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Acceleration of Electrochromic Color Change using Branched Au Nano-structured Electrode

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Abstract: Au nano-rod array membrane was prepared using a commercially-available porous anodic aluminum oxide plate as the template which consisted of branched structures. When a NiO film was immobilized on the nano-rod surface of the obtained membrane, the electrochromic response of the NiO film was remarkably accelerated: the total process including the coloring and bleaching was accelerated 1.2 times, in particular, the bleaching process was significantly accelerated 1.5 times.

Key words: Electrochromism, NiO, Au Nano-stump array membrane, Electrochromic response

1. Introduction

Electrochromism is the phenomenon related to changes in color induced in several materials by a reversible electrochemical process. One of the claimed advantages of electrochromic (EC) displays over other technologies is eye-friendly color presentation involving the high contrast, the vibrant, and rich looking color image of the display against the background. This is due to the fact that EC materials absorb some light spectra and reflect others, similar to dye and pigments used in printing. Therefore, the EC device has been attracting attention as the display of the electronic paper. In our studies, the EC characteristics of conducting polymer films have been evaluated on a Au nano-rod array membrane electrode prepared using a polycarbonate porous membrane as the template. Compared with the result in the polymer film on a planar electrode, an improved response and durability of the color change were successfully achieved using the nano-structured electrode system.[1,2] Although the electrochemical and the EC reactions can be accelerated using a thinner EC film, the optical density (coloration) of the EC film will be reduced by the shortening of the optical path. When the EC material film was immobilized on a smooth plate electrode, the direction of the light path and that of the carrier (ex. hole or electrolyte ions) transfer were always parallel in the EC film. On the other hand, the orthogonalization of these directions could be easily realized using a Au nano-rod array electrode as shown in Fig.1. [3] These 3D configurations of the EC materials produced a long light path and short carrier transfer at the same time, thereby allowing accelerated EC color changes and deep colors.

Recently, NiO films as EC materials were coaxially immobilized on the Au nano-rod array electrode prepared using an anodic porous alumina plate (AAO) template (pore diameter of 20 nm, thickness of 60 μm). After several experiments were carried out to determine the optimum relationship between the rod height and the NiO film thickness, the ultra-fast EC response within 1 s could be realized as shown in a previous report. [3] It is still necessary, however, for our system to make a breakthrough to achieve much faster response sufficient for the movie rate. In this study, we evaluated EC characteristics of the NiO film on a new branched Au nano-rod array electrode to find a remarkably accelerated EC response.

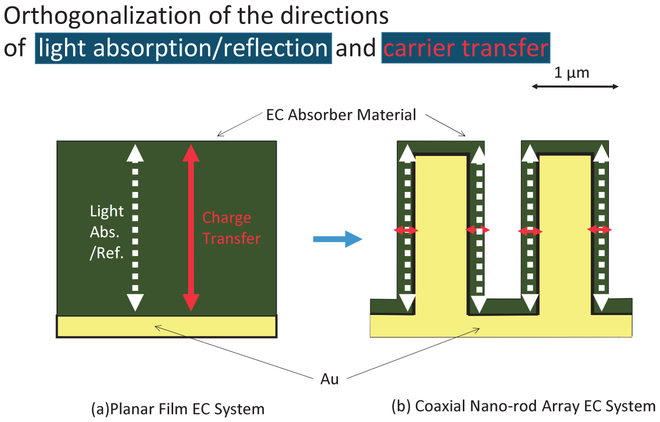

Fig.1. Schematic diagrams of planar and nano-rod architectures.[3]

2. Experimental

All electrochemical and EC measurements were performed using a potentiostat. A three-electrode cell consisting of an Au nano-structure membrane working electrode, Ag–AgCl reference electrode,

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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 AAO plate template (pore diameter of 20 nm, thickness of 60 μm) by sputter coating. The electrochemical reduction was carried out using the Au coated template in an aqueous solution (pH 10) containing gold (I) trisodium disulfite. In a typical conditions, the potentiostatic electroreduction was carried out at the applied potential of –1.0 V (vs. Ag–AgCl) for 90 minutes. Using an ultraviolet curing resin, the product template was immobilized on the glass plate. The template/glass was then immersed in 1.0 M NaOH aqueous solution for 2 hours to remove the AAO. This procedure was carried out to expose the Au nano-structure. Furthermore, the NiO/Au composite membranes were electrochemically prepared using the resulting Au nano-structure membrane 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 –0.6 V (vs. Ag–AgCl) for 15 minutes. The surface morphologies of the product membranes were observed by a scanning electron microscope (FE-SEM). A thin film (less than 50 nm thick) of Pt was sputter-coated onto the samples in order to minimize any charging effects. In order to evaluate the EC characteristics, three electrodes device with quartz cell was composed of a 1.0 M KOH aqueous solution, the NiO/Au nano-structure membrane, Ag–AgCl, and Pt wire as the electrolyte, working electrode, reference electrode and counter electrode, respectively. The reflection spectra and the EC switching of the product membranes were evaluated using a spectrophotometer equipped with a reflection probe.

