



Modification of electrodes using conductive porous layers to confer selectivity for the voltammetric detection of paracetamol in the presence of ascorbic acid, dopamine and uric acid

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ABSTRACT

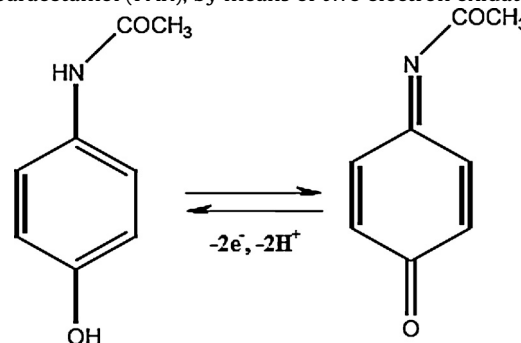
A glassy carbon electrode (GCE) has been modified with multiwalled carbon nanotubes (MWCNTs) for the selective detection of paracetamol (PAR) in the presence of ascorbic acid (AA), dopamine (DA) and uric acid (UA). The oxidation of PAR shows a quasi-reversible response on a naked GCE at which an appreciable overpotential is required to drive the two electron oxidation. However, the peak-to-peak separation is seen to reduce and the electrochemical signal appears more reversible as the GCE is modified with an increasingly thick layer of MWCNTs. The results indicate that both anodic and cathodic peaks occur at lower overpotential with increasing layer thickness on the electrode surface, and that the overall peak-to-peak separation decreases as a result. The data are consistent with a transition from planar diffusion to a thin layer character as the potential required for the oxidation of PAR shifts to lower potentials. The experimental results show that the use of conducting porous layers on the surface of electrodes can be utilised to modify the mass transport regime from planar diffusion to a thin layer character that this alteration can also favourably facilitate the electrochemical discrimination between species which oxidise or reduce at similar potentials under planar diffusion conditions. The modified electrode was used for the determination of PAR using square wave voltammetry in 0.1 M phosphate buffer solution (PBS) at pH 7. The results showed that the peak currents were proportional to the concentrations of PAR with a linear dynamic range of 2.0×10^{-10} M to 1.5×10^{-5} M and a detection limit of 9.0×10^{-11} M was obtained. The method has successfully been applied for the determination of PAR in pharmaceuticals.

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1. Introduction

Voltammetric detection provides a highly sensitive approach to the electroanalysis of a wide range of analytes [1–3]. However, this approach can sometimes be restricted by limitations of selectivity due to the interference from the other redox active molecules which may undergo electrolysis at similar potentials to the target species in the medium [4–6].

Such an example arises in the determination of the analgesic drug, paracetamol (PAR), by means of two electron oxidation:



using carbon based electrodes, since molecules such as ascorbic acid (AA), dopamine (DA) and uric acid (UA) all display redox behaviour at potentials close to those required for the oxidation of PAR. The most important strategy to overcome such problems is to modify the surface of the electrode to produce a chemically

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modified electrode, that aims to alter the electrode kinetics of both target species and the interfering species so that the potential under which the target species undergo oxidation becomes shifted from that required to electrolyse the interfering species [7–11].

Voltammetric nanosensors based on CNTs represent a new and interesting alternative for the quantification of different analytes [12–15]. The performance of CNT modified electrodes has been found to be much superior to those of other carbon electrodes in terms of response time, increased sensitivity, resistance to surface fouling, decreased overpotentials, reusability and limits of detection [16].

Paracetamol, also known as acetaminophen is an effective pain killer used for the widespread relief of pains associated with many parts of the body [17]. The overdose of PAR can lead to the accumulation of toxic metabolites which may cause hepatotoxicity and nephrotoxicity [18]. Therefore controlling the amount of PAR in pharmaceuticals is of great importance for the general public health. A number of analytical procedures have been reported for the analysis of PAR in pharmaceutical forms or biological fluids including chromatography [19], spectrophotometry [20], chemiluminescence [21], capillary electrophoresis [22], FTIR and Raman spectrometry [23] and flow injection analysis using various methods of detection [24–26]. However, these techniques are expensive and require time-consuming derivatization step and also in some cases low sensitivity and selectivity makes them unsuitable for a routine analysis. On the other hand, voltammetric methods have several advantageous owing to their simplicity, high sensitivity and rapidness [7,16]. The development and application of electrochemical sensors for the determination of PAR has received considerable interest in last few decades since PAR is an electroactive compound which can be oxidised electrochemically. Most electrochemical methods rely on the modification of electrodes such as MWCNT modified pyrolytic graphite electrode [6], carbon nanoparticles modified GCE [27], SWCNT-graphene modified GCE [28], carbon nanotube modified screen printed electrode [29], SWCNT modified ceramic electrode [30], and D50wx2-GNP-modified carbon paste electrode [31].

