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SENSING FERROCENE DERIVATIVES USING A MODIFIED GLASSY CARBON ELECTRODE WITH A PEDOT/CARBON MICROSPHERES THIN-FILM

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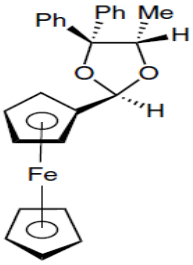
Introduction

Electrochemical technique is a powerful analytical tool that has several advantages including facile operation, sensitivity and time saving. Conducting polymers (CPs) have many superior properties such as good mechanical stability, simple preparation method, possibility of miniaturization, and interesting electrical and electrochemical properties. CPs have attracted extensive interest for the fabrication of efficient chemo/biosensors.[1] The conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT), has received attention and is broadly studied because of its important properties. In comparison with other conducting polymers, it has good electrical conductivity, low band gap, superior environment stability and good biocompatability [2-5]. Owing to these properties, PEDOT has rapidly become the subject of considerable interest for the preparation of efficient chemo/biosensors. In this work, we explore the use of thin-film deposition of PEDOT:PSS and PEDOT:PSS with carbon microspheres (CS) over glassy carbon electrode (GCE) with the aim of increasing analytical sensitivity. We proof the system using chiral acetal (2R,5R)-2-ferrocenyl-5-methyl-4,4-diphenyl-1,3-dioxalene (Scheme 1) or ferrocene. The chiral acetal shows positive response against mammalian cancer cell lines.[6] Ferrocene derivatives have been proposed for in a wide range of applications.[7]



SCHEME 1: FERROCENE ACETAL

Methods

Tetrabutylammonium perchlorate (TBAP), ferrocene, and acetonitrile were purchased from Sigma-Aldrich (USA). PEDOT:PSS was from Ossila Company (USA). Carbon microspheres were synthesized as reported previously.[8] The

cyclic voltammograms were recorded in acetonitrile solution in 0.1 M TBAP as the supporting electrolyte using a SP-150 model (Biologic, USA) electrochemical analyzer instrument controlled by EC-LAB Software Ver. 11.33. A three-electrode cell consisting of a GCE, a platinum wire auxiliary electrode and Ag/AgCl electrode as the reference electrode was used for all the experiments. Cyclic voltammograms were recorded at scan rate range of 20 to 100 mV/s. Before thin-film deposition, GCE was polished by chamois leather containing 0.05 μm alumina slurry until a mirror surface was achieved. Subsequently, the GCE was ultrasonically cleaned in nanopure water, absolute ethanol, and nanopure water each for 5 min, respectively. The electrochemical cell was saturated with nitrogen for five minutes before measurements and kept constant on the solution surface during measurements. The thin-film was prepared by placing a drop over the GCE and drying it for 24 hours. For PEDOT:PSS/CS, a vial was weighed and the required PEDOT:PSS was added with a syringe. Carbon spheres were added to the vial to the desired weight percent. Afterwards, the mixture was stirred for 30 minutes and then placed in an ultrasonic bath for one hour. A drop was placed over the GCE and dried for 24 hours. The PEDOT:PSS/CS film thickness ranged from 10 to 40 μm across the top of the GCE electrode. An irregular surface of the PEDOT:PSS/CS can be appreciated in the SEM image shown in Figure 1. For PEDOT:PSS film, the surface morphology was more uniform along the electrode, showing a thickness range of 0.4 to 2.3 μm.

