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Effects of copper precursor concentration on the growth of cupric oxide nanorods for photoelectrode using a modified chemical bath deposition method

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ABSTRACT

In this study, vertically aligned CuO nanorods were grown using a modified chemical bath deposition method with various copper precursor concentrations. The morphological, structural, optical and photoelectrochemical properties of the synthesized CuO samples were characterized using a field-emission scanning electron microscope, an X-ray diffractometer, a UV–visible spectrometer and a three-electrode potentiostat, respectively. The growth rates of the samples varied from 4.3 to 500 nm/min with the varying precursor concentrations. The vertically well-grown CuO nanorods exhibited one-dimensional growth along the (020) plane. We obtained a maximum photocurrent density of −1.05 mA/cm^2 at −0.6 V (vs. SCE) from the CuO nanorod photoelectrode grown using the 10 mM copper precursor concentration.

1. Introduction

In 1972, photoelectrochemical (PEC) cells were first embodied by Honda and Fujishima using TiO_2 as the photoelectrode material [1]. Since then, semiconductors such as $SrTiO_3$, $BaTiO_3$ and ZnO have been investigated as candidates for photoelectrode materials [2–4]. However, these materials cannot fully absorb visible light due to their large band gap energies. Cupric oxide (CuO) has attracted much attention as a promising photoelectrode candidate because of its narrow band gap energy (1.4–1.7 eV) [5,6].

CuO is also generally a p-type semiconductor. CuO has been a material of interest in many technological fields such as electronics, sensors, photovoltaic devices, batteries, field-emission devices, superconductors and photocatalysts [7,8]. For these applications, various types of CuO nanostructures have been studied, such as thin films [5], nanowires [9], nanoparticles [10] and nano-urchins [11]. One-dimensional (1-D) structures such as nanorods and nanowires have attracted attention because these materials have a large surface area and fast charge transport [12,13]. Thus, we sought a process to preferentially synthesize 1-D structures.

In the literature, many processes have been used to synthesize 1-D CuO structures, including hydrothermal methods [14,15], chemical bath deposition (CBD) [16], arc-discharge processing [17], thermal evaporation [18] and thermal oxidation using copper foil [9]. Among these processes, the CBD method is cost-effective and provides a way to easily control the growth of nanostructures by slightly adjusting parameters. Furthermore, this method is compatible with any type of substrate, including metals, polymers and semiconductors. However, conventional CBD methods also have issues, including an inconstant concentration of the precursor solution during growth and inefficient heat transfer by convective heat.

In this study, we used a modified chemical bath deposition (M-CBD) method for the growth of CuO nanorods. Our modifications overcome the issues associated with conventional CBD in that we heat the substrate directly with conduction rather than relying on convection, and we maintain a constant concentration of the solution by continuously injecting solution. This M-CBD process can provide very fast growth of 1-D nanostructures. Recently, our group reported the fast growth of ZnO nanorods using the M-CBD method, which has the advantage of growing 1-D oxide nanostructures [19]. In this work, we synthesized CuO nanorods using various copper precursor concentrations using the M-CBD method. The objective of this work was to study the effects of the copper precursor concentration on the growth of CuO nanorods for photoelectrodes through the investigation of morphological, structural, optical and PEC properties.

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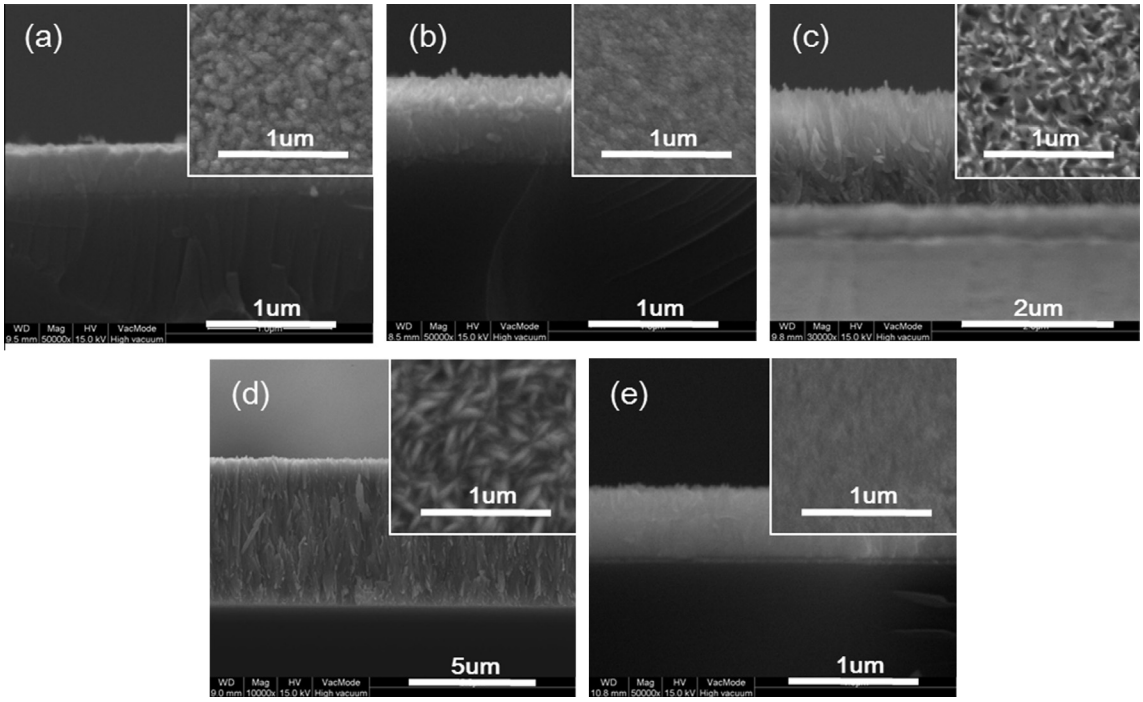

Fig. 1. SEM images of samples with various precursor concentrations: (a) 0.1 mM, (b) 1 mM, (c) 10 mM, (d) 100 mM, (e) 1 M.

