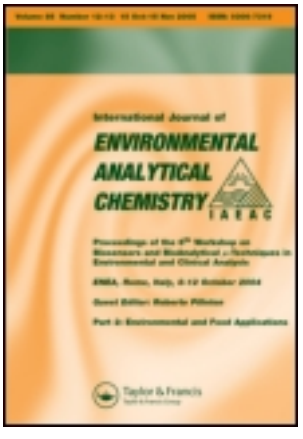

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Determination of 1-hydroxypyrene in human urine by a multi-wall carbon nanotubes-modified glassy carbon electrode

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Determination of 1-hydroxypyrene in human urine by a multi-wall carbon nanotubes-modified glassy carbon electrode

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A multi-walled carbon nanotubes (MWNTs) modified glassy carbon electrode (MWNT-GCE) was used to study the electrochemical behaviour of1-hydroxypyrene (1-OHP) and applied to its determination. The results showed that the modified electrode had a strong adsorptive ability to 1-OHP and enhances its electrochemical signal. By square wave voltammetry, the linear relationship of 1-OHP was $6 \times 10^{-9} - 8 \times 10^{-7}$ mol L^{-1} with a linear correlation coefficient of 0.996, and the detection limit was 1×10^{-10} mol L^{-1}. Compared with other published methods, this newly proposed method possesses many advantages such as very low detection limit, fast response, low cost and simplicity. And this method was applied successfully in the determination of 1-OHP in real human urine samples.

Keywords: 1-hydroxypyrene; glassy carbon electrodes; cyclic voltammetry; square wave voltammetry; multi-walled carbon nanotubes

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), are a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil, and gas, garbage or other organic substances such as tobacco or charbroiled meat [1]. According to the Protocol on Persistent Organic Pollutants signed on 24 June 1998 in Denmark [2], PAHs belong to the group of persistent organic pollutants (POPs), and they are likely to cause significant adverse effects on human health. Human biomonitoring of environmental exposures to PAHs is becoming increasingly important in the environmental and health programme of the world [3]. Because of difficulties in exposure source identification and demands of more integrated data for human exposure risk assessment, the use of biomarkers as integrated measures of exposures is increasing. Urinary 1-hydroxypyrene (1-OH-pyrene) is now largely considered to be a valuable biomarker of exposure of man and animals to polycyclic aromatic hydrocarbons (PAHs) [4], and this molecule has aroused interest among analysts. OHP in human urine has been measured with analytical equipments like HPLC with fluorescence detection (HPLC-FL) [1,5], and gas or liquid chromatography coupled to mass spectrometry (GC/LC-MS) [6,7], due to their high sensitivity and excellent selectivity. However, to our knowledge there are few published reports on the electrochemical determination of 1-OHP. Castro *et al.* proposes a new approach to the

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determination of trace amounts of 1-hydroxypyrene based on the adsorptive accumulation at the hanging mercury drop electrode [8]. The electrode response to 1-hydroxypyrene was linear up to 3.73×10^{-7} mol L^{-1} with the detection limit was 1.06×10^{-9} mol L^{-1}. Honeychurch *et al*. studied the electrochemical oxidation of 1-hydroxypyrene (1-OHP) on a screen-printed carbon electrode (SPCE), by cyclic voltammetry and bulk electrolysis [9], and this was the first detailed report on the mechanism of oxidation of 1-OHP at the carbon electrodes. After that, two modified electrodes were used to determine 1-OHP. The voltammetric determination of 1-hydroxypyrene using carbon paste electrodes modified with cyclodextrin derivatives and double stranded deoxyribonucleic acid (dsDNA) was realised [10]. The concentration range was from 2×10^{-7} to 4×10^{-6} mol L^{-1} with the limits of quantification down to 1×10^{-8} mol L^{-1}. The trace determination of 1-OHP using a disposable molecularly imprinted polymer (MIP) modified screen-printed carbon electrode (MIP-SPCE) had been developed by Kirsch *et al*. [11]. The method proved the detection of 1-OHP with a limit of detection of 182 nM and a linear range to 125 mM.

In this work, carbon nanotubes were used to modify a glassy carbon electrode due to its adsorptive accumulation. The electrochemical behaviour of 1-hydroxypyrene was investigated on the multi-walled carbon nanotubes (MWNTs) modified glassy carbon electrode and the MWNTs modified GCE was applied in the determination of trace amounts of 1-hydroxypyrene in humane urine samples.

