Surface & Coatings Technology 307 (2016) 177–181

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Controllable synthesis of bowl-like cu array prepared by electrodeposition through multilayer colloidal template

Yanbo Ding [a,b,*], Jiupeng Zhao [b], Dong Zhang [a], Shiwei Song [a], Gang Wang [a]

[a] School of Renewable Energy, Shenyang Institute of Engineering, Shenyang 110136, China
[b] School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China

ARTICLE INFO

Article history:
Received 9 July 2015
Revised 11 July 2016
Accepted in revised form 19 August 2016
Available online 21 August 2016

Keywords:
Bowl-like array
Template assistant
Electrodeposition

ABSTRACT

Macroporous materials with pores and channels are anticipated to exhibit improved performance in numerous applications due to their special structure. In this work, macroporous Cu were prepared by template-assisted electrodeposition method. The infiltration process of the film fabrication was discussed in details. Bowl-like array and three-dimensional ordered macrospores Cu film were obtained at deposition time of 1 min and 3 min, respectively. The mechanism of electrodeposition infiltrating procedures indicated that the target architectures can basically maintain its original shape, and the evolution mechanism of infiltration procedures from bowl-like array to three-dimensional ordered macroporous Cu is firstly studied systematically. Moreover, models are set up to discuss the evolution of the morphology with the process parameters, which indicated that the pore mouths and depth of the 3DOM film were deeply influenced by the deposition time.

1. Introduction

During the last decades, much effort has been directed towards the construction of devices due to the periodic arrangement of the dielectric materials, an amazing property known as the photonic crystals [1], catalysis [2], and separation [3] appears. The ordered "inverse opals" structures consist of a skeleton surrounding of uniform close-packed macrospores have attracted considerable attention due to their ordered structure and better tunable stop bands [4,5,6]. In this regard, material scientists and engineers always take common materials as a best source of inspiration for novel structures, methods, tools, systems, and other benefits.

A wide range of fabrication technologies have been reported in the literature due to the potential applications of ordered macroporous materials including multibeam interference lithography [7], bio-templating [8], direct laser writing and direct ink writing [9,10]. However, lithography, direct laser writing and direct ink writing methods are now facing the difficulty of high cost and time consumption, while bio-templating method has the disadvantage of small scale products limiting the practical applications. Template-assisted preparation using colloidal crystals with low-cost and versatile fabrication method has been proposed and widely accepted. Various methods such as wet chemistry techniques [11,12], chemical vapor deposition [13], atomic layer deposition [14] and electrodeposition [15] have been used to obtain the architectures. Electrodeposition is an effective approach to fabricate ordered macroporous materials, the morphology and thickness of the macroporous film can be easily controlled via simply adjusting the electrochemical parameters such as current, potential or deposition time. Most importantly, electrodeposited materials can be quite dense, maximizing the effective refractive index contrast, averaging the ordinary and extraordinary refractive indices [16] because of their bottom-up deposition technique, high filling ratio of materials in the interstice of the template. Hence, we considered the electrodeposition method of Cu because they possess typically conductor, and electronically interesting, which can be grown as dense crystalline films at low temperature.

In this paper, we present a method that provides a facile approach to fabricate macroporous ordered Cu films with hierarchical structures. Cu bowl-like ordered arrays prepared by template-assistant electrodeposition. The relationship between preparation parameters and formation of structure was investigated by simply vary the electrodeposition time. To the best of our knowledge, the evolution detail of bowl-like to three-dimensionally ordered array was firstly reported in this paper. Moreover, models are set up to discuss the evolution of the

* Corresponding author at: School of Renewable Energy, Shenyang Institute of Engineering, Shenyang 110136, China.
E-mail address: ybding@126.com (Y. Ding).

http://dx.doi.org/10.1016/j.surfcoat.2016.08.058
0257-8972/

morphology with the deposition time, which indicated that the pore mouths and depth of the ordered array were deeply influenced by the deposition time. This can extend the methods to prepare other metallic materials hierarchical structures.

2. Experimental

2.1. Materials and experiment

The starting materials used were cupric sulfate (A.R.), sulfuric acid (A.R.), Tetrahydrofuran (A.R.), hydrochloride acid (A.R.). All these chemicals are analytical reagents used without further purification. Monodispersed PS was obtained by using an emulsifier-free emulsion polymerization technique [17] with an average relative standard deviation smaller than 5% (on the diameter) calculated by Zetasizer NANO S90. Water used in all experiments was purified with a resistivity greater than 18 ΩM/cm. The other materials used without further purification. Monodisperse PS colloidal spheres grown on ITO by using controlled vertical drying method to form well-ordered PS template. ITO coated PS was used as working electrode with Pt parallel counter electrode. ITO was all commercially available products and washed with acetone, ethanol, and ultrapure water (respectively) under sonication for 20 min before use.

2.2. Fabrication of ordered macroporous Cu film and characterization

The electrolyte solution consisted of 200 g/L $CuSO_4$, 65 g/L H_2SO_4 and 70 mg/L HCl. Cu was grown potentiostatically in a three-electrode system controlled by CHI-660D electrochemical workstation. Platinum ($1 \times 1.5\ cm^2$) was used as counter electrode, and saturated calomel electrode (SCE) as reference electrode. The temperature in the electroplating bath kept at 25 °C during the deposition process. Samples washed with water immediately after deposition to remove other chemicals. The PS template then removed by immersing in THF for 24 h and ordered macroporous Cu products were thus obtained.

