Original Paper

Electrochromic Characteristics of NiO/Au Composite Nano-rod Array Membrane

Yasuhiro MIZUKOSHI^{*} and Katsumi YAMADA^{*}

Abstract: The Au nano-rod array membrane (Au-NRM) was prepared by using an anodic porous alumina plate (AAO) as a template. NiO films were coaxially immobilized on the surface of the Au-NRM electrode. The electrochromic (EC) characteristics of the obtained NiO/Au composite nano-rod array were evaluated in this study. Ultrafast EC color changes within 1 second were obtained by optimizations of the rod length and film thickness of the NiO films.

Keywords: Template method, Electrodeposition, NiO/Au composite nano-rod array membrane, Electrochromic characteristics

1. Introduction

For high-contrast and quick color change of reflective electrochromic (EC) devices, the EC absorber material in traditional planar film EC cells must have a minority carrier diffusion length that is long enough to allow effective transfer of the carriers over the entire light absorption depth. One approach to circumvent this issue involves orthogonalization of the directions of the light absorption and carrier transfer in the EC absorber films. For example, an absorber thin film immobilized on the surface of a vertically oriented nano-rod array with high-aspect ratio could, in principle, provide a sufficient optical absorption along its axial dimension, while facilitating radial transfer of carriers over a distance sufficiently short to compensate for the short minority carrier transfer length (Fig. 1)¹⁾. In our previous study by using a modified template method ^{2) 3)}, an Au nano-rod array membrane (Au-NRM) was prepared by removing the template in which the long rods were stacked together in large numbers on the lower Au surface layer. The Au-NRM, composed of solid nano-rods (1–10 μ m long and 50–800 nm diameter, aspect ratio = <100 : 1) has a characteristic bristle-like configuration on the Au film substrate. We adapted the Au-NRM for electrochromic applications. Conducting polymers were coaxially coated on the Au nano-rods by electropolymerization. In this case, both improvement of the EC durability and quick response of the EC color changes were realized at the same time by the nano-structure with a high aspect ratio covered with a thin conducting polymer film ^{4) 5)}.

The most commonly used anodic oxide-based EC materials are NiO and IrO_2 . They are able to change from a transparent state to



Orthogonalization of the directions of light absorption/reflection and carrier transfer

Fig. 1. Schematic diagrams of planar and nano-rod architectures.

Received 19th, March 2014; Accepted 8th, May 2014

*Department of Life Science and Sustainable Chemistry, Tokyo Polytechnic University, 1583, Iiyama, Atsugi, Kanagawa 243-0297, Japan

a neutral colored one upon the extraction of protons or insertion of OH^- ions. Charge-balancing electrons are simultaneously extracted from the valence band. The films are probably a mixture of oxide and hydroxide components in the bleached state, since a reservoir of protons seems to exist in the films. Due to the high cost and limited supply of Ir, the use of NiO is favored at least for large scale applications.

A variety of methods have been used to prepare the NiO films, such as sputtering, chemical vapor deposition, electrochemical deposition process, pulsed laser deposition, spray pyrolysis and a sol-gel process ⁶⁾⁻¹¹. Among the physical and chemical deposition techniques, electrodeposition is of particular interest due to low cost and feasibility of room temperature growth on a large area.

Since the electric conductivity of the NiO film is very low (10^{-8} S/cm) , the device with a thick NiO film would have a slower EC response due to a significant IR drop in the film. According to the consideration as mentioned above, an ideal vertical arrangement of the rods were required to provide a sufficient coloration from the NiO thin films. Therefore, we tried the electrochemical Au deposition by using anodic porous alumina plate as the template to obtain simply and easily the Au-NRM.

The detailed conditions of the Nickel oxides (NiO)/Au coaxial nano-rod membrane preparation, such as rod length and film thickness, and the electrochromic characteristics of the coaxial nano-rod membranes were evaluated in the present study.