2. Experimental

2.1 *Chemical and reagents*

The multi-wall carbon nanotubes (obtained from the Institute of nanometer materials, Central China Normal University, China) were synthesised by a catalytic pyrolysis method with a purity of 85%. Before being used, multi-wall carbon nanotubes were purified by treatment with concentrated HNO_3 as described by Tsang *et al*. [12]. Most of the multi-wall carbon nanotubes were then opened and their surface was oxidised with carboxylic, carbonyl and hydroxyl groups. But the electroactive metal impurities on/within the carbon nanotubes are not further removed and metal impurities in some instances may cause the observed 'enhancing the electrochemical current' associated with carbon-nanotube modified electrodes [13,14].

1-hydroxypyrene was purchased from Aldrich. The 3.6×10^{-3} mol L^{-1} stock solution of 1-hydroxypyrene was directly prepared in ethanol, and stored at 4°C in the dark. All the chemicals were of analytical-reagent grade unless otherwise stated and used directly without further purification. The water used in this work was re-distilled. The supporting electrolyte was 0.1 mol L^{-1} phosphate buffers and the pH was adjusted with NaOH or HCl.

2.2 *Apparatus*

All electrochemical measurements were performed with a Model CHI660C electrochemical workstation (CHI Instruments, Chenghua Instrument Co., Shanghai, China) controlled by a personal computer. A conventional three-electrode system equipped with a bare GCE or the prepared MWNTs modified GCE as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode, was used for all electrochemical measurements. All pH measurements were made with

a pHs-3 digital pH-meter (Shanghai Lei Ci Device Works, Shanghai, China) with a combined glass electrode.

2.3 *Preparation of the MWNTs-modified electrode*

A glassy carbon electrode of 3 mm diameter was used. It was polished with 0.3 μm and 0.05 μm alumna slurry (CH instrument, INC.) in sequence, then sonicated in ethanol and doubly distilled water, respectively.

Multi-wall carbon nanotube (MWNTs, 5 mg) and dihexadecylphosphate (DHP, 5 mg) were added into 5 mL doubly distilled water. A well-dispersed of MWNTs-DHP solution was obtained by ultrasonication. The GCE was coated by dropping 5 μL dispersion of MWNTs and dried under an infrared lamp. The freshly prepared MWNTs-modified electrodes were activated in 0.1 M phosphate buffer (pH 7.0) by cyclic scans from −1.0 to 1.0 V successively and continued until the shape of the cyclic curve no longer changed. After each measurement, the electrode was refreshed by potential scans mentioned above. Figure 1a and 1b show the SEM images of the bare GCE surface and MWNT-DHP on the GCE surface, respectively. From the SEM mages, it is very clear that the GCE surface is covered by many nanocarbon tubes. The active surface area of bare GCE and MWNTs modified GCE was determined by cyclic voltammetry in a solution of 5 mM $K_4[Fe(CN)_6]$ with 0.1 M potassium chloride as the supporting electrolyte. As for bare GCE, the electrode area is about 0.078 cm^2. While MWNTs modified GCE is as large as 0.253 cm^2, suggesting that MWNTs modified GCE possesses larger effective surface area.

2.4 *Analytical procedure*

Unless otherwise stated, 0.1 mol L^{-1} phosphate buffers (pH 7.0) were used as determining medium for 1-OHP analyses. The analytical procedure mainly contains two steps: accumulation step and determining step. Firstly, 1-OHP was preconcentrated onto the MWNTs modified GCE surface under 0.2 V for 120 s stirring. After that, the square wave voltammograms from 0 to 0.6 V were recorded, and the oxidation peak current at 0.30 V was measured as the analytical signal for 1-OHP.

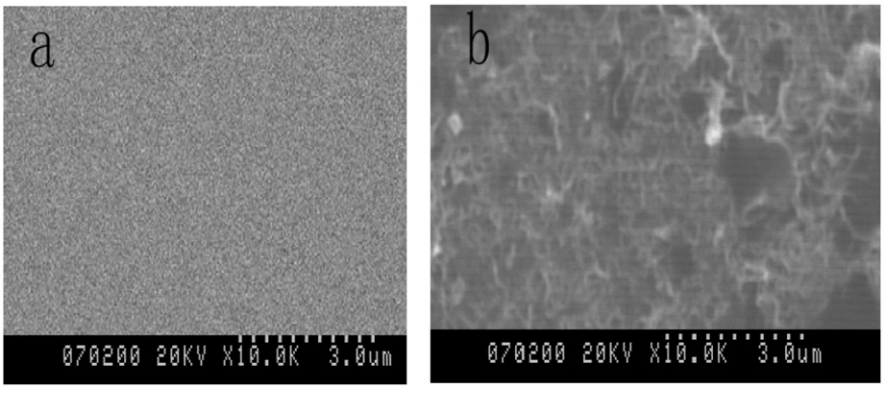


Figure 1. SEM images of GCE surface (a) and MWNT film on the GCE surface (b).

