Regular Article

Sensitive Voltammetric Determination of Acetaminophen at Poly(4-vinyl pyridine)/Graphene Composite Modified Electrode

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This study demonstrates the use of a selective and sensitive voltammetric sensor for determination of acetaminophen (AC). This was performed by modifying a glassy carbon electrode with composite film of poly(4-vinylpyridine) and graphene sheet (P4VP/GR-GCE). The redox peak currents of AC increased significantly at P4VP/GR-GCE. The result was achieved by the synergistic effect of combined electron mediator property of P4VP along with remarkable physical properties of GR which improved the kinetics of the catalytic oxidation of AC. The P4VP/GR-GCE exhibited excellent sensitivity, good reproducibilityand long-termstability for measuring AC with detection limits of 3.2 nM in the linear range of 0.04-300 µM. The novel developed sensor was not interfered by physiologically common interference, *viz.* ascorbic acid (AA) and uric acid (UA). The P4VP/GR-GCE was also successfully applied for detection of AC in tablets and urine samples, so it is reasonable to expect its broad use as AC sensor.

INTRODUCTION

Acetaminophen (AC) (N-acetyl-p-aminophenol or paracetamol) is one of the most commonly and extensively employed drugs. It is widely used as an analgesic and antipyretic drug for the reduction of fever and as a pain killer for headache, backache and arthritis [1,2]. The serum or plasma concentration of AC in humans follows a standard drug dose range from 50-100 µM [3,4]. Overdoses of AC can lead to the accumulation of toxic metabolites, which may cause kidney and liver damage [2,4,5]. Therefore, a simple, facile, sensitive and accurate method is required to determine and control the AC doses in pharmaceutical formulations and human plasma.

To date, several analytical methods such as spectrophotometry [6], high-performance liquid chromatography [7], titrimetry [8], chemiluminescence [9], capillary electrophoresis [10], flow-injection analysis [11] and electrochemical [2,4,12] have been reported for determination of AC. However, these methods are sometimes unsuitable for routine analysis due to the requirements for expensive instruments, long analysis time and sample pretreatment. Thus, a simple, sensitive, fast and accurate analytical method for determining AC in pharmaceutical preparations and human plasma is needed. Electrochemical detection is the most popular method because it is fast, simple operation, high sensitive and reproducible [1,2,4]. Determination of AC by using electrochemical methods proceeds through oxidation of AC to N-acetyl-*p*-quinoneimine on a variety of chemically modified working electrodes [1,2,13]. The improving catalytic activity, conductivity, sensitivity and easy electron transfer, are important factors in construction of these modified electrodes. Carbon-based nanomaterials such as

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multiwalled carbon nanotubes (MWCNTs), graphene (GR) and their composites have attracted more attentions in the field of chemically modified electrodes [14,15]. It is revealed that GR as a single layer of carbon atoms in a closely packed honeycomb two-dimensional lattice, has excellent conductivity, high specific surface area, high mechanical, thermal and chemical stabilities compared with CNTs [1,16]. Its unique crystal structure makes it extremely attractive as a support material to promote the electrochemical reactivity of molecules on the modified electrode surface [17]. Functionalization and dispersion of GR sheets are also crucial in their applications. The functionalized and defective GR are more hydrophilic and can be easily dispersed in solvents with long-term stability [18]. In addition, appropriate chemical functionalization of GR for example by conventional acid treatment method, for formation of -COOH and -OH groups, prevents the agglomeration of single layer GR and aggregation can also be reduced by the attachment of other small molecules or polymers to the GR sheets [18,19]. Meanwhile, non-covalent functionalization, *e.g.,* co-dispersion with polymers, has proven successful in solubilizing GR [20].

On the other hand, using of conducting polymers such as polyaniline, poly(4-vinyl pyridine) (P4VP) and polypyrrole to improve the electrocatalytic activity, electron transfer kinetics and stability of the modified electrodes have been reported [21-25]. P4VP, as a hydrophobic polymer in polar solvents and aqueous media, is a cationic polyelectrolyte at low pH [25]. The flexible chains of P4VP may act as a stabilizing agent when wrapping around the GR, preserving its intrinsic electrical and mechanical properties [25]. Besides, high electrical conductivity and good redox mediator are among the analytical advantage of P4VP in polymer nanocomposite electrodes [21,26]. Voltammetric determination of AC and 4-Aminophenol by using GR-chitosan [1], GR [16], GR-polyaniline [21] and MWCNTs/GR oxide-GCE [27] nanocomposite electrodes have been reported. Our laboratory has previously reported on the use of P4VP and MWCNT composite electrode for determination of AC [28]. In addition, we have used P4VP/GR-GCE for the simultaneous determination of the hydroquinone and catechol [29]. However, voltammetric determination of AC using P4VP/GR nanocomposite modified GCE has not yet been reported. In this study, we

report on the combination of P4VP and GR nanosheet in the fabrication of modified GCE for monitoring of AC. A synergistic effect of this modified electrode towards the oxidation of AC is expected.