In this paper, we report experiments for the detection of PAR in the presence of AA, DA and UA at a glassy carbon electrode modified with multi-walled carbon nanotubes (MWCNTs). It is shown that the use of conducting porous layers on the surface of electrodes can be utilised to modify the mass transport regime from planar diffusion to a thin layer character that can favourably facilitate the electrochemical discrimination between species which oxidise or reduce at similar potentials under planar diffusion conditions [4,32–34]. This study presents an experiment to show that the modification of an electrode with porous layers of conducting material can shift voltammetric peaks in an analytically useful manner.

2. Experimental

2.1. Chemical reagents

All chemicals were obtained from Sigma–Aldrich or Merck with highest grade available and used without further purification. Multiwalled carbon nanotubes (MWCNTs) of 95% purity were obtained from NanoLab, USA. PAR stock solution was prepared with 0.1 M phosphate buffer at pH 7 (prepared from KH_2PO_4 and Na_2HPO_4). All solutions were prepared using ultra pure water. Oxygen-free nitrogen was bubbled through the cell prior to each experiment. All experiments were carried out at room temperature.

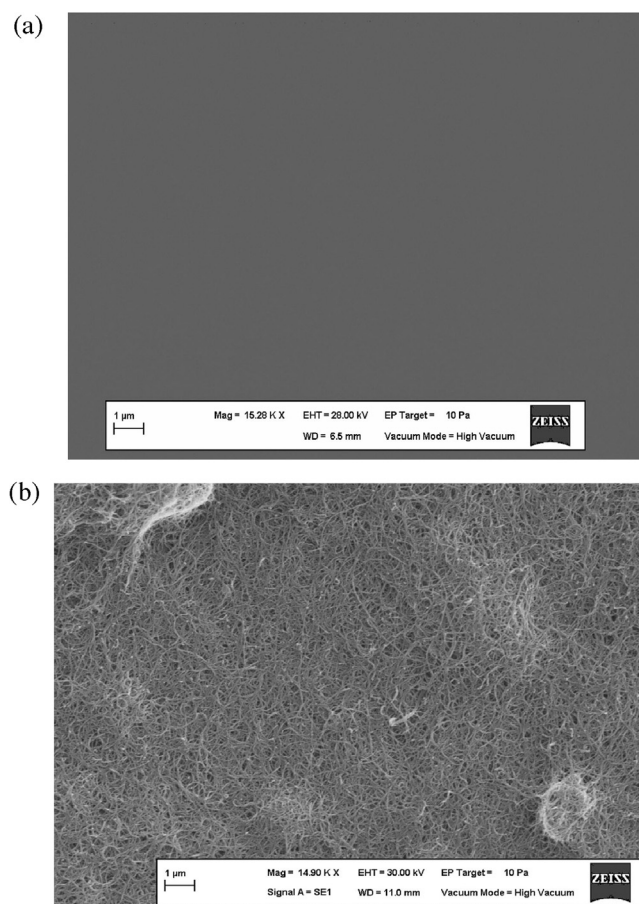


Fig. 1. SEM images of bare GCE (a) and MWCNT modified GCE (b).

2.2. Instrumentation

Electrochemical experiments were performed using an Eco-Chemie Autolab PGSTAT 12 potentiostat/galvanostat (Utrecht, The Netherlands) with the electrochemical software package 4.9. A three-electrode system was used: a glassy carbon electrode and a glassy carbon electrode modified with multiwalled carbon nanotubes as working electrodes [3 mm in diameter (Bioanalytical Systems, Lafayette, USA)], a Pt wire counter electrode and a Ag/AgCl reference electrode (Metrohm, Switzerland). Prior to modification with MWCNTs, the GCE was polished with 1 μm and 0.3 μm alumina. The electrode was then sonicated for 5 min in ethanol. All experiments were carried out at room temperature.

2.3. Preparation of MWCNT-modified electrodes

Multiwalled carbon nanotubes were first dispersed in chloroform (1 mg in 5 ml). This was placed into an ultrasonic bath for 10 min, after which an aliquot of known volume was cast onto the glassy carbon electrode and the solvent allowed to evaporate. SEM images of bare GCE (a) and MWCNT/GCE (b) are given in Fig. 1.

