Chinese Chemical Letters Vol. 10, No. 2, pp. 157–160, 1999

DNA Immobilization on Nano-Gold Modified Glassy Carbon Electrode

Xiang Qin LIN[1,*], Qian MIAO[1], Bao Kang JIN[1,2]

1. Department of Chemistry, University of Science and Technology of China, Hefei 230026
2. Department of Chemistry, AnHui University , Hefei 230039

Abstract: CT-DNA were electrochemically immobilized on the surfaces of both nano-gold modified glassy carbon electrode and bare glassy carbon electrode. The cyclic voltammetric behavior of Co $(phen)_3^{3+}$ adsorbed on the immobilized DNA was studied. Increase in the peak current of Co $(phen)_3^{3+}$ redox reaction was obtained on nano-gold modified glassy carbon electrode. The result suggests that more DNA molecules were immobilized on this electrode and nano-gold modification can enhance the heterogeneous electron transfer rate constant of the Co $(phen)_3^{3+}$.

Keywords: DNA; nano-gold; glassy carbon; cyclic voltammetry.

Introduction

The immobilization of DNA on an electronically conductive surface is of interest both in the study of DNA itself and in various applications. For example, immobilization of DNA on an electrode is used to produce DNA biosensors. Various DNA electrochemical biosensors have been prepared by immobilizing DNA on the surface of glassy carbon, carbon paste and gold electrodes[1-6].

The properties of nano-scale gold and bulk gold exhibit several differences. More noteworthy are the surface charge, high surface area and biocompatibility of nano-scale gold[7]. The strategy employed in this study was to prepare nano-scale gold modified glassy carbon electrode (NG/GCE). It is shown that more DNA can be immobilized on the NG/GCE.

Experimental

CT-DNA (calf thymus) (Sino-American Biotechnology) and $HAuCl_4$ (Shanghai Chemical Reagent) were used without further purification. The DNA solution was prepared by dissolving it in 0.02 mol/L phosphate buffer (pH 6.8). Co $(phen)_3$ $(ClO_4)_3$, tris (1,10-phenanthroline) cobalt (III) perchlorate, was synthesized as reported in the literature[8], which was used as an electrochemical indicator. Colloidal gold sols with average particle diameter of 20nm were prepared according to Frens[9]. Other reagents were of analytical grade. All solutions were prepared with doubly distilled water.

A BAS-100A Electrochemical Analyzer was used for electrochemical measurements. An Ag/AgCl electrode and a platinum wire were used as reference and auxiliary electrode, respectively. All the potentials are reported with respect to Ag/AgCl.

GC Electrode Modification and DNA Immobilization

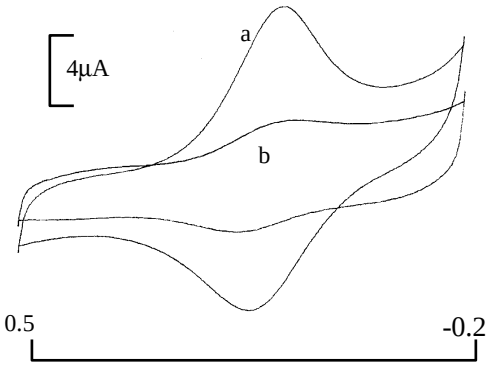
A freshly smoothed GC electrode with diameter of 3 mm was first treated by applying +1.5V for 20 min in colloidal gold sols for immobilization of nano-gold, then rinsed with water and pH 6.8 phosphate buffer solution for 20s, respectively. Then, the electrode was immersed in the DNA solution for accumulation of CT-DNA for 5min at +1.5V. Finally, the electrode was rinsed with water to remove unabsorbed DNA molecules. This DNA-adsorbed nano-gold modified GCE is denoted as DNA/NG/GCE.

Co $(phen)_3^{3+}$ cations were accumulated onto the modified electrode by immersing the electrode in 0.12 mmol/L Co $(phen)_3^{3+}$ pH 6.8 phosphate buffer solution for 5min. Then the electrode was rinsed with water and the buffer solution for 20s respectively, and ready for cyclic voltammetric experiments.

A DNA/GCE modified electrode was also prepared correspondingly by immobilization of the DNA on a bare GCE for comparison.

Results and Discussion

Figure 1. Cyclic voltammograms of Co $(phen)_3^{3+}$ on DNA modified electrodes in pH 6.8 phosphate buffer solution at 50 mV/s. (a): DNA/NG/GCE; (b): DNA/GCE



Because the binding constant between Co $(phen)_3^{3+}$ and DNA is large [10,11] the quantity of the DNA immobilized on the electrode can be determined sensitively by the electrochemical signal of coordinated Co $(phen)_3^{3+}$. In the other words, Co $(phen)_3^{3+}$ can be used indirectly to judge the quantity of immobilized DNA on the DNA/NG/GCE and DNA/GCE. As shown in **Figure 1.** the cyclic voltammograms (CVs) of Co $(phen)_3^{3+}$ on both the DNA/NG/GCE and DNA/GCE were obtained in the phosphate buffer solution. It is obvious that the peak currents corresponding to the Co $(phen)_3^{3+}$ redox reactions obtained at the DNA/NG/GCE are much larger than that obtained at the DNA/GCE. This

proves that more DNA molecules were immobilized on the nano-gold modified glassy carbon electrode.

