



Enhanced photoelectrochemical processes by interface engineering, using Cu₂O nanorods



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ABSTRACT

Here in this research, we report on surface engineering of bulk Cu₂O photocathode thorough employing nanostructured materials. Nanorods (NRs) of copper oxide with average lengths of 150 nm have been synthesized by anodization of Cu foil in aqueous KOH electrolyte, followed by annealing treatment. Several heating processes were examined to reach pure Cu₂O nanostructures and lastly the moderate annealing procedure at 700 °C under Ar gas flow resulted in pure Cu₂O nanostructures, confirmed by XRD analysis. Surface modified nanorod/bulk Cu₂O electrode was prepared by spin coating of sediments suspension of anodized drop on bulk Cu₂O film fabricated through thermal oxidation method, followed by final heating process. Photoelectrochemical analysis indicates that nanorod/bulk Cu₂O electrodes have noticeable enhancement in photocurrent, around 76% at –0.6 V and the favorable decrease in interface resistance about 10³ Ω in comparison to the bulk Cu₂O thermal oxidized electrode. This novel bulk Cu₂O electrode with modified nanostructured surface can be a good candidate as the electrode of either photoelectrochemical systems for hydrogen generation or the photocathode of bulk heterojunction photovoltaic cells.

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1. Introduction

The development of cost effective and promising photovoltaic (PV) systems is an important aim to manage the growth of PV-generated energy and reducing the greenhouse gas emission. To develop up-scaling fabrication process for PV cells, Metal oxide (MO) semiconductors are attractive candidates. Being chemically stable, earth abundant and low-cost manufacturing process in ambient condition [1] make metal-oxide-based photovoltaics a capable candidate. Utilizing inexpensive materials or employing easy fabrication methods typically results in photoactive materials with high density of defects and impurities which causes low-minority carrier diffusion length [2]. Using the absorbing nanostructured material in bulk-hetero-junction scheme can be a solution to resolve carrier collection length limitation [3]. It is more promoted if carrier collection achieved in a path perpendicular to light absorption, by using nanorod or nanotubular structures [1–3].

Among the inexpensive MO semiconductors, cuprous oxide

(Cu₂O) exhibits great potential for solar energy conversion due to direct band gap about 2.1 eV, good majority carrier mobility about 100 cm²/Vs at RT and appropriate absorption coefficient about 1000 cm⁻¹ at 600 nm [4–6]. There are few reports on fabrication of freestanding Cu₂O nano-architectures. However consuming additives make process complicated, majority of chemical processes by using various kinds of ligands and surfactants has been reported [7–12]. Electrodeposition based template process to gain nanowire Cu₂O branches are most informed [13], but etching templates away usually makes some defects and surface trap states in final structure. Among available procedures, electrochemical anodization is cost effective surface treatment process to grow several nano-architectures on lots of metals such as copper [14]. There are some reports based on this method to fabricate Cu₂O nanostructures in presence of either Cu or CuO [15–18]. In this research, copper oxide nanorod arrays were formed thorough anodic oxidation of polished pure copper foil in the aqueous alkaline. Several annealing treatment were examined to find the proper condition to get pure crystalline Cu₂O nanostructures. Hetero-structure of nanorod/bulk Cu₂O fabricated by deposition of copper oxide anodized nanostructures on bulk Cu₂O film followed by proper heat treatment which takes the both advantages of long diffusion length of charge carriers in bulk crystalline Cu₂O and

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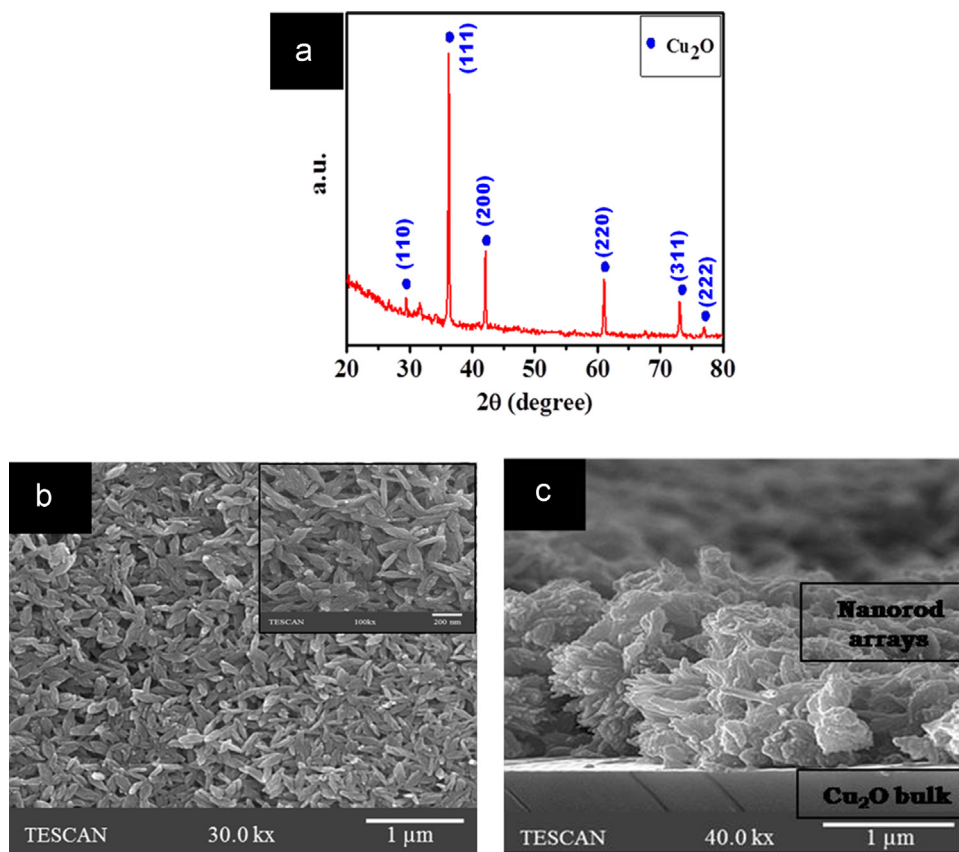


