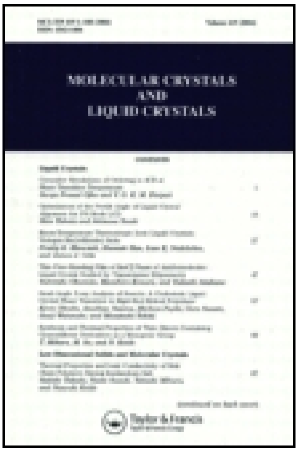

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Fabrication of Thin Film from Conducting Polymer/Single Wall Carbon Nanotube Composites for the Detection of Uric Acid

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Fabrication of Thin Film from Conducting Polymer/Single Wall Carbon Nanotube Composites for the Detection of Uric Acid

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Poly(2–aminobenzylamine)/single wall carbon nanotube (P2ABA/SWNTS) thin films were fabricated for the detection of UA by using electrochemical surface plasmon resonance spectroscopy (EC–SPR) technique. The suspension of 0.01% wt of carboxylated SWNTSs was assembled on the polymer film because of the electrostatic and van der Waals interactions between the $-COOH$ *and* $-NH_2$*. The P2ABA/SWNTS thin film formation on gold electrode was studied by EC–SPR technique. In this work, uric acid was detected by EC–SPR in PBS buffer comparing with the interference response with ascorbic acid. EC–SPR uric acid sensor using P2ABA/SWNTS thin film can be applied for the detection of uric acid in urine.*

Keywords Ascorbic acid; conducting polymer/SWNTS composites; detection; fabrication; thin films

1. Introduction

Uric acid (UA) is a product of purine metabolism and abnormal level of UA in urine and serum cause several diseases such as gout, hyperuricemia and Lesch–Nyhan syndrome [1–2]. Development and optimization of methods for the selectivity and rapid detection of UA are of important significance. The electrodes modified with a self–assembled monolayers (SAMs) alkanethiol and aromaticthiol have received considerable because their higher selectivity and rapid detection. Recently, 11-amino-1-undecanethiol was formed a thiolate bond on gold electrode and functionalized SWNTs were assembled on the modified gold

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electrode for application to UA detection [3]. However, this method requires a SAM process and stabilization of alkanethiol monolayer on gold electrode. In this work, we report the simple and rapid methods in real–time for detection of UA by EC–SPR technique. The P2ABA has received considerable attention due to its high conductivity, simple and nanoscale controlled for electropolymerization on gold electrode. The P2ABA has a $-NH_2$ group in the structure, which can form electrostatic and van der Waals interactions with the $-COOH$ in carboxylated SWNTs structure [3]. The surface plasmon resonance (SPR) spectroscopy is the technique for surface characterization, P2ABA/SWNTS thin film interface and kinetic process at the surface. EC–SPR spectroscopy has been applied for monitoring the interaction between UA and P2ABA/SWNTs thin film electrochemical sensor. We detected the response in both electrochemical current and optical signal of UA in real–time comparing with the response detected of major interference of ascorbic acid (AA) because the oxidation potential of AA close to that of UA.

2. Experimental

2.1 Chemicals and Apparatus

2–Aminobenzylamine (2–ABA) was purchased and used as received from Tokyo Kasei Kogyo Co. Ltd. UA was purchased from Sigma–Aldrich. L–ascorbic acid was purchased from Tokyo Kasei Kogyo Co. Ltd. Single Wall carbon Nanotube (SWNTs) was purchased from Nanolab, Inc. and used as received.

Cyclic voltammetry and amperometry were performed using a potentiostat HZ–5000 (Hokuto Denko Ltd., Japan) interface with a conventional three electrode cell. The reference electrode was a Ag/AgCl (3 M NaCl, BAS Inc.) aqueous electrode, a platinum wire was served as counter electrode and the gold film was used both excitation surface plasmon and used as working electrode. The thickness of gold film about 47 nm was chosen for optimum excitation of the surface plasmon.

2.2 Electropolymerization of 2–ABA

The gold–coated high reflective index glass substrate was washed with 0.5 M sulfuric acid and deionized water before thin film formation. The P2ABA thin film was grown on the working electrode by electropolymerization of 50 mM 2–ABA monomer in 0.5 M H_2SO_4 by cycling the potential between –0.2 and 0.1 V vs. Ag/AgCl for 10 cycles at a scan rate of 20 mV/s.

2.3 Preparation of the P2ABA/SWNTS Thin Film

The deposited P2ABA film (thickness $\sim$10 nm) on gold–coated high reflective index glass substrate electrode was washed 3 times with 0.5 M sulfuric acid and distilled (DI) water before assembled carboxylated SWNTs. The carboxylated SWNTs were prepared by follow–up Zhang et al. and the details of the carboxylated SWNTs have been reported at applied surface science [4]. The 0.5 mL suspension of 1, 0.1 and 0.01%wt of carboxylated SWNTs in DI water were assembled on the P2ABA film for 20 min. Finally, the P2ABA/SWNTs/Au was rinsed with DI water just before use.