2.5 *Synchronous fluorescence spectroscopy*

Synchronous fluorescence spectroscopy was performed on a Hitachi F-2500 spectrofluorometer equipped with a 1 cm quartz cell and a thermostat bath. Synchronous fluorescence spectrometry of 1-OHP was obtained by setting $\Delta\lambda = 34$ nm with 10 nm slit widths on the emission and excitation channels, a PMT voltage of 700 V and a response time of 0.1 s. Appropriate blanks corresponding to the buffer were subtracted to correct background fluorescence.

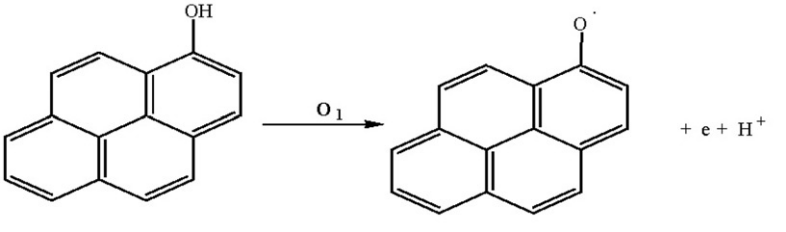
2.6 *Pretreatment of urine sample*

A urine sample was collected from a local smoker. After centrifugal separation at 5000 rpm for 15 min, 10 mL topper suspension of urine sample was collected and then was hydrolysed by adding 2 ml of 1.5×10^{-3} mol L^{-1} sodium hydroxide, and heated for 3.5 h in a boiling water bath away from light. After heating, the hydrolysed sample was adjusted to pH 3 with HCl solution. Then the above solution was extracted four times by using 6 ml of hexane. The organic collection was dried in a rotary evaporator and dissolved again in 1 mL ethanol.

3. Results and discussion

3.1 *Electrochemical behaviour of 1-OHP at MWNTs-modified GCE*

The cyclic voltammograms of a MWNT-modified GCE in phosphate buffer at pH 7.0 with and without of 1-OHP are illustrated in Figure 2. In the potential range from −1.0 to 1.0 V, there is a redox peaks for a MWNT-modified GCE (solid line), which attributes to the oxidation and reduction of MWNT [15]. Upon addition of 6×10^{-7} mol L^{-1} 1-OHP, three well-defined oxidation peaks are observed and the peak potential are at −0.11 V, 0.28 V and 0.48 V, which were denoted as O_1, O_2 and O_3, respectively (dashed line). On the reverse potential scan from 1.0 to −1.0 V, there are two reduction peaks observed for 1-OHP and the peak potential are at −0.12 V and 0.25 V, which were denoted as R_1 and R_2, respectively. However, on the second sweep, the oxidation peak current of O_2 and O_3 were reduced and the oxidation peak current of O_1 and the reduction peak current of R_1 were increased simultaneously (which were denoted as O_1' and R_1, respectively). Based on the well-established mechanism [9], the peaks O_1, O_1'/R_1, O_2/R_2, O_3 were discussed. Initially, 1-OHP is oxidised by loss of one electron and one proton to form the radical species and yielded the oxidation peak of O_1 (Equation 1).



(1)

The radical species formed the electrophlilic dimerisation and the dimerisation was oxidised and yielded the oxidation peak of O_2. So, the redox peak of R_2/O_2 can be

