

Room temperature growth of CuO nanorod arrays on copper and their application as a cathode in dye-sensitized solar cells

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Abstract

Vertically aligned CuO nanorod arrays on copper electrodes with diameters of ~5 nm and lengths of hundreds of nanometers were synthesized successfully using a simple wet chemical method at room temperature. The composition, morphology, and growth conditions of the nanorods were characterized. We also show that the as-prepared CuO nanorod arrays are promising hole-transport media of dye-sensitized hetero-junctions for solar energy conversion.

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1. Introduction

One-dimensional nanomaterials are currently considered to be key structural components of future electronic, optical, and mechanical devices [1]. Their unique properties could be harnessed for the design and fabrication of nanosensors, switches, nanolasers and transistors [1–4]. Practical applications of nanowires/nanorods often require them to be regularly patterned. To this end, various techniques including arc discharge, laser ablation, template, precursor thermal decomposition, etc. have been developed to prepare well-aligned nanowires/nanorods [5–10]. However, it is still a challenge to develop simple methods for the fabrication of uniform nanowire or nanorod arrays that are cost-effective and allow large-scale production. In this letter, we report on the fabrication of robust CuO nanorod arrays on copper electrodes at room temperature using a simple wet chemical method. The possible application of these materials as cathodes of

dye-sensitized photovoltaic devices has also been demonstrated.

CuO is a p-type semiconductor with a narrow bandgap (1.2 eV), which has interesting photovoltaic, electrochemical, and catalytic properties [11–14]. The large surface area, excellent stability, low production cost, and good electrical properties of the CuO nanorod arrays we prepared are all favorable characteristics for the cathode materials of dye-sensitized solar cells.

CuO nanowhiskers were prepared as early as 1950s by Nabarro et al. [15] and recently Xia and coworkers [16] by heating copper foils in an O₂ atmosphere. Our group obtained CuO nanoribbon arrays on copper converted from Cu(OH)₂ nanoribbon arrays prepared by solution-solid reactions [17,18]. Solution syntheses of CuO nanofibres, nanorods, nanowires, and nanoribbons have also been reported by a number of research groups [19–23]. A common feature of these methods for the synthesis of CuO nanowires is so far the requirement of high temperature. Although the temperatures for the solution methods are somewhat lower, the precipitated nanowires are normally in a powder form. The uniform CuO nanorod arrays we prepared in the present work are roughly aligned and firmly adhered on copper substrates.

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2. Experimental

A typical synthesis of p-CuO nanorods was carried out as follows. First, a copper foil (1 cm²) was washed with a 4 M HCl solution for ~15 min and subsequently with de-ionized water three times to remove surface impurities. The washed copper foil was then immediately immersed into 400 ml of water containing 1 ml of ammonia (13 M) and 2 ml of NaOH (1 M) solutions at room temperature (pH is 11 at this concentration). After a given reaction time (96 h), the sample was taken out of the solution, washed with deionized water three times, and dried in air. A black film was obtained (viewed through naked eye), which covered uniformly on the Cu substrate. The pH of the solution was varied for growing the CuO nanorods by changing the amount of NH₃ and NaOH solutions. For pH 11.5, 400 ml of water containing 2 ml of NH₃ (13 M) and 3 ml of NaOH (1 M) solution was used. Whereas for pH 12, 400 ml of water containing 1 ml of NH₃ (13 M) and 10 ml of NaOH (1 M) and for pH 12.3, 400 ml of water containing 5 ml of NH₃ (13 M) and 15 ml of NaOH (1 M) were used. Different growth times were also investigated. The morphology of the synthesized nanorod was characterized using JEOL 6300F scanning electron microscopy at an accelerating voltage of 15 kV. The phase identification and the chemical composition were carried out using powder X-ray diffraction (XRD; Philips PW-1830) and X-ray photoelectron spectroscopy (XPS; Physical Electronics PHI 5600). Reflectance spectra were recorded using a UV–vis spectrometer (Perkin Elmer, Lambda 20). More experimental details are provided in Supporting Information (S-1).

