

Nanoarchitected metal film electrodes with high electroactive surface areas

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Abstract

Well-defined nanoarchitected metal film electrodes (NMFs) with high electroactive surface areas relative to corresponding metal macroelectrode have been fabricated by direct evaporating metal onto porous anodic aluminum oxide films in a two-step route. The so-prepared metal electrodes have high dense hollow nanostructure arrays upstanding on their surfaces and thin thickness within several hundred nanometers, which endow them with enhanced electroactive surface areas relative to disk-shaped electrodes of macroscopic dimensions and the feature of reduction of cost. Because of the rich nano-surface, these NMFs will find use in a number of applications that involve sensing, analysis, and catalysis.

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1. Introduction

The fabrication and use of high efficient nanoarchitected electrodes is of current interest in a number of fields, which range from electrochemical analysis (environmental and medical) to chemical and biological sensing and diagnosis, catalysis, separation, nanoelectronics, and basic neuroscience and neurobiology. Several template-based methods, including the templates of surfactants [1], inorganic-block copolymer micelles [2], polystyrene spheres [3], nanochannel glass [4], and filtration membranes [5,6], have been used for preparing these electrodes. Among the templates reported, the generally used two types of templates are track-etched polymeric membranes and porous anodic aluminum oxide (AAO) membranes, as pioneered by Martin [7,8] and

other groups such as Gösele [9–11] and Masuda [12,13]. Using the two templates, metal (Au and Pt) nanoelectrode ensembles and nanotubule membranes have been fabricated and studied extensively by Martin's group [14–16]. Au nanowell electrode array has also been prepared by Myrick and co-workers using a similar template synthesis method [17]. These electrodes have shown distinguished advantages in electroanalysis, molecular sieving, and selective ion transport [7,8,14–20]. For example, ensembles of nanoscopic disk-shaped electrodes have been shown to offer enhancements in electroanalytical detection limits relative to electrodes of macroscopic dimensions [21,22]. In this work, a thin layer of Ag or Cu was often evaporated onto one side of an anopore template in order to form an electrode for subsequent electrodeposition of Au or Pt, and finally removed to expose the Au or Pt nanostructures. Until now there have been few attentions on the evaporated metal film. Herein, we discuss the neglected metal film on the motivation to address the following questions: (1) Can a freestanding nanoarchitected metal film be directly fabricated by evaporating metals onto porous membranes? (2) What is

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the structure and morphology of the film? and (3) Can the film be used as an efficient electrode?

2. Experimental details

AAO membranes obtained from Whatman were used as the template material for metal (Au and Ag) electrode fabrication. The templates are sold as having 200 nm pores. Fig. 1 shows a schematic of the electrode preparation process. A two-step evaporating process was used. First, a thin (100 nm) layer of Au was evaporated onto one side of the AAO membrane using a DZ-400 evaporating system at a very slow evaporating rate (0.05 nm/s) and under a high vacuum of $\sim 8.7 \times 10^{-5}$ Pa. The AAO membrane was positioned with pores normal to the evaporating target. The metal nanoparticle with small size formed under the high vacuum will not cover (i.e., plug) the pores but will penetrate into the pores and deposit onto the pore walls. After this evaporating, another layer of Au (200 nm) was subsequently evaporated at a fast evaporating rate (0.2 nm/s) and under a low vacuum of $\sim 4.4 \times 10^{-4}$ Pa relative to that of the first layer. The metal nanoparticles formed in this condition will become larger and consequently cover and seal the pores, which results in the formation of a continuous film on the surface of AAO template. To form the nanoarchitected Au film electrode (NAuFE) the AAO template was completely removed in 4 M NaOH for 6 h, followed by thoroughly rinsing with distilled water. A

Hitachi S-4300F field-emission scanning electron microscope operated at 15 kV was used to determine the morphology of the metal electrode. X-ray diffraction (XRD) analyses were carried out using a Rigaku D/max-2500 using filtered Cu K α radiation.

