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Synthesis and properties of iridescent Zn-containing anodic aluminum oxide films

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ABSTRACT

A simple method of fabricating Zn-containing anodic aluminum oxide films for multifunctional anticounterfeit technology is reported. The resulting membranes were characterized with UV–vis illumination studies, natural light illumination color experiments, and electron microscopy analysis. Deposition of Zn in the nanopore region can enhance the color saturation of the thin alumina film with different colors dramatically. Both the anodization time and etching time have great influence on the structural color. The mechanisms for the emergence of this phenomenon are discussed and theoretical analysis further demonstrates the experimental results.

1. Introduction

It has been found that structural color exists commonly in the biological world [1–4]. Owing to the many useful characters [5,6], structural color may have a wide range of applications in environment-monitor, interior decoration, liquid sensors and anti-counterfeiting. Many researchers have attempted to replicate the biological structures, they have focused efforts on finding and preparing ordered nanostructure materials with bright structural color in the visible light range. In recent years, PAA membrane [7], a nanostructure material with highly ordered nanopore arrays, has been studied extensively. For instance, Diggle *et al.* [8] had reported that a PAA thin film supported on an Al substrate can produce bright color on reflection in the visible light range. It is worth noting that the films they achieved show a low saturated structural color due to the high reflectivity for visible light of the Al substrate. Xu *et al.* [9] introduced a technique to enhance the saturation of the interference color by removing the Al substrate. Zhao *et al.* [10] found that depositing carbon in the PAA nanopores can improve the color saturation of PAA film supported on Al substrate greatly. Zhang *et al.* [11] devised color tunable PAA thin films embedded with Ni nanowires, and an enhanced color saturation was achieved in this system without getting rid of the Al substrate.

In this paper, we report a more economical and more efficient preparation technology of PAA thin film with brilliant structural colors by means of embedding metal Zn in the pore of it. In the process, the oxidation time is about 10 to 14 min only, which shortens materially the traditional two-step anodic oxidation process [12–14]. In addition, compared with oxalic acid and sulfuric acid, PAA films produced in phosphoric acid [15–20] have irregular pores and more branched arrays. It is therefore reasonable that the quasi-ordered microstructure might scatter the light reflected from the PAA/Al interface more effectively than the regular arrays ones, and thereby leading to more highly saturated color. More importantly, deposition of Zn in the nanopore region can further enhance the color saturation of the film, and the mechanism of it will be analyzed in detail. The detailed fabrication process and optical properties of the Zn@PAA films we produced are given.

2. Experiment

2.1. Preparation of PAA/Al templates

PAA thin films were prepared by one-step anodization procedure. However, there are several steps that had been completed before implementing the anodization. Firstly, high-purity aluminum foils (99.999%) were annealed at 673 K for 4 h in argon. Secondly, the annealed aluminum foils were tailored to be disks with a diameter of 20 mm. Then, the processed aluminum disks were electropolished with a voltage of 30 V for 5 min to smooth the surface, and the mixed solution of ethanol and perchloric acid (1:4) was used as the polishing solution. Subsequently, aluminum disks were cleaned and degreased by ultrasonication in acetone, anhydrous ethanol, and deionized water. Finally, the one-step anodization process was carried out at room temperature. A 45 g/L phosphoric acid solution was used as electrolyte, the applied direct current voltage was kept at 30 V. In particular, the anodization time was varied from 10 to 14 min.

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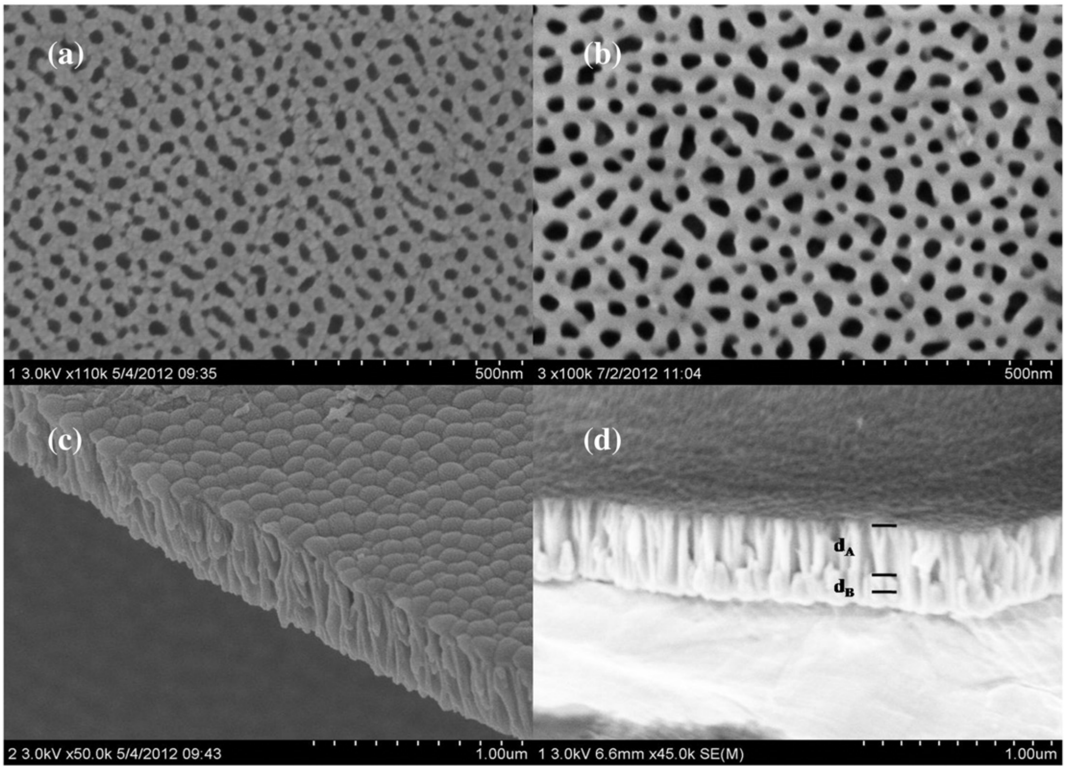

