Graphene-modified CPE as a disposable electrochemical sensor for rapid determination of fluoranthene

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Abstract. A disposable electrochemical sensor (ES) was developed by embellishing graphene on carbon paste electrode (CPE), and the electrocatalytic activity of fluoranthene (Frτ) was investigated. An anodic peak of Frτ-acetonitrile-NaClO₄ appeared at 1.6 V based on the cyclic voltammetry. The peak current of Frτ at graphene-modified CPE was increased compared with that of unmodified electrode. The differential pulse voltammetry revealed a linear relationship between peak current and Frτ concentration within 2–140 ng mL⁻¹, and the LOD was calculated to be 0.95 ng mL⁻¹. Also, the ES method was effective for rapid determination of Frτ in black rubbers on modified CPE.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are known as persistent organic contaminations with carcinogenicity and mutagenicity [1-3]. The main sources of fluoranthene (Frτ) were biomass combustion and coal burning [4]. Frτ is commonly found in black rubber products which include preformed and antiskid rubbers. Electro-oxidation route was shown to be one of the effective manners to the removal of PAHs [5,6].

Current assay methods for Frτ include real-time polymerase chain reaction [7], high-performance liquid chromatography (HPLC) [8], gas chromatography-mass spectrometry [9] and atmospheric pressure chemical-ionization mass spectrometry [10]. However, these techniques require large equipment and expensive instrumentation, which are unsuitable for field related studies [11]. Based on facile pretreatment steps of routine quality control, carbon paste electrode (CPE) is mainly used in electroanalysis owing to its slight voltammetric background current and low-cost device [12,13]. For carbon electrodes, the design of chemically functionalized electrodes specific to Frτ determination still remains challenges.

This work showed the differential pulse voltammetry (DPV) and cyclic voltammetry (CV) of Frτ-acetonitrile-NaClO₄, which were characterised using CPE filled with graphite paste and embellished with graphene. The modified CPE was impregnated with Frτ at open-circuit potential and then transferred to a three-electrode system. The influence of different mass concentrations of Frτ (C Frτ) on the sensor performance was investigated, and the electrochemical sensor (ES) data were compared with
those of HPLC methodology. Finally, the electroanalysis of Frt in rubber products at modified CPE was expected to establish field test of PAHs.

2. Experimental section

2.1. Instruments and reagents

A CorrTest CS350M electrochemical workstation (China), an Agilent 1290 Infinity II high performance liquid chromatograph (USA), a Hitachi TM4000 scanning electron microscope (Japan), a CEM Mars6 microwave extractor (USA), an Eppendorf 5810R multi-purpose desktop centrifuge (Germany) and a JingChong 3-mm diameter paste electrode shell (China) were utilized.

Graphene, N,N-dimethylformamide, graphite, acetonitrile, HCl and NaClO₄ were purchased from Macklin Biochemical, China. 1000 μg mL⁻¹ Frt in methanol was purchased from TMRM, China. Water (electrical resistivity of 18.25 MΩ cm) was obtained using a ULUP-I water purifier.

2.2. Preparation of graphene-modified CPE

The CPE was obtained by mixing 70% (w/w) graphite powder with 30% (w/w) paraffin oil in an agate mortar [14]. The well-stirred paste was added to the cavity of electrode body, and the electrode surface was smoothed on a filter paper. The CPE was immersed in 0.2 mol L⁻¹ HCl, and the potential value (E) was increased from open-circuit potential to 0.3 V for 1 min.

Next, graphene was added to 50 mL N,N-dimethylformamide (via sonication for 5 min) to prepare a 0.4% (w/w) graphene suspension. The modified liquid (20 μL) was then applied to the electrode surface with infrared drying to obtain the modified CPE.

2.3. DPV measurement

The as-prepared electrodes need to be polished before each measurement. For the electroanalysis of Frt, a three-electrode system is employed, and the DPV parameters are shown in Table 1.

| Variables               | Conditions                  |
|-------------------------|-----------------------------|
| Working electrode       | Graphene-modified CPE       |
| Reference electrode     | Ag/AgCl electrode           |
| Auxiliary electrode     | Pt electrode                |
| Potential range         | 1.3–1.8 V                   |
| Pulse amplitude         | 70 mV                       |
| Pulse width             | 50 ms                       |
| Step time               | 0.1 s                       |
| Potential scan rate     | 50 mV s⁻¹                   |

The C₅ in 2, 10, 40, 80, 120 and 140 ng mL⁻¹ were prepared with 0.1 mol L⁻¹ electrolyte (NaClO₄ was dissolved in 85% acetonitrile as the electrolyte; the pH value of electrolyte was adjusted at 4.0). The modified CPE was immersed in Frt standards for 10 min and conducted for DPV analysis. The mean value of current response was recorded as the anodic peak current (I). The ES tests were measured in triplicate.

2.4. Sample’s pretreatment and HPLC analysis

0.3 g black rubbers and 15 mL acetonitrile was incubated by microwave extraction, and extracted at 80 °C for 20 min. The mixture was centrifuged at 2500 rpm for 3 min, and then filtered by 0.45 μm organic membrane. The extract was next transferred into acetonitrile-NaClO₄ for ES tests.
Through silica gel solid-phase extraction, 1.2 mL extract in chromatic bottle was prepared for HPLC analysis. Chromatographic grade acetonitrile and water in certain proportions were used as mobile phases on C18 reverse-phase column. The qualitative experiment was determined derived from retention time at 1.5 mL min⁻¹ of flow rate. The integral areas of LC peaks were used to acquire the \( C_{FrT} \) of black rubbers, comparing with those of ES.

