Electrochromism in mesoporous nanowall cobalt oxide thin films prepared via lyotropic liquid crystal media with electrodeposition

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ABSTRACT

Mesoporous nanowall cobalt oxide (Co_3O_4) thin films were prepared by a liquid crystal templated electrodeposition method. The as-prepared Co_3O_4 thin films exhibited a highly porous nanowall structure composed of many interconnected nanoflakes with a thickness of 10–25 nm. The nanoflakes showed continuous mesopores ranging from 4 to 15 nm and formed a net-like structure leaving pores of 20–250 nm. The electrochromic performances of the Co_3O_4 thin films were characterized by means of transmittance, cyclic voltammetry (CV) and chronoamperometry (CA) measurements. The Co_3O_4 thin film annealed at lower temperature exhibited better electrochromic performance. The film annealed at 200 °C exhibited a transmittance modulation of 40% at 633 nm with a coloration efficiency of 31 cm^2 C^{-1}, and fast response times with 2.5 s for coloration and 2 s for bleaching. The high porosity and big surface area were responsible for the enhanced electrochromic properties.

1. Introduction

Electrochromic materials present a reversible change in optical properties as the result of electrochemical oxidation or reduction [1,2]. Generally, electrochromic materials are categorized into organic and inorganic materials including transition oxides, inorganic coordination complexes, organic molecules, conducting conjugated polymers and so on. Early studies of electrochromism mainly focus on inorganic and small-molecule organic electrochromes, which suffer from processing, compatibility and performance problems. More recently, electrochromic researches have heavily focused on electrochromic conducting polymer films because of their high color contrast, multiple color possibilities, rapid response times and ease of processing. Transition metal oxides such as WO_3, NiO, MoO_3 and Co_3O_4 have been extensively studied as electrochromic layers for smart windows [1,3–5]. Among them, Co_3O_4 is an attractive electrochromic material due to its high electrochromic efficiency, good cyclic reversibility and low material cost. Various deposition techniques have been developed for the preparation of electrochromic Co_3O_4 thin films, such as chemical vapor deposition (CVD) [6], sputtering [7], spray pyrolysis [8], sol–gel process [9], electrochemical deposition [10] and chemical bath deposition [11,12]. Compared with other physical techniques and template synthesis, the electrodeposition methods show unique principles and flexibility in the preparation of transition metal oxide films because of the lower cost, lower temperature, higher quality and better processability.

In the past few years, porous electrochromic films containing nanometer sized pores have attracted great attention due to their large specific surface area and inner space [13,14]. It is believed that the highly porous structures can provide short diffusion pathway for the counter ions as well as a large active surface, leading to decreased response time and enhanced optical modulation [15]. To date, there are a few reports on electrochromic properties of porous Co_3O_4 thin films. Xia et al. [16–18] reported several Co_3O_4 films with highly porous structures such as nanowire array and bowl-like array, and their improved electrochromic properties. However, there is little literature about electrochromic performance of mesoporous nanowall Co_3O_4 thin films. On the other hand, fabrication of porous-structured films using lyotropic liquid crystalline templates (such as surfactant Brij 56) has been proved to be a very promising research area [19,20]. This soft template would maintain the topology of the phase and possess the ability to fabricate thin films with high porosity. Recently, Zhou et al. [21] reported ordered mesoporous cobalt hydroxide and nickel hydroxide films via lyotropic liquid crystalline template and their improved electrochemical capacitor performances. These results provide impetus for the preparation of mesoporous nanowall Co_3O_4 thin films for electrochromic application. In the present work, mesoporous nanowall

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Co_3O_4 thin films were prepared by a liquid crystal templated electrodeposition method and their electrochromic properties were investigated in detail.

2. Experimental

2.1. Chemical materials

All solvents and chemicals were of reagent quality and used without further purification. Nonionic surfactant polyoxyethylene (10) cetyl ether (Brij 56, $C_{16}EO_{10}$) was purchased from Aldrich. The cobalt nitrate, sodium nitrate, ethanol (99.9%) and 2-propanol (99%) were obtained from Shanghai Chemical Reagent Co. All aqueous solutions were freshly prepared with high purity water (18 MΩ cm resistance).

2.2. Preparation of mesoporous nanowall Co_3O_4 thin films

The Co_3O_4 thin films were prepared by a cathodic electrodeposition as follows. The electrodeposition was performed in a standard three-electrode glass cell at 25 °C, ITO substrate with a size of 2.5 cm × 2.5 cm as working electrode, saturated calomel electrode (SCE) as reference electrode and a Pt foil as counter-electrode. Before electrodeposition, the ITO substrate was cleaned ultrasonically in ethanol and acetone for 15 min, respectively. The electrolyte for electrodeposition was a binary system of a 50 wt.% surfactant Brij 56 and a 50 wt.% aqueous solution containing 0.9 M $Co(NO_3)_2$ and 0.075 M $NaNO_3$. Firstly, the surfactant Brij 56 was heated to around 60 °C (above the melting point of the surfactant), and then the aqueous solution containing 0.9 M $Co(NO_3)_2$ and 0.075 M $NaNO_3$ was added dropwise. Afterwards, the mixture was sealed in a capped vial and allowed to stand in a thermostated oven at 75 °C for about 1 h to keep the mixture melted. The electrolyte was vigorously stirred again to ensure a homogeneous mixture. The electrodeposition was carried out at a constant cathodic current of 0.5 mA cm^{-2} for 300 s through a Chenhua CHI660C electrochemical workstation. The electrodeposition process of the $Co(OH)_2$ precursor film would include an electrochemical reaction and a precipitation reaction expressed as follows [16]:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \qquad (1)$$

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

After deposition, the precursor film was placed consecutively in ethanol, 2-propanol and high purity water for 2 days to remove surfactant and other soluble materials. After washed and dried, the samples were heat-treated in a quartz tube furnace at different temperatures (200, 250 and 300 °C) for 1 h in air. The thickness of the annealed films was about 300 nm.

