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An Integrated DNA Modified Dual-microelectrode Sensor Probe

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Abstract: A unique method for preparing a coaxial dual-microelectrode sensor by vaporizing the nano-thickness Au layer on the DNA modified carbon fiber micro-column electrode was illustrated. The dual-electrode showed particular merit for determination in biological systems.

Keywords: DNA, dual-electrode, coaxial, microelectrode, biosensor.

Voltammetric techniques employing microelectrodes are extremely useful in the research aimed at understanding biochemical processes in living organs and even in cells. The small size of the microelectrodes benefits to position them very closely to the cells or even inside the cells without causing serious damage. Furthermore, microelectrodes are well suited to high-speed voltammetric measurements, which permit, for example, the observation of individual exocytosis events[1-3]. In this paper, we describe an effort to fabricate a sensing micro-probe containing a micro-column working electrode and a coaxial counter electrode based on conventional simple techniques.

Recently, we found that DNA molecules such as calf thymus DNA (ct-DNA) can directly attach onto carbon surfaces through covalent bonds under controlled potentials[4-5]. Using this method, a carbon fiber micro-column electrode (CFME) can be electrochemically modified with a uniform layer of ct-DNA as reported in the previous work[4]. Then the ct-DNA modified CFME was treated in a vacuum compartment for Au vapor deposition, producing a thin layer of conductive Au porous coverage. After leading out of the Au layer acting a coaxial Au counter electrode (CACE), a ct-DNA sandwiched CFME and CACE microprobe was ready for application, denoted as ct-DNA//CFME-CACE. This fabrication was rather facile with a well-controlled route and good reproducibility. A diagram of the ct-DNA//CFME-CACE is shown in **Figure 1**.

A scanning electronic microscopy (SEM) image of the cut end is shown in **Figure 2a**. It reveals that the thickness of the sandwiched DNA layer as well as the Au cover layer is as only about 20-50 nm.

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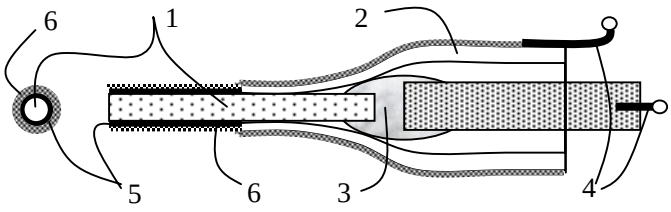
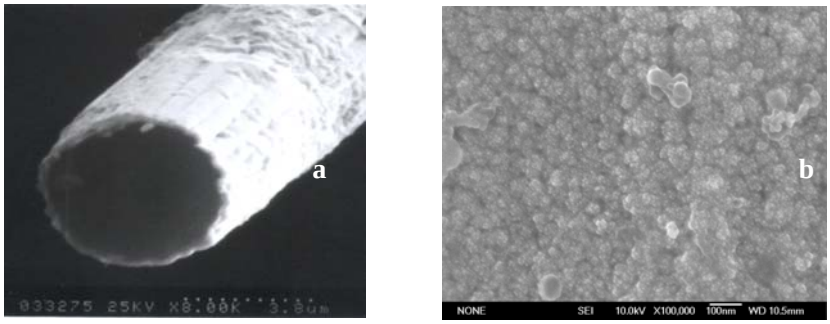
Figure 1 Schematic diagram of the ct-DNA//CFME-CACE microprobe



Top view Side view

1. Carbon fiber, 2. glass capillary, 3. silver conductive glue, 4. copper wires,
5. DNA sandwiched layer, 6. porous Au cover layer.

Figure 2 SEM images of the ct-DNA//CFME-CACE microprobe



top view side view

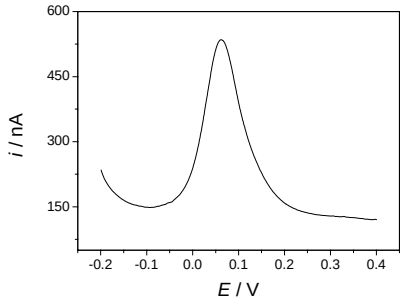
The image for the Au covered micro-column of the ct-DNA//CFME-CACE is shown in **Figure 2b**. It reveals that the surface layer was formed by aggregated Au particles of about 20-50 nm in diameter. The close parking of the nano-Au particles ensured the electric conductivity of the layer required for acting the counter electrode, and also generated diffusion conductivity through its porous structure with nano-holes. Although the DNA double helix chain is electronic conductive, however, it was demonstrated that the DNA layer sandwiched in ct-DNA//CFME-CACE is an electronically insulate.

The ct-DNA//CFME-CACE was used for electrochemical sensing of catecholamine neurotransmitters and related biomolecules. It shows that some small molecules such as dopamine (DA) can penetrate the Au layer and be accumulated on the sandwiched DNA layer for obtaining facilitated electron transfer reactions. The sensitivity of the DA detection by either cyclic voltammetry or differential pulse voltammetry (DPV) was almost the same as that at the corresponding DNA modified CFME[4, 5]. **Figure 3** shows the DPV of DA oxidation at the electrode. The potentials *versus* the CACE of the dual-electrode were relatively stable during the experiment. Only about 10% enlargement on the peak current was observed in comparison with a ct-DNA/CFME, which could be attributed to an effect of redox cycling between the CFME-CACE. In

mimic biological conditions, the overlapped responses of ascorbic acid (AA) and DA could be resolved into two well-defined voltammetric peaks, hence AA did not interfere the DA determination, as reported previously[4-5]. The following compounds did not interfere the detection of 10 μmol/L DA (the tolerance ratio is shown in the blanket): bovine serum albumin (100), bovine pancreas (100), glucose (100), citric acid (100), glutamic acid (150), NH_4NO_3 (200), and NaCl (400).

Finally, similar method can be used for fabrication of coaxial dual-electrode microprobes with various sandwiched substances for obtaining different function. As an example, phenol-2-allylphenol can be electropolymerized on the CFME before CACE coating for obtaining a thin film insulated coaxial ring-disk dual-electrode microprobe.

Figure 3 DPV curve of DA oxidation reaction at the ct-DNA//CFME-CACE.



Scan rate: 20 mV/s; pulse amplitude: 50 mV; pulse width: 50 ms; pulse time: 200 ms; DA concentration: 20 μ mol/L.

Acknowledgment

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