2. Experimental details

CuO nanorods were grown on fluorine-doped tin oxide (FTO) substrates using a M-CBD process. The FTO substrates were sonicated in acetone and methanol for 10 min each, rinsed in distilled water and dried by filtered air. After drying, the substrates were treated for 10 min with a UV–ozone cleaner. A seed layer was deposited on the FTO substrates. A seed layer solution containing 1 M copper acetate was prepared using copper acetate monohydrate ($Cu(OAc)_2{\cdot}H_2O$), 2-methoxyethanol and monoethanolamine as the precursor, solvent and stabilizer, respectively. The solution was spin-coated on the FTO substrates at 4000 rpm for 30 s and dried at 120 °C for 10 min in an electric oven. This spin-coating and drying process was repeated three times. Then, the FTO substrates were annealed in air at 300 °C for 10 min.

For the M-CBD process, copper acetate aqueous solutions with the following concentrations were used: 0.1 mM, 1 mM, 10 mM, 100 mM and 1 M. The solutions contained copper acetate monohydrate, distilled water and 25% ammonia aqueous solution. The volume ratio between the copper acetate aqueous solution and the 25% ammonia solution was fixed at 10:1. The pH values of solutions for 0.1 mM, 1 mM, 10 mM, 100 mM and 1 M were 11.6, 11.5, 11.4, 10.9 and 6.5, respectively. To grow the CuO nanorods, a constant concentration and constant amount of solution was fed into the M-CBD reactor, which was placed on the seeded substrate using a peristaltic pump (Masterflex L/S, EW-7523-90). During deposition, the substrate was placed on a hot plate for conductive heating and heated to 175 °C for 15 min. The solution was maintained at 65 °C before feeding. $Cu(OH)_2$ was formed in the solution as precipitates. In addition, continuous heating transforms the hydroxides into oxides by dehydration. The reactions for CuO growth can be expressed as follows:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2$$

$$Cu(OH)_2 \underset{heat}{\rightarrow} CuO + H_2O$$

After growth, the samples were rinsed with distilled water and dried with filtered air. A more detailed M-CBD process description is reported elsewhere [19].

The sample morphology was examined using field-emission scanning electron microscopy (FE-SEM, Quanta 200FEG), and the structural properties were analyzed using X-ray diffraction (XRD) with Cu Kα radiation. The optical absorption was recorded using UV–visible spectroscopy. The PEC performance was measured using a three-electrode cell. For the PEC measurements, a grown CuO sample, a graphite rod and a saturated calomel electrode (SCE) were used as the working electrode, counter electrode and reference electrode, respectively. The PEC measurements were performed with a potentiostat (Digy-Ivy, DY2111) interfaced with a computer. A voltammetric sweep was performed from 0 V to −0.7 V. A 1 M KOH aqueous solution (pH = 13.5) was used as the electrolyte. For the analysis of the pH effect of electrolyte, a 0.5 M Na_2SO_4 aqueous solution (pH = 6.5) was also used. A 300-W arc Xe-lamp with 1-sun illumination (AM 1.5 filter, 100 mW/cm^2) was employed as the light source.

3. Results and discussion

Top-view and cross-sectional SEM images of the copper oxide nanostructures grown on FTO substrates with copper precursor concentrations of 0.1, 1, 10, 100 mM and 1 M are presented in Fig. 1. Nanoparticles are observed on the FTO substrate for the 0.1 mM sample. Short nanorods were grown irregularly on the 1 mM sample. At these low precursor concentrations (0.1 mM and 1 mM), there are not enough Cu^{2+} ions to grow nanorods, and consequently, nanoparticles and thin films consisting of irregular short nanorods were grown. However, vertically well-aligned copper oxide nanorods were grown when using the 10 mM and 100 mM precursor concentrations, as observed in Fig. 1(c) and (d). These concentrations were observed to be the most suitable concentrations for the growth of nanorods in this study. At the highest precursor concentration tested, 1 M, there were excessive Cu^{2+} ions, resulting in a film-like smooth copper oxide, as observed in Fig. 1(e). The growth of CuO nanorods may have been suppressed by a homogeneous reaction between the primary particles due to excessive Cu^{2+} ions. In addition, because the pH value of the 1 M solution is 6.5, which is much lower than that of the other solutions, the 1 M solution can dissolve Cu on the surface of the sample more easily and hindered the growth of copper oxide [20]. The vertical lengths of the samples were measured to be 65, 280, 1700, 7500 and 250 nm from Fig. 1(a)–(e), respectively. The maximum growth rate of the copper oxide nanorods was calculated to be 500 nm/min and occurred during deposition using the 100 mM concentration. This growth rate was significantly higher than that previously reported [14,15,21] and highlights a potential advantage of the M-CBD method.

In Fig. 2(a), XRD patterns of the samples using various copper precursor concentrations are presented. The peaks in the XRD patterns at $2\theta = 32.48°$, 35.61°, 38.71° and 53.52° are identified as the (110), ($\bar{1}11$) and (002), (111) and (200) and (020) planes, respectively, of monoclinic-phase cupric oxide (CuO) (ICSD card file: 01-089-5897). The peaks at $2\theta = 33.88°$, 37.96° and 51.78° are from SnO_2 in the FTO substrate (ICSD card file: 01-077-0452). In the 10 mM and 100 mM samples, the crystalline peaks of CuO