2.3. Characterization

The powder from the as-deposited films was analyzed by thermogravimetry (TG) and differential thermal analysis (DTA) under N_2 atmosphere at a heating rate of 10 °C min^{-1} in a temperature range of 25–575 °C. The as-deposited and annealed films were characterized by X-ray diffraction (XRD, Philips PC-APD with Cu Kα radiation). The morphologies of all films were observed by field emission scanning electron microscopy (FESEM, FEI SIRION) and transmission electron microscopy (TEM, JEM 200 CX 160 kV). The transmission spectra of Co_3O_4 thin films in the fully colored and fully bleached states were measured over the range from 200 to 900 nm with a UV-2550 spectrophotometer. The cyclic voltammetry (CV) and chronoamperometry (CA) measurements were carried out in a three-compartment system containing 0.1 M KOH as electrolyte, Hg/HgO as reference electrode and a Pt foil as
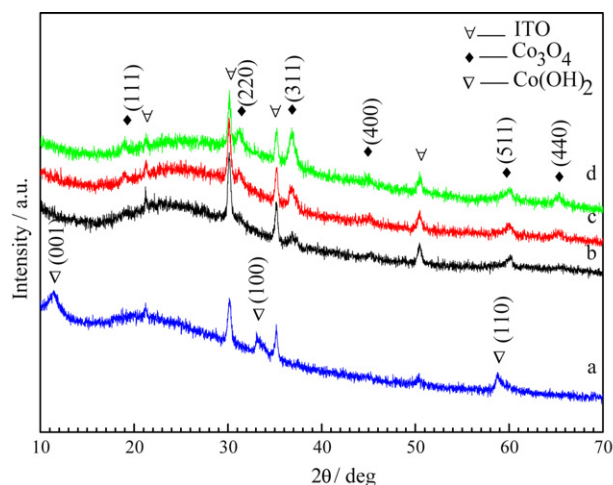

Fig. 1. XRD patterns of (a) as-deposited precursor film and the films annealed at (b) 200 °C, (c) 250 °C, (d) 300 °C for 1 h.

counter-electrode. Cyclic voltammetry (CV) measurements were performed using a CHI660c electrochemical workstation with a scanning rate of 10 mV s^{-1} between −0.15 and 0.65 V at 25 °C.

3. Results and discussion

3.1. Structure characterization

Fig. 1 shows the XRD patterns of as-deposited precursor and annealed films on ITO substrates. The diffraction peaks for precursor film is consistent with layered α-$Co(OH)_2$ phase (JCPDS 74-1057). Three annealed samples show similar diffraction peaks at 19.1°, 31.3°, 36.9°, 44.8°, 59.3° and 65.2°, which correspond to (1 1 1), (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) crystal planes of spinel Co_3O_4 phase (JCPDS 42-1467), respectively. XRD results indicate that the precursor film changes into Co_3O_4 films after heat treatment. The intensities of these diffraction peaks increase with the increasing annealing temperature, indicating that the crystalline degree of films increases as the temperature increases. The phase change is also supported by thermal analysis (Fig. 2), the main weight loss of the precursor film happens in the temperature range of 170–300 °C, which is ascribed to the decomposition of $Co(OH)_2$ to Co_3O_4. In addition, 12 wt.% of mass loss is also consistent with the calculated value from $Co(OH)_2$ to Co_3O_4. In this temperature range, the DTA curve exhibits a dominant endothermic peak centered at 270 °C attributed to the formation of crystalline Co_3O_4 film.
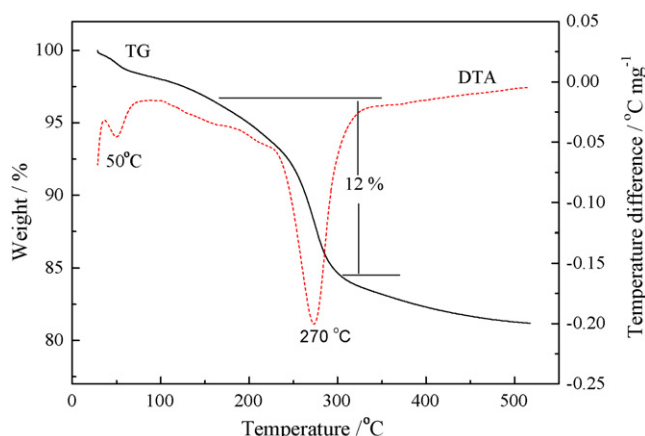

Fig. 2. TG–DTA curves of as-deposited precursor film.