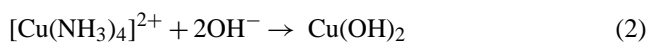
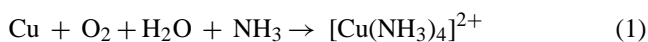
3. Results and discussion

Fig. 1 shows the SEM images of p-CuO nanorods grown on copper foil substrates at different pH and reaction time intervals. As can be seen from the top view, the nanorods cover the copper surface uniformly, smoothly and compactly. In addition, the nanorods are roughly aligned perpendicular to the substrate surface. When the reaction time was increased from 96 to 130 h, the lengths of the nanorods were increased as shown in Fig. 1a and b. Preliminary transmission electron microscopy examination showed that the CuO nanorods are about ~5 nm thick (see also Supporting Information (Fig. S2)) and a few hundred nanometers long. When the solution pH was varied from 11.0 to 12.3, the black nanorod film was very compact (see Fig. 1a–f) and the colorless solution became bluish, indicating the dissolution of Cu²⁺ under the strong basic condition. At pH 12, the nanorods were visibly formed within 96 h. However, when the pH was increased to 12.3, the CuO nanorod growth was much slower and in fact only visible after a period of 7 days. To cover the complete surface of the copper substrate took nearly 14 days. The observed surface of the CuO nanorod array film at this pH is somewhat shiny compared to the samples prepared under lower pH conditions. Also, the

growth is more compact as can be seen from the SEM image (Fig. 1f).

Fig. 2 shows the XRD pattern of an as-synthesized p-CuO nanorod/Cu sample. It matches quite well with the XRD diffraction data of the monoclinic CuO powder (JCPDS 45-0937). By comparing to the standard XRD pattern of the CuO powder, the peaks at 32.5, 35.4, 38.7 and 38.9 can be attributed to the Miller indexes of ($\bar{1}$ 1 0), (0 0 2) and ($\bar{1}$ 1 1), (1 1 1), and (2 0 0) for CuO, respectively. Note that the peaks at 2θ values (43.3 and 50.4 °C) are due to the substrate copper. The observed peaks are similar for all the samples prepared at different pH values and growth time intervals. The chemical identity of the CuO nanorods is also confirmed by XPS (see Supporting Information (Fig. S1)).

The chemical reactions that are involved in the room temperature growth of the CuO nanorod arrays on copper are believed to proceed as follows:



The reactions (1) and (2) were used previously for the synthesis of Cu(OH)₂ nanoribbons [17,18]. The key difference here is that the solution used is much more basic so that Cu(OH)₂ is unstable and thus immediately decomposed to CuO. This is consistent with the fact that the blue color characteristic of Cu(OH)₂ never appeared on the copper surface during growth. As a result, we obtained an excellent adhesion of the CuO nanorods to the Cu substrates.

Solar energy conversion processes have garnered much attention of late as the most attractive methods to generate useful form of alternative energy. In particular, dye-sensitized solar cells based on TiO₂ nanoparticles have reached an overall energy conversion efficiency as high as ~10% [24]. Here, photoexcited dye molecules such as *cis*-di(thiocyanato)*N,N'*-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid)-ruthenium (II) [N3 dye] anchored to the TiO₂ nanoparticle surfaces could inject electrons to the conduction band (CB) or holes to the valence band (VB). In these cells, a thin layer of Pt ($\Phi = 5.65$ eV) coated on a conducting glass is normally as the counter electrode [25,26]. It seems worthwhile to study the possibility of replacing the more expensive Pt/conducting glass electrode by our p-CuO-nanorod/Cu electrode. First, the work function of CuO is close to that of Pt (i.e., $\Phi = 5.3$ eV) [25,26]. Second, p-CuO has a relatively high hole mobility (0.1 cm² V⁻¹ s⁻¹) [25]. Third, the aligned CuO nanorods synthesized in situ with excellent adhesion on the copper substrate have a high surface area and may serve as convenient cathode for the dye-sensitized heterojunctions in solar photovoltaic applications. In addition, the reflectance spectrum of the p-CuO nanorods in Fig. 3 shows strong absorption below 850 nm, suggesting that the nanorod films can also harvest the solar energy efficiently.

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