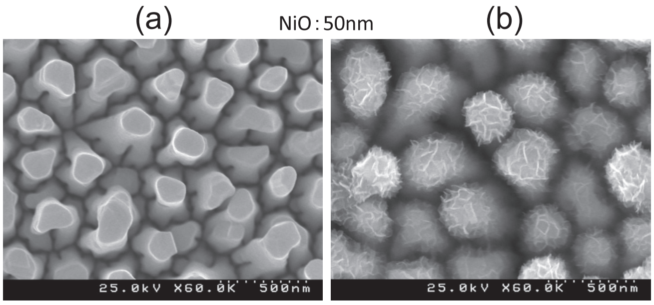

Fig.2. FE-SEM images of (a) the product membranes from AAO template with the branched pores and (b) the product film on the Au nano-structured membrane after electroreduction of $NiCl_2$.

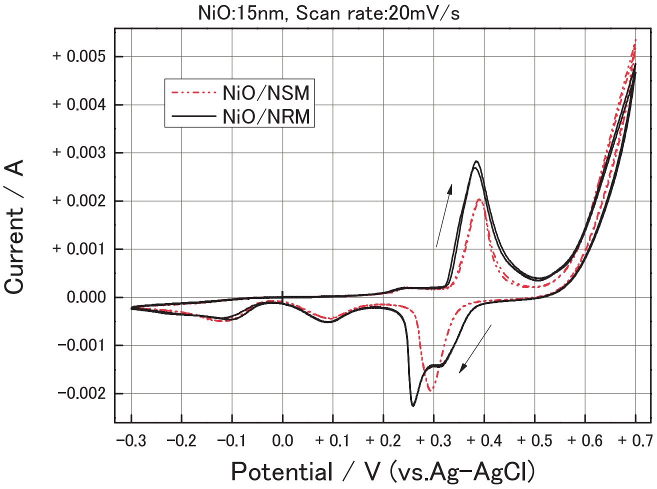

Fig.3. Cyclic voltammograms of the NiO(15 nm)/NSM and the NiO(15 nm)/NRM in the 1.0 M KOH aqueous solution.

3. Results and Discussion

Surface observations of the obtained Au membrane were carried out by FE-SEM, and the resulting image is shown in Fig.2a. Complex structures were found in the image which contained some branched nano-rod structures. The average height (length) of the rod structure was about 2 μm by the electrolysis for 90 min. The diameters of the nano-rods changed from 20 nm near the Au base plate (the length is about 50 nm) to 200 nm at the top of the rod. In this study, we labelled the straight rod membrane NRM and the branched rod membrane NSM. After electroreduction of the nickel (II) chloride, NSM was covered with flaky deposit of NiO, the thickness of which was about 50 nm. In the FE-SEM observation, relatively thicker film of 50 nm was immobilized to confirm the formation of NiO easily.

The electrochemical characteristics of the thin NiO film were evaluated in a 1.0 M KOH aqueous solution using the NRM and NSM electrodes. The NRM was composed of the smooth and straight rods with the height of 2 μm and the diameter of 200 nm. The cyclic voltammograms (CV) are shown in Fig.3 which were obtained at the scan rate of 20 mV/s. The NiO film on the NRM was slightly thicker than that on the NSM; the film thickness was around 15 nm. For both electrodes, the redox couple (Ni II/Ni III) was approximately +0.35 V (vs. Ag–AgCl) based on the CV. Their currents were also about the same values. In contrast, the different feature was the shape of the reductive wave from the NiO/NRM. The reductive wave appeared to contain two peaks at +0.26 V (vs. Ag–AgCl) and +0.31 V (vs. Ag–AgCl). A $Ni(OH)_2$ thin layer was formed on the NiO film in the KOH aqueous solution. The $Ni(OH)_2$ thin layer would be NiOOH by electrochemical oxidation. The color change in the metal oxide from colorless to brown occurred during this reaction. These peaks were probably attributed to the electrochemical reduction of β-NiOOH at the positive potential and γ-NiOOH at the negative potential. γ-NiOOH was formed by over-oxidation of β-NiOOH, and was hard to reduce compared to the β-NiOOH.[4] Since the small shoulder of the oxidation current was found at +0.55 V (vs. Ag–AgCl) in the CV with the NRM, the formation of γ-NiOOH was probably facilitated on this electrode. Concerning the redox reaction between $Ni(OH)_2$ and NiOOH, the reduction of γ-NiOOH on the NRM required the more negative applied potential compared to the reduction of β-NiOOH on the NSM.