3. Results and discussion

3.1. Microstructure of surface-modified electrode and redox behavior of FrT

The CPE was modified with 20 µL graphene suspension under infrared drying. The microstructure of CPE was observed using scanning electron microscopy (SEM) at an accelerating voltage of 15.0 kV. The bare CPE surface was relatively flat before deposition (Figure 1A), but variations occurred on its microstructure after modification. The graphene was dispersed in N,N-dimethylformamide, and the SEM revealed an uneven deposition on CPE surface with a cauliflower-like appearance (Figure 1B).

![Figure 1. SEM images of the bare CPE (A) and modified CPE (B) surfaces.](image)

After 10 min open-circuit state, the CV curves of bare CPE and modified CPE were performed in FrT-acetonitrile-NaClO₄. No distinct peaks were surveyed in 0.1 mol L⁻¹ electrolyte (Figure 2A) and 50 ng mL⁻¹ FrT-acetonitrile-NaClO₄ (Figure 2B) on bare CPE. A current signal at 1.6 V appeared that was owing to the oxidation of adsorbed FrT on modified CPE, while a cathodic peak at 0.33 V appeared in the negative potential scan (Figure 2C). After modification, graphene provided enhanced the activity of electron-transfer reaction. The oxidation potential of FrT was normally required to ensure high selectivity.
Figure 2. CV curves of 0.1 mol L⁻¹ electrolyte (A) and 50 ng mL⁻¹ Frt-acetonitrile-NaClO₄ (B) on bare CPE, and Frt-acetonitrile-NaClO₄ on graphene-modified CPE (C).

For enrichments on CPE surface, the graphene suspensions were embellished and the anodic current was significantly affected by modified liquid volume (Figure 3). The $I$ of 50 ng mL⁻¹ Frt-acetonitrile-NaClO₄ increased within volume of 15–19 μL. The $I$ reached a maximum as the volume increased to 20 μL at high redox potential. When the volume was >20 μL, the $I$ decreased in a nonlinear manner. This might be the modified film was comparatively thick, which hindered the electron-transfer reactions in electrolyte.
Figure 3. Effect of modified liquid volume on the $I$ of graphene-modified CPE.

3.2. Electrochemical determination of Frt in rubbers

The working electrodes were immersed in Frt-acetonitrile-NaClO$_4$ at 2–140 ng mL$^{-1}$, and the Frt standards were determined by DPV (Figure 4A). The relation between $I$ and $C_{\text{Frt}}$ was as follows: $I = 0.336C_{\text{Frt}} + 15.71$, squared correlation coefficient $R^2 = 0.9982$ (Figure 4B). The limit of detection (LOD) was calculated to be 0.95 ng mL$^{-1}$ using formula: LOD = $3\sigma/k$; where $\sigma$ is the standard deviation of the peak currents for blank sample ($n = 9$), and $k$ is the slope of the calibration curve. Hence, the ES constructed has high sensitivity for Frt.

Figure 4. DPV responses of adsorbed Frt-acetonitrile-NaClO$_4$ on modified CPE ($A$), and calibration curve of Frt standards ($B$).
C_{Fr}t of the black rubbers were detected by ES and HPLC method. The specific concentrations of spike-in sample at 10, 40 and 80 ng mL\(^{-1}\) were sequentially prepared. The mean C_{Fr}t of the positive samples was 12.1 ng mL\(^{-1}\) by ES and 12.5 ng mL\(^{-1}\) by HPLC, of which the deviation was \(\leq 3.4\%\). The mean recoveries for ES were 93.7\%–104.2\%, while the mean recoveries for HPLC were 97.0\%–108.1\% (Table 2). Their deviation was considered acceptable, and the proposed electrochemical method was favourable in terms of inexpensive in price. The relative standard deviations (RSD) of modified CPE and HPLC were \(\leq 5.8\%\) and \(\leq 5.2\%\). The reproducibility of modified CPE was good in terms of ES detection, indicating that the ES system was applicable for PAHs quantification.

| Sample               | Added (ng mL\(^{-1}\)) | Found (ng mL\(^{-1}\)) | Recovery (%) | RSD (%) |
|----------------------|-------------------------|-------------------------|--------------|--------|
| Positive rubbers     | 80                      | 96.0                    | 95.2         | 104.2  | 5.5  | 4.7 |
|                      | 40                      | 51.4                    | 50.9         | 98.6   | 97.0 | 5.0 | 5.2 |
|                      | 10                      | 20.7                    | 24.3         | 93.7   | 108.1| 5.8 | 4.9 |

4. Conclusion
A disposable CPE modified with graphene showed good electrocatalytic properties for the oxidation of Frt-acetonitrile-NaClO\(_4\) due to its high surface area and charge-transfer reaction. The redox behavior of Frt and the \(I\) at modified CPE were enhanced compared with that of unmodified electrode. The mean recoveries of Frt in black rubbers using ES method were from 93.7\% to 104.2\%. The results confirmed a quantitative approach of Frt and indicated the characteristics of current responses. The oxidizing conditions of Frt were optimized, which was opportune to develop a controlled electro-oxidation system in the domain of PAHs assay.

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