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Synthesis of pod-like Cu_2O nanowire arrays on Cu substrate

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ABSTRACT

A new structure of Cu_2O nanowires was synthesized by a two-step thermal decomposition method of Cu $(OH)_2$ precursor, which operated at 570 K and 770 K respectively. The final samples show pod-like morphology with length about 50–60 um of each nanowire and about 200 nm of each grain. Compared to smooth nanowires, increased surface area was obtained with this structure. Meanwhile, the joint position of two grains was well crystallized corresponding to (1 1 1) growth orientation. Small amount of wires with branches were also found. We attributed formation of this unique morphology to addition of heating step at 570 K during which both CuO and Cu_2O were formed.

1. Introduction

In recent years, nanomaterials with special physical and chemical properties have been widely applied in photovoltaics, photocatalysis and sensors or been used as electrodes. In all of these usages, devices made up with nanostructures perform better through increasing the surface area. So it is important to optimize the structures for higher specific surface area [1,2]. Among all of these materials, Cu_2O is attracting more interests for its unique optical and electronic properties [3]. The current known natural crystal structures of p-type semiconductors are much less than that of n-type, while Cu_2O is a p-type semiconductor [4]. With direct band gap of 2.17 eV, Cu_2O has high absorption coefficient in the visible light, so it has been regarded as potential material in solar energy conversion [5–11]. The ability to process Cu_2O into nanomaterials could enrich our understanding of its properties and enhance its performance in current applications [12].

Nanowires have the capability of independently modulating carrier diffusion length and light absorption depth of a semiconductor. Over the past several years, various synthetic procedures of Cu_2O nanostructures have been developed, particularly using $Cu(OH)_2$ nanowires as templates is a novel fabrication route [13]. Wang et al. [14] synthesized Cu_2O nanowires by the redox reaction $Cu(OH)_2$ nanowires with hydrazine hydrate. Qian et al. [15] used Cu_2O nanowires, synthesized by thermal decomposition of $Cu(OH)_2$ nanowires, as photocathode. But these Cu_2O nanowires were all from in situ evolution with regular morphologies, hard to further increasing the surface area.

Compared with those regular nanowires, we report a pod-like structure of Cu_2O nanowires grown on Cu foil. The structure is obtained by a two-step thermal method, which uses the same regular $Cu(OH)_2$ nanowires precursor, while it requires a lower temperature annealing step before the normal heating process. Different from in situ evolution products, the surface of new samples is irregular, thus surface area increases remarkably and there exists a more element to adjust the area of nanostructure. To our best knowledge it is a new morphology and unique to copper oxides for now.

2. Experimental

The cuprous oxide nanowires were synthesized by thermal decomposition of $Cu(OH)_2$. First, $Cu(OH)_2$ nanowires were grown on Cu substrate. Cleaned Cu foils (purity: 99.5%) were immersed in mixed aqueous solution of 20 mL 2.5 M NaOH and 20 mL 0.2 M $(NH_4)_2S_2O_8$ for 30 min. When a blue layer was formed, the foils were taken out, rinsed with distilled water and dried with N_2 flow. Then the obtained foils were annealed using muffle furnace in two different temperatures.

Step 1: when the temperature was raised to 570 K, the foils were put in and maintained for 30 min.

$$Cu(OH)_2 \rightarrow CuO + H_2O,\ CuO + Cu \rightarrow Cu_2O$$

Step 2: the foils were heated to 770 K and maintained for another 30 min.

$$CuO + Cu \rightarrow Cu_2O$$

Finally, the foils were taken out as soon as the furnace was turned off and cooled to room temperature on paper stack. Surface of the foils turned to brick color and attached to the Cu substrate.

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Since Cu substrate served as reactant in both steps, tight bonding was formed between substrate and nanowires. The final samples could be curved without surface layer peeling.

The samples were characterized by scanning electron microscope (SEM, Hitachi S-4800), transmission electron microscopy (TEM, FEI Tecnai G2 20), X-ray diffraction (XRD, Rigaku D/Max-IIIC, Cu Kα, radiation $\lambda = 0.15406$ nm).

3. Results and discussion

Observation of the morphology of prepared samples was achieved by SEM. Fig. 1a shows the morphology of $Cu(OH)_2$ layer on Cu substrate, showing high density of straight nanowires. From the images, we can see that the nanowires have sharp tips and some of them show flatten structure. The SEM image at a higher magnification (shown in inset of Fig. 1a) reveals that the flatten structure is formed by some nanowires bundled together. Size of the nanowires is uniform, with lengths ranging from 20 um to 30 um and diameters about 100 nm. SEM image of the products after step 1 was shown in Fig. 1b, pod-like nanowires were found. Compared with $Cu(OH)_2$, the lengths did remain the same, while the morphology changed a lot. Pod-like structure was observed with bulges grown on cylinder surface. Straight nanowires became slight curved and the bundled ones turned to scattered. The morphologies of final products were shown in Fig. 1c. Morphologies barely change after step 2.