EXPERIMENTAL

Instrumentation

Electrochemical measurements were carried out on electrochemical workstation BAS Epsilon (Bio analytical system, USA). A conventional three-electrode system including a platinum wire as an auxiliary electrode and an Ag/AgCl (3 M NaCl) as a reference electrode were used. The working electrodes were bare GCE and P4VP/GR-GCE. Unless otherwise stated all potentials were obtained against the reference electrode. The surface morphologies of the P4VP/GR-GCE were characterized by scanning electron microscopic (SEM) model Leo Supra 50 VP (Oxford INCA 400, UK) and the energy-filtering transmission electron microscope (EF-TEM) LIBRA 120 equipped with an Olympus SIS ITEM Version 5.0 (build 1243) (Carl Zeiss, Germany).

Materials

GR nanopowder was purchased from Graphene Supermarket, Calverton, NY. The P4VP cross linked with 6% ethylene dimethacrylate (mesh size 50 μm) from Fluka Chemie, Switzerland, was used as obtained. All other chemicals were of analytical grade from E. Merck, Germany and used directly without further purification. All solutions were freshly prepared with pure water (18.2 MΩ cm) from Milli-Q plus (Millipore, USA).

Procedure

The electrochemical determination of AC using P4VP/GR-GCE were investigated by studying the cyclic voltammetric behavior of the reagent in phosphate buffer (pH 7) as supporting electrolyte and buffer at a potential range of 0.0-0.8 V. The CV was swept at scan rates between 10 and 300 mV s^{-1}. The DPV was performed with potentials from 0.0-0.8 V, a step potential of 2 mV, modulation amplitude of 50 mV and a scan rate 10 mV s^{-1}. Experiments were conducted at 25 ± 5 ºC. All potentials were measured against reference electrode Ag/AgCl (3 M NaCl).

Determination of AC in Tablets' Formulation

The developed electrode was tested for the determination of AC in tablets (Pharmaniaga, Malaysia). The tablets were ground to a powder and mixed with a mortar. A portion of the sample (equivalent to 0.05 g acetaminophen) was accurately weighed and dissolved in 25 ml of distilled water. The solution was then diluted to 50 ml with 0.1 M phosphate buffer (pH 7). A portion of the resulting solution (25 ml) was then used as the sample for the determination of AC using differential pulse voltammetry.

Determination of AC in Urine Mid-samples

The use of P4VP/GR-GCE is investigated for the measurement of AC in three human urine Mid-samples. Recovery tests were carried out by adding 25 μM of AC standard solution to the diluted urine samples of healthy specimens. The urine samples were collected 4 h after the introduction of a 0.5 g AC tablet. The unpretreated samples (250 ml) were then collected and diluted 30 times with phosphate buffer (pH 7).

Preparation of P4VP/GR Modified GCE

The GC electrode was modified according to the previous procedures described in literature [29]. Briefly, the polished and clean GC electrode was dried in ambient temperature. The mixture of GR and P4VP in a weight ratio of 4:2 was dispersed in 1 ml dimethylformamide (DMF) for 3 h. A 15 μl of P4VP/GR solution (1.0 mg ml^{-1}) was drop-casted onto the surface of GCE and dried at room temperature. The resulting nanocomposite P4VP/GR-GCE was then used for further experiments.

RESULTS AND DISCUSSION

Surface Morphology of the P4VP/GR-GCE

The surface morphology of the P4VP, GR and P4VP/GR composite has been described in detail previously [29]. Here, we just demonstrate the SEM and EF-TEM images of P4VP/GR nanocomposite (Fig. 1A and 1B). The SEM image (Fig. 1A) shows that microspheres of P4VP are well distributed between or on the paper like GR nanosheets, indicating that GR is densely covered by P4VP. The TEM analysis in Fig. 1B also confirms these findings. The P4VP

appear as dark spots homogeneously distributed throughout the composite material and adherent to the GR surface and even embedded in the entangled transparent GR sheets. These results clearly revealed that the P4VP along with GR exists as a composite and demonstrated the formation of dense films in the GCE.

