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Detection of Catecholamines with Poly(3-aminobenzylamine) Thin Films Using Electrochemical-Surface Plasmon Resonance Spectroscopy

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1. Introduction

Conducting polymers have been shown as sensitive materials to monitor and manipulate biological interactions. This is attributed to the high conductivity and specific redox properties of conducting polymers which is essential for biological communications.[1] Since the redox property of conducting polymers changes upon biological interactions, the change can be detected either as an electrochemical signal or an optical signal. Electroactive conducting polymers provide the media for electron transfer to the electrode that allows one to detect the electrochemical signals.

Surface plasmon optical technique has been known to be a powerful tool for the characterization of surfaces, interfaces, and thin films. In bio-sensor applications, this technique allows for the investigation of adsorption/desorption of biomolecules onto surfaces and *in-situ* time dependent surface coverage without labels. We have previously demonstrated the electrochemical-SPR (EC-SPR) technique for the characterization of conducting polymer thin films.[2] In EC-SPR measurements, the gold substrate that carries the optical surface mode, simultaneously is used as the working electrode in electrochemical experiments. One of the advantages in using the EC-SPR technique is that the electrochemical and optical properties are simultaneously obtained on surfaces at the nanometer scale. This involved the *in-situ* monitoring of the specific adsorption and of electrochromic properties of deposited conducting polymers.

In this research, we report a simultaneous detection of optical and electrochemical signals from the specific adsorption of catecholamines on poly(3-aminobenzylamine) (PABA) using electrochemical-surface plasmon resonace spectroscopy. Since PABA is a polyaniline derivative, bearing benzylamines in the structure which can act as specific adsorption sites to catecholamines. PABA was electropolymerized from electroactive 3-aminobenzylamine monomers. The deposition process was investigated by EC-SPR. Electroactivity of PABA was confirmed from cyclic voltammetry in PBS solution, indicating that the signals can be enhanced on the event of specific adsorption. Large signal enhancements both in optical and electrochemical signals were obtained in the case of PABA mediator, while polyaniline thin film showed little enhancement.

2. Experimental

Materials.

3-aminobenzylamine (ABA) was purchased and used as received from Tokyo Chemical Industry Co.

Electrochemistry.

All potentiostatic and cyclic voltammetry measurements were carried out using a one compartment, three-electrode cell driven by an Hokuto Potentiostat (Model HZ-5000). In all the measurements, the working electrodes consisted of gold films (d ~ 47 nm) vacuum evaporated onto an S-LAH66 glass substrate (with an adhesion layer of 2nm Cr, previously evaporated on glass). The counter electrode was a Platinum wire and the reference an Ag/AgCl aqueous electrode. All the potentials reported in this paper are relative to this reference electrode.

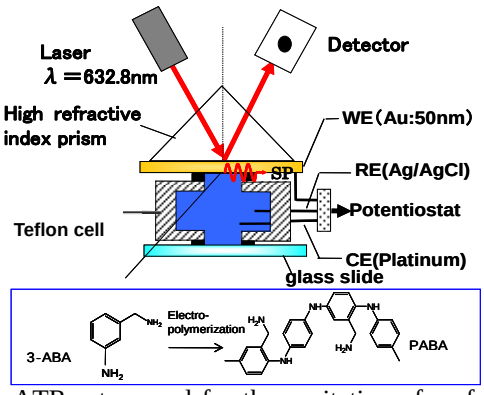

Fig. 1. ATR setup used for the excitation of surface plasmons in the Kretschmann geometry

Electrochemical-Surface Plasmon Resonance Spectroscopy (ESPR) Measurement.

The ATR set-up combines the three-electrode electrochemical cell with a Kretschmann configuration for the excitation of surface plasmons (Fig. 1). Details of this set-up can be found elsewhere.[3] Surface plasmons are excited by reflecting p-polarized laser light (λ = 632.8 nm) off the Au-coated base of the prism. Kinetic measurements

were performed in order to monitor the formation of the poly(3-aminobenzylamine) (PABA) film and the oxidation /reduction and doping/dedoping properties of deposited PABA thin film via reflectivity changes as a function of time. Angular measurements were also performed by scanning an incident angle range while the potential was held constant. The electrode surface area was 0.785 cm^2.