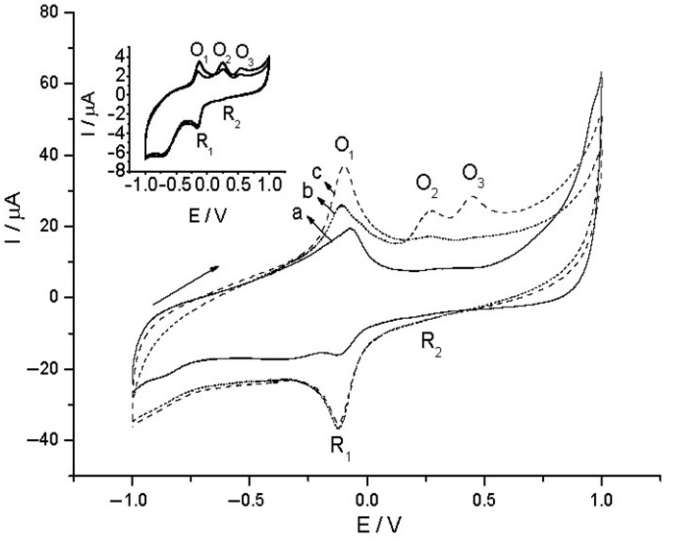
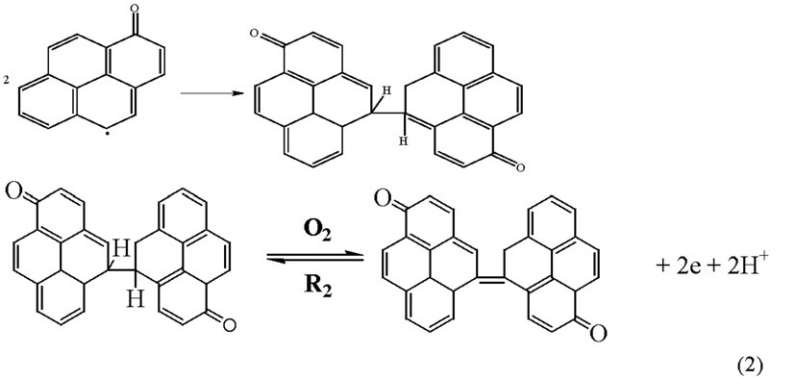


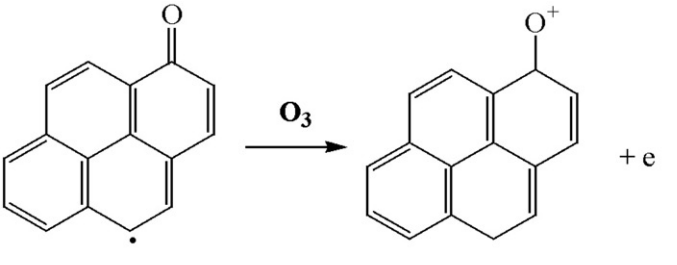
Figure 2. Cyclic voltammograms of MWNT-modified GCE in absence (a, solid line) and presence of (dash line) 6.0×10^{-7} mol L^{-1} 1-OHP in 0.1 mol L^{-1} pH 7.0 phosphate buffer at the first cycle (b) and the second cycle (c) at scan rate of 100 m Vs^{-1}. Inset: Cyclic voltammograms of bare GCE presence of 6.0×10^{-7} mol L^{-1} 1-OHP in 0.1 mol L^{-1} pH 7.0 phosphate buffer at scan rate of 100 m Vs^{-1}.

described by Equation (2).



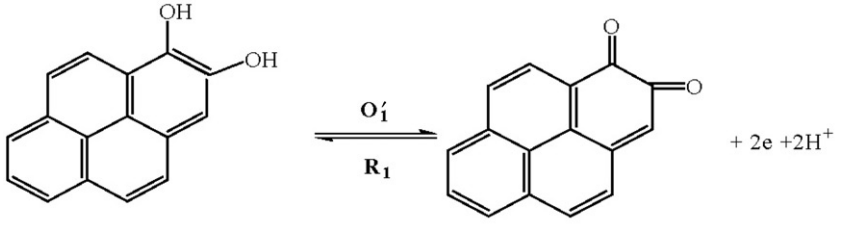
(2)

Meanwhile, the radical species in Equation (1) is oxidised by loss of one electron to produce the cation and result in the oxidation peak of O_3 (Equation 3).



(3)

The cation reacts with water and produces the hydroxylated substance. The hydroxylated substance is also electrochemically active and can be oxidised at the electrode to produce the quinoid species. The redox peak of R_1/O_1' is shown in Equation (4).



(4)

In order to illustrate the activity of MWNT towards 1-OHP, the electrochemical properties of 1-OHP at bare GCE using cyclic voltammetry was investigated, and the results are shown in the inset of Figure 1. At bare GCE, 6.0×10^{-7} mol L^{-1} 1-OHP also yields three oxidation peaks and two reduction peaks, and the peak potential are the same as at MWNTs-modified GCE. However, the peak current of 1-OHP at the MWNT-modified GCE increases almost six times as that at bare GCE. The remarkable peak current enhancement is attributed to the special properties of MWNT such as huge surface area and strong adsorptive ability. The pyrenyl group of 1-OHP, being highly aromatic in nature, can interact strongly with MWNT via π-stacking [16]. In the experiments it was found that 1-OHP adsorb strongly on the surface MWNTs-modified GCE. Thus, after each measurement the electrode was to regenerate in pH 7.0 phosphate buffer by potential scans from -1.0 to 1.0 V for 20 cycles. To avoid the interference of oxidation peak of MWNTs at -0.11 V, the oxidation peak O_2 in the first anodic sweep was recorded for the analyses of 1-OHP in the following studies.

