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A facile fabrication of Cu_2O nanowire arrays on Cu substrates

Research article

Zhichuan Xu[1]*, Zhuanfang Bi[2], Chengmin Shen[1]

1 *Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, 100080 P. R. China*

2 *School of Physics, Shandong University, Jinan, Shandong 250100, China*

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Abstract: Nanomaterials play an important role in modern science and engineering. The ability to fabricate nanomaterials with high quality and low cost is a primary stage for further discovering their applications. This research article presents a facile fabrication of Cu_2O nanowires on Cu substrate. It was found that simply heating Cu in air leads to the growth of Cu_2O nanowires. The Cu_2O nanowires are aligned in one direction and vertically grown on the Cu substrate. The growth process of nanowires was tracked by SEM and the root at the initial stage was observed by HRTEM. The access to oxygen is critical to the growth of Cu_2O nanowires and the patterned nanowire arrays can be readily fabricated by using a mask. The method reported here offers a great potential route toward a large scale manufacture of Cu_2O nanowires.

Keywords: Cuprous oxide • Nanowires • Copper

1. Introduction

One-dimensional (1D) nanostructures are desirable for a wide range of applications in electronic, optical and mechanical devices due to their unique electronic confinement in radial-direction and large surface-to-volume ratio [1]. Semiconductive nanowires, nanotubes and nanobelts are typical 1D structures that have attracted much attention [2]. Cuprous oxide, Cu_2O, is a p-type semiconductor materials with a narrow band gap (2.2 eV) [3] and has shown great potential for gas sensing [4], solar energy conversion [5], and Bose-Einstein condensation study [6]. Nanostructured Cu_2O are commonly synthesized by solution phase reaction. For examples, monodisperse Cu_2O nanocubes are produced in a reversal micelle formed by cetyltrimethylammonium bromide (CTAB) [7]. Octahedral Cu_2O nanocages with tunable band gap energy in the range from 2.6 to 2.2 eV are prepared by a self-template route [8]. More interestingly, Cu_2O nanowires have been produced in an anodic aluminum oxide (AAO) template [9], a polymer assisted wet chemical method [10], a metal complex chain based reduction [11], or by a chemical conversion from the pre-formed $Cu(OH)_2$ nanowires [12]. To understand the chemical and physical properties of these Cu_2O nanostructures and to fabricate functional Cu_2O nanowire-based devices, it is necessary to have 1D Cu_2O nanostructures assembled along a specified direction and anchored on a conductive substrate. This, however, has not been achieved fully from any of the previous syntheses.

*E-mail: xuzc@mit.edu

In this article, we present a facile and template-free fabrication of Cu_2O nanowire arrays directly on a Cu substrate. Different from the previous approaches, this method does not involve solution phase reaction and the starting materials for the synthesis are just air and Cu substrate. The substrate can be either a Cu foil, or a plain Cu grid used in TEM experiments.

2. Experimental

In a typical Cu_2O nanowire synthesis, Cu substrates (Cu foil or Cu TEM grid) were washed with acetone and ethanol to remove organic impurities. Then, the substrate was treated with 2 M HCl solution to eliminate surface oxidation layer and was further rinsed with O_2 free deionized water and dried by N_2. The Cu substrate was then annealed at 400°C in air for 2 h to produce Cu_2O nanowires. The Cu surface changed from copper yellow into dark brown.

Scanning electron microscope (SEM) study was carried out in a XL30 S-FEG FEI field emission type scanning electron microscope at 10 kV. Transmission electron microscopy (TEM) was preformed by a JEOL 200CX transmission electron microscopy at 120 kV. High resolution TEM was performed on a Tecnai F20 (FEI Corp.) microscopy. Nanowires were scratched off from Cu substrate surface and dispersed in hexane by sonication. The nanowire solution was then dropped onto the amorphous carbon coated copper grid for imaging. X-ray powder diffraction patterns were recorded on a Rigaku D/MAX 2400 X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å).

3. Results and discussion

The morphology of the Cu_2O nanowires on the Cu foil surface was characterized by scanning electron microscopy (SEM). Figure 1a is the SEM image of a typical area of the dark brown Cu surface. It can be seen that the surface is covered with Cu_2O nanowire arrays. The side view of the nanowire array in Figure 1b shows that the nanowires are ~ 50 nm in diameter and over 10 μm in length. These nanowires are free standing on Cu substrate and are nearly perpendicular to the substrate. The powder scratched off from the Cu foil were suspended in hexane by sonicating and further characterized by TEM (Figure 1c). The bright-field TEM image (Figure 1c) shows that the diameter is about 50 nm and is consistent with the one observed by SEM. The inset is the selected area electron diffraction (SAED) recorded from a single nanowire and the pattern shows a single crystal feature. The zone axis can be identified as 2-1-1 according to the PDF#05-0667,