Electrochemical Behavior of AC on the P4VP/GR-GCE

Figure 2 show CVs obtained for the bare GCE, GR-GCE and P4VP/GR-GC Eelectrodes in supporting electrolyte (buffer pH 7). A bare GCE in the absence of AC has only capacitive current with poor electrochemical response (Fig. 2a). However, for the GR (Fig. 2b) and P4VP/GR-GCE (Fig. 2c), in particular, the peak current is more noticeable, which indicates the greater electroactive surface area of the P4VP/GR-GCE.

The electrochemical response of 100 μM AC in 0.1 M phosphate buffer (pH 7) at three different electrodes have been studied by using CV (Fig. 3). The broad redox couple peaks of AC at the bare GCE and GR (Figs. 3a and 3b) could indicate a sluggish rate of electron transfer. However, the P4VP/GR-GCE displays well-defined redox peaks with E_{pa} at 441 mV and E_{pc} at 369 mV. The peak separation (ΔE_p) calculated for AC at the P4VP/GR-GCE is 72 mV indicates a quasi-reversible electrode process (Fig. 3c). While at GR-GCE, ΔE_p values for AC is 111 mV. Hence, smaller ΔE_p for AC at the P4VP/GR-GCE is indicative of high reversibility of the electrode process as a result of faster kinetics of electron transfer when P4VP is present in the nanocomposite modified electrode as compared to the GR-GCE and bare GCE. Moreover, based on electrochemical impedance spectroscopy (EIS) studies that have been already reported [29], the charge transfer resistance (R_{ct}) indicates that the kinetics of charge transfer at the P4VP/GR-GCE is very favorable. It is obvious that the increase in peak currents is due to the huge increment in the area of the electrode surface modified with P4VP and GR.