The surface morphology was performed using a Hitachi-S-4800 SEM (FEI, Japan) scanning electron microscope operating at an accelerating voltage of 30 kV. The samples were sputter-coated with gold before examination. The phase composition of the crystalline structure of products was analyzed by X-ray diffraction (XRD) on a Phillips X Pert diffractometer equipped with CuKα radiation at a scan rate of $5°\ min^{-1}$. The surface morphologies of PS colloidal crystals and electrodeposition coating were observed using XSZ-H type optical microscope with 220 W high pressure mercury lamp for excitation light source.

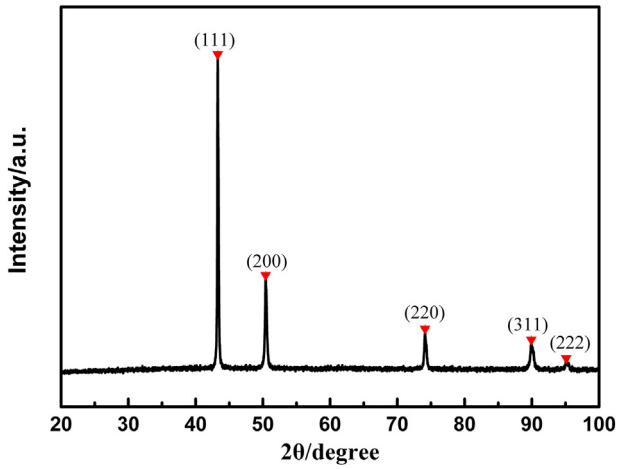

Fig. 1. X-ray diffraction pattern of sample prepared by electrodeposition.

3. Results and discussion

3.1. XRD analysis of as-prepared films

Fig. 1 shows the X-ray diffraction pattern of ordered macroporous Cu film electrodeposited on the ITO substrate after PS template removed. It is obviously seen that there are five distinct diffraction peaks at 2θ = 43.32°, 50.44°, 74.12°, 89.92°, 95.14°can be indexed as (111), (200), (220), (311) and (222) reflections of the Cu, respectively. The diffraction pattern illustrates typical reflection peaks of cubic Cu (JCPDS card File No. 04-0836) and displays a (1 1 1) preferred orientation. The sharp diffraction peaks indicate a high purity and crystalline of the final product.

3.2. Cyclic voltammetry behavior of Cu electrochemical deposition process

Current-potential studies in Fig. 2 are performed to analyze the behavior of copper electrodeposition. The catholic electrodeposition process of copper in the aqueous solution was studied through electrochemical testing methods. The curve start from 3.0 V to −2.0 V at a scan rate of 50 mV/s at 25 °C. The current is relatively stable with no significant reduction of the cathode reaction at the beginning as shown in Fig. 2 (I-regional). The cathodic reduction and hydrogen evolution reaction occurred in the potential sweep at −2.0 V vs SCE as shown in Fig. 2 (II-region). There was no redox reaction occurs due to the negative current value increased dramatically with the increase of the potential value, which indicating the corresponding electrochemical reaction rather than diffusion-controlled reaction step controlling. Oxidation-reduction reaction took in the anodic oxidation (III-region) according to the following equation:

$$Cu^{2+} + 2e^- = Cu^0 \quad (1)$$

3.3. Morphology variation of ordered macroporous metals

Typical morphology of assembled PS thin film is presented in Fig. 3. The top surface of the film is in a close-packed hexagonal array. The ordered colloidal crystal is composed of a face centered cubic lattice of spheres. The top (1 1 1) surface of which is parallel to the substrate, giving rise to an ideal duplicated architecture as template.

Morphology of copper deposited with or without templates as shown in Fig. 4. It is obviously seen that the composed film with Cu filled in the interspaces of PS template is flat and the interspaces of PS template are uniform filling as show in Fig. 4(a). A bigger air sphere which

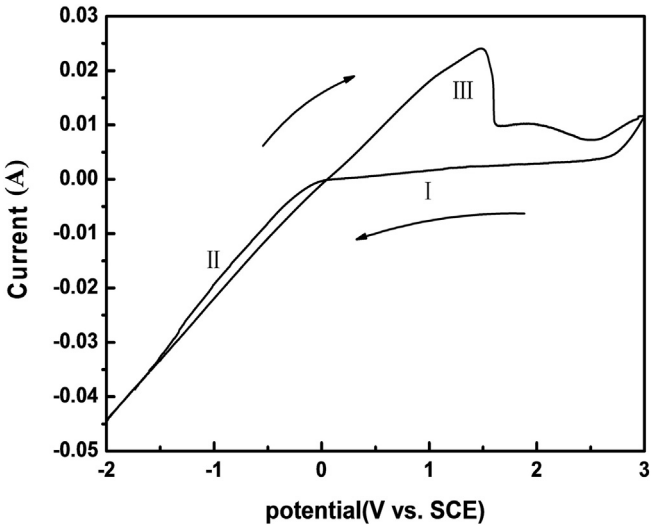

Fig. 2. Cyclic voltammogram of copper electrodeposition on the ITO substrate at 50 mV/s.