Electrochromism of poly(3,4-ethylenedioxythiophene) films on Au nano-brush electrode

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\begin{abstract}
Au nano-brush membranes were prepared using a modified template method. Poly(3,4-ethylenedioxythiophene) (PEDOT) films were immobilized by an electropolymerization with the product membrane as the working electrode. The PEDOT film on the nano-brush electrode showed higher electrochromic (EC) coloration compared to the PEDOT film on an Au planar electrode.
\end{abstract}

\section{Introduction}

Many physical studies are currently underway regarding microcapsule-type, electrophoretic-type, and cholesteric liquid crystal (LC)-type devices in order to develop electronic paper displays. However, we have placed significant focus on a chemical approach using reflective electrochromic devices with conducting polymers. Electrochromism is a color changing phenomenon due to the redox reaction of the material. However, the development of electrochromic (EC) displays based on conducting polymer materials involves several problems. In particular, the switching response and the repetition stability of EC devices were very poor compared to commercially available electronic displays. Among the studies to improve the EC performance with conducting polymers\cite{1,2}, our current focus on the flexibility of the electrode materials and the high aspect ratio of the electrode configuration has been a very new approach\cite{3}. Namely, the polypyrrole (PPy) films electropolymerized on a Au nano-brush electrode have exhibited improved EC switching life-times, higher EC coloration, and the potential of high-speed EC switching response. This is due to the high aspect ratio (15:1) of the nano-brush structures. High-speed EC switching is expected from a display device composed of a thin conducting polymer film and a Au nano-brush electrode. Furthermore, the electrochemical and electrochromic stabilities of the PPy film have been significantly improved using the Au nano-brush electrode. The flexible structure of the Au nano-brush electrode probably contributes to enhancing the adhesion between the PPy film and the electrode.

In the present study, Au nano-brush electrodes were prepared by an advanced template method, and were used to evaluate the electrochemical characteristics and the EC characteristics of the conducting polymer film. Of the conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives are ideal EC materials for electronic paper displays\cite{4,5}. Therefore, PEDOT was utilized as the EC material in order to demonstrate the advantage of this new nano-structured electrode.

\section{Experimental}

Commercially available ‘track-etched’ poly-carbonate (PCTE, Poretics) filter membranes were used as the templates to prepare the Au nano-brush membrane. The polycarbonate membranes used for this study had nominal pore diameters of 200 nm and a thickness of 10 \mu m. The electroless plating method was used to deposit Au nano-wires within the pores of these membranes, as previously reported, but with some modification\cite{6,7}. The difference in the procedures was the application of a cover film on the template membrane before immobilization of the Sn ions and additional processing for 5 min with a 2\% PdCl\textsubscript{2} hydrochloric acid solution prior to Au plating. The Au nano-brush electrode fabrication procedure is schematically shown in Fig. 1. After removal of the cover film, a small piece (10 mm \times 15 mm) of the Au membrane was immobilized on the glass substrate using an ultraviolet curing...
resin (Norland Products, Norland Optical Adhesive 81). The Au membrane was placed on the glass substrate so that the Au film covering the rough face of the membrane was facing downward. After UV illumination for 36 min, the Au membrane was then immersed in chloroform for 25 min to remove the template polycarbonate. A nano-brush structure was then obtained in which the Au nanowires are aligned together in large numbers on the lower Au surface layer. A rectangular strip (8 mm \(\times\) 40 mm) of Cu foil was then fixed to the brush surface, so that it covered only approximately 3 mm of the 15 mm long Au nano-brush membrane. The Cu foil acts as a current collector and working electrode lead for the nano-brush electrode. The electrode assembly was then connected to an electrolyte cell for electropolymerization via a silicon O-ring. The O-ring defines the area (0.22 cm\(^2\)) of the Au nano-brush electrode that is exposed to the electrolyte solution.

All the electrochemical measurements were performed in a N\(_2\) gas atmosphere using a potentiostat (EG&G PAR model 283) and a vacuum glove box (Miwa Seisakusho Co., Ltd.). A three-electrode cell consisting of an Au nano-brush membrane working electrode, Ag–Ag\(^+\) reference electrode (BAS, Inc.), and Pt wire counter electrode, was used. All potentials are quoted vs. Ag–Ag\(^+\). The electropolymerization solution was 1 mM 3,4-ethylenedioxythiophene (EDOT) and 0.1 M LiClO\(_4\) dissolved in acetonitrile. The nano-brush electrode was exposed to this solution for 30 min prior to the start of the electropolymerization. The potential cycle polymerization on the Au nano-brush electrode was continued for 8 cycles. Fig. 3 shows FE-SEM surface views of the Au membrane (a) before and (b) after polymerization. Based on the FE-SEM observations after the polymerization (Fig. 3(b)), the PEDOT film thickness on the Au fiber was approximately 50 nm after 8 polymerization cycles. The neighboring nano-fibers were still independent after the polymerization. The surface condition of the obtained PEDOT film was relatively smooth, and with dense packing. On the other hand, after the potential cycle polymerization on the Au planar electrode was continued for 6 cycles, the polymer thickness obtained was approximately 400 nm. A close fibrillar structure was found over the densely packed polymer layer (thickness: <100 nm) for the PEDOT film obtained on the planar electrode.

3. Results and discussion

Solid Au nano-wires could be easily obtained in the small pores (pore diameter: <200 nm) by attachment of the cover film to the PC template membrane, similar to a previous study using an alumina template [8]. Fig. 2 shows a FE-SEM surface view of the Au membrane after the exposure procedure. Nano-fibers (aspect ratio 50:1) 10 m long and with 200 nm diameter were observed in the FE-SEM image. This could be evidence that these Au fibers are not hollow, but are completely solid rods that possess sufficient strength for the template removal procedures, which involves swelling of the template polymer. The fine paper fiber-like structure produces a mild light-scattering characteristic of the reflective EC device.