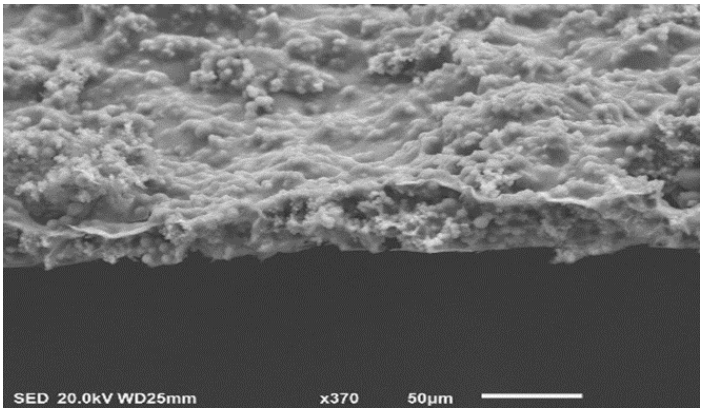


Figure 1: SEM image of PEDOT:PSS/CS film

RESULTS

The background corrected CV of ferrocene acetal using bare GCE and PEDOT:PSS/CS electrode against Ag/AgCl electrode are shown in Figure 2. Oxidation and reduction peaks are observed at 0.38 and 0.46 mV, respectively ($E_{1/2}$ = 0.42 mV).

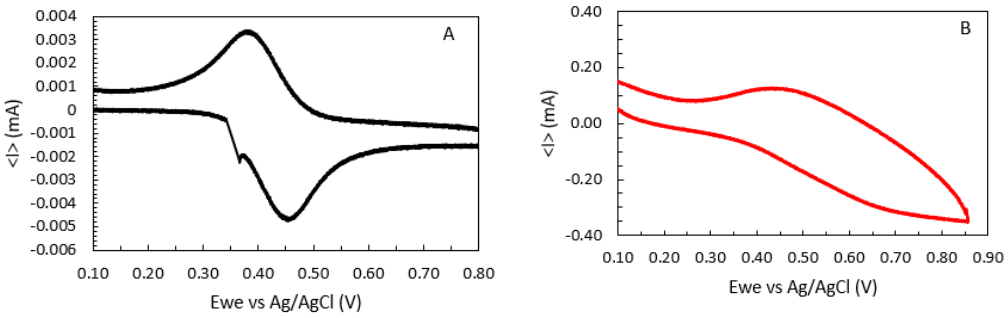


Figure 2: Cyclic voltammogram of 2-diphenyl ferrocene (0.50mM) in CH3CN/TBAP/N_2 saturated solution at 20mV/s: A) bare GCE electrode and B) GCE/PEDOT electrode.

On the other hand, the thin-film deposition of PEDOT:PSS shifts the oxidation and reduction peaks to 0.45 and 0.66 mV, respectively. This shift can be explained in terms of slower electron transfer reaction. Interestingly, the current amplitude is higher for PEDOT:PSS electrode than for bare GCE. Therefore, we explore this observation for quantitative analyses. Oxidation peak integration at different concentrations of ferrocene acetal and ferrocene were used to build the linear calibration curves shown in Figure 3. It is observed that the calibration sensitivity increases from GCE (1.10 ± 0.01 A/(V*M)) < PEDOT (1.66 ± 0.07 A/(V*M)) < PEDOT/CS(5% w/w) (8.3 ± 0.3 A/(V*M)) all with correlation coefficients (R^2) better than 0.99.

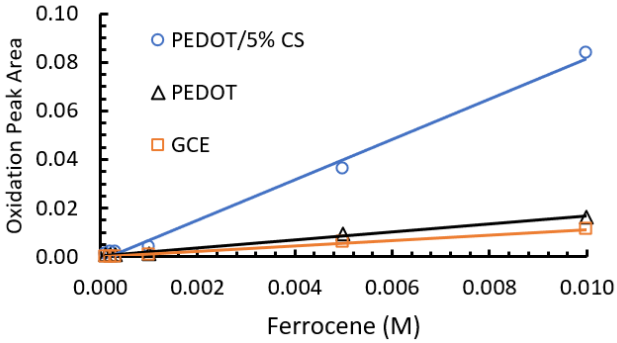


Figure 3: Calibration curves for ferrocene in CH3CN/TBAP/N2 saturated solution at 40 mV/s. Solid lines correspond to linear regression analysis.

Conclusions

In summary, GCE modified with thin-film of PEDOT:PSS or PEDOT:PSS with carbon microspheres increases cyclic voltammogram current amplitude of ferrocene and ferrocene acetal. The calibration curve sensitivity increases by a factor of 7.5 times for PEDOT:PSS/CS relative to GCE.

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Acknowledgments

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