3. Results and Discussions

Electropolymerization of 3-aminobenzylamine (ABA)

Electrochemical polymerization of 3-aminobenzylamine (ABA) on the gold surface was achieved by applying potential cycling between –0.2 and 1.1 V at a scan rate of 20 mV/s. The cyclic voltammogram (CV) obtained during the electropolymerization is shown in Figure 2 up to 10th cycle. As shown in this Figure, the redox process (ca. 0.6 V in the anodic scan and 0.2 V in the cathodic scan) corresponds to the electron transfer from/to the electrodeposited poly(3-aminobenzylamine) (PABA) film. In order to compensate the charge of the PABA film, anion transport from/to the electrolyte solution, i.e. anion doping and dedoping,[4] should occur. As is known for polyaniline films, this phenomenon should also responsible for the dramatic change in the conductivity of the PABA

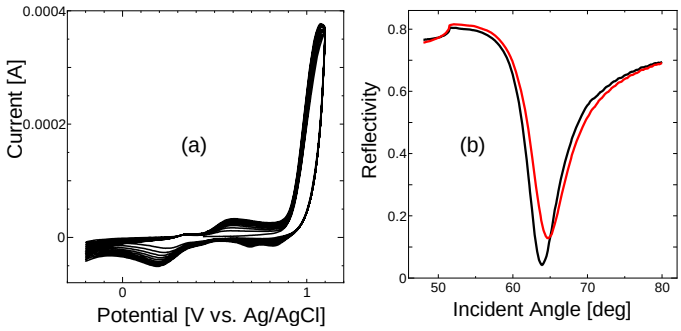

Fig. 2. Cyclic voltammogram of the electropolymerization of 3-aminobenzylamine (ABA) (0.05 M) in H_2SO_4 (0.5 M) solution (a) and angular SPR reflectivity curve measured before and after potential cyclings. (b)

film. The electrodeposition of PABA on the Au electrode proceeds via a radical cation mechanism. The large currents observed at the positive end of the CV are due to the superposition of two distinct processes: one is the electron transfer from the PABA film corresponding to the oxidation of the PANI film and the other is the electron transfer from the ABA monomer to the electrode corresponding to the oxidation of the ABA monomer to produce a precursor for the PABA film. Angular SPR curves taken before and after potential cycling were shown in Figure 2(b). These scans were measured in the solution at open circuit potential. A shift of the dip angle in the SPR curves was observed indicating that PABA was deposited onto the gold film electrode during the potential cycling.

Simultaneous detection of optical and electrochemical signals by EC-SPR

Figure 3 shows simultaneous observation of current change and SPR reflectivity change on injection of 0.4 mM catecholamin. Both the current and reflectivity increased when 0.4 mM glucose was injected into buffer solution. In a controlled experiment using polyaniline which does not have specific adsorption site to catecholamines, both the current and SPR reflectivity did not show obvious increase as compared to the PABA mediator. Hence, the large increase both the signals in Fig. 3 indicates the possibility to develop high sensitive EC-SPR catecholamine sensor using electropolymerized PABA film.

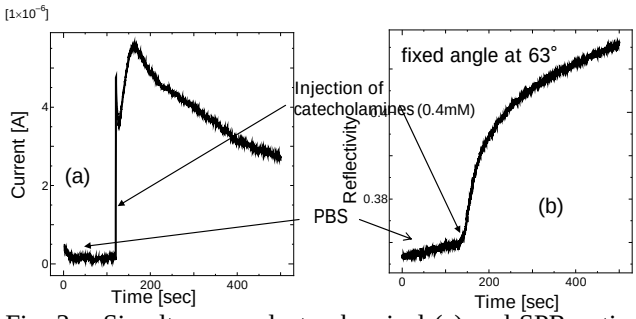

Fig. 3. Simultaneous electrochemical (a) and SPR optical (b) detection of catecholamine (0.4 mM) at a constant potential, 0.65 V.

3. Conclusions

In summary, we have successfully prepared poly(3-aminobenzylamine) (PABA) thin films by electropolymerization. As PABA is polyaniline-based conducting polymer bearing a specific adsorption sites to catecholamines, large signal enhancements both in SPR optical and electrochemical signals were obtained when catecholamines were injected on PABA, while polyaniline thin film showed little enhancement. Signals were detected immediately after injections. Further developments of fast and high sensitive detections are underway.

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