



Fabrication and characterization of micro/nanoporous Cr film for sensing applications



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ABSTRACT

A novel technique is developed to fabricate micro/nanoporous Cr film on an Al substrate using DC electrodeposition via the simultaneous etching of the porous anodic alumina (PAA) membrane. The structures and morphologies of the fabricated structures were characterized by field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray (EDX), and X-ray diffraction (XRD). Vertically aligned and highly ordered alumina (Al₂O₃) nanowires of length 4 μm, diameter 36 nm, and yield of 2×10^{11} wire/cm² are observed over etching time of 30 min at a current density of 2 A/cm². In addition, nanoconcaves array is formed on the Al substrate at a current density of 4 A/cm². This array was used as a substrate for the growth of micro/nanoporous Cr film after a deposition time of 45 min. For the morphological comparison, Cr electrodeposition on the Al substrate was carried out at the same conditions and shown a nonporous film of Cr spheroids. The nanoporous Cr film was used as a substrate for the detection of Hg²⁺ based on laser induced fluorescence (LIF). Upon the increase of the concentration of Hg²⁺ ions from 1 to 10 μM, additional emission peak is observed and showed a blue-shift of 100 nm. In addition, the coordination between the nano-rough surface and Hg²⁺ ions disrupted the photo-induced electron transfer process leading to the increase of the intensity of fluorescence emission as the concentration of Hg²⁺ ions increased.

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1. Introduction

Heavy metal ions such as mercury (Hg), cadmium (Cd), and lead (Pb) pose significant public health hazards when present in drinking water in parts per million (≥ 0.002 , 0.005, and 0.015 mg/L, respectively) [1,2]. In particular, mercury ions are widely distributed in the environment causing serious problems in the agricultural yields, which increases human health threats through accumulation in the food chain. Therefore, the detection of these ions becomes important and necessary. Laser-induced fluorescence (LIF) is a spectroscopic method for the sensitive detection of small traces of impurities in several media such as bulk materials, liquids, and gases. The fluorescence chemo-sensor is becoming more popular with its easy use, low-cost and high efficiency. Different principles to design the fluorescence sensors have been used; photo-induced electron transfer (PET), fluorescence resonance

energy transfer (FRET), intermolecular charge transfer (ICT), and excimer/exciplex formation. In thin film area, the LIF measurements are rarely used so far for the investigations, due to the extremely weak fluorescence signal that produced from the very small interaction volume. In addition, the density of the defects in the thin film is expected to be larger than for that of the corresponding bulk material. One promising method to defeat this problem is to apply a nanostructured metal surface (usually Ag or Au) as a substrate to enhance the fluorescence signals [3,4]. This enhancement is usually explained by a combination of two different mechanisms; the electromagnetic mechanism and the chemical mechanism. The electromagnetic mechanism is induced by the excitation of the surface plasmon resonances and the chemical mechanism is derived from the charge transfer between the molecules and the substrates [5,6]. However, it is challenging to achieve high reproducibility, good uniformity, and long-term stability for the substrates. Moreover, the fabrication of the substrates is a time-consuming and expensive process. A possible answer to the aforementioned challenges is to utilize the nanoporous metallic substrate that supports surface plasmon interactions for the detection of Hg²⁺ ions based on LIF spectroscopy. In recent years, the fabrication of plasmonic

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nanoarrays has attracted much interest for their potential use in many applications such as surface enhanced Raman scattering (SERS) substrates [7–9]. However, there is a strong demand for a cheap and reliable material that can be patterned in two and three dimensions. We believe that chromium (Cr) is, in many ways, an excellent material for the fabrication of nanostructured substrate. It possesses surface plasmon interactions and hence can enhance the interaction between the incident light and the analyte solution. In addition, the Cr grain size is typically very small (≤ 5 nm) with very low surface mobility and excellent stability under exposure to air. The typical growth properties of Cr produce a very thin (~ 1 nm) passivating oxide layer, acting as a protective coating against further corrosion and allowing it to be conveniently stored and analyzed in the air. However, the synthesis of Cr nanostructures, especially the Cr nanoporous morphology, which is suitable for sensing applications for its extremely high surface area, is very difficult because the adhesion property of the Cr atoms. Consequently, there is very limited number of studies on Cr nanostructures [10–14]. In these studies, the common serial top-down nanofabrication techniques such as laser-focused atomic deposition, glancing angle deposition (GLAD), focused ion beam (FIB), and radio frequency (r.f.) magnetron sputtering are used to fabricate Cr nanostructures. However, the long time for these methods makes fabrication of large-area ordered structures expensive and inefficient.