Effects of Solution pH

Because a proton takes part in the electrode reaction process of AC, the effect of different pH solutions on the electrochemical behavior of 100 μM AC at the P4VP/GR-
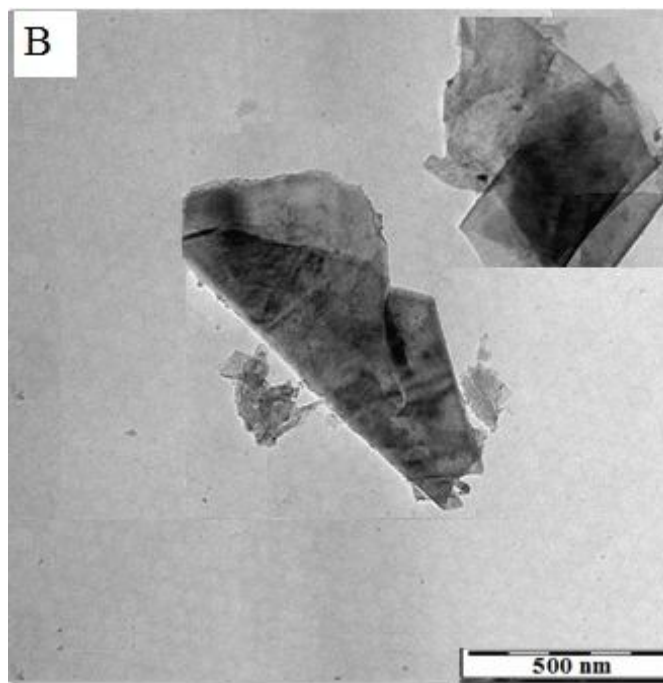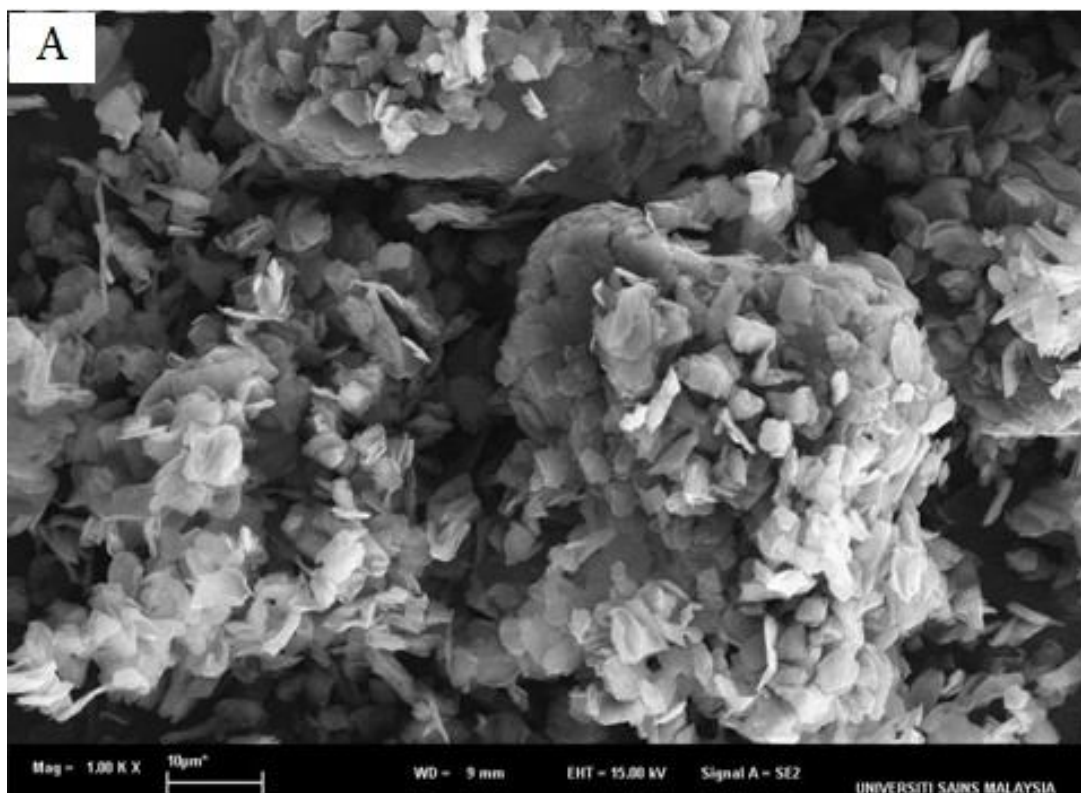
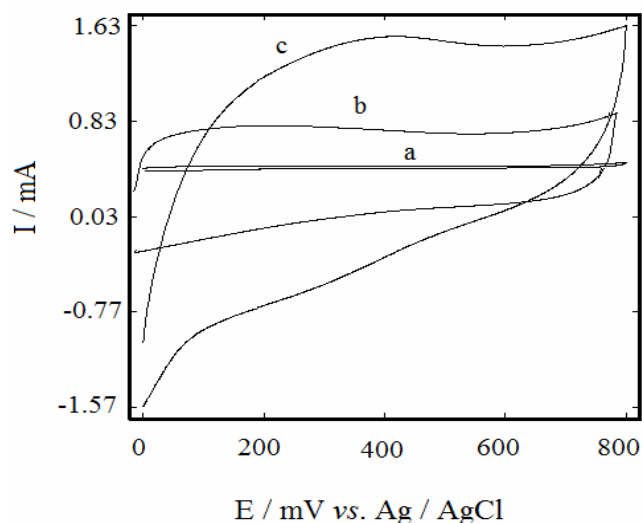**Fig. 1.** (A) SEM image of P4VP/GR and (B) EF-TEM image of P4VP/GR.

Fig. 2. CVs obtained for the (a) bare GCE, (b) GR and (c) P4VP/GR-GCE in 0.1 M phosphate buffer solution (pH 7) at scan rate 20 mV s^{-1}.
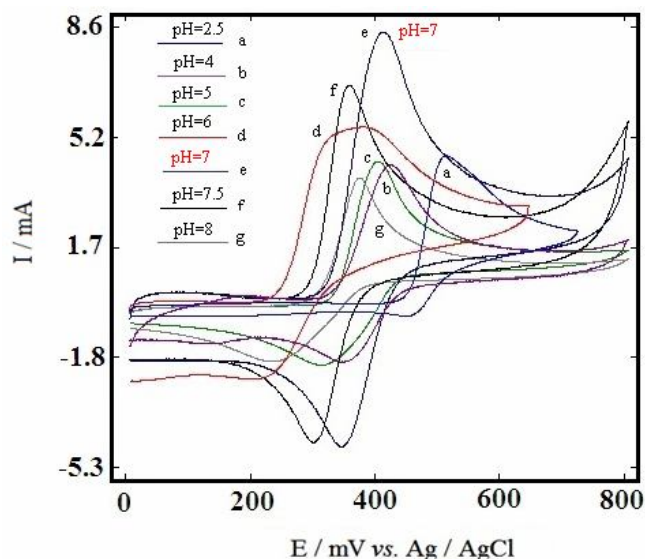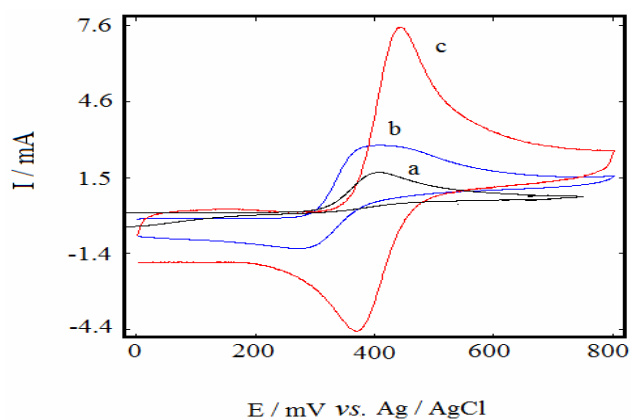

