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In situ Electrochemical and Transmission Surface Plasmon Resonance for Studies of Electropolymerized Poly(3-Aminobenzoic acid) Thin Film

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1. Introduction

Electrochemical method represents a great interest for the synthesis of conducting polymers since 1979. Recently, many in situ techniques such as electrochemical-surface plasmon resonance (EC-SPR) spectroscopy, electrochemical-quartz crystal microbalance (EC-QCM) had been used for simultaneous monitoring the electropolymerization and doping-dedoping process of conjugated polymers.

Transmission surface plasmon resonance (T-SPR) spectroscopy, which based on the exploited of localized surface plasmon resonance (L-SPR), is the technique for monitoring changes in surface plasmon absorbance of the discontinuous Au film in transmission configuration. Many studies using T-SPR for monitoring the binding process of biomolecules or biosensing such as antigen-antibody, protein-DNA and biotin-avidin interactions, had been recently reported because it serves as the inexpensive and simple method. Moreover, the commercial available CD, DVD or Blu-rays can serve as inexpensive grating substrates in this technique.

Polyaniline and its derivatives have become one of the most interest conducting polymers due to their electrical, optical and also chemical properties. The carboxylated polyanilines had recently been employed in the application of biosensors and immunosensors.

In this study, the electropolymerization process and doping/dedoping properties of carboxylated polyaniline, poly(3-aminobenzoic acid) (PABA), films on commercial Blu-rays and DVD grating substrates were simultaneously studied by the combination of electrochemical technique and T-SPR spectroscopy at the fixed incident angle.

2. Experimental

Materials

All materials used in the experiments were purchased from Sigma-Aldrich and used without further purification.

Electrochemistry and T-SPR instrument

The electrochemical experiment was performed using conventional single compartment three-electrodes cell with computer-controlled potentiostat HZ-5000 model (Hokuto Denko Ltd., Japan). The gold-coated commercial available DVD and Blu-ray grating substrates which used as working electrode were prepared by vacuum evaporation of 2.5 nm chromium and 50 nm gold, respectively. The counter electrode was a platinum wire and the reference electrode was a silver wire. Transmission surface plasmon resonance spectra were obtained with home-made configuration instrument.

Electropolymerization of 3-aminobenzoic acid monomer

The electropolymerization was performed using a solution of 50 mM 3-aminobenzoic acid (3-ABA) monomer in 0.5 M H_2SO_4 on the gold electrode with an applied potential ranging from -0.2 V to 0.9 V at a scan rate of 20 mV/s for five cycles. The electropolymerized electrode was then rinsed several times with 0.5 M H_2SO_4 and deionized water. The electropolymerization process was monitored in situ by electrochemical T-SPR measurement. The transmission spectra in water at the fixed incident angle were obtained before and after electropolymerization.

3. Results and Discussion

Fig. 1 shows cyclic voltammogram (CV) during the electropolymerization on Blu-ray grating substrate. From CV trace, the oxidation onset peak at about 0.9 V corresponds to the formation of PABA on gold working electrode with dedoping peak at about 0.02 V in the cathodic scan and doping peak at about 0.2 V in the anodic scan.

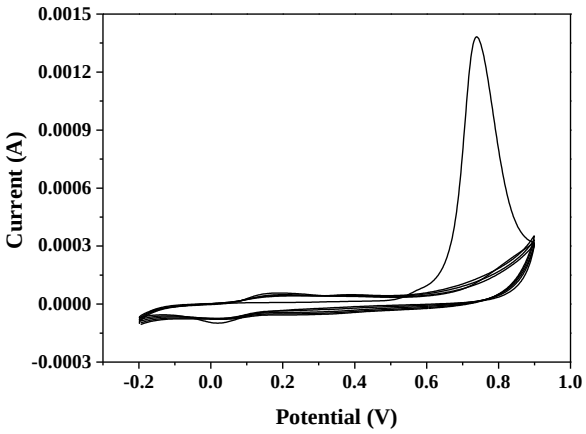

Fig. 1 CV trace during electropolymerization of 3-ABA in 0.5 M H_2SO_4 at scan rate of 20 mV/s for 5 cycles.

The T-SPR spectra were obtained in water before and after electropolymerization as shown in Fig.2. It can be seen that the transmission peak on both substrates was shifted to higher wavelength, about 7 nm comparing with Au substrate, after electropolymerization which indicating the formation of PABA film on the substrates. However, the peak intensity on DVD grating substrate increased which in contrast with the peak intensity on Blu-ray grating substrate decreased. The in situ kinetic data during electropolymerization was also obtained in this study.

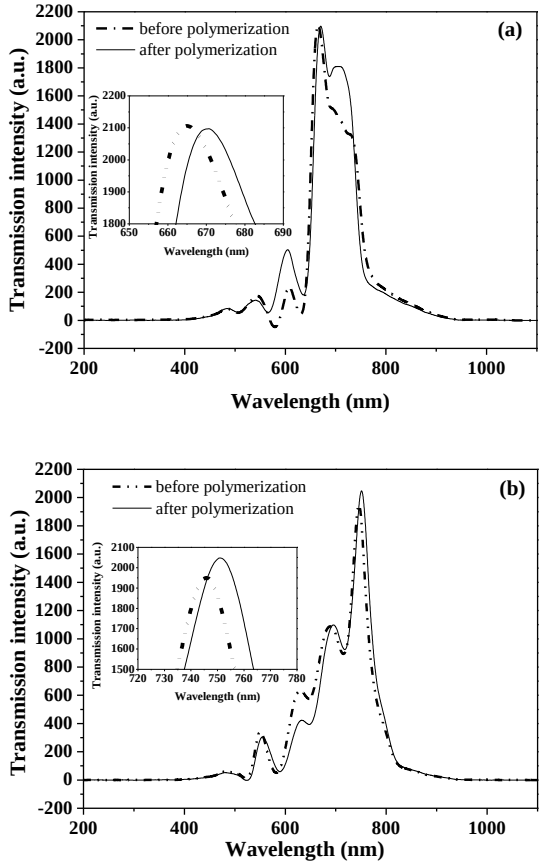

Fig. 2 T-SPR spectra taken in water before and after electropolymerization of 3-ABA on (a) Blu-ray and (b) DVD grating substrates.

4. Conclusions

The electropolymerization and doping-dedoping property of poly(3-aminobenzoic acid) were simultaneously studied using the combination of electrochemical method and transmission surface plasmon resonance spectroscopy. The technique shows the powerful potential to be further used for studying in the immunosensor application.

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