3. Results and discussion

3.1. Voltammetric behaviour of paracetamol

Cyclic voltammetry was performed at a bare glassy carbon electrode for a 1.0×10^{-6} M solution of PAR in 0.1 M phosphate buffer at pH 7. The oxidation of PAR shows a quasi-reversible response on a naked glassy carbon electrode at which an appreciable

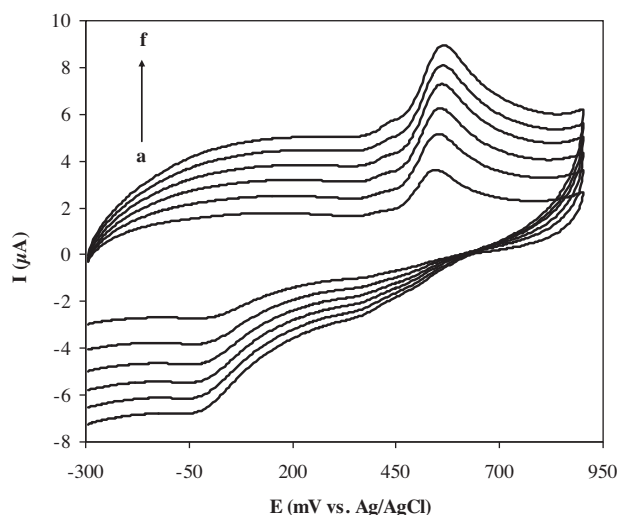


Fig. 2. Cyclic voltammograms of 1.0×10^{-6} M PAR at bare GCE in 0.1 M PBS at pH 7.0. Scan rates increasing from 25 mV/s to 150 mV/s. (a) 25 mV/s; (b) 50 mV/s; (c) 75 mV/s; (d) 100 mV/s; (e) 125 mV/s; (f) 150 mV/s. Equilibrium time: 5 s.

overpotential is required to drive the two electron oxidation. Fig. 2 shows cyclic voltammograms of PAR recorded at different scan rates. Log of peak current against log of scan rate showed slope close to 0.5, suggesting that the redox wave is diffusional in nature.

The cyclic voltammograms of 1.0×10^{-6} M PAR recorded at different scan rates using a GCE modified with MWCNTs are shown in Fig. 3. The peak current was observed to vary linearly with scan rate for an electrode modified with 0.15 μg MWCNTs. The change in the peak current response from a square root to a linear dependence on scan rate is attributed to the transition from planar diffusion to thin layer behaviour [4,32]. As the signals were seen immediately on exposure of the electrode to solution, and changed only a little over a period of ca. 10 min from which it was inferred that adsorption effects were considerably less than solution-phase signals. Although, the distinction between thin layer diffusion and adsorption effects is not easy to make, especially where the adsorption is rapidly reversible we infer that thin layer effects may dominate in the oxidation of PAR as strong oxidative signals are seen immediately on exposure to the solution, changing relatively little with prolonged immersion of the electrode prior to oxidation [32].

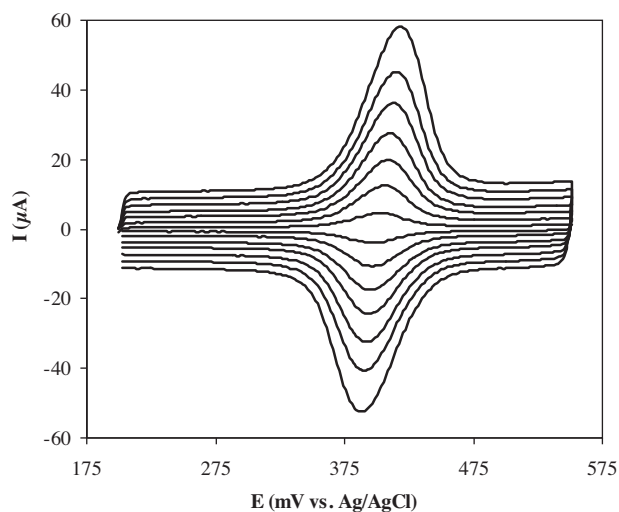


Fig. 3. Cyclic voltammograms of 1.0×10^{-6} M PAR at 0.15 μg MWCNT/GCE in 0.1 M PBS at pH 7.0. Scan rates increasing from 25 to 175 mV/s. Equilibrium time: 5 s.