2.4 Electrochemical–surface Plasmon Resonance Measurement

The SPR setup combined the three electrode electrochemical cell with a Kretschman configuration for the excitation of surface plasmon. The excitation source was a He–Ne laser with $\lambda = 632.8$ nm. Kinetic measurements were performed to monitor both the P2ABA thin film grown on gold film surface and the oxidation/reduction, doping/dedoping properties of the deposited P2ABA thin film and the catecholamine (CA) sensing via reflectivity changes (fixed incident angle lower than dip angle) as a function of time.

2.5 Methods

All experiments were carried out at room temperature and the solutions for electrochemistry measurement were degassed in water bath sonicator for five minutes. A phosphate buffered saline (PBS, pH 7.4) was used as the supporting electrolyte for UA and AA detections. The solutions of UA and AA were prepared daily by using PBS solution. The cyclic voltammetry was employed at the potential cycling between –0.2 and 0.9 V with a scan rate of 20 mV/s and the amperometry was performed to investigate the interaction of UA and AA with the P2ABA/SWNTs thin film. The real–time detection of optical and electrochemical signals from the reaction of UA and AA with P2ABA/SWNTs composite thin films was reported by EC–SPR.

3. Results and Discussion

3.1 EC–SPR Spectroscopy Measurement of P2ABA/SWNTs Thin Film Formation

Electropolymerization of 2–ABA on the gold–coated high reflective index glass substrate was performed by cycling the potential between –0.2 and 0.9 V for 10 cycles at a scan rate 20 mV/s. During cyclic voltammetry scan, the first oxidation peak at about 0.85 V is corresponding to the oxidation of 2–ABA monomer and P2ABA film. After the first oxidation, the dedoping peak at about 0.4 V in the cathodic scan and doping peak at about 0.55 V in the anodic scan of the second cycle are corresponding to the electron transfer to the formation of redox couple during the oxidation of P2ABA on electrochemical sensor. SPR curves in Fig. 1a were taken by scanning an incident angle range of deionized water

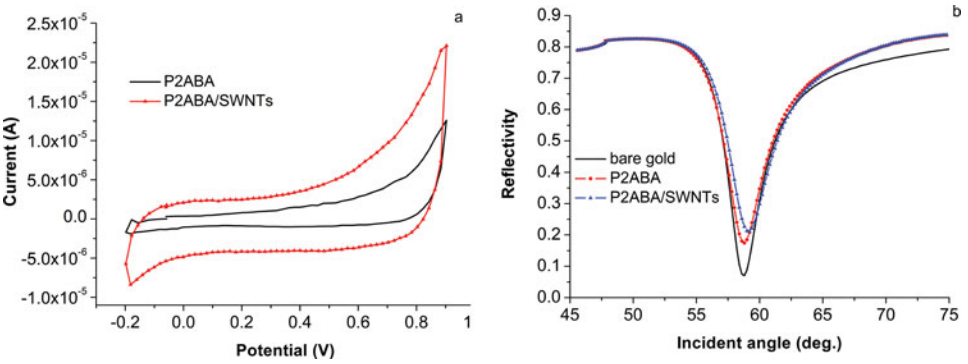

Figure 1. (a) Cyclic voltammoframs of P2ABA/SWNTS and P2ABA in PBS solution and (b) SPR angular reflectivity curves before and after electropolymerization and after assembling of carboxylated SWNTS on the P2ABA thin film.

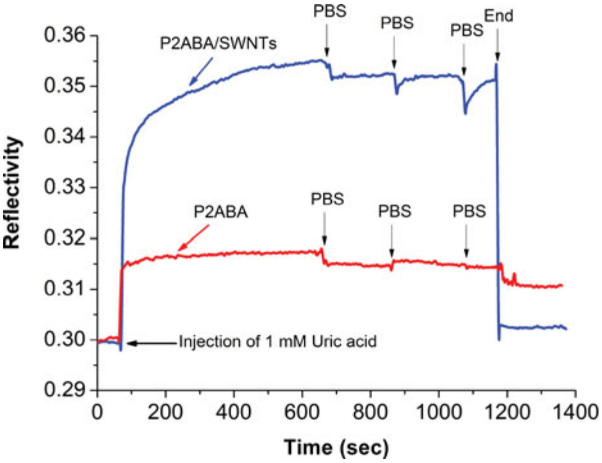

Figure 2. SPR reflectivity responses upon injection of 1 mM UA into P2ABA and P2ABA/SWNTS thin film.

before and after electropolymerization of 2–ABA monomer. The SPR curves were shifted to the higher dip angle after electropolymerization indicating that P2ABA was deposited on to gold film electrode. The suspension of 0.01%wt of carboxylated SWNTs in DI water was optimum for assembled on the P2ABA. The SWNTs can be dispersed in the water without surfactants because the incorporation of the carboxylic group for their hydrophilicity [5]. The SPR dip angle shifted to a higher angle corresponding to the electrostatic and van der Waals interactions between the —COOH in SWNTs structure and $-NH_2$ in P2ABA structure [3]. Figure 1(a) shows the cyclic voltammetry of P2ABA and P2ABA/SWNTs thin film in the PBS solution (pH 7.4) by potential cycling between –0.2 and 0.9 V at a scan rate of 20 mV/s. The cyclic voltammetry measurement result, the redox current of P2ABA/SWNTs thin film was higher than P2ABA thin film because P2ABA/SWNTs thin film has more charge capacitance [6].