3.2 *Effects of pH and scan rates on the oxidation of 1-OHP at MWNTs-modified GCE*

The electrochemical oxidation behaviours of 1-OHP in phosphate buffer with different pH values were studied using linear sweep voltammetry (LSV). Figure 3 shows the influence of pH on the i_{pa} and E_{pa} of peak O_2 at the at MWNTs-modified GCE. The i_{pa} increases when pH increases from 2.0 to 4.0. As further increasing pH value, the i_{pa} of peak O_2 shows decline. The i_{pa} change indicates that the i_{pa} is highest at pH 4.0. In the present study it was also found that peak O_3 merged with peak O_2 at pH from 2.0 to 6.0 and E_{pa} of peak O_3 was independent of pH. At pH above 7.0, peak O_3 and peak O_2 were split off. And the pH value is similar to physiological pH, thus, pH 7.0 phosphate buffer was employed for the determination of 1-OHP. Unlike i_{pa}, the E_{pa} of peak O_2 shifted linearly towards less positive values with increasing the pH by 0.0454 V/pH, which indicates that proton is involved in the process of electrochemical reaction of 1-OHP.

The effect of potential scan rate, ν, on the peak current and peak potential of peak O_2 were evaluated by cyclic voltammetry from -1.0 V to 1.0 V. The result showed that from 20 m Vs^{-1} to 400 m Vs^{-1}, the peak current was proportional to the scan rate (the inset in Figure 4), suggesting an adsorption-controlled process was involved in the process of electrochemical reaction of 1-OHP. For an adsorption-controlled and totally irreversible electrode process, the relationship between the peak potential E_p and the scan rate ν in the cyclic voltammogram have been expressed in Equation (5) by Laviron [17]:

$$E_p = E^{\circ\prime} + (RT/\alpha nF)\ln(RTk_s/\alpha nF) - (RT/\alpha nF)\ln \nu \quad (5)$$

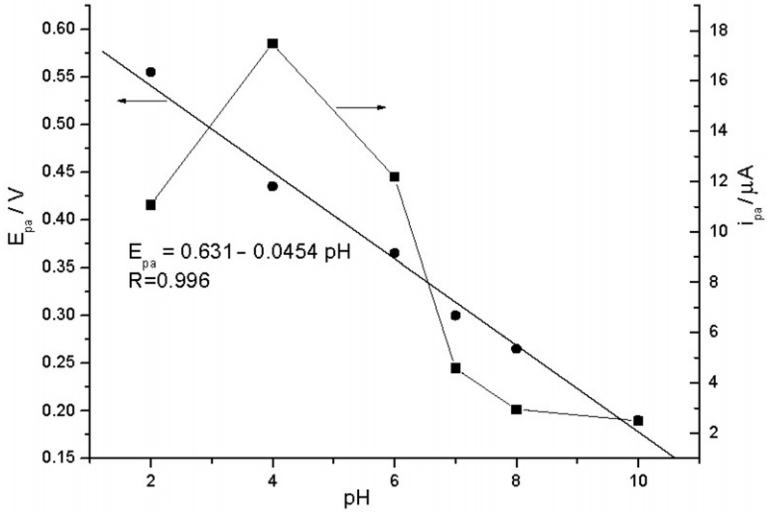


Figure 3. Effect of pH on i_{pa} and E_{pa} of peak O_2 of 1-OHP.

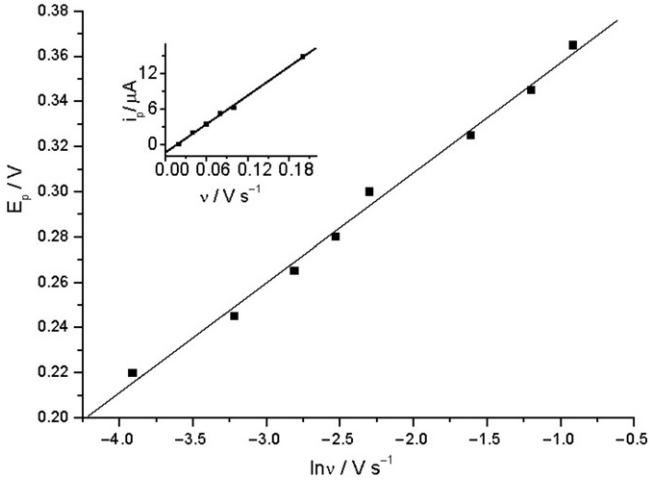


Figure 4. Dependence of peak potential, Ep, on the scan rates, lnν. Inset: Effects of scan rates on peak currents ipa.

where α is the transfer coefficient, k_s, the standard rate constant of the reaction, and $E^{\circ\prime}$ is the formal potential. According to Equation (5), the plot of $E_p \sim \ln \nu$ is linear with a slope allowing αn determined. From slope of the $E_p \sim \ln \nu$ plot in Figure 4 (0.049), $\alpha n = 0.52$ was calculated.