Fig. 3. CVs of 100 µM AC at the (a) bare GCE, (b) GR and (c) P4VP/GR-GCE in 0.1 M phosphate buffer solution (pH 7) at scan rate 20 mV s^{-1}.

Fig. 4. Overlay CVs of 100 µM AC at P4VP/GR-GCE at various pH and at scan rate 20 mV s^{-1}.

Fig. 5. Effect of the pH on the (A) anodic peak currents and (B) peak potential.

GCE are investigated (an overlay of the CVs as shown in Fig. 4). As can be seen, the anodic peak currents increase with increasing the pH value from 2.5 to 7.0, and then decrease with increasing the pH value from 7.0 to 8.0, suggesting that the oxidation reaction of AC is kinetically less favorable at higher pH [28,30]. Variation of peak currents with respect to pH of the electrolyte is then shown in Fig. 5A. The maximum I$_{pa}$ is obtained at pH 7.0. Hence,
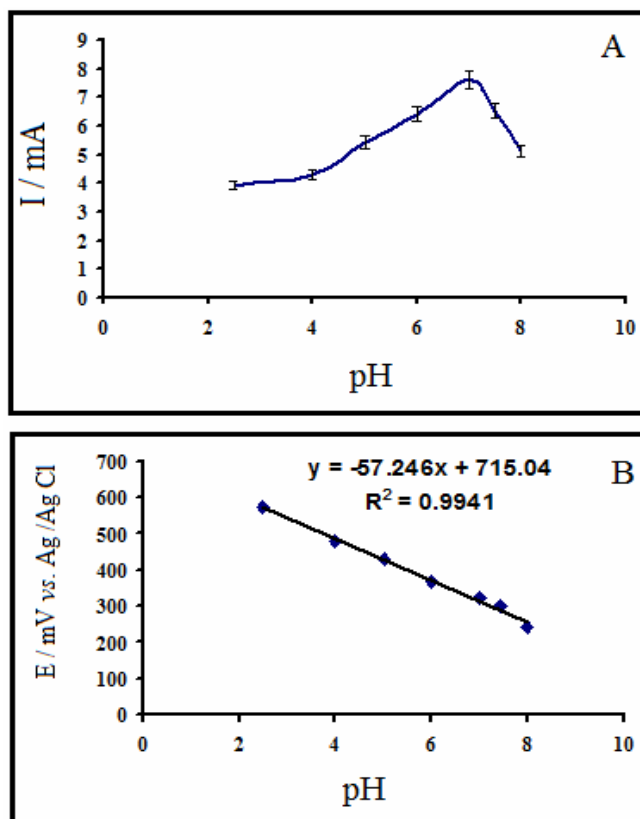
the 0.1 M phosphate buffer (pH 7) is chosen as supporting electrolyte in the subsequent experiments. Moreover, the buffering at pH 7, near to the physiological pH, will be used for the rest of the work. Effect of phosphate buffer pH on E_{pa} has been also investigated in the mentioned range (Fig. 5B). The peak potentials shifte negatively with increasing the pH value from 2.5 to 7.0, indicating that the redox reaction involve protons [30,31]. A linear relationship of E_{pa} (V) = -0.057 pH + 715.04 is obtained with (R2 = 0.994). The E_{pa} is shifted with a slope of -57 mV decade^{-1}, which is very close to the Nernstian value of -59 mV decade^{-1}. This suggests that the number of protons and electrons transferred in the redox reaction of AC are equal and likely to be two [28,30,32,33]. The anodic peak at 441 mV is ascribed to the oxidation of AC to form N-acetyl-*p*-quinone imine, and the peak reduction at 369 mV is ascribed to the reduction of AC to form N-acetyl-*p*-quinone imine. Thus, the mechanism in Scheme 1 for oxidation of AC is proposed. This is in agreement with previous studies [30,33-35].

