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A heated pencil lead disk electrode with direct current and its preliminary application for highly sensitive detection of luteolin

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A B S T R A C T

A indirectly heated pencil lead disk electrode (HPLDE) with direct current was fabricated. The dramatic temperature effect on the adsorptive accumulation of luteolin was demonstrated. A detection limit of 1.0×10^{-9} M could be obtained (S/N=3) with an electrode temperature of 44 °C, which was more than one magnitude lower than that at room temperature. It was applied to the determination of luteolin in simulated human urine with good accuracy. This heated electrode shows many merits such as easy fabrication and simple heating equipments, low cost, high thermal stability, high sensitivity and good reproducibility.

1. Introduction

Electrically heated metal wire microelectrodes (HMWEs) were invented in the early 1990s [1,2]. The major advantage of this technique lies in that by heating the electrode rather than the solution, the temperature at the electrode surface can be well controlled. The HMWEs have been widely used in electroanalytical chemistry [3–8] due to the enhanced convection and the accelerated redox reaction rates with elevated electrode temperature. In order to improve biological compatibility, various carbon-based heated electrodes have been designed, such as heated carbon paste electrodes [9,10], heated graphite cylinder electrodes [11,12], and heated screen-printed carbon electrodes [13].

These heated electrodes were symmetrically designed with a couple of sides and heated directly by alternative current in order to eliminate the interferences with the electrochemical signal from the simultaneously enforced heating current. Alternatively, indirectly electrically heated gold disk electrodes based on LTCC (low temperature co-fired ceramic) technology were introduced later [14]. This construction consisted of an insulated resistance heater inside the ceramic body right below the screen-printed metal electrode layer. They were applied to enzyme-modified sensors [14,15], the investigation of DNA melting curves [16], and ion-selective electrode for copper [17]. Because of the separation between heating and electrochemical circuits, the simultaneously enforced heating current even with direct current would not interfere with the electrochemical signal. But the fabrication of this kind of heated electrode was quite complicated. Recently, a very indirectly heated copper microdisk electrode (HCME) with direct current was fabricated and applied to the capillary electrophoresis (CE) and CE-Chip as an electrochemical detector in our group [18]. But the HCME was only suitable for determination of very limited kinds of substances such as polyhydroxy compounds. Likewise, indirectly heated gold disk electrode [19] and heated glassy carbon disk electrode [20] were presented, but they were both very expensive.

In addition, pencil leads have long been used as electrodes for electroanalytical applications due to their low background current, favorable anodic potential range, low cost and commercial availability [21–23].

In this paper, a novel heated pencil lead disk electrode (HPLDE) heated indirectly with direct current similar to the HCME was firstly designed. This heated electrode exhibits simple fabrication and heating equipments, low cost, high thermal stability, high sensitivity, and a wide range of analytes. Furthermore, the heated electrode could be renewed easily by mechanical polishing. The adsorptive stripping analysis of luteolin was established for preliminary evaluating the analytical performance of this new heated electrode.

2. Experimental

2.1. Chemicals and apparatus

Pencil lead (0.5 mm in diameter). Cu enameled wire (100 µm in diameter). Luteolin was obtained from the National Institute for Control of Pharmaceutical & Biological Products, Beijing, China. The other chemicals were of analytical grade.

The heating current was provided by a DC power supplier (Zaoxin DC Power Supply RXN-303A, Shenzhen Zaoxin Electronics Co. Ltd.,

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China). Electrochemical experiments were performed with CHI440 (CH Instruments, Inc., USA). An electrochemical cell with conventional three-electrode system was used, an HPLDE as working electrode, a platinum foil as counter electrode and a saturated calomel electrode as reference electrode.

2.2. Preparation of HPLDE

Preparation of HPLDE was similar to the HCME [18]. In brief, one pencil lead was wound by a double parallel Cu enameled wire as a heater. Then the electrode was inserted into a plastic tube, which was further sealed with epoxy resin. Fig. 1 (Top) shows the scheme of the HPLDE configuration.

2.3. Procedure for adsorptive stripping measurement

All measurements were conducted in 0.2 M phosphate buffer solution (PBS, pH 5.0) unless otherwise mentioned. The electrode was subjected to cyclic scanning in a 0.2 M PBS (pH 10.0) before every measurement in order to remove the adsorbed luteolin. For accumulation, the electrode was immersed into PBS containing luteolin for 3 min. Then it was transferred into blank PBS for square wave voltammetry (SWV) stripping measurements. In the case of heated measurements, the DC was turned on only during accumulation step and turned off for 10 s prior to stripping.