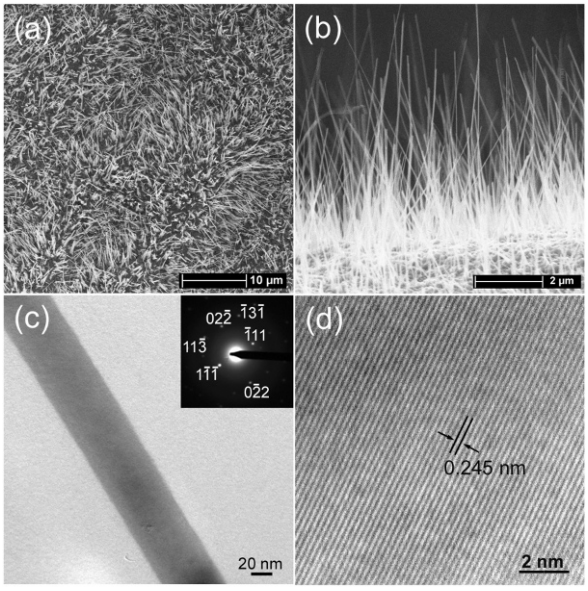

Figure 1. SEM images of Cu_2O nanowires: top view (a) and side view (b). (c) TEM image of a single nanowire. The inset is the corresponding SAED pattern. (d) HRTEM image of Cu_2O nanowire. The nanowire consists of well-defined continuous (111) planes (d = 0.245 nm), which pack parallely along the direction of nanowire growth direction.

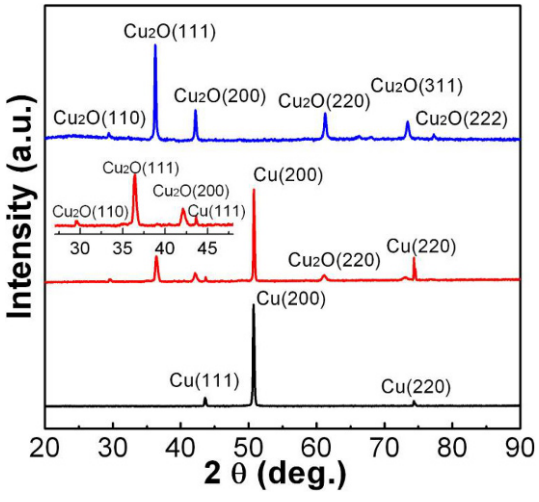

Figure 2. XRD patterns of Cu foil before (the bottom black one) and after heat treatment (the middle red one). The top blue one is the XRD pattern of the surface oxidation layer after heat treatment.

indicating the existence of (111) planes. High resolution TEM study (Figure 1d) further revealed that the nanowire consists of well-defined continuous (111) planes (d = 0.245 nm), which pack parallely along a growth direction of [0-11] [13].

Figure 2 shows the X-ray diffraction (XRD) patterns of Cu foil before and after annealing and the dark brown

