



Electrocatalytic determination of Reduced Glutathione using rutin as a mediator at acetylene black spiked carbon paste electrode



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ABSTRACT

The electrocatalytic oxidation of glutathione based on rutin as a mediator was studied at acetylene black (AB) modified carbon paste electrode (CPE). The results of cyclic voltammetric experiments showed that rutin could catalyze oxidation of GSH in PBS (pH 7.0) and the oxidation current was greatly increased by using AB-CPE compared to the nonmodified CPE. The kinetic parameters such as catalytic rate constant and diffusion coefficient were obtained using double potential step chronoamperometry. Under the optimum conditions, the electrocatalytic oxidation peak current was linear to the glutathione concentration range from 0.5 μM to 3.5 μM and 2.5 μM to 25 μM with the detection limit of 0.080 μM ($S/N = 3$) by differential normal pulse voltammetry (DNPV). The proposed method has been applied to the determination of glutathione in pharmaceutical sample with satisfactory results.

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1. Introduction

Acetylene black is a special kind of carbon black which is made by the controlled combustion of acetylene in air under pressure. On account of its porous structure and many fascinating properties such as excellent electric conductivity, large specific surface area and strong adsorptive ability [1–3], AB has attracted more and more attention to the researchers and was widely used in electrochemistry for various purposes such as electric double layer capacitor and electrode material. Glutathione (GSH, L- γ -glutamyl-L-cysteinylglycine), which is present in virtually all mammalian tissues and function as an antioxidant [4], plays an important role in detoxification of peroxides and free radicals [5]. It has been well founded that a decrease in GSH concentration may be correlated with aging and pathogenesis of several diseases, including rheumatoid arthritis, muscular dystrophy, amyotrophic lateral sclerosis, AIDS, Alzheimer disease, and Werner syndrome [6–9].

As the fact of many important functions of GSH in biological process, much effort has been made to develop novel and sensitive methods for GSH detection. So far, various methods have been reported for the determination of GSH in the literatures. The instrumental techniques included flow injection [10], spectrophotometry [11], fluorimetry [12], capillary zone electrophoresis [13,14], high performance liquid chromatography [15–17], proton nuclear magnetic resonance [18], and electrochemical method

[19–21]. Electrochemical approach [2,3,22] has been investigated for GSH determination due to its inherent advantages of simplicity, easy miniaturization, high sensitivity and relatively low cost. However, direct amperometric detection of GSH at common electrode (C, Pt and Au, except mercury electrode) is somewhat difficult due to the slow electron transfer rate will result in a high anodic potential [23–25]. Also, strong absorption of GSH at the surface of metallic electrodes will lead to the fouling of electrodes [26–29]. Therefore, indirect electrochemical method was proposed in this paper for the sensitive detection of GSH based on rutin as a catalytic mediator at AB modified carbon paste electrode (CPE).

To the best of our knowledge, there is no report concerning GSH determination using rutin as a mediator at AB-CPE. Therefore, the suitability in electrocatalytic determination of glutathione was investigated by cyclic voltammetry and chronoamperometry in this paper.

2. Experimental

2.1. Chemicals

Glutathione was obtained from Sigma and rutin from J&K Chemical. High-viscosity paraffin oil and graphite powder were obtained from Aladdin. Acetylene black (AB, purity >99.99%, avg. particle size 0.042 μm) came from Strem Chemicals, Inc. USA. Other chemicals of analytical grade were purchased from Sino-pharm Chemical Reagent Co. Ltd., or J&K Chemical. All reagents

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were the highest purity and used without further purification. All solutions were prepared with doubly distilled water.

2.2. Apparatus

A computerized electrochemical workstation CHI660D (Chenhua Instrument Co., Shanghai, China) was used for electrochemical measurements in a conventional three-electrode cell. Unmodified or acetylene black modified carbon paste electrode were served as the working electrodes, Ag|AgCl|KCl_{sat} as the reference electrode and a Pt wire as the counter electrode. A pH-meter (PHS-3C, Shanghai Dapu, China) was applied for pH measurements.

2.3. Preparation of working electrode

The modified electrode (AB-CPE) was prepared by mixing 5% (w/w) AB, 30% (w/w) paraffin oil and 65% (w/w) graphite powder in a mortar to form a homogeneous carbon paste which was then packed into a plastic tube (25 mm i.d. × 35 mm o.d.). The electrical contact was made by pushing a copper wire down the plastic tube into the back of the mixture. Carbon paste electrode (CPE) was constructed in the same way as AB-CPE except that AB was absolutely replaced by graphite powder. A new electrode surface was obtained by wiping and smoothing the electrode surface on a weighing paper. All electrodes were stored at 4 °C in a refrigerator before use.

2.4. Pharmaceutical sample determination

Reduced Glutathione Eye Drops was prepared by completely dissolving of each tablet (100 mg) of glutathione in 5.0 mL giving solution by ultrasonication. The above solution was diluted 1000 times with phosphate buffer solution (PBS, 0.1 M NaH₂PO₄+0.1 M Na₂HPO₄, pH 7.0) and used for electroanalysis.

