

# Durability Improvement of Electrochromic Display with Nano-Structured Electrode

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## ABSTRACT

*Au nano-islands were immobilized on ITO electrodes by pulse electrolysis. Poly(pyrrole) [PPy] was electrochemically polymerized using the nano-structured electrode (Au-ITO). The electrochromic changes of PPy on the Au-ITO could be more stable than one on an untreated ITO electrode.*

## 1. INTRODUCTION

Recently, we reported that the electrochromic (EC) response of conductive polymers could be improved by using Au nano-particles with island structure immobilized on transparent electrode. These nano-structures were easily obtained by sputtering or electrochemical deposition. In order to improve the EC response, the enhancement of coloring by plasmonic electric fields of Au nano-particles (with a particle size of several tens of nanometers) contributes to the thinning of EC material films. [1,2] The dielectric-metal-dielectric (DMD) structure formed between these particles probably improve the electrical conductivity of the EC material.

The stability of EC changes was focused on this study as the effect on the EC characteristics by using the nano-structured electrode. It is well known that the redox reaction of conductive polymer is accompanied by a large and powerful volume changes. We believe that the polymer film detachment from the electrode due to volume changes play the great role to the deactivation of the EC changes.

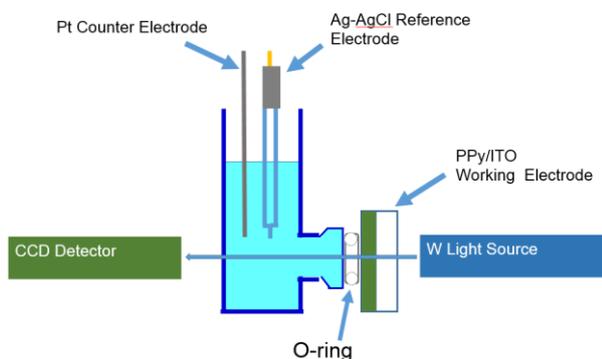


Fig. 1 Schematic diagram of the transparent glass cell.

## 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 Poly(pyrrole) Film

The PPy films were prepared on the electrode by an electropolymerization with a cyclic potential application between -500 mV and +800 mV (vs. Ag-AgCl, scan rate: 50 mV/s). The polymerization solution was 10 mM pyrrole and 0.1 M lithium perchlorate (LiClO<sub>4</sub>) 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. Fig. 1 shows the schematic diagram of the transparent glass cell.

## 3. RESULTS AND DISCUSSION

### 3.1 Polymerization

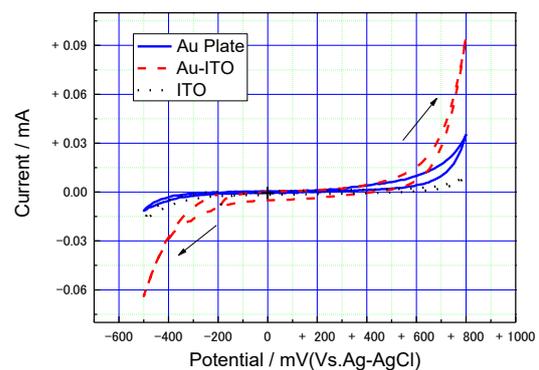
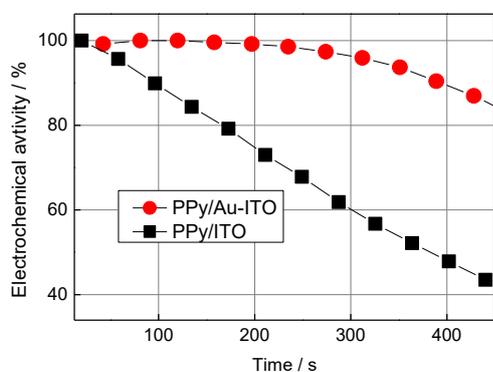


Fig. 2 Cyclic voltammograms (scan rate : 50 mV/s) of the pyrrole polymerization on ITO, Au-ITO and Au plate electrodes at the first potential scanning.