Influence of Scan Rate

Figure 6 shows the CV of 100 μM AC at the P4VP/GR-GCE at different scan rates. With the increase of scan rate from 10 to 400 mV s^{-1}, the I_{pa} increased gradually along with the ΔE_p values. Then, a good linear relationship between the peak current (I_{pa}) and the scan rate (v) was plotted (Fig. 6B) with the regression equation as: I_{pa}/mA = 3.33X - 4.52 v/mV s^{-1} (R = 0.998) and I_{pc}/mA = -1.57X - 4.22 v/mV s^{-1} (R = 0.992), respectively. It indicates that an adsorption process occurs at the electrode and this result
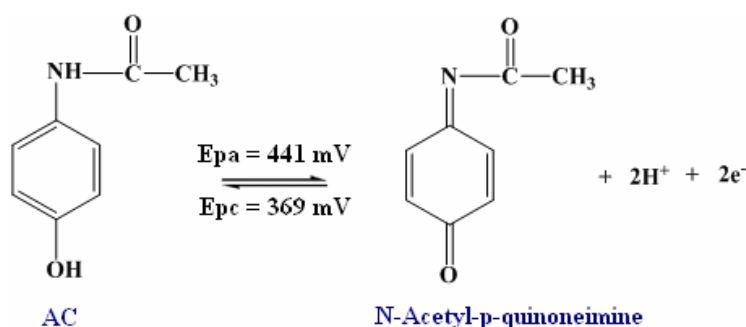
matches the EIS results [29]. Hence, it is obvious that the P4VP/GR-GCE possess faster charge-transfer kinetics which is attributed to the presence of P4VP and GR as modifiers. The results indicate that the electrochemical reaction of AC on the P4VP/GR-GCE is a surface-controlled process [2,36].

Determination of AC by Differential Pulse Voltammetry

DPV was applied for the identification of the AC in 0.1 M phosphate buffer (pH 7) with applied potentials of 0 to 0.8 V, step potential of 2.0 mV, modulation amplitude of 50 mV and a scan rate of 10 mV s^{-1} (Fig. 7). The I_{pa} is linearly proportional to the concentration of AC in the range of 0.04-300 μM. A linear equation of I_{pa} (mA) = 0.0378[AC] (μM) + 2.260 with (R = 0.997), was obtained. The detection limit of AC at P4VP/GR-GCE is found to be 3.2 nM (S/N = 3). The comparison of P4VP/GR-GCE with other modified electrodes for AC detection is listed in Table 1. It is evident that the present modified electrode shows better or comparable analytical results including detection limit and linear range than the previously reported works.

Determination of AC in Pharmaceutical and Biological Samples

Determination of AC in tablets' formulation. P4VP/GR-GCE is tested for the determination of AC in tablets. The recovery was obtained by using DPV to evaluate the accuracy of the method. The relative standard deviation of this method, based on three replicates (n = 3), is presented in Table 2. Satisfactory recoveries of AC at

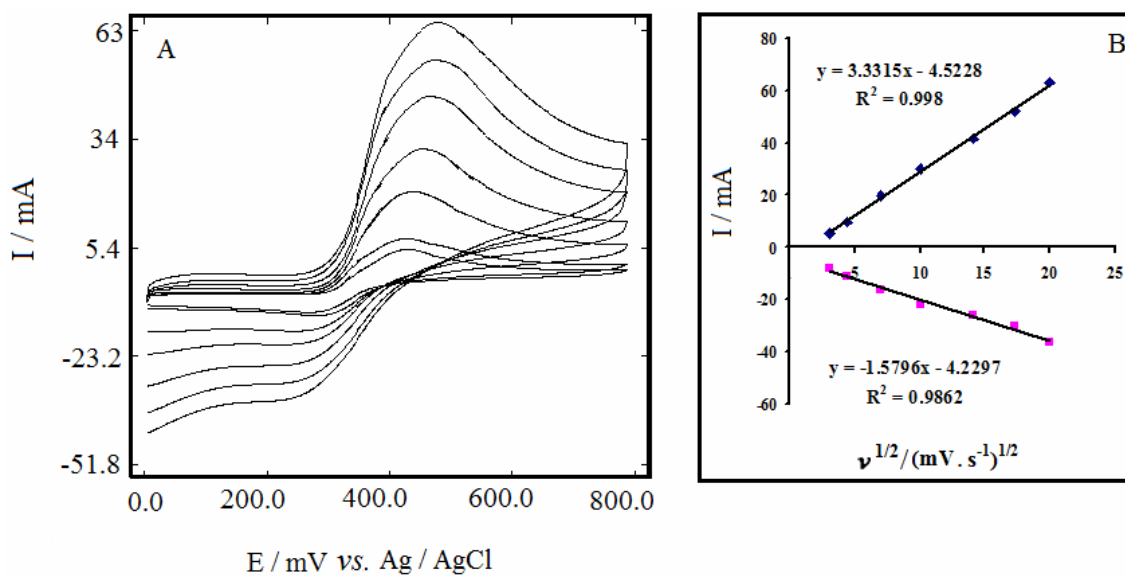*Scheme 1.* The proposed mechanism for the oxidation of AC

