Applied Surface Science 361 (2016) 11–17

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Hierarchically porous micro/nanostructured copper surfaces with enhanced antireflection and hydrophobicity

Ming Li, Yanjie Su, Jing Hu, Lu Yao, Hao Wei, Zhi Yang, Yafei Zhang*

Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Department of Micro/Nano Electronics, School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

ARTICLE INFO

Article history:
Received 25 September 2015
Received in revised form 23 October 2015
Accepted 28 October 2015
Available online 1 November 2015

Keywords:
Porous micro/nanostructured Cu foil
Antireflection
Superhydrophobicity
Anticorrosion
Hydrothermal

ABSTRACT

A facile hydrothermal method has been proposed to fabricate hierarchically porous Cu micro/nanostructures on Cu foil, whose growth can be controlled by the reaction time and the amount of ethylene glycol added into the precursor. Compared to commercially available Cu foil, the micro/nanostructured Cu surfaces exhibit not only greatly enhanced ability to absorb light over a wide range of wavelengths from 250 to 1000 nm, but also improved hydrophobicity from 90.4° to 151.2° without any low-surface-energy chemical modification. The reflectance can reach a lowest value of 10% at 300 nm and show a biggest decrement of 53% at 582 nm. Due to their superhydrophobicity, the micro/nanostructured Cu foils demonstrate an improved anticorrosion ability against 3.5 wt% NaCl solution compared with a bare one. The proposed mechanism indicates that the combination of the dual-scale roughness and the adsorbed air in pores account for the enhanced antireflection and hydrophobicity.

1. Introduction

The micro/nanostructured metallic film/foams have been considered to have enormous potential in improving the functional efficiencies of high-current-density batteries, energy conversion in solar cells, and highly efficient water splitting, which are regarded as the three pillars carrying a green and sustainable energy future [1–3]. By controlling the pore, ligament sizes, and surface properties, novel physical and chemical properties can be observed for the micro/nanostructured metallic film/foams. To date, significant efforts have been devoted to exploring effective approaches for realizing various controllable micro/nanostructured metals, including gold, silver, platinum, nickel, and copper (Cu) [4–9].

Among them, the hierarchically micro/nanostructured Cu film/foams have aroused much interest of researchers in various fields due to their large surface-to-volume ratios, excellent electrical, thermal conductivities, and mechanical workability [10–12], which have been widely used as electrode materials, catalysts, surface-enhanced Raman scattering (SERS) active substrates and sensors [10–14]. Up to now, a variety of methods have been presented to fabricate micro/nanostructured Cu film/foams with different morphologies. Typically, the electro/chemical dealloying methods are adopt to prepare nanoporous Cu foams with tunable nanoporosity, exhibiting applications of SERS, catalyst, and biosensor [11,12]. However, the methods easily lead to miscible metals remaining and formation of metal oxides in the nanoporous Cu [11]. Niederberger et al. [2] introduced a template-assisted wet-chemical deposition process to produce nanostructured Cu foam monoliths with relative mass densities from 7 to 21%. Nevertheless, this method needs templates to induce the formation of nanoporous structures, which increases the complexity of preparation. Li et al. [15] reported that hierarchically micro/nanostructured Cu/Ni film with superhydrophobic property could be prepared by a two-step electrodeposition process. Sun et al. [16] employed one-step electrodeposition method to fabricate porous nanostructured Cu film, showing an extraordinary hydrazine oxidation reaction performance and potential promise for direct hydrazine fuel cells. Even though such progresses have been made toward determining the complex structures of Cu as well as establishing structure–function relationships for them, to the best of our knowledge, little work has been done with a focus on the fabrication of hierarchically porous micro/nanostructures on Cu foil by a facile hydrothermal method.

On the other hand, one of the major challenges in Cu applications is the prevention of Cu corrosion, which leads to inferior device performance and failure [17,18]. It is believed that constructing superhydrophobic surface on a Cu substrate can improve its corrosion resistance. Yuan et al. [19] assembled a

* Corresponding author.
E-mail address: yfzhang@sjtu.edu.cn (Y. Zhang).