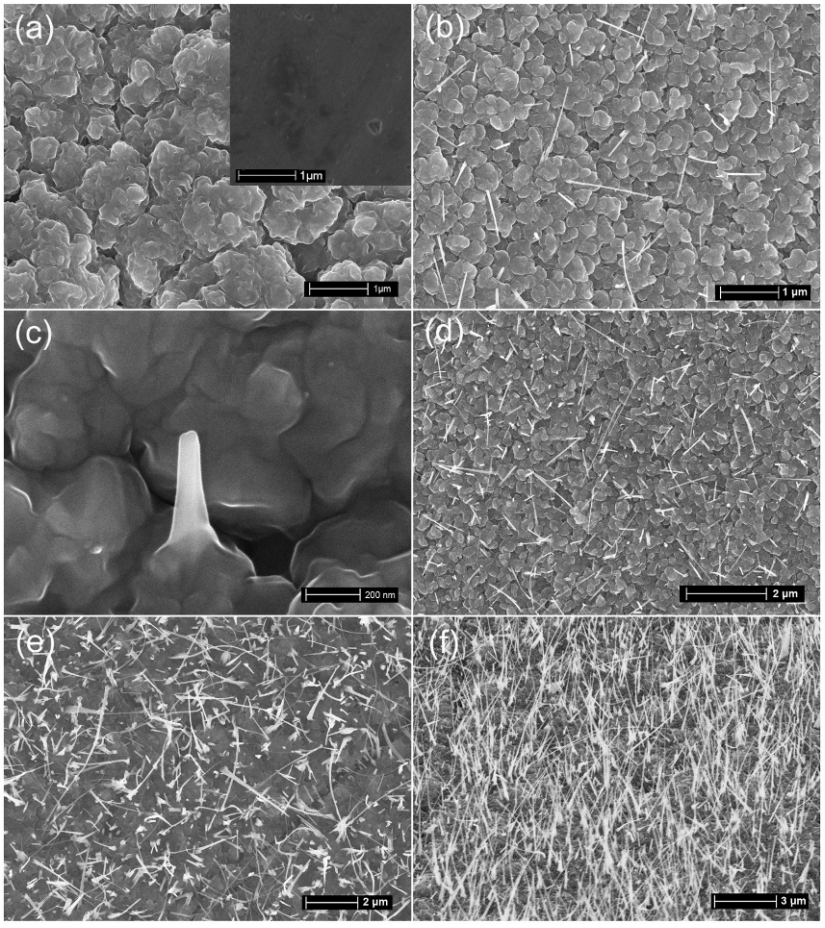

Figure 3. SEM images of the morphology of Cu foil surface heat-treated at 1 min (a), 5 min (b), 10 min (d), 30 min (e) and 60 min (f). (c) A close view of a nanowire in growth. The inset of a is the Cu foil before the heat treatment.

powder at the surface of Cu foil after annealing. The Cu foil before annealing shows characteristic peaks of pure Cu (bottom black line) at 43.5, 50.6, and 74.4°, corresponding to Cu (111), Cu (200), and Cu (220), respectively. After annealing, the Cu foil surface turned to dark brown and its XRD pattern (middle red lines) shows both characteristic peaks of Cu and Cu_2O. The peaks at 29.6, 36.3, 42.1, and 61.1° are ascribed to Cu_2O (110), Cu_2O (111), Cu_2O (200), and Cu_2O (220), respectively. Again, the peaks at 43.6, 50.6, and 74.4° are corresponding to Cu (111), Cu (200), and Cu (220), respectively. The dark brown surface layer after annealing was scratched carefully off from the Cu foil and the resulting powder was examined by XRD. Its XRD pattern (top blue line) shows a pure phase of Cu_2O with characteristic diffraction peaks at 29.3, 36.3, 42.1, 61.1, 73.3, and 77.2°, corresponding to Cu_2O (110), Cu_2O (111), Cu_2O (200), Cu_2O (220), Cu_2O (311), and Cu_2O (222), respectively. The XRD pattern recorded here confirmed that so-fabricated nanowires are in Cu_2O stucture. It should be noted that the intensity of Cu_2O (111) peak is much stronger than the expected intensity from a randomly oriented Cu_2O powder (PDF#05-0667); in consistent with the cylindrical symmetry of the nanowires with (111) planes parallel to the growth direction [0-11]. This is consistent with what has been observed in HRTEM in Figure 1d.

To further observe the growth of Cu_2O nanowires, the surface morphology of Cu foil was investigated by SEM at various stage of the heat treatment. Figure 3 shows the SEM images of the Cu foil surface after heat-treated at 1 min (a), 5 min (b and c), 10 min (d), 30 min (e), and 60 min (f). It can be seen that the heat treatment immediately caused a rough oxidation surface layer in 1 min (Figure 3a). After 5 min of annealing, some nanowires appeared on the surface (Figure 3b). A close view of a nanowire root shows clearly a direct connection to the oxidation layer (Figure 3c). Figure 4b shows the HRTEM image of a nanowire root, which shows polycrystalline feature and is different from the structure of nanowires. It indicates

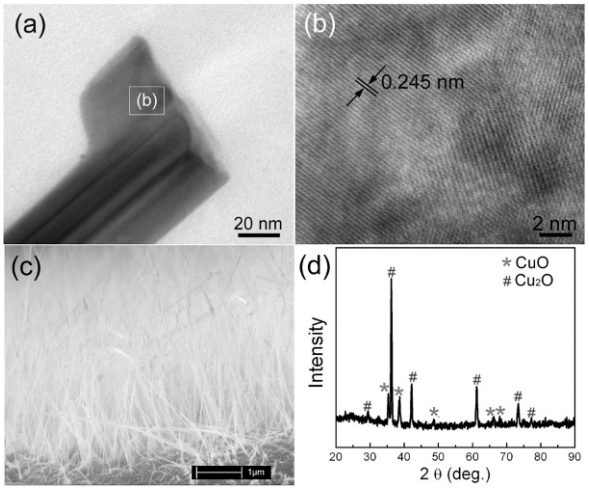

Figure 4. The TEM image of a nanowire root (a) and HRTEM image of the root. The SEM image and XRD pattern of nanowires produced by annealing Cu foil at 500°C.