The surface morphologies of the Au nano-brush electrode were observed before and after electropolymerization using a field emission-scanning electron microscope (FE-SEM, Hitachi S-5000). A thin layer (<50 nm) of Pt was sputter-coated onto the samples to minimize any charging effects.

Simple two-electrode devices were assembled to evaluate the EC characteristics as follows. A 0.1 M LiClO\(_4\) propylene carbonate electrolyte solution containing was held by a silicon O-ring between the PEDOT film coated Au nano-brush electrodes and the indium tin oxide (ITO) transparent electrodes. The EC switching of the device was evaluated using a UV–vis spectrophotometer (Ocean Optics USB-2000) with a reflection probe.
Fig. 2. FE-SEM image of the Au nano-brush membrane obtained by electroless plating reaction for 25 h.

As explained in Section 2, the EC behavior of the PEDOT film on the Au nano-brush electrode was evaluated using a simple reflection device. Changes in the reflectance between 380 nm and 800 nm were measured from the ITO electrode side using a reflective probe. The reflectance was measured on the basis of the bare Au planar electrode device. It is well known that absorption changes in the visible band around 600 nm due to π-π* transitions induced by the redox reactions of the PEDOT films. When the PEDOT film was immobilized on a white substrate, an EC color change should be observed between dark blue (for the reductive state) and light blue (for the oxidative state) [4]. For the Au nano-brush electrode device, the maximal change in reflectance was observed around 610 nm by switching of the applied voltage as shown in Fig. 4. The reflectance at 610 nm increased in the oxidative state (+2.5 V) of the PEDOT film, and recovered in the reduced state (−2.5 V). The EC color change between yellow green and dark green was easily recognized visually. The maximum difference in reflectance (Δref.) from the device with the PEDOT film (film thickness: 50 nm) on the Au nano-brush electrode was found to be 27% at 610 nm. The solid line in Fig. 4 indicates the spectrum including the reflectance of the Au nano-brush electrode and the PEDOT film in the oxidative state. It is well known that an oxidative PEDOT film with a thickness of 50 nm exhibits a relatively small absorption from 500 nm to 700 nm. Therefore, the strong coloration above 500 nm shown in Fig. 4 (solid line) is attributed to plasmon scattering by Au nano-particles with a high aspect ratio. In contrast to the light blue color for the oxidized PEDOT film on a white substrate, the yellow green color may be due to the gold colored nano-brush substrate and plasmon scattering. The very low reflectance of 10% above 650 nm (broken line in Fig. 4), was induced by plasmon scattering and the EC coloration of the reduced PEDOT film. Δref. for the device (PEDOT film thickness: 400 nm) with a planar electrode, was found to be only 14% at 610 nm. Δref. generally,

Fig. 3. FE-SEM images of the Au nano-brush electrode (a) before and (b) after 8 electropolymerization potential cycles in a solution of 0.1 M LiClO₄ and 1 mM EDOT in acetonitrile. (c) SEM image of the Au planar electrode after the electropolymerization (6 cycles).
corresponds to the film thickness or the light-path lengths of the EC material. Electrode configurations particularly affect the light-path lengths of a PEDOT film on an electrode. In the case of the planar electrode, the light-path lengths correspond to the thickness (400 nm) of the PEDOT film electropolymerized on the electrode. The light-path lengths of the PEDOT film are extended by the configuration of the nano-brush electrode with a high aspect ratio. That is, the maximum light-path length is identical with the length of the Au nano-fiber (10 μm), due to additional contributions by the light incident to the cross-sectional direction of the PEDOT film. The Au nano-brush membranes prepared in the present study contain some imperfections in the rod arrangement such as scattering intervals, shallow depths and crossings; however, the PEDOT films on the Au nano-brush electrode exhibited increased EC coloration compared to films on the Au planar electrode.

The color-switching response time of the same device was optically measured from the reflectance at the 610 nm wavelength as a function of the time after voltage application. Voltage was continuously applied by stepping the voltage between +2.5 V and −2.5 V with a switching interval of 9 s. The response time is defined as the time required for the system to reach 80% of its full response. Fig. 5 shows a portion (5 cycles) of the results. The de-coloring and coloring processes of the nano-brush electrode device had switching times of 0.6 s and 2.4 s, respectively, whereas those for the planar electrode device were 0.6 s and 1.8 s, respectively. According to a previous report regarding the relationships between the PEDOT film thickness and the EC response, a thicker film has a slower EC response than a thinner film [9]. The difference in polymer thickness was a factor of approximately 8; however, there was only a small difference in the EC response of both devices in the present study. However, there was a significant difference in the morphology of the PEDOT films on the different electrodes, as shown in Fig. 3. In particular, it is supposed that the fine fibrillar structure of the PEDOT film on the planar electrode contributes to the rapid transfer of dopant ions in the film. This mass transport is the rate-determining process of the entire EC reaction; therefore, morphological optimization of the PEDOT film is an important feature to realize a high-speed EC response.

4. Conclusions

Fine solid Au nano-wires could be prepared for a Au nano-brush electrode, even in small pores, using a modified template method with a cover film. PEDOT films prepared on the Au nano-brush electrode showed higher EC coloration (∆ref. = 27%) compared to PEDOT films on a Au planar electrode. This is due to the high aspect ratio (50:1) of the nano-brush structures. However, there are some concerns when developing a practical EC device using PEDOT films. In order to improve the EC characteristics, optimization of the electrode nano-structures and detailed study of the electropolymerized PEDOT film morphology are necessary.
References