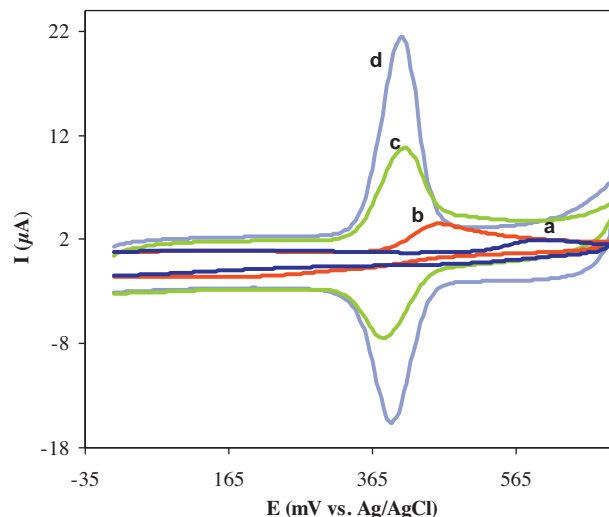


Fig. 4. Cyclic voltammograms of 1.0×10^{-6} M PAR in 0.1 M PBS at pH 7.0 at a GCE electrode modified with 0.00 μg (a), 0.025 μg (b), 0.1 μg (c) and 0.15 μg (d) MWCNTs. Scan rate: 100 mV/s. Equilibrium time: 5 s.

The effect of the mass of MWCNTs on the electrode surface was then examined. Cyclic voltammograms were recorded at a glassy carbon electrode modified with varying amounts of MWCNTs, shown in Fig. 4. The peak-to-peak separation is seen to reduce and the electrochemical signal appears more reversible as the glassy carbon electrode is modified with an increasingly thick layer of MWCNTs. A plot of peak potential vs. mass of MWCNTs is shown in Fig. 5. The results indicate that both anodic and cathodic peaks occur at lower overpotential with increasing layer thickness on the electrode surface, and that the overall peak-to-peak separation decreases as a result. The data are consistent with a transition from planar diffusion to a thin layer character as the potential required for the oxidation of PAR shifts to lower potentials [4,32–34].

3.2. The effect of pH

Fig. 6 shows that the effect of pH on the peak potential of PAR using cyclic voltammetry at GCEs modified with 0.15 μg MWCNTs in 0.1 M PBS at pH 7. The results show that the oxidation peak potential shifts towards negative potential with increasing pH. This

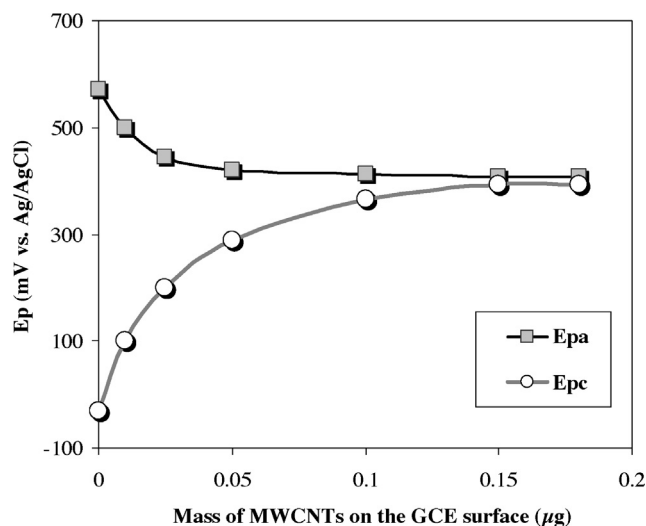


Fig. 5. Plot of peak potentials of 1.0×10^{-6} M PAR solution vs. mass of MWCNTs on the electrode surface.

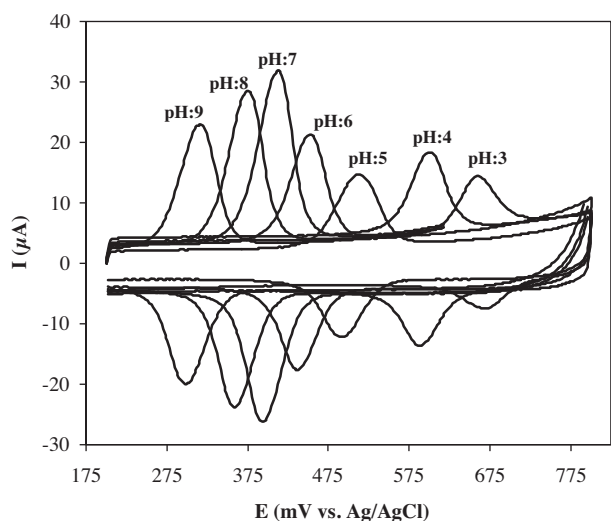


Fig. 6. Cyclic voltammograms of 1.5×10^{-6} M PAR at $0.15 \mu\text{g}$ MWCNT/GCE in 0.1 M PBS at different pH values. pH: 3.0; 4.0; 5.0; 6.0; 7.0; 8.0; 9.0. Scan rate: 100 mV/s. Equilibrium time: 5 s.

