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High-Sensitive and Label-Free Detection of Biomolecules Using Single-Walled Carbon Nanotube Modified Microelectrodes

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1. Introduction

We have fabricated high-sensitive and label-free amperometric biosensors with microelectrodes modified by single-walled carbon nanotubes (SWNTs), as shown in Fig. 1. SWNTs have been known to have the high ability to promote electron-transfer reactions in electrochemical measurements, because SWNTs have a high aspect ratio that the total surface area for electrodes becomes significantly larger on the same site. In this study, the electrochemical characteristics of the devices were investigated using $K_3[Fe(CN)_6]$ and electro-active amino acids; such as tyrosine using cyclic voltammetry (CV) and differential pulse voltammetry (DPV), as shown in Fig. 2. Furthermore, the electrochemical label-free detection of a cancer marker, prostate specific antigen (PSA), was carried out by DPV after the immobilization of PSA antibodies onto the SWNT-arrayed electrodes.

2. Results and discussion

The SWNT-arrayed electrodes were directly formed on Pt surfaces by thermal chemical vapor deposition (Fig.1). The electrodes with various areas were also arrayed on the device in order to investigate the area dependence of the electrochemical current intensities.

Figure 3 shows the electrochemical signals of $K_3[Fe(CN)_6]$ with SWNT- or bare-Pt-arrayed electrodes by CV. The strong peaks from oxidation and reduction are clearly observed. And the peak distance is about 0.1V, which is almost the same as the ideal value. Moreover, the peak intensity from SWNT electrodes is much higher than that from bare-Pt electrodes. Figure 4 shows SWNT-area dependence of electrochemical signals. The peak current linearly increases as a function of SWNT area. These results indicate that SWNT-arrayed electrodes work well as working electrodes.

Figure 5 shows the electrochemical signals of tyrosine with SWNT- or bare-Pt-arrayed electrodes by DPV. The peak intensity from SWNT electrodes is more than 100 times higher than that from bare-Pt electrodes. SEM observations revealed that oxidized tyrosine adsorbed on SWNT-arrayed electrodes after tyrosine detection by DPV. These results indicate that the devices with SWNT-arrayed electrodes provide a much higher sensitivity to detect biomolecules.

Next, the electrochemical detection of a cancer maker, PSA was carried out by DPV, as shown in Fig. 6. First, SWNT electrodes were modified with linkers. Second, PSA antibodies were immobilized onto the SWNT electrodes. Third, PSAs were introduced onto the electrodes. After that, the samples were rinsed with buffer solution. Finally, the electrochemical signals were measured by DPV method. Figure 7 shows the electrochemical signals of proteins with SWNT-arrayed electrodes by DPV. The electrochemical signal is obtained from only PSA antibodies, as shown in Fig. 7(a). After introduction of 1 ng/mL PSA onto the SWNT electrodes with PSA antibodies, the electrochemical current signals significantly increase, as shown in Fig. 7(b), which results form the formation of antigen-antibody complexes. On the other hand, when another protein, nontarget bovine serum albumin is introduced onto the SWNT electrodes with PSA antibodies, electrochemical signals do not increase, as shown in Fig. 7(c), indicating that the reactions of antigen-antibody do not occur. Therefore, the devices have high selectively. Moreover, PSA concentration dependence is clear observed, as shown in Fig. 8. Therefore, PSA at 0.5 ng/mL can be effectively detected. The concentration of 0.5 ng/mL is much smaller than cut-off limit of 5 ng/mL. The biosensors are useful for clinical diagnosis for prostate cancers.

3. Conclusion

In conclusion, our devices with SWNT-arrayed microelectrodes are useful as amperometric biosensors to high sensitivity detect biomolecules without any labeling and in real time.

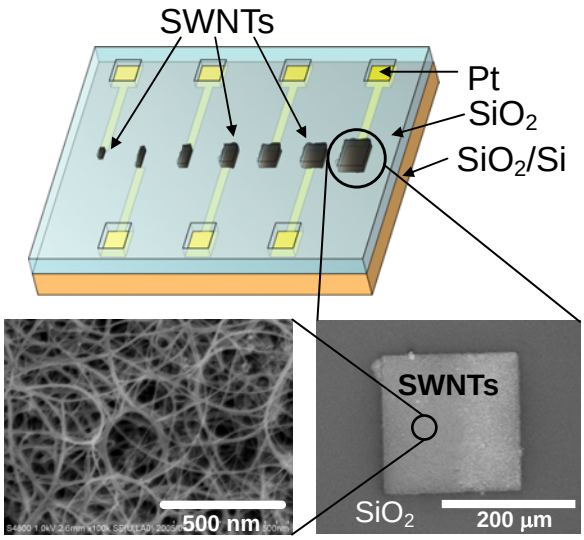

Fig. 1. Amperometric biosensors based on SWNT-arrayed microelectrodes.

