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Vertical CuO nanowires array electrodes: Visible light sensitive photoelectrochemical biosensor of ethanol detection

Weiting Zhan[a,b,*], Zhe Chen[a,b], Ji Hu[a,b], Xiongjie Chen[a,b]

[a] The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China
[b] Key Laboratory for Ferrous Metallurgy and Resource Utilization of Ministry of Education, Wuhan University of Science and Technology, Wuhan, China

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ABSTRACT

Photoelectrochemical (PEC) sensing using visible light has attracted great attention for high sensitivity with low undesired background noise. A CuO electrode with nanowires on Cu foil was synthesized by thermal oxidation and the devices was used to explore the PEC sensing for ethanol detection under visible light. The morphology, composition, optical, and PEC properties of CuO nanowires have been systematically investigated. The results showed that the CuO nanowires were present on the top surface of specimens with single phase and the thick interface layer were made of Cu_2O between CuO nanowires and Cu foil substrate. The CuO nanowires on surface contained two types of nanowire (bend CuO Nws and vertical CuO Nws). With the temperature increasing, the Nws of first type decreased, and the Nws of second type started to increase. When the Cu foil were annealed at 700 °C, densely bundled CuO Nws array was vertically fabricated on the foil. The band gaps of CuO nanowires annealing at 400 °C, 500 °C, 600 °C, and 700 °C, were 1.715, 1.714, 1.698, 1.691 eV, indicating that CuO nanowires annealing at 700 °C can obtain the highest photoreponse. The photocurrent of the vertical CuO nanowires array annealing at 700 °C were calculated with 668 μA cm^{-2} about 2-fold, 6-fold and 10-fold higher than that to CuO nanowires annealing at 600 °C, 500 °C and 400 °C, respectively. Combing with the morphology of CuO nanowires annealing at different temperature, the vertivally-aligned nanowires array at 700°Cwas attractive than others. This vertical CuO nanowires device prepared at 700 °C is visible-light irradiation and shows the fast photoresponse, present a detection limit of 23.2 nM, which is much lower than those with the similar configurations reported previously. It is probable that the vertical CuO nanowires array may be applied as the proposed PEC sensor to determine ethanol in further.

1. Introduction

The photoelectrochemical (PEC) sensors, as a new and green bioanalysis, have arisen widespread interest due to its unique benefits such as low cost, simple and convenient [1–3]. The separation between the source of excitation and photocurrent detector offers high sensitivity with low undesired background signal. For the successful development of PEC sensors, the photoactive materials with excellent PEC properties appears vital in particular [4–6].

TiO_2 and ZnO, as traditional semiconductor materials, have been applied widely in photoelectrochemical sensors. However, the wide band-gaps of TiO_2 (3.2 eV) and ZnO (3.4 eV) limit the efficiency of the visible light and their application in biosensors [7–9]. Copper oxides (Cu_2O and CuO), is multifunctional p-type semiconductor for visible light photocatalysis, with band gaps ranging between 1.5 and 2.2 eV. Copper oxides has already received high attention in the field of chemosensing, photocatalysis, photovoltaics, and photoinduced water splitting with visible light-driven proton reduction [10–12]. Recent measurement of the carrier diffusion length suggests that nanostructured copper oxides would exhibit an improved performance for photoelectrochemical applications. Some efforts have been made to prepare copper oxides nanowires include electrodeposition of copper salts, solution-based method, template electrodeposition and thermal oxidation [13–16]. As shown in Table 1, compared to methods mentioned above with complex and multi-step synthesis procedures, the direct and simple thermal oxidation used to synthesize CuO NWs has been recently given considerable attention due to its simplicity growth capability with no catalyst and template assisted. Over here, a visible light photoelectrochemical immunosensor based on copper oxides nanowires was fabricated by heating Cu foil in air.

Ethanol plays an important role in biomedicine, food fermentation, brewing, and other chemical processes. Several strategies for ethanol detection have been proposed to meet the growing demands, such as hydrometry [17,18], gas/liquid chromatography [19,20],

* Corresponding author.
E-mail address: zhanwt@wust.edu.cn (W. Zhan).

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Table 1
Summary of CuO nanowires obtained by different methods and their synthesis conditions.

