A Ca^{2+} and Thiols Sensor Based on Pyrroloquinoline Quinone (PQQ) and Single-Walled Carbon Nanotubes Modified Electrodes

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Single-walled carbon nanotubes (SWNTs) are molecular wires that exhibit interesting structural, mechanical, electrical, and electromechnical properties. The unique features of SWNTs make them extremely attractive for wide range of sensing applications. Carbon nanotube-modified electrodes have shown a superior performance as compared to other carbon electrodes. PQQ is a redox coenzyme, which serves as a cofactor for a number of enzymes (quinoproteins) and particularly for some bacterial dehydrogenases. Direct electrochemistry of PQQ in aqueous solution at conventional electrodes, such as glassy carbon, gold, platinum and carbon-fiber packed column electrodes exhibits a quasi-reversible electron transfer.

In this study, a new way for investigating the electron-transfer properties of PQQ and also a study on the interaction between Ca^{2+} and PQQ at the SWNT-modified glassy carbon (GC) electrodes are described. The reversible electron transfer was observed for PQQ at the SWNT-modified GC electrodes. The cyclic voltammetry showed the direct electrochemical response of PQQ on the SWNT-modified electrodes, and anodic and cathodic peak potentials were observed at -0.085 and -0.125 V (vs Ag/AgCl), respectively. Ca^{2+} stabilized the semiquinone radical of PQQ which caused the decrease of the PQQ redox currents. The decrease of PQQ redox peak currents was proportional to the increase of Ca^{2+} concentration. Other cations such as Al^{3+}, Cr^{3+}, Ba^{2+}, Cu^{2+}, K^{+}, and Na^{+} showed no effects on the PQQ redox currents. One exception was Mg^{2+} : its effect on the PQQ redox currents was less than 1% of that of Ca^{2+}. Results showed an excellent linearity in the range of 10 μM – 10 nM Ca^{2+}.

The PQQ modified SWNT/GC electrode is also used for the detection of thiols. Thiols are important marker molecules in biological systems, and an accurate determination of the change in thiol levels provides critical insight into proper physiological functions and can be used in the diagnosis of disease states. A major barrier for developing electrochemical methods for thiols is that the direct oxidation of thiols at solid electrode is slow and usually requires large overpotentials to proceed.

The SWNT-modified GC electrodes are used for the detection of 14 thiols including cysteine and glutathione. SWNT modified electrodes show very stable electrochemical behavior and can be used to catalyze the electrochemical reactions of thiols. Cyclic voltammetry shows that cysteine can be oxidized at much less positive potential (peak potential of 420 mV vs Ag/AgCl) than those at other electrodes such as bare GC and diamond electrodes. The PQQ/SWNT/GC electrode showed an improved catalytic behavior compared with the SWNT/GC electrode by reducing the peak oxidation potential of cysteine to 270 mV. The less positive potential applied at the PQQ modified CNT/GC electrode is helpful to minimize the effects of potential interferents for the amperometric determination of cysteine.

References

1. Davis, J. J.; Coleman, K. S.; Azamian, B. R.; Bagshaw, C. B.; Green, M. L. H. *Chem. Eur. J*. **2003**, *9*, 3732 .
2. Inoue, T.; Kirchhoff, J. R. *Anal. Chem*. **2000**, *72*, 5755.
3. Sato, A.; Takagi, K.; kano, K.; Kato, N.; Duine, J. A.; Ikeda, T. *Biochem. J*. **2001**, 3*57*, 893.

Acknowledgements

This work was supported in part by the National Institutes of Health (Grant SO6GM08047).