The reason for using P2ABA/SWNTs thin film to detect uric acid is that P2ABA thin film showed lower SPR reflectivity than P2ABA/SWNTs as shown in Fig. 2.

3.2 *Detection of UA by EC–SPR*

The EC–SPR responses on the determination of UA were observed in both the current and reflectivity responses at a constant applied potential of 0.5 V. Figure 3(a) shows the SPR reflectivity response changes upon injection of 1 mM UA compared with the response detection of AA. The SPR reflectivity change in the AA addition is observed smaller than the reflectivity change in UA, which suggests that UA can effectively accumulate at the carboxylated SWNTs surface [3] and this method is possible to detect UA in urine. The SPR responses after finishing the detection, the reflectivity rapidly decreased to the original. This indicates that UA did not accumulate at P2ABA/SWNTs surface. Figure 3(b) shows the current responses upon the injection of UA and AA into carboxylated P2ABA/SWNTs thin film. The current initially increased rapidly then decreased rapidly and gradually decreased for UA and significantly decreased for AA, corresponding to the electrochemical double layer [7–8] at P2ABA/SWNTs thin film and electrolyte interface

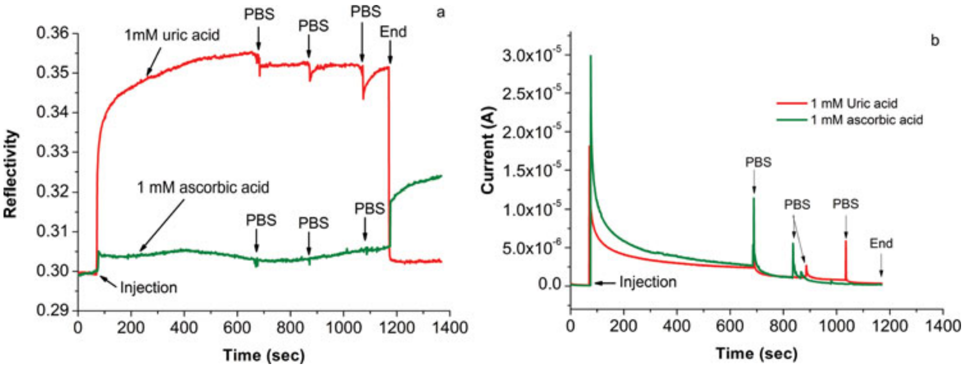

Figure 3. (a) SPR reflectivity response upon injection of 1 mM UA and AA. (b) The current response upon injection of 1 mM UA and AA at a constant applied potential of 0.5 V.

and diffusion of UA. This result indicated that the distinct response in the current for UA on P2ABA/SWNTs is responsible for the oxidation of UA with SWNTs as reported by Kalimutha et al. [1].

Conclusions

UA was detected at a constant applied potential of 0.5 V, which showed the SPR reflectivity response of UA separate from the SPR reflectivity response of AA. P2ABA/SWNTs thin films based electrochemical sensor showed a possibility to develop high sensitive EC–SPR UA sensor using electropolymerized P2ABA film and suspension of carboxylated SWNTs were assembled on the P2ABA film, which can be applied for rapid measurement of UA in urine.

Acknowledgments

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References

[1] Kalimuthu, P., Suresh, D., & John, S. A. (2006). *Anal. Biochem.*, *357*, 188.
[2] Zhao,Y., Bai, J., Wang, L. E. X. H., Huang, P., Wang, H., & Zhang, L. (2006). *Int. J. Electrochem. Sci.*, *1*, 363.
[3] Huang, X. J., Im, H. S., Yarimaga, O., Kim, J. H., Lee, D. H., Kim, H. S., & Choi, Y. K. (2006). *J. Phys. Chem. B*, *110*, 21850.
[4] Zhang, L., Ni, Q. Q., Fu, Y., & Natsuki, T. (2009). *Appl. Surf. Sci.*, *255*, 7095.
[5] Ansón–Casaos, A., González–Domínguez, J. M., Terrado, E., & Martínez, M. T. (2010). *Carbon.*, *48*, 1480.

[6] Tian, S., Baba, A., Liu, J., Wang, Z., Knoll, W., Park, M. K., & Advincula, R. (2003). *Adv. Funct. Mater.*, *13*, 473.

[7] Baba, A., Tian, S., Stefani, F., Xia, C., Wang, Z., Advincula, R. C., Johannsmann, D., & Knoll, W. (2004). *J. Electroanal. Chem.*, *562*, 95.

[8] Baba, A., Mannen, T., Ohdaira, Y., Shinbo, K., Kato, K., Kaneko, F., Fukuda, N., & Ushijima, H. (2010). *Langmuir.*, *26*(23), 18476.