To avoid this obstacle, template synthesis is a common tool for the preparation of porous materials [15]. Porous anodic alumina (PAA) membranes with nanoporous structure have been widely used as templates for the fabrication of a variety of nanostructures because of the cheap equipment, easy technology, high-throughput, and high controllability of the process [16–18]. For an instant, the nanoporous metal structures have more possibilities to touch the reactant than the thin film. Then, a new methodology is required to coat a conducting substrate with well-defined nanoporous Cr structure for sensing applications. The present work describes the growth and characterization of Cr nano/micro structures on the Al substrate simultaneously with the etching of the PAA membrane by using the DC electrodeposition method. Furthermore, we study the different morphologies of Cr nanostructures at various fabrication conditions. Moreover, we measure and analyze the emission for the blank nanoporous Cr film and the contaminated nanoporous Cr film upon addition of low concentrations Hg^{2+} ions (1–10 μM).

2. Experimental details

2.1. Preparation of PAA membrane

The porous anodic alumina membrane (PAA) was prepared by a two-step anodization process [19]. The Al foil (99.99%) was electropolished with a mixture of H_3PO_4 and H_2SO_4 to improve the surface smoothness. The electropolished Al foil was anodized in 0.3 M oxalic acid electrolyte at a constant anodizing voltage of 50 V for 5 h. After the removal of the porous oxide layer, the second anodization was performed under the same anodization conditions for 8 min. Then, the barrier layer was thinned by a successive drop of the DC voltage at a rate of 0.1 V/s from 50 to 15 V. The layer was eventually maintained under DC voltage of 15 V for 15 min. The pores were widened by immersing the PAA into 6 wt.% phosphoric acid for 45 min.

2.2. Fabrication of porous Cr film

The Cr electrodeposition was carried out in a two-electrode electrochemical cell. The used anode was a Pt plate while the PAA substrate acted as a cathode. An electrolytic bath containing

chromic acid (250 g/l CrO_3) and sulfuric acid (1 ml/l H_2SO_4) in de-ionized (DI) water was used. Sulfuric acid was used as a catalyst in the Cr electrolyte as it was commonly used in Cr electroplating [20–22]. It is also used as an etching solution for walls of PAA. The electrodeposition process was carried out at high current densities of 2 and 4 A/cm^2 and a temperature of 60 °C for 45 min. For the sake of morphological comparison, Cr was electrodeposited directly on the Al substrate at 4 A/cm^2 and 60 °C for 45 min.

2.3. Characterization of PAA membrane and Cr nanostructures

Field emission-scanning electron microscope (FE-SEM, ZEISS SUPRA 55 VP and ZEISS LEO Gemini Column), X-ray diffraction (XRD, Philips X'Pert Pro MRD) using $\text{Cu } K_\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), and energy dispersive X-ray spectrometer (EDX; Oxford Link ISIS 300 EDX) were used to characterize the morphologies and structures of the PAA membrane and Cr nanostructures.

2.4. Hg^{2+} ion detection

LIF spectroscopy was used to detect Hg^{2+} ions in the nanoporous Cr substrate at the room temperature. Small amount (100 nL) of water contaminated with Hg ions was injected into the nanoporous Cr substrate. Excitation laser was directly focused onto the surface of the substrate with integration time of 5 s for each run. The wavelength of the excitation laser is 532 nm. The laser spot size is 1 μm . We could detect Hg^{2+} ions of 1–10 μM concentration.

3. Results and discussion

3.1. PAA membrane morphology

Fig. 1 illustrates (a) top view and (b) cross-sectional view SEM images of PAA membrane anodized for 8 min and pore widened for 45 min. The figure shows a typical hexagonal nanoporous Al_2O_3 array with an interpore distance of ~ 125 nm, pore diameter of ~ 79 nm, and pore density of $\sim 1.1 \times 10^{11} \text{ cm}^{-2}$.

The grown PAA membranes on the Al substrates have a double-layered structure: a porous Al_2O_3 layer is formed on the top and a semi-spherical Al_2O_3 barrier layer is formed on the bottom of the pore [23]. It is impossible to deposit Cr atoms inside the pores directly using the electrodeposition without removing this Al_2O_3 barrier layer. This is due to the high resistivity of such a layer [17]. Thus, the electrodeposition of Cr in PAA membrane occurs in two simultaneous steps; electrochemical etching of the Al_2O_3 barrier layer and electrochemical deposition of the Cr atoms. Other research groups [24,25] have confirmed that the side walls of the PAA pores are composed of duplex oxide layers as shown in the enlarged parts of Fig. 1. The outer pore wall (the junction zone between the three neighboring cells) contains pure Al_2O_3 , while the inner pore wall consists of contaminated Al_2O_3 with acid negative anions (OH^- and $\text{C}_2\text{O}_4^{2-}$). The duplex oxide layers exist not only in the pore wall, but also in the barrier layer at the pore bottom. The inner pore wall with negative anion-incorporated Al_2O_3 is more prone to be etched, while the outer pore wall is more resistant [26].

3.2. Al_2O_3 and Cr nanostructures

The Cr electrodeposition was carried out at two high current densities 2 and 4 A/cm^2 for 45 min using CrO_3 (250 g/l)/ H_2SO_4 (1 ml/l) electrolyte at a temperature of 60 °C. Different surface morphologies of Cr/PAA films were obtained from top to bottom during the high-temperature electrodeposition process as a result of the vaporization of the electrolyte solution. This process allowed

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