shows that the redox couple of PAR includes transfer of protons in oxidation and reduction process. The slope of oxidation peak potential (E_{pa}) vs. pH is 56.9 mV/pH (Fig. 7). The linear regression equation is $E_{\text{pa}} \text{ (mV)} = 820.0714 - 56.8929 \text{ pH}$ with a correlation coefficient of 0.9920. This indicated that the proportion of electrons and protons involved in the reaction is 1:1. Since equal numbers of electrons and protons should be involved in the electrode reaction, the number of hydrogen ions involved in the whole electrode reaction is 2. The proposed PAR reaction at a GCE modified with MWCNTs is given in Scheme 1.

3.3. Calibration equation for the determination of paracetamol

The square voltammetric determination of the concentration of PAR at glassy carbon electrodes modified with $0.15 \mu\text{g}$ MWCNTs was performed in 0.1 M PBS at pH 7 (Fig. 8). The anodic peak currents were plotted against the concentration of PAR

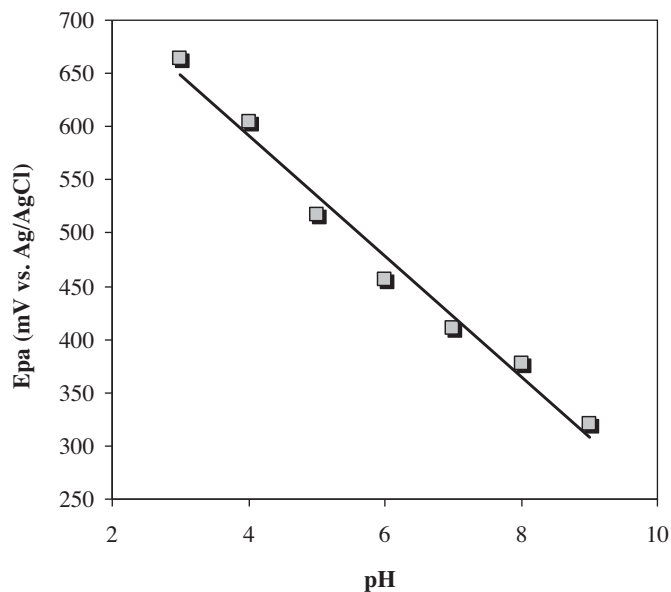
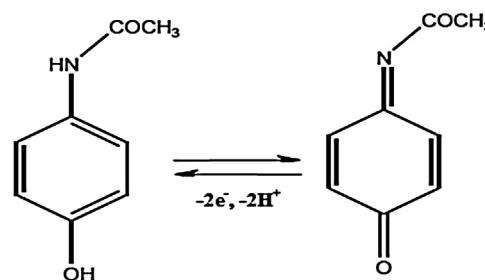


Fig. 7. A plot of anodic peak potentials of PAR vs. solution pH at $0.15 \mu\text{g}$ MWCNT/GCE.



Scheme 1. Proposed PAR reaction at a GCE modified with MWCNTs.

as shown in Fig. 8 inset (A and B). The anodic peak currents were linear with the concentrations of PAR over two intervals in the range of 2.0×10^{-10} M to 2.5×10^{-8} M (A) and 2.5×10^{-8} M to 1.5×10^{-5} M (B). The first linear regression equation was $I_{\text{pa}} \text{ (}\mu\text{A)} = -0.06185 + 202.1743C \text{ (}\mu\text{M)}$ with a correlation coefficient of 0.9993. The second was $I_{\text{pa}} \text{ (}\mu\text{A)} = 6.7992 + 0.6025C \text{ (}\mu\text{M)}$ with a correlation coefficient of 0.9962. The detection limit was 9.0×10^{-11} M ($S/N = 3$). Also, the analytical parameters obtained by the proposed method are well compared with several methods for the determination of PAR as shown in Table 1.