Synthesis method	Catalyst	Processing steps	Application	Ref.
Solution-based method	NaOH and $(NH_4)_2S_2O_8$	2 steps	Nonenzymatic glucose and H_2O_2 biosensor	[13]
template electrodeposition technique	Au, $CuSO_4$ and H_2SO_4	3 steps	nonenzymatic glucose sensor	[14]
electrochemical dissolution and deposition	–	2 steps	–	[15]
Thermal oxidation	–	1 steps	O_2,SO_2 and NO_2 gas sensor	[16]

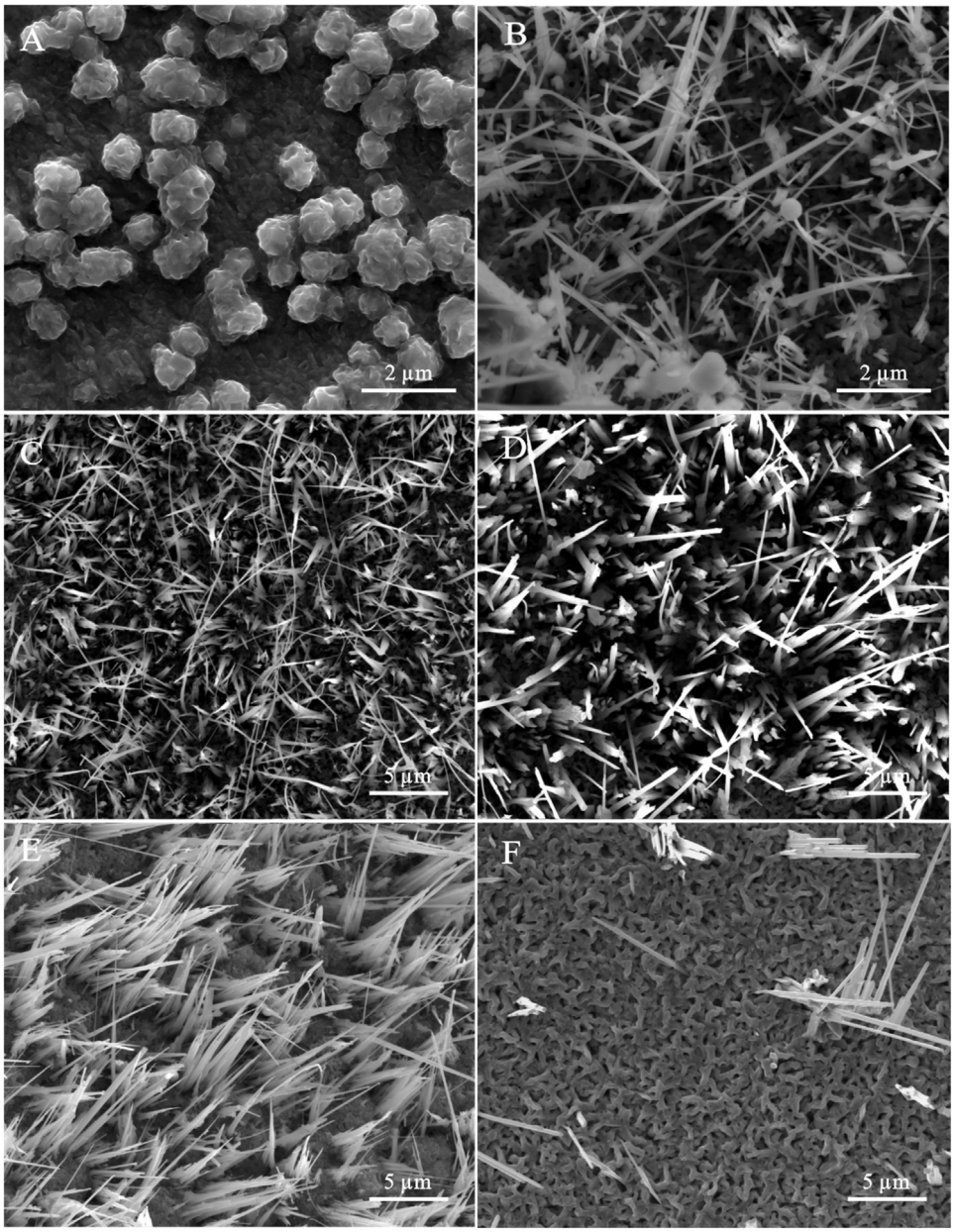

Fig. 1. FE-SEM images showing the morphology of the Copper oxide after annealed at 300 ˚C (C3) (A); 400 ˚C (C3) (B); 500 ˚C (C3) (C); 600 ˚C (C3) (D); 700 ˚C (C3) (E); 800 ˚C (C3) (F).

refractometry [21,22], and infrared spectroscopy [23,24]. These methods usually suffered from series of problems, e.g. high working temperature (≥300 ˚C), complicated fabrication and high cost, which greatly limits the application of semiconductor-based sensors for ethanol. Thus, the development of simple, convenient and reliable amperometric sensors to monitor ethanol is of great importance [25,26]. In this study, we demonstrate the fabrication of vertical copper oxides nanowires array on Cu foil as ethanol sensors. The resulting CuO nanowires devices exhibited high sensitivity for ethanol detection by photoelctrochemical sensing under visible light. The PEC sensors showed a lower limit of detection than the literatures [23,24], which exhibited its potential applications in many biological targets detection.

2. Experimental section

Cu foil (99.9%) of 10 × 10 × 1 mm were purchased from Aldrich.