3. Results and discussion

3.1. Temperature calibration and thermal response of HPLDE

Temperature calibration of the surface of the electrode was according to the previous literature [11,24]. The results (Fig. 1A) show that the temperature rise over room temperature of the HPLDE is linear with the square of the heating current. It is worthwhile to note that significant temperature rise of the pencil lead electrode surface could be obtained through controlling suitable fabrication conditions, although carbon is a bad conductor, in great contrast with Au and Cu.

The thermal response of the HPLDE was shown in Fig. 1B, which was measured by open circuit potential method during heating and after heating [11]. After beginning heating at "on", the electrode temperature rises promptly from the bulk temperature to its maximum and reaches a steady value after heating ca. 15 s. As the heating currents are turned off, the electrode temperature decreases quickly to the bulk temperature within 15 s. Because of being indirect heating, the thermal response rate of HPLDE was lower than that of heated graphite cylinder electrode [11], but this did not affect the application of the heated electrode.

Fig. 1C showed the cyclic voltammograms of $K_3[Fe(CN)_6]$. As shown in Fig. 1C, increasing the electrode surface temperature resulted in the increase of the peak current. Note that no interference of the electrochemical signal was observed at elevated electrode temperature.

3.2. Effects of electrode temperature on the SWV stripping signal of luteolin at HPLDE

The effects of electrode temperature upon the SWV stripping response of luteolin are illustrated in Fig. 2. The electrode was heated only during the 3 min accumulation step in 1×10^{-7} M luteolin solution and the stripping was carried out in blank PBS at room temperature. The response signal was significantly enhanced with increasing the electrode temperature from 25 °C to 44 °C. It was estimated that the forced thermal convection induced by heating the electrode would be mainly responsible for this signal enhancement [25].

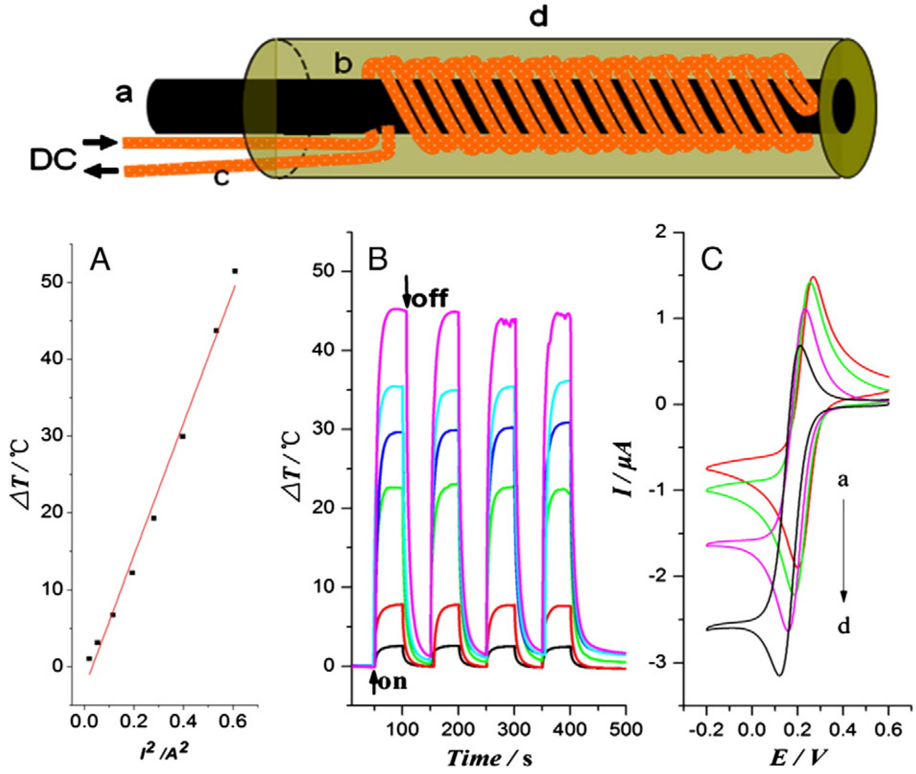

Fig. 1. (Top) scheme of the HPLDE configuration. a: pencil lead, b: epoxide resin, c: Cu enameled wire, d: plastic tube, and DC: direct current power supply. (A) Relationship between the temperature rise over room temperature of the HPLDE and the square of the heating current. (B) Time profile of temperature rise during heating (on) and after heating (off) at HPLDE. (C) CVs of 5 mM $K_3[Fe(CN)_6]$ with 0.5 M KCl at HPLDE with different electrode temperatures, (a)20, (b) 35, (c) 60, and (d) 75 °C. Scan rate: 0.1 V s^{-1}.