http://dx.doi.org/10.1016/j.apsusc.2015.10.217
0169-4332/

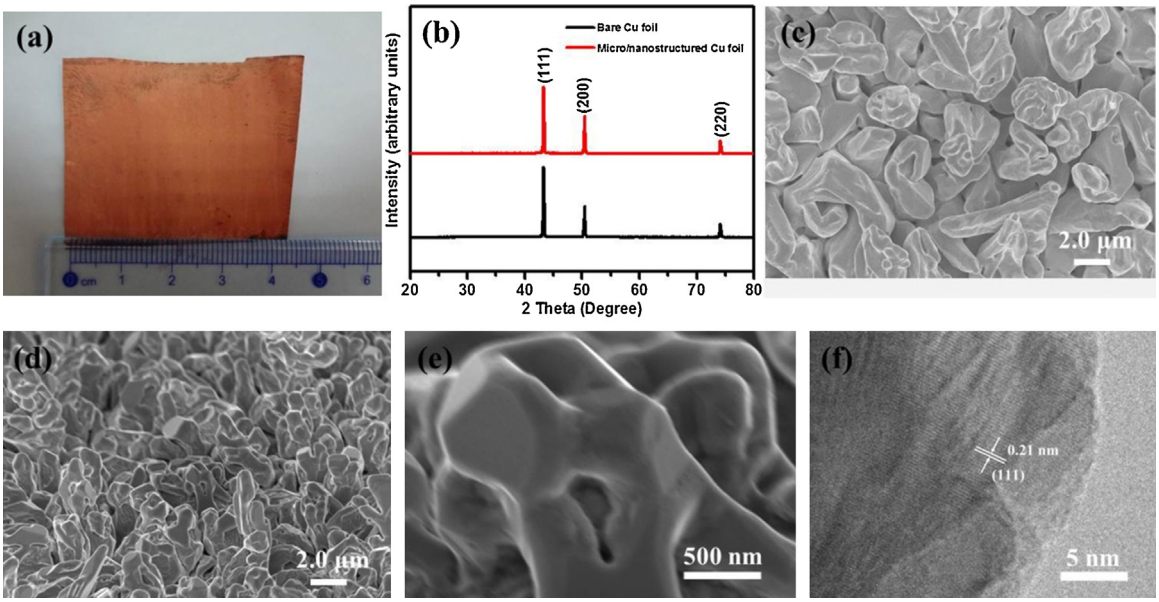

Fig. 1. (a) Digital photograph of a micro/nanostructured Cu foil (EG, 7 mL; reaction time, 12 h). (b) XRD patterns of the bare and micro/nanostructured Cu foils. (c–e) SEM images of the porous Cu micro/nanostructures. (f) HRTEM image of the edge of an irregular Cu branch.

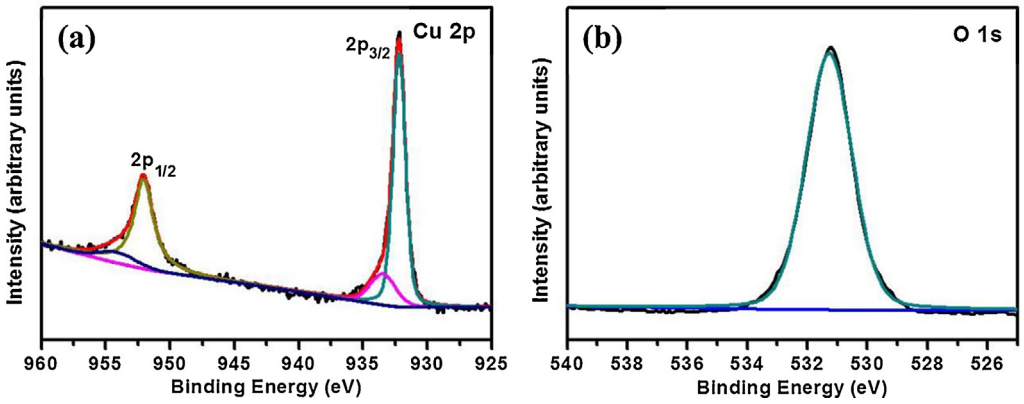

Fig. 2. XPS spectra of the micro/nanostructured Cu foil (EG, 7 mL; reaction time, 12 h): (a) Cu 2*p*; (b) O 1*s*.

superhydrophobic fluoropolymer film on a Cu substrate to improve the corrosion resistance. Su et al. [18] proposed an electrodeposition method to fabricate hierarchically Ni micro/nanostructures on Cu surface, which exhibited superhydrophobicity and excellent corrosion resistance after being modified with low-surface-energy fluorinated components. Cu nanocone structures were also electrodeposited on Cu substrates, and showed superhydrophobicity after chemical modification by hexadecyl mercaptan [20]. Liu et al. [21] fabricated Cu micro/nanostructures on Cu substrates by a selective etching of high-energy facets, which also demonstrated superhydrophobicity and anticorrosion against electrolyte solution after chemical modification. However, little work has been proposed to prepare superhydrophobic Cu surfaces without any chemical modification.

Herein, we propose a facile hydrothermal method for the fabrication of hierarchically porous Cu micro/nanostructures on Cu foil. The amount of ethylene glycol (EG) added into the precursor was used to control the growth of Cu micro/nanostructures, and further tune their antireflective and hydrophobic properties. Additionally, the improved corrosion resistance against electrolyte solution of the superhydrophobic Cu surfaces was investigated by electrochemical analysis.

2. Experimental details

2.1. Preparation of porous Cu micro/nanostructures

All chemical reagents used in the experiments were of analytical grade and used without further purification. Deionized water (DIW, 18 MΩ cm) was used throughout all of the experiments. Cu foil (99.9%), $Cu(CH_3COO)_2{\cdot}H_2O$ and NaCl were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). NaOH and EG were purchased from Pinghu Chemical Reagent Company (China) and Shanghai Lingfeng Chemical Reagent Company (China), respectively.

In a typical procedure, a piece of cleaned Cu foil substrate (4 cm × 3 cm) was curled to attach the inwall of 100 mL Teflon-lined autoclave containing 40 mL of 0.1 M $Cu(CH_3COO)_2{\cdot}H_2O$, 4 M NaOH and 7 mL EG aqueous solution followed by 12 h heating at a constant temperature of 200 °C. The products were washed using DIW and ethanol, and then dried in a vacuum oven at 70 °C.

2.2. Characterization

The crystal structure identification was performed by X-ray diffraction (XRD) using an advanced X-ray diffractometer (D8