3.3 *Analysis application*

3.3.1 *Optimisation of experimental parameters*

Since square wave voltammetry possesses high sensitivity and excellent resolution, the electrochemical response of low concentration of 1-OHP was determined using square

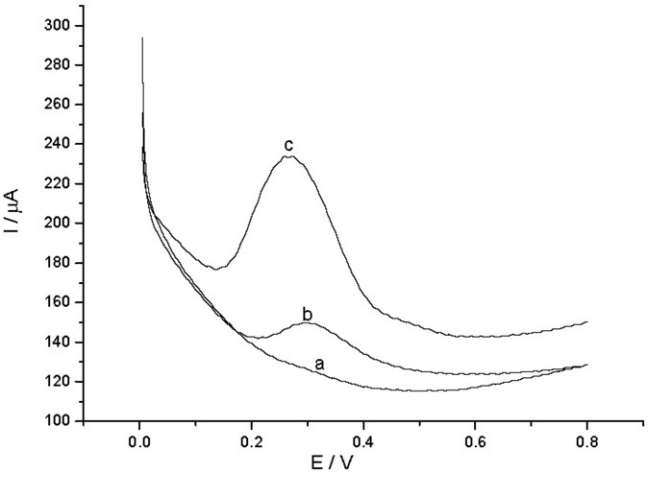


Figure 5. Square wave voltammetric responses at MWNT-modified GCE in absence (a) and presence (c) of 6.0×10^{-8} mol L^{-1} 1-OHP. Square wave voltammetric responses at bare GCE in presence of 6.0×10^{-8} mol L^{-1} 1-OHP (b). Accumulation time = 120 s, Incr E (V) = 0.004, Amplitude (V) = 0.025 and Frequency (Hz) = 15.

wave voltammetry (SWV). Under the condition of Incr E (V) = 0.004, Amplitude (V) = 0.025 and Frequency (Hz) = 15, in pH 7.0 phosphate buffer, 6.0×10^{-8} mol L^{-1} yields a well-shaped oxidation peak at 0.30V at the MWNTs-modified GCE after 120 s accumulation (Figure 5).

The relationship between the amount of MWNTs-DHP dispersion on the GCE surface and the oxidation peak current of 1-OHP were tested. The oxidation peak current is very high when using 5 μL of 1 mg L^{-1} MWNTs-DHP dispersion to coat GCE. On further increasing the amounts of MWNTs-DHP dispersion, the peak currents begin to decrease gradually. However, the amounts of MWNTs-DHP dispersion exceed 10 μL, the peak currents greatly decrease. It is mainly due to the blocking behaviour of DHP.

In this work, the effects of accumulation potential and accumulation time on the oxidation peak O_2 current of 1-OHP were also investigated. In order to evaluate the influence of accumulation potential on the determination of 1-OHP, the oxidation peak currents of 6.0×10^{-8} mol L^{-1} 1-OHP after 120s accumulation under different accumulation potentials as well as under open-circuit were measured by SWV. The influence of accumulation potential on the oxidation peak current of 1-OHP was illustrated in Figure 6. It was found that under negative potential accumulation the oxidation peak current is smaller than that at the accumulation potential of 0V. When the accumulation potential is more positive than 0V, the oxidation peak current gradually becomes higher, and at the accumulation potential of 0.2 V the oxidation peak current reached the maximum. However, when the accumulation potential is more positive than 0.2 V, the oxidation peak current gradually decreases. It may be the polarisation of the electrode influence the oxidation of 1-OHP. The influence of accumulation time on the oxidation peak current of 1-OHP was also investigated (Figure 7). The oxidation peak current increases greatly within 120 s and then remained unchanged, suggesting that the accumulation of 1-OHP at the surface of MWNTs-DHP modified GCE is saturation after accumulation of 120 s.