2. Experimental

All electrochemical and electrochromic measurements were performed by using an EG&G PAR model 263 potentiostat. A three-electrode cell consisting of an Au-NRM working electrode, Ag-AgCl reference electrode, and Pt wire counter electrode, was used. All potentials are quoted vs. Ag-AgCl.

The Au thin films (thickness of 50 nm) were immobilized on the template polycarbonate (PC) membrane (thickness of 5–10 μ m) and the template anodic porous alumina plate (AAO) (pore diameter of 200 nm, thickness of 60 μ m) by sputtering coating. The electrochemical reduction was carried out by using the Au coated template membrane in aqueous solution (pH 10) containing gold (I) trisodium disulfite. As the typical conditions, potentiostatic electroreduction was carried out at the applied potential of -1.2 V (vs. Ag-AgCl) for 3 hours.

Furthermore, the NiO/Au coaxial nano-rod membranes were electrochemically prepared by using the resulting Au-NRM as the working electrode (A 0.283 cm^2 area is exposed to the electrolyte solution). An aqueous solution containing nickel (II) chloride 6-hydrate (25 mM) was employed as the electrolyte solution. As the typical conditions, the potentiostatic electroreduction was carried out at the applied potential of -0.7 V (vs. Ag-AgCl) for 45 min¹²).

The surface morphologies of the product membranes were observed by using a Hitachi S-5000 scanning electron microscope (FE-SEM). A thin film (less than 50 nm) of Pt was sputter-coated onto the samples to minimize any charging effects. The reflection spectra and the EC switching of the product membranes were evaluated by using an Ocean Optics USB 2000 spectrometer equipped with a reflection probe.

3. Results and discussion

Fig. 2 shows FE-SEM images of the surface condition of the product membranes prepared by using typical two conditions. As shown in Fig. 2, a remarkable difference in the surface condition was found between the Au-NRM obtained from the PC template and that from the AAO template. The orientation of the rod directions and intervals between the rods were not very uniform for the Au-NRM obtained from the PC template. In contrast, the distributions of the rods obtained from the AAO template were quite perpendicular and densely packed. The obtained rod diameter is about 200 nm, and the rod density was 8 to 16×10^8 rod/ cm². Therefore, the rod density was 2.7 to 5.3 times the product from the PC template. Their rod shape reflected the pore shape of the AAO template. It is anticipated that an ideal light absorption by the EC material along the axis of the nano-rod will be realized by using the Au-NRM obtained from the AAO template. During the electrodeposition of the Au rod, the current-time characteristic showed almost constant values except for the initial process. Although the depositions were carried out in the potentiostatic mode, the charge amount was simply proportional to the deposition time due to the constant current values. The relationship



Fig. 2. FE-SEM images of the product membranes from PC template and AAO template.



Fig. 3. Reflection spectra of obtained Au-NRMs.

between the charge amount and the rod length was not directly discussed in this study. The Au deposition proceeded on both the inside of the AAO pores and back side surface of the sputtered Au layer, then most reaction current was consumed by the Au under layer formation except for the rod formation. Since the reaction of Au ions needs to pass through the small pores with the length of 60 μ m, the net current for the rod formation is about 1/5 of the observed current. Actually, the rod length can be controlled by the deposition time.

The reflection spectra of the obtained Au-NRM are shown in Fig. 3. The shape of the spectra was fundamentally similar to that from the PC template, and the reflectance were lower than that from the PC template (20-50%)¹³⁾. The spectrum involved the absorption due to the Au inter-band transitions shorter than the wavelength of 500 nm and plasmon scattering to the longer wavelength. It was found that the reflectance value decreased with a change in the rod length to $2-3 \mu m$, then no drastic drop in the value would be observed for Au-NRM with longer rods. Since the reflection includes both the head of the rod and Au under layer, the high reflectance value was observed from Au-NRM with shorter rods. In contrast with Au-NRM with longer rods where incident light could not reach the reflective Au under layer, in the case of Au-NRM with shorter rods, the reflection came from both the head of the rod and Au under layer, thereby showing higher reflectance. If the EC films were coaxially immobilized on the longer nano-rods, the incident light into the EC film would not be reflected on the under layer of the Au-NRM. Cyclic voltammetries of a redox reagent were carried out with Au-NRM of different rod lengths. Fig. 4 shows the relationship between the obtained oxidative peak current and the scan rate. Between the cases of Au-NRMs with rod length of 1 µm and 3 µm, definitive differences in the redox current were found with increment of the electrode surface area. When the rod length increase from $3 \, \mu m$ to 6 µm, only a slight enhancement in the redox current could be observed. Even if the rod length of the Au-NRM changes, the surface area of the Au under layer is always constant. Therefore, total surface area of the Au-NRM is the addition of the surface area for the side wall of the all rods (multiplication of the rod circumference by the rod length) and the surface area for the under