Fig. 6. (A) CV of 100 µM AC in 0.1 M phosphate buffer (pH 7) at P4VP/GR-GCE at scan rates 10, 20, 50, 100, 200, 300, 400 mV s^{-1} and (B) Linear relationship of anodic and cathodic peaks currents for 100 µM AC *vs.* square root of scan rate.
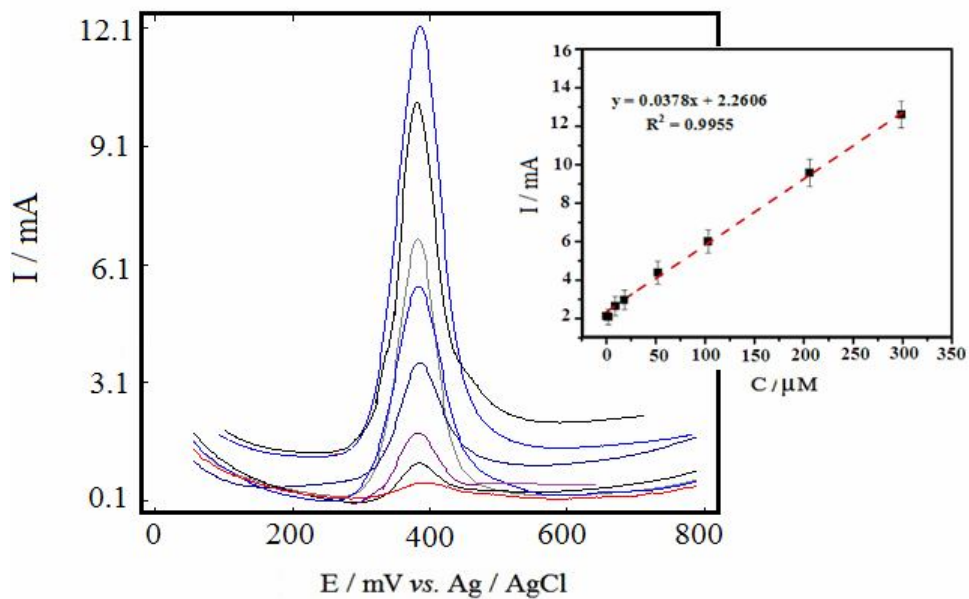

Fig. 7. Differential pulse voltammogram of AC in 0.1 M phosphate buffer (pH 7) with concentration (µM) 0.04, 2, 5, 20, 50, 100, 200 and 300 at P4VP/GR-GCE. Inset: The corresponding calibration curve.

Table 1. Comparison of Different Modified Electrodes for AC Detection

Electrode materials	Technique	Detection limit	Linear range (µM)	Ref.
Graphene	DPV	0.032 µM	0.1-20	[37]
Polyaniline-MWCNT	SWV	0.25 µM	1-2000	[38]
Nanoparticles Bi_2O_3/GCE	CV	0.2 µM	0.5-1500	[39]
PVC/TTF-TCNQ modified with gold nanoparticles	Amperometric determination	0.66 µM	1-800	[40]
Poly(thaurine)/MWCNT modified GCE	DPV	0.5 µM	1-100	[41]
MWCNT-alumina-coated silica nanocomposite modified electrode	SWVs	0.05 µM	0.05-2	[2]
Carbon paste electrode modified with CNT/Poly$_3$(aminophenol)	SWV	1.1 µM	10-100	[42]
	CV	0.01 µM	0.1-65	[43]
Poly(4-aminobenzoic acid)/graphene oxide composite modified GCE	CV	0.78 µM	0.9-80	[44]
Flavonoid nanostructured modified GCE	DPV	0.04 µM	0.1-190	[45]
Carbon paste electrode modified with Co(II)-exchanged zeolite				
Chitosan modified carbon paste electrode	SWV	0.508 µM	0.8-400	[46]
P4VP/MWCNT modified GCE	DPV	1.69 nM	0.04-450	[28]
MWCNTs and chitosan-copper complex	DPV	0.24 µM	0.1-200	[30]
P4VP/GR-GCE	DPV	3.2 nM	0.04-300	This work

P4VP/GR-GCE in the range of 0.04-300 µM revealed that this method is effective and reliable. These findings indicate a successful application of the proposed method for determination of AC in commercial pharmaceutical formulations.