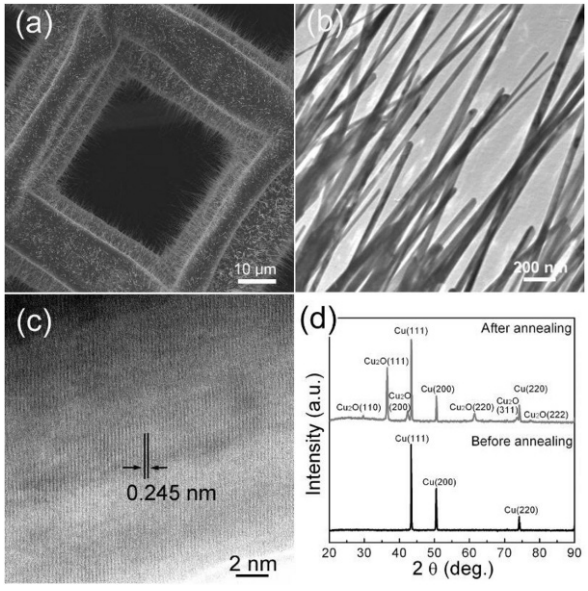

Figure 5. The SEM image (a) and the TEM image (b) of Cu_2O nanowires produced by heat treatment on Cu grid. (c) a HRTEM image of a so-produced Cu_2O nanowire. (d) XRD patterns of Cu grid before (the bottom) and after heat treatment (the top).

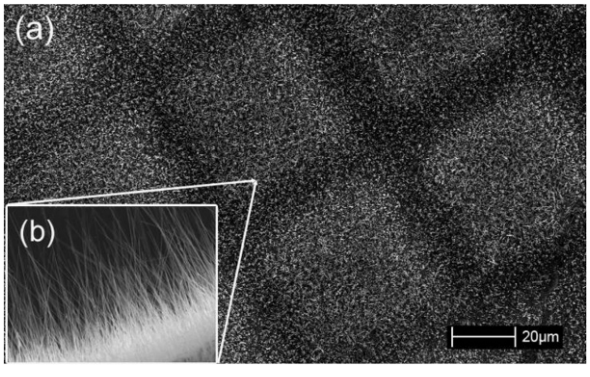

Figure 6. (a) The SEM image of a patterned Cu_2O nanowire array fabricated by partially covering Cu foil. (b) The SEM image of the side view of these nanowires.

that the growth of Cu_2O nanowire probably is induced by a crystal reconstruction of the rough oxidation layer from multi crystal to lower energy (111) plane prevailed structure. Well-arranged (111) planes accumulated parallely along [0-11] direction enable the continued growth of nanowires. The similar growth direction has been found in the Cu_2O nanowires synthesized by a wet-chemical method, where the growth was along the direction of [110] [13]. This is also similar to what has been observed in Au nanorods, where the growth of cubic (fcc) structured Au is along the direction of [110] with the (111) planes packed parallely [14, 15] The Cu foil annealed with 10 min, 30 min, and 60 min shows an increase in nanowire density and length (Figure 3d–f). The increase in density implies a continual nucleation process during thermal treatment and further indicates that the formation of Cu_2O nanowires was thermodynamically facilitated at this temperature. The excessive oxidation to a mixture of Cu_2O and CuO was found an annealing temperature went higher than 500° (Figure 4c,d). But annealing at 300° is insufficient for nanowire growth.

The Cu_2O nanowires can also be grown on a Cu grid, which is used as a sample holder for regular TEM investigation. Under similar annealing condition as those in Cu foil (in air at 400C for 1 h), Cu_2O nanowires grew along the Cu bar of the grid. Figure 5a and 5b show SEM and TEM images of Cu_2O nanowires produced on Cu grid. The HRTEM (Figure 5c) and XRD (Figure 5d) further confirmed that these Cu_2O nanowires are structurally the same as those grown on Cu foil.

Since the Cu_2O nanowires are fabricated by oxidation of Cu in air, the access to oxygen is critical for Cu surface to grow nanowires. This technically enables the fabrication of Cu_2O nanowires in a desired pattern. A simple experiment was demonstrated to form a patterned nanowire array. A bare Au TEM grid was pressed on a pre-treated Cu foil and then the Cu foil was annealed in air at 400C for 2 h. The Au grid prevented the Cu surface underneath from accessing oxygen. The SEM image (Figure 6) shows that the area without Au grid cover has dense nanowires on the top, but the area covered with Au grid does not. This again convinced that Cu_2O nanowires were produced by oxidation of Cu surface and exhibited the great potential of this method for manufacturing control.

4. Conclusions

In summary, this work demonstrated a facile method for the fabrication of Cu_2O nanowire arrays. Simple heat treatment on any Cu substrates in air results in a dense Cu_2O nanowire arrays on the top. The as-prepared nanowires are $\sim$ 50 nm in diameter and $\sim$ 10 µm in length. The growth of Cu_2O nanowires was characterized by electron microscopy. The optimal temperature for Cu_2O nanowire production is 400°C. This method provides a great potential route for a large scale fabrication of Cu_2O nanomaterials based devices, such as sensors [4] and solar cells [5].

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