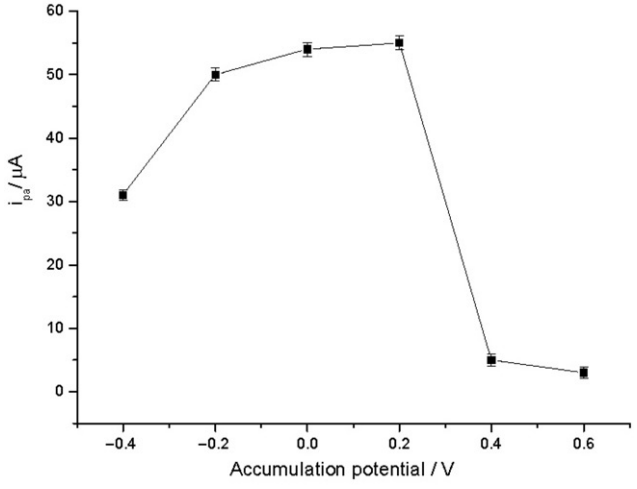


Figure 6. Effect of accumulation potential on oxidation peak current of 6.0×10^{-8} mol L^{-1} 1-OHP.

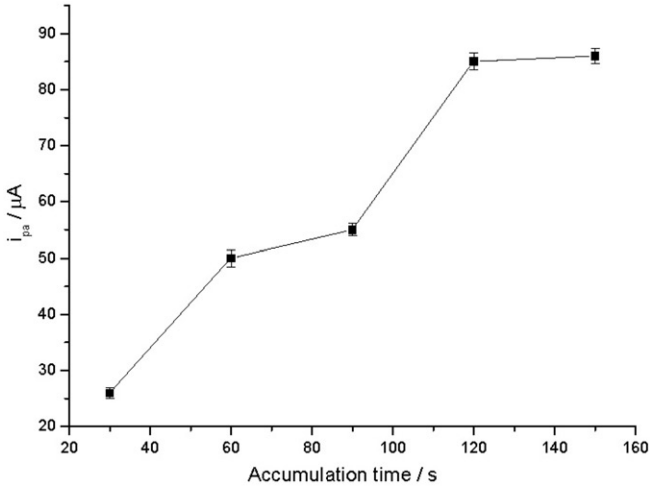


Figure 7. Effect of accumulation time on oxidation peak current of 6.0×10^{-8} mol L^{-1} 1-OHP.

3.3.2 *Calibration graph*

Under optimised experimental parameters, the calibration curve was obtained in pH 7.0 phosphate buffer by SWV. The linear segment increases from $6 \times 10^{-9} - 8 \times 10^{-7}$ mol L^{-1} with a regression equation of $i_p = 1.87 + 7.02c$ ($r = 0.996$, C in 10^{-7}mol L^{-1}, i_p in μA). It is found that this method can detect 1×10^{-10} mol L^{-1} 1-OHP after 2 min of accumulation via this method. The relative standard deviation (R.S.D.) of 3.5% for 6×10^{-8} mol L^{-1} 1-OHP ($n = 7$) showed good reproducibility. The linearity and LOD for 1-OHP by this electrochemical method was compared with other method, such as HPLC with fluorescence detection [5] and liquid chromatography coupled to mass spectrometry [6] and the results were listed in Table 1. It indicated that the presented method possessed the advantages of wide linearity range and very low detection limit for 1-OHP.

Table 1. The linearity and LOD for 1-hydroxypyrene by various method.

Analyte	Linearity	LOD	Ref.
1-hydroxypyrene		1.12×10^{-10} mol L^{-1}	5
1-hydroxypyrene	$5.96 \times 10^{-7} - 5.96 \times 10^{-5}$ mol L^{-1}	1.83×10^{-9} mol L^{-1}	6
1-hydroxypyrene	$6 \times 10^{-9} - 8 \times 10^{-7}$ mol L^{-1}	1×10^{-10} mol L^{-1}	This method

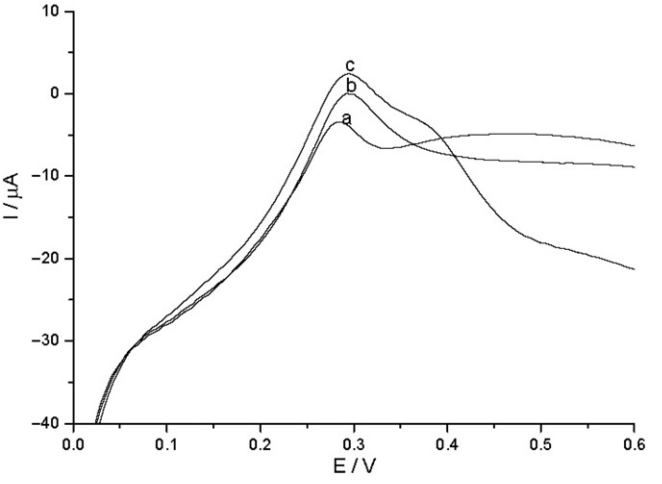


Figure 8. Baseline-subtracted square wave voltammograms of urine sample at MWNTs-modified GCE in pH 7.0 phosphate buffer (a); a + 3.0×10^{-8} mol L^{-1} PCP (b); a + 6.0×10^{-8} mol L^{-1} 1-OHP (c). Other conditions are the same as in Figure 5.