Fig. 4. Relationship between the obtained oxidative peak current and the scan rate. Cyclic voltammetric analyses of $K_3Fe(CN)_6$ (2 mM) were carried out in the KNO₃ aqueous solution with Au-NRM of different rod lengths.

layer, and depends only on the rod length. In the cases of the rod length of 1, 3 and 6 μ m (Average rod density : 12×10^8 rod/cm²), the theoretical surface areas of the Au-NRM are 2.42, 6.68 and 13.1 cm², respectively. When the electrochemical measurement is carried out with a flat surface electrode, the redox currents are proportional to the surface area of the electrode. As shown in Fig. 4, it was found that the redox currents from three-dimensional electrode as the Au-NRM were not simply proportional to the electrode surface area. Since these redox currents had a linear relationship with the square root of the scan rate, these redox reactions were controlled by diffusion process of the redox agents in the solution. This suggests that it is hard to migrate redox species into deeper areas of the rod array.

Fig. 5 shows the FE-SEM image of the obtained the product film on the Au-NRM prepared by a typical condition (Rod from 1h deposition, and product film from 40 min. deposition). The flaky morphology was found on the Au nano-rod, which reflected the NiO formation. Fig. 6 shows the cyclic voltammograms of the product membrane (Rod from 3 h deposition, and product film from 40 min. deposition) in the 1.0 M KOH aqueous solution. A pair of well-defined redox peaks at +0.4 and +0.2 V were clearly observed at the scan rate of 50 mV/s. Their peaks are due to the reversible reactions of Ni²⁺/Ni³⁺ associated with the OH⁻ anions. On the base of these results, the product films were identified as NiO. As in the other nano-structured NiO films, almost no charging current due to the electric double layer was observed in Fig. 6¹⁴⁾.

Fig. 7 shows the changes in the reflection spectrum of the NiO/ Au composite nano-rod array membrane (Rod from 3 h deposition, and NiO film from 40 min. deposition) induced by an applied potential switching between +0.7 V and -0.3 V. Brightness changes were visually observed from the membrane. Especially, the difference in the reflection values (Δ Ref.) was maximum (around 5.5%) from the wavelengths of 650 nm to 750 nm. Upon immersion of NiO into an alkaline solution, a spontaneous chemical conversion of NiO into a hydrous metal oxide phase Ni(OH)₂ takes place. The Ni²⁺/Ni³⁺ couple responsible for the reversible



Fig. 5. FE-SEM image of the obtained product film on the Au-NRM prepared by a typical condition (Rod from 1h deposition, and product film from 40 min. deposition).



Fig. 6. Cyclic voltammograms of the product membrane (Rod from 3 h deposition, and product film from 40 min. deposition) in the 1.0 M KOH aqueous solution.

color change upon electrochemical cycling has been identified as the nickel hydroxide/oxy-hydroxide phases as shown in the followed equation $^{15) 16)}$.

$$Ni(OH)_2 \leftrightarrow NiOOH + H^+ + e^-$$
 (1)

Thus, the NiO film exhibited an anodic coloring at +0.7 V and cathodic bleaching at -0.3 V. This change in the redox states would be visually observed as the color change. The changes in the reflectance value at the wavelength of 700 nm for the NiO/Au composite nano-rod array membrane (Rod from 3 h deposition, and NiO film from 40 min. deposition) during the continuous potential switching between +0.7 V and -0.3 V were measured to evaluate the color switching speed. The response (coloring and bleaching) times are defined as the time required for an 80% change in the total reflectance modulation at the wavelength of 700 nm. The obtained EC response was quite fast, which involved the coloring for 0.65 s and bleaching for 1.3 s.