3. Results and discussions

3.1. Characterization of electrodes

The electrochemical behavior of different working electrodes was first investigated using [Fe(CN)₆]^{4-/3-} as redox probe and their cyclic voltammograms of CPE (a) and AB-CPE (b) in 1 mM [Fe(CN)₆]^{4-/3-} solution containing 500 mM KCl were shown in Fig. 1. A pair of redox peaks was observed at CPE with peak-to-peak

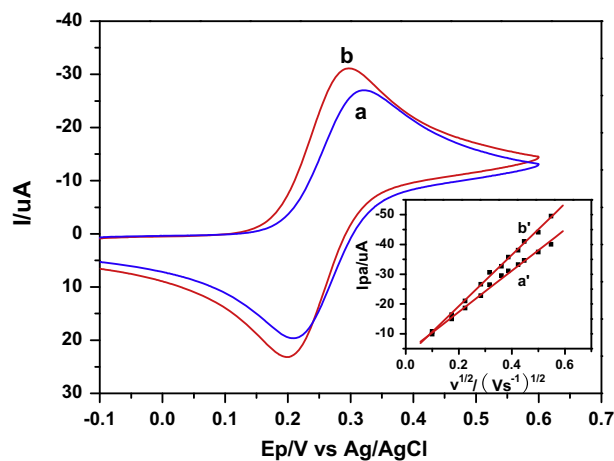


Fig. 1. Cyclic voltammograms of (a) CPE, (b) AB-CPE in 1 mM [Fe(CN)₆]^{4-/3-} + 0.5 M KCl solution with scan rate of 100 mV s⁻¹. Inset Plot of I_{pa} versus $v^{1/2}$ (V s⁻¹)^{1/2} (0.03–0.3 V s⁻¹) in 1 mM [Fe(CN)₆]^{4-/3-} + 0.5 M KCl solution at (a') CPE (b') AB-CPE.

separation (ΔE_p) of 113 mV at the scan rate of 100 mV s⁻¹ (a). While at AB-CPE, both cathodic and anodic peak currents increased with ΔE_p value of 98 mV (b). By comparing the two electrodes, the peak current obtained at AB-CPE is about 20% greater than that obtained at CPE and peak to peak separation (ΔE_p) was smaller. This indicates that AB could effectively increase the electron transfer rate between electrode surface and [Fe(CN)₆]^{4-/3-}. These effects confirm the large surface area and electrostatic adsorption of AB.

Inset of Fig. 1 showed peak currents (I_p) versus square root of scan rate (v , 0.01–0.3 V s⁻¹) for CPE (a') and AB-CPE (b') in 1 mM [Fe(CN)₆]^{4-/3-} containing 500 mM KCl solution, and I_p was linear to $v^{1/2}$ for two electrodes. According to the Randles–Sevcik equation: [30]

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} c \quad (1)$$

The values of the effective surface area (A) could be calculated. Where n refers to the number of transfer electron, A refers to the effective surface area, D refers to the diffusion coefficient of the electroactive molecule at electrode surface, c refers to the concentration of the probe molecule, and v refers to the scan rate. For [Fe(CN)₆]^{4-/3-}, $n = 1$, $D = 7.6 \times 10^{-6}$ cm² s⁻¹, so the effective surface of AB-CPE and CPE can be calculated to be 0.12 cm² and 0.09 cm², respectively.

To further characterize the electrodes, electrochemical impedance spectrum (EIS) was used to investigate the interface information on the impedance changes after modification. Electrochemical impedance spectra of unmodified CPE and AB-CPE were conducted in 1 mM [Fe(CN)₆]^{4-/3-} containing 500 mM KCl solution with frequency varied from 0.1 to 100,000 Hz. The corresponding Nyquist diagram was shown in Fig. 2. As can be seen, the electron transfer resistance of the redox at AB-CPE was obviously lower than that of CPE, suggesting the presence of AB in the carbon paste could enhance the conductivity of the electrode and make it easier for the electron transfer between the electrode and electrolyte.

3.2. Electrocatalytic oxidation of glutathione

The voltammetric behavior of 20 μ M GSH in the presence or absence of rutin in PBS (0.1 M NaH₂PO₄ + 0.1 M Na₂HPO₄, pH 7.0) at AB-CPE and CPE was given in Fig. 3. Curve a and curve b showed the cyclic voltammogram of buffer solution at CPE and AB-CPE, while curve c and curve d showed the responses of 20 μ M GSH at CPE and AB-CPE, respectively. It can be clearly seen that GSH

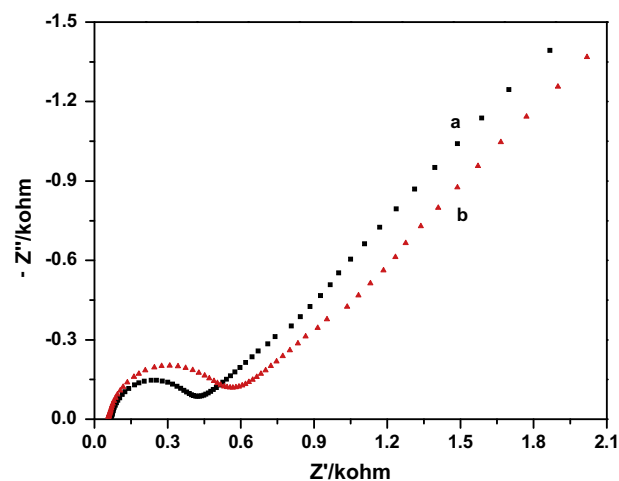


Fig. 2. Nyquist plots for the Faradaic impedance measurements of 1 mM [Fe(CN)₆]^{4-/3-} + 0.5 M KCl solution performed on AB-CPE (a) and CPE (b).

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