Figure 2. Cyclic voltammograms of Co $(phen)_3^{3+}$ on DNA/NG/GCE in pH 6.8 phosphate buffer solution at different scan rates (v=10, 20, 30, 40, 50, 60, 70, 80 mV/s). The initial potential: +0.5V.

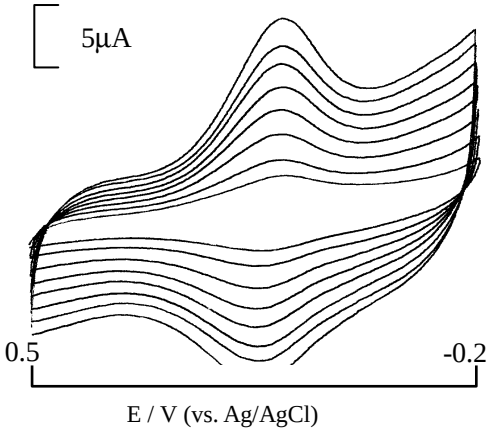


Figure 3. Plot of i_{pc} *vs.* v for the data in **Figure 2.**

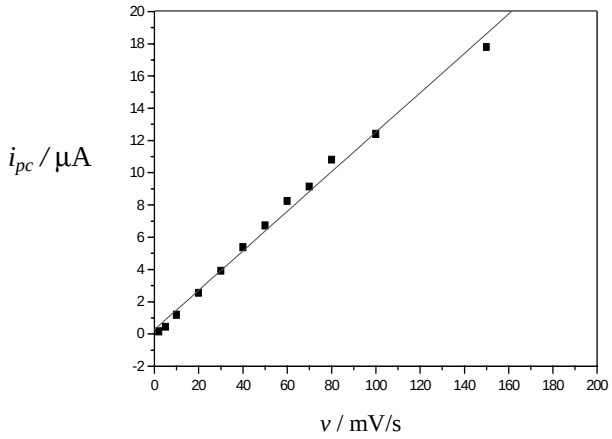


Figure 2. shows the CVs at various scan rates on the DNA/NG/GCE modified electrode in the phosphate buffer solution. **Figure 3.** shows a linear dependence of the cathodic peak current on scan rate in the range of 2 to 180 mV/s, indicating that Co $(phen)_3^{3+}$ is strongly bound to the DNA/NG/GCE surface. From the slope of the i_p-v curve, a total surface concentration of Γ=1.87x10^{-11}mol/cm^2 Co $(phen)_3^{3+}$ on the DNA/NG/GCE surface can be calculated, according to the equation[12]: $i_p=n^2F^2v\Gamma A/4RT$. This value is about 4 times the 4.91x10^{-12}mol/cm^2 obtained for the DNA/GCE (CVs not shown).

CV peak separations were also measured from the cyclic voltammograms, and listed in **Table 1**.

Table 1. Dependence of peak separation (ΔE_p) and scan rate (*v)*

v, V/s		2	5	10	20	50	80	100	150
ΔE_p, mV	DNA/NG/GCE	15	28	33	39	52	60	66	81
	DNA/GCE		38	51	57	68	74	79	92

It can be seen from the table that the values of ΔE_p increase with increasing scan rate. This shows that the cyclic voltammograms obtained on both modified electrodes are quasi-reversible wave. One can also find that the ΔE_p value for the DNA/NG/GCE is smaller than that for the DNA/GCE in the whole range of scan rate. It suggests that the electron transfer rate of Co $(phen)_3^{3+}$ on the DNA/NG/GCE is faster than that on the DNA/GCE.

Acknowledgments

The financial support from the CAS Key Project is greatly acknowledged.

References

1. J. Wang, M. Chicherro, G. Rivas, X. Cai, N. Dontha, D. Farias, H. Shiraishi, *Anal. Chem.* , **1996**, *67*, 251.
2. A. M. O. Bert, S. H. P. Serrano, I. Gutz, M. A. La-Scdea, *Bioelectrochem. Bioenerg*., **1997,** *42*, 175.
3. X. Xu, A. J. Bard, *J. Am. Chem. Soc*., **1995**, *117*, 2627.
4. K. Hashimoto, K. Ito, Y. Ishimorl, *Anal. Chem.*, **1994**, *66*, 3830.
5. D. Pang, M. Zhang, Z. Wang, Y. Qi, J. Cheng, Z. Lin, *J. Electroanal. Chem*., **1996**, *403*, 183.
6. S. Liu, J. Ye, P. He, Y. Fang, *Anal. Chim. Acta*, **1996**, *335*, 239.
7. C. R. Martin, D. T. Mitchell, *Anal. Chem*., **1998**, *70***,** 322A.
8. L. S. Dollimere; R. D. Gillard, *J. Chem. Soc. Dalton Trans*., **1973**, 933.
9. G. Frens, *Natutre Phys. Sci*., **1973**, *241*, 20.
10. M. T. Carter, A. J. Bard, *J. Am. Chem. Soc*., **1987,** *109*, 7528.
11. M. T. Carter, M. Rodriguez, A. J. Bard, *J. Am. Chem. Soc*., **1989**, *111*, 8901.
12. S. Dong, G. Che, Y. Xie, "*Chemically Modified Electrodes*", Sci. Press, Beijing, **1994**, 53.

Received 10 September 1998