The stability of the MWNT-modified GCE was evaluated by measuring the current responses at a fixed 1-OHP concentration of 6×10^{-8} mol L^{-1} over a period of 3 weeks. The MWNT-modified GCE was used daily and stored in the air. The experimental results indicated that the current responses deviated only 2.3%, revealing that the MWNT modified GCE fabricated by this method possesses long-term stability.

3.3.3 *Interferences*

To evaluate the potential effect of foreign species on the determination of 1-OHP at 6.0×10^{-8} mol L^{-1} level, a systematic study was carried out under the above optimised conditions. The peak currents of 1-OHP in the absence and presence of foreign species were measured by SWV, respectively, and the error was consequently obtained. It is found that 6.0×10^{-6} mol L^{-1} Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, Cu^{2+}, and some organic compounds such as urea, galactose, lactic acid, vitamin A and serotonin did not interfere with the oxidation signal of 1-OHP (signal change below 5%). But the compounds perhaps exist in urine such as ascorbic acid, uric acid and cytochrome c interfere largerly the oxidation signal of 1-OHP because they could possibly be oxidised on the carbon nanotubes modified electrode nearby at the oxidation potential of 1-OHP. These results indicate that pretreatment of urine sample before analysis is necessary.

Table 2. 1-hydroxypyrene recovery studies in urine from a frequent smoker ($n = 7$).

	$C_{1\text{-OHP}}$/mol L^{-1}					
Sample	Found before adding	Added	Expected	Found after adding	RSD (%)	Recovery (%)
1	6.78×10^{-8}	3.0×10^{-8}	9.78×10^{-8}	1.007×10^{-7}	3.6	102.9
2	6.75×10^{-8}	6.0×10^{-8}	1.275×10^{-7}	1.224×10^{-7}	4.5	96.0
3	6.80×10^{-8}	9.0×10^{-8}	1.580×10^{-7}	1.575×10^{-6}	2.3	99.6

Table 3. 1-OHP in urine from a smoker comparision between results obtained with the voltammetric method and a synchronous fuorescence spectrometric method.

	$C_{1\text{-OHP}}$/mol L^{-1}		
Sample	Voltammetric method	Spectrophotometric method	Relative error (%)
1	6.78×10^{-8}	6.69×10^{-8}	1.3
2	6.75×10^{-8}	6.58×10^{-8}	2.5
3	6.80×10^{-8}	6.56×10^{-8}	3.5

3.3.4 *Determination of 1-OHP in urine samples by MWNT-modified GCE*

In order to ascertain its potential application, this developed electrochemical method was employed to detect 1-OHP in a pretreated fresh urine sample of a frequent smoker. After 1 mL of the extract solution from the urine sample was placed in the electrochemical cell, 5 ml of pH 7.0 phosphate buffers was added. The extract solution from the above samples was detected on MWNT-modified GCE by SWV. After accumulation for 120 s at the accumulation potential of 0.2 V, the baseline-subtracted SWV were recorded (curve a in Figure 8). In order to establish the suitability of the proposed method, known amounts of the standard 1-OHP were added into the analytical solution and the same procedure were applied (curves b and c in Figure 8). The amount of 1-OHP present in each sample is obtained by the standard addition method and the results are listed in Table 2. The recovery is excellent, indicating that this method can be used in the practical sample analysis. Comparative determinations of the concentration of 1-OHP in urine sample were carried out by the synchronous fluorescence spectrometric method [18]. The results are shown in Table 3 with a good agreement.

4. Conclusions

In this work, the electrochemical behaviour of 1-OHP was studied on the MWNTs modified glassy carbon electrode MWNTs and the mechanism for oxidation of 1-OHP was also discussed. On account of the strong adsorptive ability of MWNTs with the pyrenyl group of 1-OHP, the oxidation peak current of 1-OHP greatly increases at the MWNT-modified GCE compared with the bare GCE. Based on this, a sensitive and

convenient electrochemical method was developed for the determination of 1-OHP and the analytical parameters were optimised. This method was applied successfully in the determination of 1-OHP in real human urine samples. Compared with other method, this new method possessed higher sensitivity, extreme simplicity and rapid response. This method is also suitable for environmental samples after the pretreatment of the samples.

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