Fig. 1. SEM images for the top view of the samples (a) the PAA thin film, (b) the Zn@PAA nanocomposite film and the cross-sections of the samples, (c) the PAA thin film, and (d) the Zn@PAA nanocomposite film.

2.2. Deposition of Zn into the PAA/Al template

Concerning the characteristics of the two different deposition methods dc electrodeposition and ac electrodeposition, ac deposition has been adopted in this work because it can obtain a more uniform deposition inside the pores. In our cases, the electrodeposition process was carried out in a mixture of 80 g/L $ZnSO_4 \cdot 7H_2O$ and 20 g/L H_3BO_3 under an ac voltage of 15 V (50 Hz) for 1.5 min. What is important to point out is that the pH value of the electrolyte needs to be controlled at 2.5 for it determines whether the film deposited uniformly successfully or not. In the ac deposition process, graphite plate and the as-prepared template with aluminum substrate (PAA/Al templates) are used as counter electrode and working electrode, respectively.

2.3. Characterization of PAA/Al templates and Zn@PAA/Al nanocomposite films

In this manuscript, we report on the effects of electrodepositing Zn into PAA/Al on the optical properties of the composite film. Optical digital camera (Canon IXUS 9515) was used to record the color of PAA/Al templates and Zn@PAA/Al nanocomposite films. The crystal structure and morphology of PAA/Al templates and Zn@PAA/Al nanocomposite films were characterized by X-ray diffraction (XRD) with Cu K_α radiation, and field emission scanning electron microscopy (FE-SEM, Hitachi S-4800), respectively. The chemical composition of the samples was determined by an energy dispersive X-ray spectrometry (EDS). Optical properties of the samples were measured via the UV–vis spectrophotometer (Hitachi U-3010) equipped with an integrating sphere and $BaSO_4$ was used as a reference.

3. Results and discussion

Fig. 1(a) shows a SEM image of the PAA template anodized for 13 min. The average pore diameter and interpore distance are estimated as 40 nm and 80 nm, respectively. It can be seen that the distribution of the pores is not uniform as those in films formed in oxalic acid solution [21]. The thickness, *d*, of PAA template is about 400 nm, as shown in the inset of Fig. 1(a). The surface morphology of the Zn@PAA nanocomposite film is

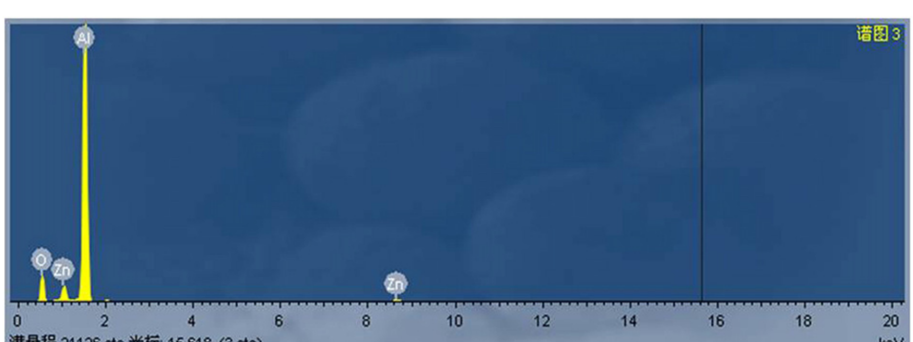

Fig. 2. EDS spectra of the Zn@PAA nanocomposite film with Al substrate.