The dependences of the EC characteristics on the rod length were discussed for the coaxial membrane with the same NiO film thickness (85 nm). Fig. 8a shows the relationship between the Δ Ref. and rod length. According to the tendencies as shown in



Fig. 7. Changes in the reflection spectrum of the NiO/Au composite nano-rod array membrane (Rod from 3h deposition, and NiO film from 40 min. deposition) induced by applied potential switching between +0.7 V and -0.3 V. (a) Photographs of the NiO/Au composite nano-rod array membrane in the colored (Ox.)/bleached (Red.) states of -0.7 and -0.3 V. (b)



Fig. 8. Relationship between Δ Ref. and rod length. (a) The dependences of the Δ Ref. on the rod length were discussed for the coaxial membrane with the same NiO film thickness (85 nm). Relationship between Δ Ref. and the film thickness. (b) The dependences of the Δ Ref. on the NiO film thickness were discussed for the coaxial membrane with the same rod length (3 μ m).



Fig. 9. Relationship between the response time and the NiO film thickness. The dependences of the response time on the NiO film thickness were discussed for the coaxial membrane with the same rod length (3 μ m).



Fig. 10. Changes in the reflectance at 700 nm for the NiO/Au composite nano-rod array membrane (Rod from 3h deposition, and NiO film from 40 min. deposition) during continuous potential switching between +0.7 V and -0.3 V.

Table 1. The comparison of the EC performance between our reflective system and other selected NiO-based transparent systems. (t_c) and (t_b) are the response time for coloring and bleaching, respectively.

λ (nm)	ΔT (%)	t_{c} (s)	t_b (s)	ref.
550	28	0.88	0.74	Cai et al. 14
550	66.2	3.5	4	Lin et al. 17
550	76	3	5	Yuan et al. 18
550	82	8	10	Xia et al. 19
630	45	1.7	2	Sonavane et al. 20
630	79.6	0.063	0.053	Scherer et al. 21
λ (nm)	∆Ref. (%)	t_{c} (s)	t_b (s)	ref.
700	5.5	0.62	0.85	Our Result

the Fig. 4, further increase in the $\Delta Ref.s$ were not found over the rod length of 3 μm . Since the response would be slower with the increasing rod length, it was concluded that the rod length of 3 μm was the optimum condition for the EC performance.

The dependences of the EC characteristics on the NiO film thickness were discussed for the coaxial membrane with same the rod length (3 μ m). Fig. 8b shows the relationship between the Δ Ref. and the film thickness. The Δ Ref. increased to 5.5% with

an increase in the thickness, while further increases in the Δ Ref. were not found over the film thickness of 50 nm. Fig. 9 shows the relationship between the response time for the color change and the NiO film thickness. When the film thickness was 50 nm, the EC response time was 0.62 s for coloring and 0.85 s for bleaching as shown in Fig. 10. The optimum condition for the EC response has so far been the film thickness of 50 nm and the rod length of 3 μ m. Table 1 shows the comparison of the EC performance be-

4. Summary

The Au-NRMs were prepared with AAO as the template. As a result, the distributions of the rod obtained from the AAO template were ideally perpendicular and densely packed. The NiO films were coaxially immobilized on the Au rod surface by an electrodeposition by using the Au-NRM as the electrode. It was found from this study that the fabrication conditions for best EC performance were the rod length of 3 μ m and the NiO film thickness of 50 nm. An ultrafast EC response was achieved by the NiO/Au composite nano-rod array membrane under the optimum conditions.

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