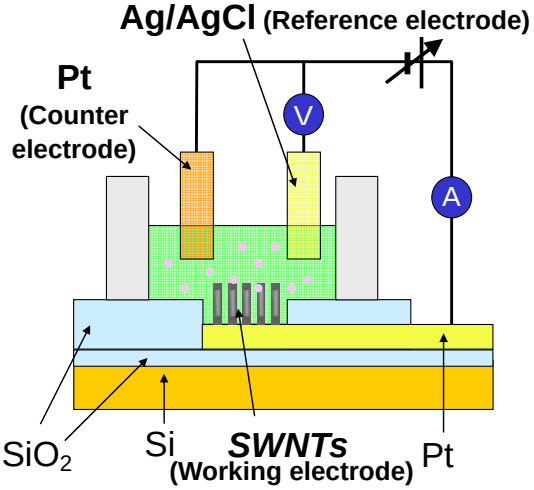

Fig. 2. Three-electrode system for amperometric biosensors.

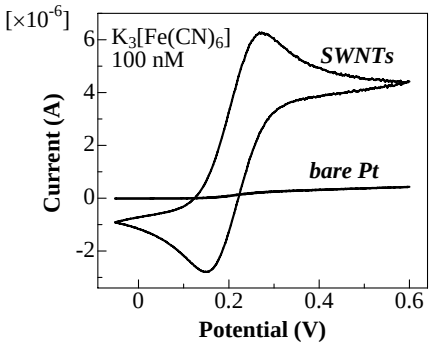

Fig. 3. Electrochemical signals of $K_3[Fe(CN)_6]$ with SWNT and bare-Pt electrodes by CV.

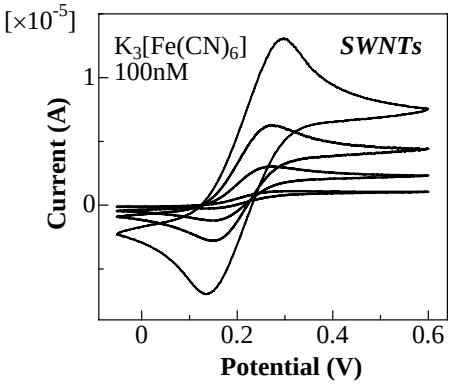

Fig. 4. SWNT-area dependence of electrochemical signals by CV.

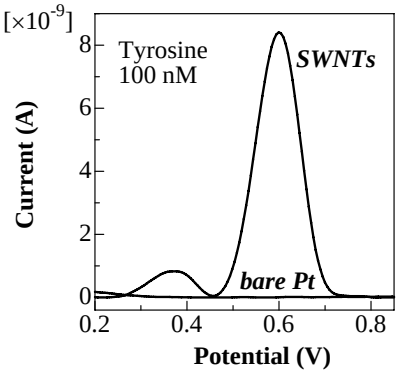

Fig. 5. Electrochemical signals of tyrosine with SWNT and bare-Pt electrodes by DPV.

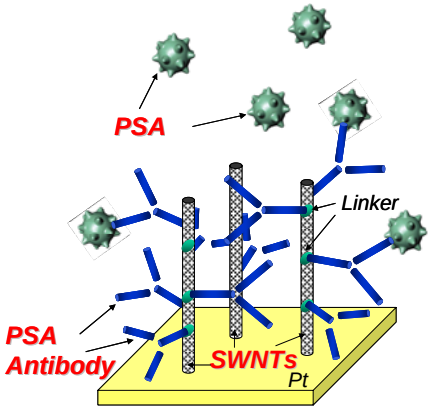

Fig. 6. Amperometric PSA biosensors.

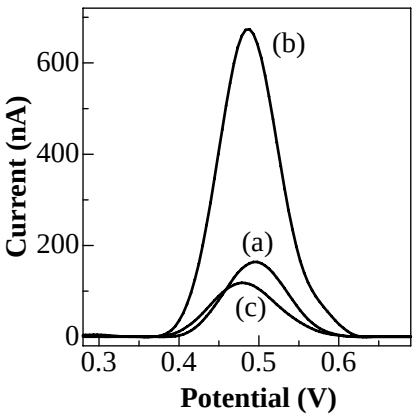

Fig. 7. Electrochemical signals by DPV, (a) PSAAb, (b) PSAAb + PSA (1ng/mL), (c) PSAAb + BSA.

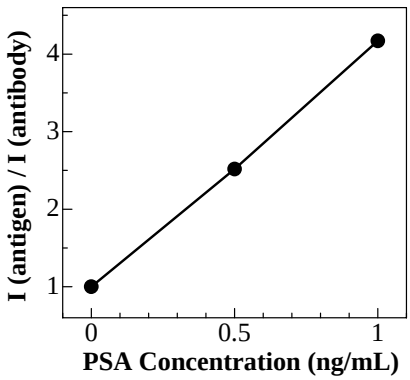

Fig. 8. PSA concentration dependence of electrochemical signals.