

Durability Improvement of Electrochromic Display with Nano-Structured Electrode

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ABSTRACT

Island-shaped Au nano-particles were immobilized on an ITO transparent conductive film by a pulse electrolysis method capable of controlling the nucleation and the nuclear growth. Using this as an electrode, a polypyrrole thin film was immobilized by electrochemical polymerization. It was confirmed that the electrochromic durability of the polypyrrole film was greatly improved on the ITO electrode modified with the Au nano-islands.

1. INTRODUCTION

In the study of electrochromic (EC) displays using conductive polymers, improving the responsiveness and durability of the color changes associated with the electrochemical redox reaction is the most important subject for their practical application. Nevertheless, there are not many direct studies for improving the durability of the EC changes.

In this study, using the island-shaped Au nano-particles immobilized ITO electrode, the durability of the change in transmittance of the polypyrrole (PPy) film due to EC was evaluated and compared to the normal ITO electrode.

2. EXPERIMENTALS

2.1 Preparation of ITO Electrode Modified with Au Nano-island (Au-ITO)

Au nano-island was immobilized on ITO electrode by electrochemical deposition with pulse voltage (11 V) and constant voltage (1.0 V). This reaction was carried out using an aqueous solution of Au (I) trisodium disulphite and potassium sulfite at room temperature.

2.2 Preparation of PPy Film

The PPy films were prepared on the electrode by an electropolymerization with a cyclic potential application between -500 mV and +1000 mV (vs. Ag-AgCl, scan rate: 50 mV/s). The polymerization solution was 10 mM pyrrole and 0.1 M lithium perchlorate (LiClO₄) dissolved in water.

2.3 Transmittance measurement

The EC characteristics of the PPy on the electrode were evaluated by the transmittance measurement in the transparent glass cell.

3. RESRESULTS AND DISCUSSION

When constant potentials of -400 mV and +800 mV were applied to the PPy films on the electrode in an aqueous solution containing lithium perchlorate, color changes were observed due to their electrochromism. The PPy films (film thickness: 100 nm for ITO and 150 nm

for Au-ITO) formed by potential scanning polymerization of 20 cycles on both electrodes showed a change in the transmission spectrum as shown in Figure1.

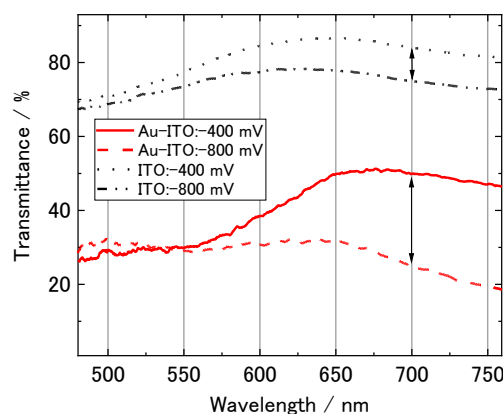


Fig. 1 Transmittance spectra of the PPy films (20 cycles polym.) on the ITO and the Au-ITO in the redox states at the applied potentials of -400 mV and +800 mV.

In the case of the normal ITO electrode, the transmittance decreased to about 80% at the wavelength of 700 nm after 20 cycles of polymerization, and a 9.0% electrochromic change in the transmittance was obtained between both redox states. In the case of the Au-ITO electrode, plasmon scattering of the Au nano-particles immobilized on the ITO surface probably included to the absorption of the ITO electrode. Therefore, the transmittance of the Au-ITO electrode decreased to about 50% at a wavelength of 700 nm after 20 cycles of polymerization, and a 25.0% electrochromic change in transmittance was obtained between both redox states. Since the thickness of the PPy film on the ITO electrode was around 100 nm, and on the Au-ITO electrode, it was around 150 nm, it is considered that the amount of EC change in transmittance (ΔT) was mainly due to the difference in the film thickness.

Using the same sample as in Figure 1, the time dependence of the transmittance at a wavelength of 700 nm was measured when cyclic scanning was performed between the applied potentials of -400 mV and +800 mV at the rate of 50 mV/s. The results of the comparison between the normal ITO electrode and the Au-ITO

electrode are shown in Figure 2. With the ITO electrode, the change in transmittance, which was initially 9.0% (ΔT_1), decreased to 2.2% (ΔT_{20}) after 20 redox cycles. On the other hand, with the Au-ITO electrode, the change in transmittance, which was initially 25.0%, decreased to 13.4% after 20 redox cycles.