The XRD patterns of the pod-like nanowires modified foils after step 1 and step 2 were shown in Fig. 2a,b. After step 1 CuO peaks were apparent and content of CuO phase is 28%. In final products a small amount of impurity peaks are observed, because Cu_2O is an active material and partially converted to CuO after annealing. The content of CuO phase is 5.8%. The results indicate that Cu_2O is the main product after two-step annealing. All the Cu_2O peaks could be clearly indexed to cubic phase Cu_2O, which were consistent with the literature values (JCPDS No. 78-2076). No peaks of Cu are found, indicating Cu_2O film's sufficient thickness. We infer that pod-like structure is caused by local shrinkage and expansion in step 1, when $Cu(OH)_2$ was dehydrated.

Fig. 3a shows TEM image of the same pod-like Cu_2O nanowires used in SEM. Test samples are prepared by ultrasonicated extraction and place a drop of precipitate on a copper grid, so single nanowire could be observed. Consistent with the SEM observations, the Cu_2O nanowires all show pod-like structure. To observe clearer, enlarged TEM images with detail local morphology features are shown in Fig. 3b. Straight $Cu(OH)_2$ nanowire is also shown as comparison. The uniform diameter of $Cu(OH)_2$ nanowire is about 100 nm, while diameters of Cu_2O ranging from 50 nm to 200 nm, which fluctuate around the former. It is obvious that surface area increases tremendously than original structure. The increment could be estimated by a spheres string approximation with 100 nm in radius of each sphere compared to a column with 50 nm in radius. So the surface ratio of new structure and smooth one is Ssphere/Scolumn, about 200%. Although most nanowires remain one growing orientation, there are special samples with branches (Fig. 3c shows TEM image of an example with branches). From HRTEM image (Fig. 3d), it can be seen that distance between two neighboring lattice planes is about 0.25 nm, corresponding to

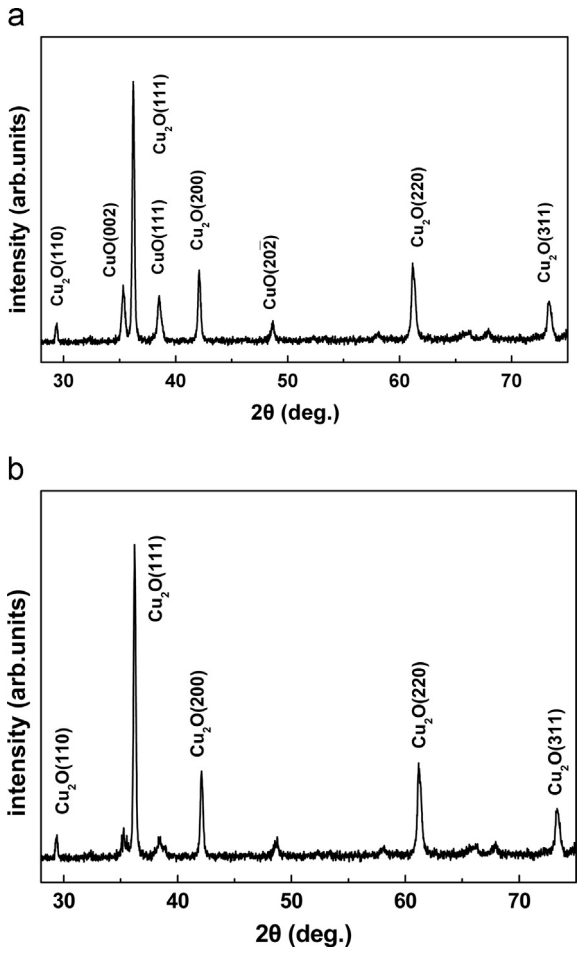

Fig. 2. XRD patterns of the nanowires (a) after the first step and (b) after the second step.

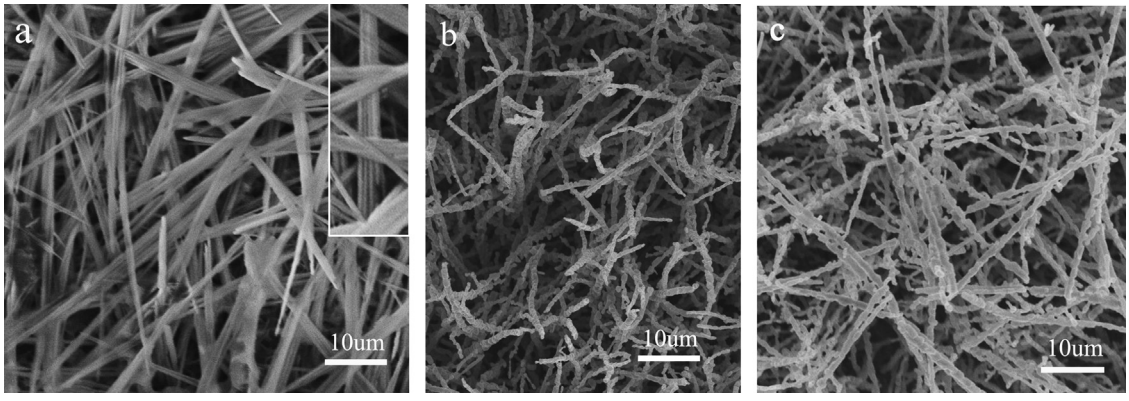

Fig. 1. (a) SEM images of the $Cu(OH)_2$ nanowires. The inset shows SEM images of $Cu(OH)_2$ nanowires bundled together. (b) pod-like nanowires after the first step and (c) after the second step.