3.4. Reproducibility and stability of modified electrode

The relative standard deviation (RSD) of 10 successive scans was 2.5% for 1.5×10^{-6} M PAR. This indicated that the reproducibility of the modified electrode was excellent. However, the modified electrode should be well treated to maintain its reproducibility. It was found that 20 cycles of scanning in 0.1 M PBS in the potential range 0.0–0.8 V could regenerate clean background CV curves and the modified electrode was ready for the next experiment or storage in 0.1 M PBS. Also, the current response decreased only by 5–6% over a week for storage in 0.1 M PBS.

3.5. Detection of paracetamol in the presence of AA, DA and UA

Electrochemical detection provides a sensitive approach to the detection of a wide range of analytes [1–3]. However, this approach is sometimes restricted due to the interference from the other redox active molecules which may undergo oxidation/reduction

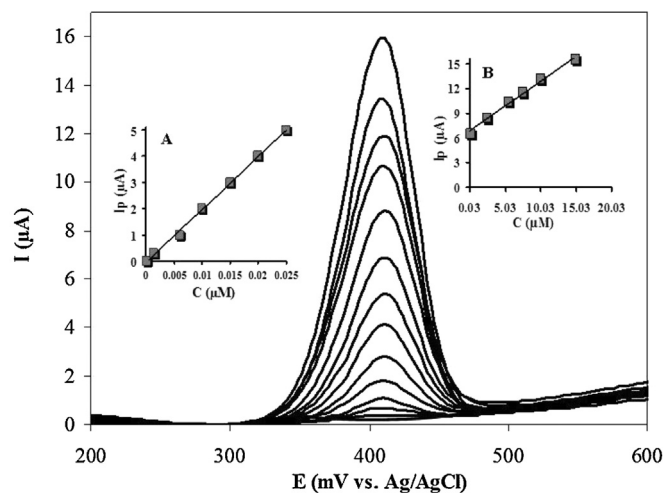


Fig. 8. Square wave voltammograms of increasing concentrations of PAR at $0.15 \mu\text{g}$ MWCNT/GCE in 0.1 M PBS at pH 7.0. PAR concentrations: 0.00; 0.0002; 0.0015; 0.006; 0.010; 0.015; 0.020; 0.025; 0.125; 2.50; 5.50; 7.50; 10.0; 15.0 μM . Frequency: 22 Hz. Step potential: 100 mV/s. Amplitude: 50 mV/s. Equilibrium time: 5 s. Inset: plots of peak currents vs. concentration of PAR.

Table 1
The application results of various electrodes for the determination of PAR.

Electrode	pH used	Linear range (μM)	Detection limit (nM)	Reference
C ₆₀ /GCE	7.2	50–1500	50,000	[37]
N-DHPB-MWCNT/CPE	7.0	15–270	10,000	[38]
PANI-MWCNT/GCE	5.5	1–100	2500	[39]
PAY/nano-TiO ₂ /GCE	7.0	12–120	2000	[40]
PEDOT/SPE	5.0	4–400	1390	[41]
ZrO ₂ /CPE	7.0	1–2500	912	[42]
C-Ni/GCE	3.0	2–230	600	[43]
f-MWCNT/GCE	8.0	3–300	600	[44]
PR/MCPE	5.0	0.7–100	530	[45]
IL/CNTPE	7.0	1–600	500	[46]
PSS-PDDA/GE	7.0	25–400	500	[47]
Poly(taurin)-MWCNT/GCE	7.3	1–100	500	[48]
CoOx/CCE	13	5–35	370	[49]
Carbon ionic liquid electrode	4.6	1–2000	300	[50]
Nafion/TiO ₂ -graphene	7.0	1–100	210	[36]
Chitosan-MWCNT/GCE	7.0	1–145	100	[51]
Ppyox/AZ/Au	2.8	0.2–100	80	[52]
MWCNT-ACS/GCE	9.0	0.05–2	50	[35]
MWCNT/CPE	4.0	0.1–100	50	[53]
Carbon NP/GCE	7.0	0.1–100	50	[27]
Graphite oxide/GCE	2.0	0.165–26.5	40	[54]
SWCNT-DPF/GCE	6.5	0.1–20	40	[55]
SWCNT-graphene/GCE	7.0	0.05–64.5	38	[28]
Graphene/GCE	9.3	0.1–20	32	[56]
ISSM-CNT/PE	7.0	0.112–69.4	25.8	[57]
MWCNT/BPPGE	7.5	0.01–20	10	[6]
Poly(CCA)/GCE	6.0	0.1–10	10	[58]
D50wx2-GNP/GCPE	6.0	0.0334–45.5	4.71	[31]
MWCNT/GCE	7.0	0.0002–15	0.09	This work