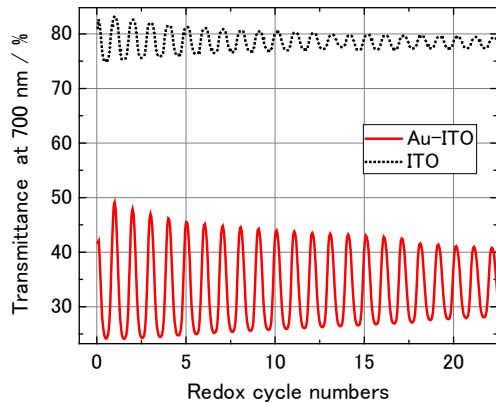


Fig. 2 Time dependences on the transmittance of PPy films (20 cycles polym.) on the ITO electrode and the Au-ITO electrode at the wavelength of 700 nm during the applied potential cycling between -400 mV and +800 mV.

The decay of ΔT was evaluated as the ratio of ΔT_{20} to ΔT_1 , [Decay of $\Delta T = ((\Delta T_{20}) / (\Delta T_1)) \times 100$] to be 25.0% for the ITO electrode and 54% for the Au-ITO electrode. The decay was significantly suppressed by using the Au-ITO electrodes, thus resulting in an improved durability.

The decay process of the ΔT was discussed for the PPy film thickness in the latter half. Figure 3 shows the results of comparing the relationship between the decay and the number of redox cycles at each electrode by the number of polymerization cycles of PPy. On the ITO electrode, the film thickness was about 100 nm after 20 polymerization cycles, and about 150 nm at the 40th cycle. On the other hand, on the Au-ITO electrode, the PPy film thickness was about 150 nm after 20 polymerization cycles, and about 200 nm at the 40th cycle. For both electrodes, the PPy film thickness tended to increase as the polymerization cycle increased. The PPy film thickness on the Au-ITO electrode was thicker than that on the ITO even for the same polymerization cycles. This suggested that the Au nano-particles can promote the deposition of the PPy polymer. The Au nano-particles obtained on the ITO electrode were slightly flattened in the plane direction, so it could not be simply determined, but it was one of the factors affecting the increase in the film thickness of the PPy obtained on the Au-ITO electrode. As shown in Figure 3, the decay of ΔT progressed as the number of redox cycles increased on both electrodes. The large difference between the two electrodes was that a rapid drop was found on the ITO electrode during the initial

stage. During the subsequent stage, however, the two decays seemed to have almost the same slope on both electrodes. It is considered that the decay in the subsequent stage is due to the reason that an aqueous solution is used as the electrolyte solution, so that the hydrolysis of PPy occurs due to peroxidation, and the electrochemical activity is gradually deteriorated. The rapid drop in the initial stage of the ITO electrode suggested that the volume of the PPy film changes with the redox reaction, and the PPy film is peeled off from the electrode. In fact, in the ITO electrode, it was confirmed that the PPy film was peeled off when the electrode was removed from the electrolytic cell after the experiment. Regarding the difference in the PPy film thickness, the initial decay occurred on both electrodes, but the steeper decay was found from the thicker PPy film. The volumetric change of the PPy film associated with the redox reaction must be greater on the electrolyte solution side than on the electrode substrate side. Because the freedom of movement is limited on the electrode substrate side, the mechanical stress of the PPy film is enhanced by the continuous redox reaction. It is considered that this tendency becomes stronger as the film thickness increases.

An aqueous electrolyte solution was used in the study so that the decay of the EC change of PPy strongly took place on both electrodes by hydrolysis due to over-oxidation. However, the stacking between the electrode and PPy film was strengthened by using the Au-ITO electrode, which had nano-structures consisting of Au nano-particles. This can suppress peeling of the PPy film due to the redox reaction, and the durability of the EC changes would be finally improved.

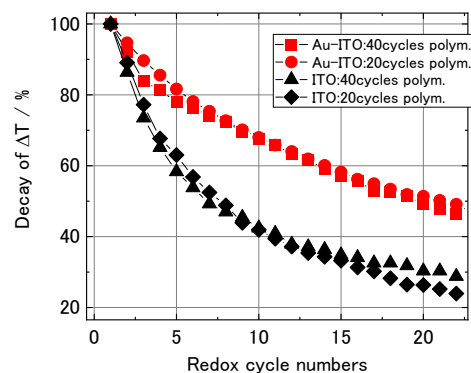


Fig. 3 Electrochromic durabilities of the PPy films on the ITO electrode and the Au-ITO electrode for 22 applied potential cycles between -400 mV and +800 mV at the scan rate of 50mV/s. The decay of ΔT was calculated from [Decay of $\Delta T = ((\Delta T_{20}) / (\Delta T_1)) \times 100$].

4. REFERENCES

- [1] K. Yamada, E. Kanazawa, S. Tsuneyasu, F. Koshiji, T. Uchida, T. Satoh, Bull. Soc. Photogr. Imag. Japan, 30,19 (2020).