Determination of AC in urine samples. P4VP/GR-GCE is investigated for the measurement of AC in three human urine samples. The percentage of recovery of the spiked sample is in the range between 99.4 and 101 (Table 3). The results show that the developed electrode is suitable for the determination of AC in biological fluids.
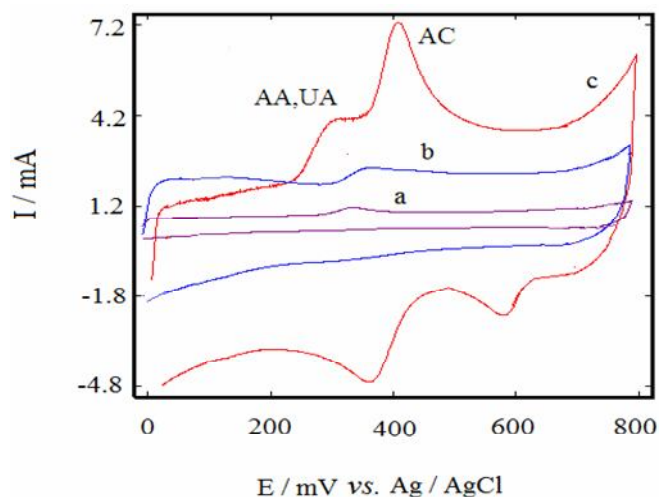
Reproducibility and Stability of P4VP/GR-GCE

The regeneration of the surface of electrode was examined by cyclic voltammetric studies of seven different electrodes constructed by the same procedure. A relative

Table 2. Determinationof AC in Formulation Tablets Using P4VP/GR-GCE (n = 3)

Sample	AC (µM)			RSD (%)	Recovery (%)
	Contents	Spike	Found		
1	59.25	0	60.35	2.40	101.85
2	59.25	10	68.16	1.11	98.42
3	59.25	20	79.23	1.96	99.97

Table 3. Determination of AC in Human Urine Samples Using P4VP/GR-GCE

Sample	AC (µM)			RSD (%)	Recovery (%)
	Detected	Spike	Found		
1	98.94	25	125.20	1.12	101.01
2	104.23	25	128.40	1.64	99.35
3	112.16	25	136.36	1.53	99.41

Fig. 8. CV of 100 µM AA, 100 µM UA and 100 µM AC at the (a) bare GCE, (b) GR-GCE and (c) P4VP/GR-GCE in 0.1 M phosphate buffer (pH 7) at scan rate 20 mV s^{-1}.

standard deviation (*RSD*) of the I_{pa} is 3.88% which indicates good reproducibility. In addition, the long-term stability of the modified electrode was also evaluated. The modified electrode was constantly used for two months. It has retained 99% of its current response to AC.

Interference Studies

Ascorbic acid (AA) and uric acid (UA) are the most common constituents found with AC [47]. The interference of UA and AA on the measurement of AC on bare GCE, GR-GCE and P4VP/GR-GCE were studied using CVs. Figures 8a and 8b indicate that the oxidation peaks of AC and UA and AA cannot be separated on the bare GCE and GR-GCE. At the P4VP/GR-GCE, the E_{pa} of AA is close to that of UA at the same potential range. The well-defined wave of AC was obtained at the P4VP/GR-GCE with good separation from AA and UA. The anodic peak potentials of AA, UA and AC were 300, 310 and 441 mV, respectively. This shows that the voltammetric determination of AC in biological samples is devoid of any

interference from AA and UA.

CONCLUSIONS

A novel P4VP/GR composite modified GC electrode and its application for the voltammetric determination of AC in neutral buffer solution has been reported. The P4VP/GR-GCE demonstrates higher electrocatalytic activity toward the oxidation of AC with remarkably improved oxidation peak current response compared with GCE and GR. The result indicates that P4VP incorporated into the GR-based composite sensor significantly increase the conductivity and effective electroactive surface area of the modified electrode. The polymer nanocomposite electrode with low detection limit and wide linear range exhibits a stable and reproducible response for AC. The selectivity of developed electrode shows it does not have any influence of common physiological interference, AA and UA. The P4VP/GR-GCE could be applied for detection of AC in urine samples with a commendable result. Therefore, it is promising for determination of other analgesic drugs. This could be identified as a target research for our future studies.

ACKNOWLEDGEMENTS

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