at similar potentials to the target species in the medium as shown in Fig. 9 where only one broad oxidation peak is observed for a mixture of AA, DA, UA and PAR at a naked glassy carbon electrode in 0.1 M PBS at pH 7. However, 4 well-defined peaks were observed for a mixture of AA, DA, UA and PAR at a GCE modified with 0.15 μg MWCNTs (Fig. 10). The peak current increases linearly with the concentration of PAR in the presence of AA, DA and UA indicating that these three potential interfering molecules do not interfere with the determination of PAR. It is clearly shown that modification of glassy carbon electrodes using conductive porous layers enables selective detection of PAR in the presence of AA, DA and UA. The modified electrode also exhibits a high electrocatalytic effect towards AA, DA and UA with a distinct shift of the oxidation potential of AA, DA

and UA in the cathodic direction and a marked enhancement of the current response and also provides larger peak to peak separation between AA, DA, UA and PAR for their easier simultaneous determination. Therefore, the proposed electrode is selective not only for the detection of PAR in the presence of AA, DA and UA but also selective for the simultaneous determination of these four species present in a mixture as shown in Fig. 11. These results indicate that covering electrode surfaces with porous layers can modify the mass transport regime from planar diffusion to a thin layer character and this alteration can in favourable circumstances facilitate the voltammetric discrimination between species in the target medium

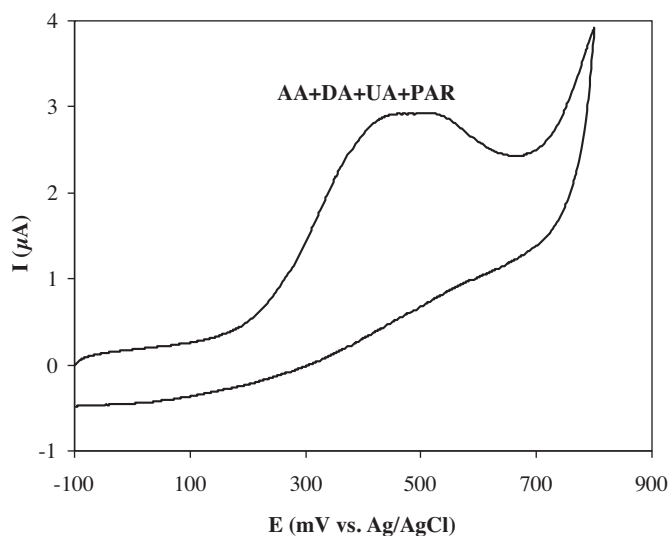


Fig. 9. A cyclic voltammogram of the mixture of 1.25×10^{-4} M AA; 1.75×10^{-7} M DA; 2.0×10^{-4} M UA and 7.5×10^{-6} M PAR at 0.15 μg MWCNT/GCE in 0.1 M PBS at pH 7.0. Scan rate: 100 mV/s. Equilibrium time: 5 s.

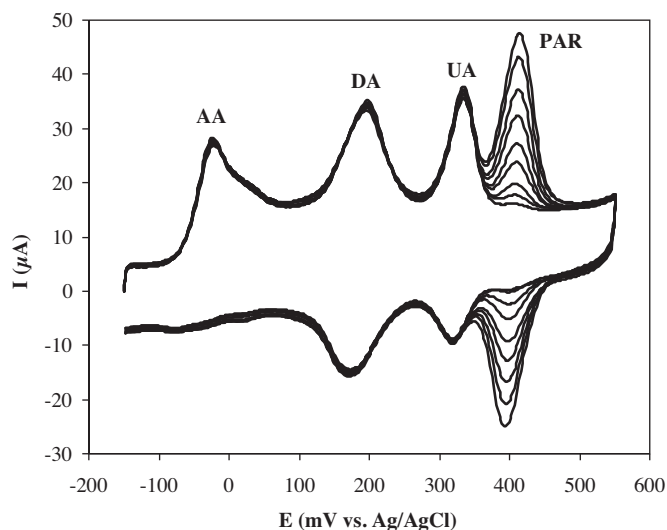


Fig. 10. Cyclic voltammograms of the mixture of 1.25×10^{-4} M AA, 1.75×10^{-7} M DA, 2.0×10^{-4} M UA and increasing concentrations of PAR at 0.15 μg MWCNT/GCE in 0.1 M PBS at pH 7.0. Scan rate: 100 mV/s. Equilibrium time: 5 s. PAR concentrations: 0.00; 5.0×10^{-7} M; 7.5×10^{-7} M; 1.0×10^{-6} M; 1.2×10^{-6} M; 1.5×10^{-6} M; 3.0×10^{-6} M; 5.0×10^{-6} M; 7.5×10^{-6} M.