For electrochemical characterization of the electrode, a specially constructed cell was used, consisting of a planar gold base onto which the Au-coated membrane was placed. This base was screwed into a Teflon cell, with an O-ring to ensure sealing, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. An EG and G PAR Basic Electrochemical System was used for the electrochemical measurement.

3. Results and discussion

Fig. 2a and b are the typical scanning electron microscopy (SEM) images of the surface view of as-prepared NAuFE. A uniformly nanoarchitected Au film having highly dense Au nano-ring array upstanding on the surface can be clearly seen in the images. The average outer diameter of the nano-ring is about 300 nm, which is much larger than the nominal pore diameter (200 nm) of the AAO template. Furthermore, these nano-rings are not well separate but contact somewhat. This is because the Au film was evaporated onto the branched-pore surface of the AAO membrane [23,24] with large mouths of 300 ± 50 nm according to our SEM measurements. The result also indicates that the evaporated Au have entered into the channels of the AAO templates within a short distance and formed a hollow structure as expected. It should be noted that the other side of the AAO membrane has well separate pores with small mouths of 240 ± 50 nm. Therefore, well separate hollow metal nanostructures with the similar diameter of ~ 240 nm can be fabricated when the metal is evaporated onto the corresponding surface of the AAO membrane, as demonstrated in the following text on the nanoarchitected Ag film electrode.

These Au nano-rings are located on an impermeate and continuous Au film, which can be confirmed by our SEM observation of the bottom of the evaporated film. The absence of Au nano-rings in the surface resulting from the removal process of AAO is also visible, as indicated by the arrows in Fig. 2b. The feature of impermeate of the Au substrate film can also be observed at these points. This feature ensures the electrode application of the Au film.

Fig. 2c and inset are the typical SEM images of the as-prepared NAuFE near the edge. It can be seen that the thickness of the Au film including the nano-rings is no more than 500 nm. This feature endows the Au electrode with the feature of less material and reduction of cost.

The crystal structure of the NAuFE was investigated by XRD, as shown in Fig. 2d. The result clearly shows that the NAuFE has a characteristic face-center-cubic (fcc) polycrystalline structure. The XRD pattern also indicates a high

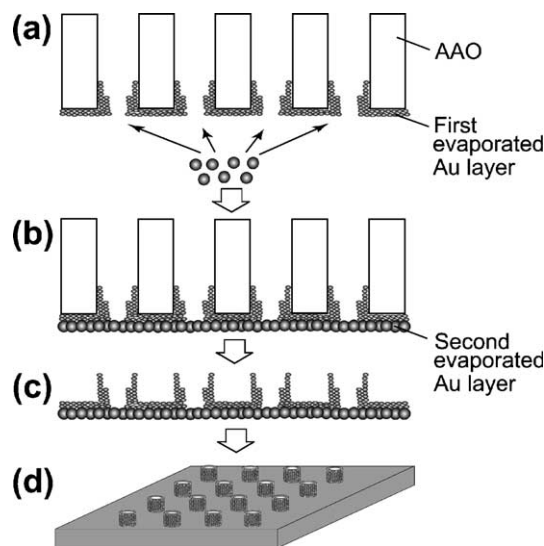


Fig. 1. Fabrication procedure for nanoarchitected Au-film electrode (NAuFE). (a) The first layer of Au is evaporated on one side of a host AAO membrane at a very slow evaporating rate and under a high vacuum. This layer does not cover the pores but penetrate into the pores and deposit onto the pore walls in a short distance of the AAO template. (b) The second layer of Au is subsequently evaporated at a fast evaporating rate and under a low vacuum relative to that of the first layer. This layer finally seals the pores and forms a continuous film. (c) AAO is removed using NaOH, revealing an array of hollow nanostructures on the surface of Au film. (d) Schematic illustration for the oblique top view of the NAuFE.

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