Fig. 2 shows cyclic voltammograms at the time of the first scan during polymerization using the ITO electrode and the Au-ITO electrode. Comparing the monomer oxidation currents at +800 mV, the Au-ITO shows about 10 times larger current value than the ITO electrode. Generally, this current is considered to be a mixture of a current for monomer oxidation and a current for oxidation of a polymer adsorbed (or deposited) on an electrode. On the cyclic voltammogram, oxidative currents for potential scan in negative direction from +800 mV were smaller than that in positive direction to +800 mV. It indicates that conductive polymers have never deposited on the electrode surface. These results suggest that the Au-ITO electrode, in which three-dimensional Au nano-structures are present in the form of islands, has a significantly larger effective electrode surface area for monomer oxidation than the ITO electrode. In particular, there is a large difference in the monomer oxidative potentials between Au-ITO and ITO. The value of the Au-ITO electrode is more negative (at least 200 mV) than the ITO electrode). By lowering the applied potentials for the electropolymerization of pyrrole in an aqueous solution, it is possible to suppress a degradation reaction such as hydrolysis occurring simultaneously with the polymerization reaction. Decomposition sites generated during the polymerization with positive potentials have a disconnection of  $\pi$ -conjugate structure, which probably accelerates the decomposition reaction in entire film.

### 3.2 Electrochemical Activity



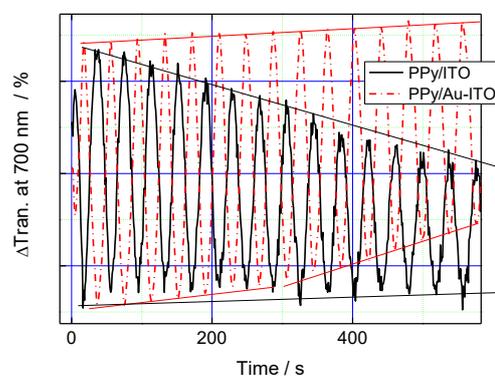
**Fig. 3 Electrochemical stabilities of the PPy films on the Au-ITO or ITO electrodes for applied potential cycles.**

In order to compare the decay in the electrochemical activity of PPy film on each electrode, continuous cyclic scans (50 mV/s) of the applied potential between -500 mV and +450 mV were carried out for the PPy films on each electrode in the polymerization solution. Fig. 3 shows the electrochemical activities of the PPy films for each cycle, where the activity value of 100% was the reduction current at 0 mV in the first cycle. In the case of ITO electrode, a

continuous activity decay was observed from 2nd cycle. On the other hand, in the case of Au-ITO, the decay is suppressed up to 7th cycle. A significant difference in the stability was found between Au-ITO and ITO.

### 3.3 EC stability

As the demonstration of EC stability, fig. 4 showed a change in transmittance at a wavelength of 700 nm when continuous cyclic scans (50 mV/s) of the applied potential between -500 mV and +450 mV were carried out on PPy film immobilized on each electrode. For PPy films on both electrodes, the transmittance increased and decreased periodically due to redox reaction. In the ITO, the amount of change in transmittance had been reduced since the 2nd cycle. On the other hand, in the case of the Au-ITO, the amount of change was stable until the 7th cycle. In addition, subsequent decay (after 8th cycle) of the change was slower than that of ITO.



**Fig. 4 Electrochromic stabilities of the PPy films on the Au-ITO or ITO electrodes for applied potential cycles.**

The decomposition reaction seemed to be faster, probably because the aqueous solution was used as the electrolyte. About both electrochemical activity and EC stability, better results were obtained from the Au-ITO. It is concluded that the detachment of the polymer film is suppressed by the three-dimensional nano-structure existing on the ITO electrode surface.

## 4. REFERENCES

- [1] Y. Tanaka and K. Yamada, J. Soc. Photogr. Sci. Technol. Jpn., pp.60-61, Vol. 80, (2017)
- [2] K. Yamada, F. Koshiji and T. Uchida, Bull. Soc. Photogr. Imag. Japan, pp.18-22, Vol. 28, (2018)