Fig. 1. (a) XRD analysis of anodizing sediments heated at 700 °C for 15 min under Ar flow. FESEM images of anodizing sediments at 10 V in KOH electrolyte of pH=11 spin coated on Cu₂O bulk, (b) top view, and the inset shows the high resolution, (c) cross sectional view of bulk hetero-junction nanorod/bulk layer.

enhanced surface properties modified by nanostructures.

2. Experimental

Pure copper foil (99.9%, 0.1 mm thick) was acquired from Iran industry. Before anodization pieces of Cu foils were polished with 50 nm alumina powder to remove any native oxide. The anodization was performed in two-electrode cell with platinum and copper foil as counter and working electrode respectively. It is reported that Cu foil is dissolved in aqueous KOH with pH ≤ 10 [16]. So three aqueous KOH electrolytes with pH=11, 11.5 and 12 was selected for anodization at 10 V. The light blue precipitate was created on the Cu foil which can be collected and transferred to any arbitrary substrates. The time-dependent anodization currents were recorded using computer controlled multimeter. The morphology of the anodized samples was studied using a TESCAN field emission scanning electron microscope (FESEM). The crystalline structure was analyzed by XRD, SPECTRO AMATEK with Cu K α ($\lambda=0.1506$ nm) and interpreted through X'pert high score plus software. A conventional three electrode contained Pt wire, Ag/AgCl and nanorod/bulk Cu₂O and bare bulk Cu₂O photocathode as counter, reference and working electrodes respectively was adjusted for the photoelectrochemical investigation. The chopped light source was a 10 W white LED, irradiated the samples at the rate of 5 s exposure followed by 5 s darkness periodically. The behavior of the Cu₂O electrodes in 1 M aqueous Na₂SO₄ was recorded by Autolab potentiostat/galvanostat. The Mott-Schottky analysis was performed at 45 KHz in the potential range of chemical stability, and electrochemical impedance spectroscopy (EIS) was accomplished at frequency range of 0.01 Hz to 10 KHz at open circuit voltage under dark condition.

3. Results and discussion

3.1. Anodization in KOH aqueous electrolyte

The current–time graphs of anodizing process illustrated that as pH increased the corresponded current density also improved (Fig. S1a) which can be related to pH dependence of the solubility of Cu⁺ in aqueous electrolyte (Eq. (1)) [16]. The reduction in transient current value is a result of formation of metal oxide layer near the surface.



FESEM analysis of as fabricated sediments shows that the size of NRs became finer as the pH of electrolyte increased (Fig. S1b and c). It seems that the formation of these NR arrays took place by initial pits created in the surface of Cu in anodizing process (Fig. S2) and then grew in one direction faster which is common process for metal oxide formation [17]. XRD analysis indicates that the formed structures were composed of copper oxide composition before any heating processes. To reach pure Cu₂O crystalline phase, proper annealing treatment is needed. At the temperatures higher than 400 °C CuO converted to Cu₂O [18]. Here various heating temperatures were applied at 500 °C, 600 °C, 700 °C and 800 °C for 2 h under Ar gas flow. The XRD investigation illustrated at higher temperature CuO phase reduced as well Cu phase increased and at 800 °C Cu phase appears abundantly (Fig. S3a–d). Additionally annealing at high temperature could cause some shrinks in the structures which may be due to releasing of H₂O and O₂ in them which cause losing weight as in this experiment was about 0.05 gr through heating at 700 °C for 2 h. Therefore optimum temperature should be selected around 700 °C under Ar gas

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