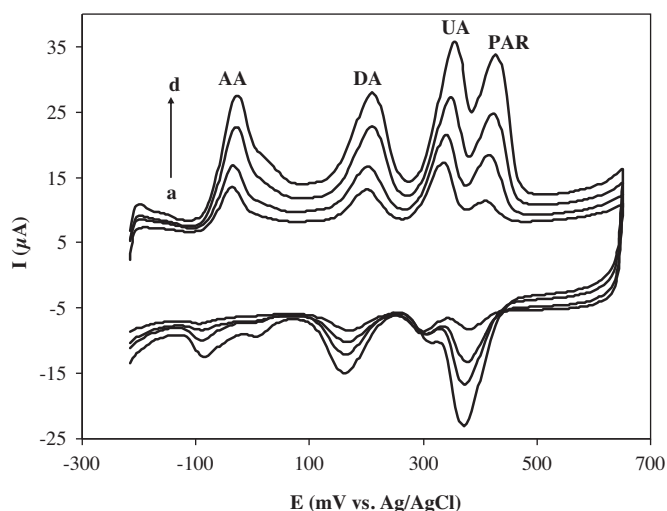


Fig. 11. Cyclic voltammograms of the mixture of simultaneously increasing concentrations of AA, DA, UA and PAR at 0.15 μg MWCNT/GCE in 0.1 M PBS at pH 7.0. Scan rate: 100 mV/s. Equilibrium time: 5 s. (a) 2.5×10^{-5} M AA; 1.0×10^{-7} M DA; 1.0×10^{-4} M UA; 3.0×10^{-7} M PAR. (b) 5.0×10^{-5} M AA; 1.25×10^{-7} M DA; 1.25×10^{-4} M UA; 7.5×10^{-7} M PAR. (c) 1.0×10^{-4} M AA; 1.50×10^{-7} M DA; 1.5×10^{-4} M UA; 1.0×10^{-6} M PAR. (d) 1.25×10^{-4} M AA; 1.75×10^{-7} M DA; 2.0×10^{-4} M UA; 1.5×10^{-6} M PAR.

Table 2

Results of the determination of PAR in tablets.

Content (mg)	Found (mg)	Recovery%	RSD%
500.0	495.0 ± 7.2	99.0	1.6

Mean \pm standard deviation ($n = 5$).

[4,32–34]. This study presents an experiment to show that the modification of an electrode with porous layers of conducting material can shift voltammetric peaks in an analytically useful manner [32].

3.6. Determination of paracetamol in pharmaceutical preparations

Square wave voltammetric determination of PAR in tablets on a glassy carbon electrode modified with 0.15 μg MWCNTs was referred to the regression equation. The analysis of tablets using the proposed method is summarised in Table 2. A mean recovery of 99.0% with RSD of 1.6% was obtained using the proposed method for the voltammetric analysis of tablets. The results of the drug analysis obtained from the proposed method are in close agreement with the claimed value. The results obtained are also comparable with the results obtained from square wave voltammetry at multiwalled carbon nanotube-alumina coated silica nanocomposite electrode with a recovery of 98.2% [35], differential pulse voltammetry at nafion/TiO₂-graphene modified electrode with a recovery of 98.6% [36]. However, the experimental results indicate that the proposed procedure is more precise and accurate for the determination of PAR in drug samples.

4. Conclusion

We have presented experiments to show that the modification of a glassy carbon electrode with porous layers of conducting material can shift voltammetric peaks in an analytically useful manner. The change in the peak current response from a square root to a linear dependence on scan rate is attributed to the transition from planar diffusion to thin layer behaviour. The results indicate that both anodic and cathodic peaks occur at lower overpotential with

increasing layer thickness on the electrode surface, and that the overall peak-to-peak separation decreases as a result. It is clearly shown that modification of glassy carbon electrodes using conductive porous layers enables selective detection of PAR in the presence of AA, DA and UA. It is shown that the peak currents are proportional to the concentrations of PAR with a two linear dynamic range of 2.0×10^{-10} M to 1.5×10^{-5} M and a detection limit of 9.0×10^{-11} M is obtained.

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