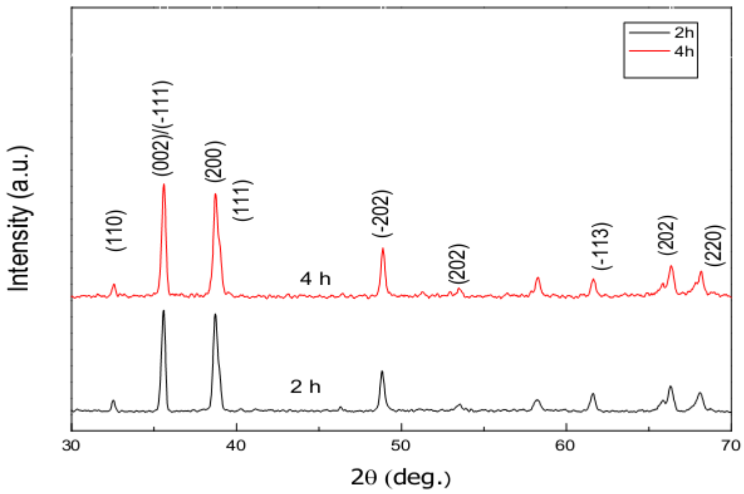

Figure 4. XRD patterns of CuO nanowires prepared in 2 h and 4 h in air.

All diffraction peaks could be well indexed as those of CuO of monoclinic structures both in relative intensities and positions. The average size of the CuO nanocrystals is estimated to be 25 nm and 20 nm for sample according to the Debye-Scherrer formula: $D= (0.9\ \lambda)/ (B \cos\theta)$, where D is the particle size, B is the full width at half maximum intensity of the peak and λ is the monochromatic wavelength of X-ray used in the equipment. The lattice constants are calculated for the two samples and shown in Table 1. These values are similar to the reported values for CuO materials in literature [4-6]

Table 1. Lattice parameters of CuO nanowires prepared at 500°C in 2 and 4 h.

Lattice parameters	a (Å)	b (Å)	c (Å)	B
2 h	4.7	3.4	5.1	99°40'
4 h	4.7	3.3	5.1	99°20'

4. Conclusion

Well-aligned CuO nanowires were successfully prepared by thermal oxidation methods. By controlling annealing time, annealing temperature, we could control the density and the aspect ratio of the as-produced nanorods. When varying temperature from 400 to 600 °C, we obtained nanowires of diameter ranging from 30 to over 100 nm, and length from 1 µm up to 20 µm with high density. The nanorods prepared at 500°C have highest crystal quality, uniformity as well as well-orientation. The successful preparation of CuO nanowire with low-cost thermal oxidation method may lead to the enhancement of performance in its applications.

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