According to the CV, the NiO films on the NSM and NRM exhibited an anodic coloring at +0.7 V (vs. Ag–AgCl) and cathodic bleaching at –0.3 V (vs. Ag–AgCl). These changes in the redox states could be visually observed as brightness changes. The changes in the reflectance value at the wavelength of 600 nm for the NiO films on the NSM and NRM during the continuous potential switching between +0.7 V (vs. Ag–AgCl) and –0.3 V (vs. Ag–AgCl) were mea-

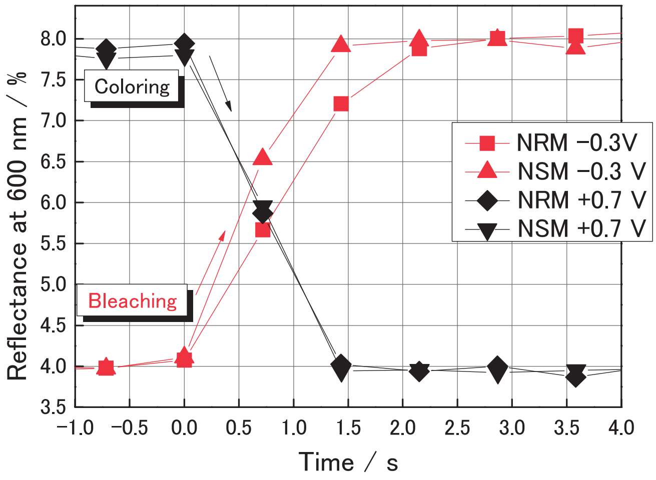

Fig.4. Changes in the reflectance at 600 nm for the NiO(15 nm)/NSN and the NiO(15 nm)/NRM induced by the switching of potential applications between +0.7 V and –0.3 V (vs.Ag-AgCl).

sured in order to evaluate the color switching speed. As a result, the time dependences of the reflectance after a potential application are shown in Fig.4. The response (coloring or bleaching) times are defined as the time required for a 70% change in the total reflectance modulation at the wavelength of 600 nm. The EC response for the NSM was quite fast: 1.01 s for coloring and 0.83 s for bleaching. For the NRM, the response time was 0.98 s for coloring and 1.26 s for bleaching. This result indicates that the total response time (coloring and bleaching) for the NSM will be about 82% of that for the NRM. Thus, a considerable acceleration of the NiO EC change was achieved using the NSM.

Concerning the coloring process, this acceleration was attributed to the change from $Ni(OH)_2$ to NiOOH. Since the electric conductivity of NiOOH was higher than that of $Ni(OH)_2$, the conductive layer would be smoothly extended from the electrode side to the solution side. In the bleaching process, an insulating layer ($Ni(OH)_2$) was formed by the reduction of NiOOH in the area nearest to the electrode. The reduction of NiOOH in an area slightly distant from the electrode was then inhibited by the formed insulating layer. In most cases, the EC bleaching process of NiO required a longer time compared to the coloring process. We are now proposing a mechanism for the acceleration of the bleaching process on the NSM. The only difference in the experimental conditions was the shape of the nano-rod; the other conditions, such as the NiO immobilization, were common to both of the nano-electrodes. According to the peak separation on the CV (as shown in Fig.3), the conductivities of the NiO film were probably different on the NRM versus on the NSM. It is expected that a difference in the electric environment on the electrode surface is present between the NRM and the NSM. The dielectric-metal-dielectric (DMD) structure must be discussed as the potential candidate mechanism. Many studies about the DMD structure were carried out to improve the electric conductivity and the transmittance of the transparent electrode.5-7) At first, metals such as Ag and Au were used as the thin layer in these studies, but metal nano-particles with island structures were actually immobilized on the substrate. The localized surface plasmon resonance on the metal layer of the DMD structure has been discussed in recent years.8) Although the comments about the reflectance spectrum of both electrodes (NRM and NSM) were omitted in the letter, the drop in the reflectance for the NSM was enhanced at a wavelength longer than 500 nm compared with the NRM. This drop is due to plasmon scattering, which is often observed from a metal nano-structure. As mentioned above, the nano-rods of the NSM were branched and ranging in the diameter from 20 nm to 50 nm near the Au substrate. Since the NiO films were coaxially immobilized on the branched Au nano-rod, the DMD (NiO/Au/NiO) structure might be formed in this system. There is a possibility that the conductivity of the NiO film on the NSM is enhanced by the DMD structure. Therefore, we plan to study the influence of the plasmon electric field of the NSM on the conductivity of the prepared NiO film.

4. Summary

Array membranes of the Au nano-rod with a branched structure were prepared in this study. NiO films were electrochemically immobilized using the obtained nano-rod membrane as the electrode. The EC response of the NiO film which included a coloring and bleaching process was accelerated 1.2 times by a branched nano-rod electrode compared to a straight nano-rod one. The difference in the electrochemical transformation from NiOOH to $Ni(OH)_2$ is responsible for the acceleration of the EC response. The experimental results obtained in this study seem to be stimulating for such studies as rechargeable batteries and sensor devices.

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