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Sensor based on Copper Nanoparticles Modified Electrochemically Activated Glassy Carbon Electrode for Paracetamol Determination

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In this paper, copper was electrodeposited by means of cyclic voltammetric technique on the electro-activated glassy-carbon electrode (GC_{EA}). Voltammetric techniques had been utilized for studying the electrochemical behavior of paracetamol (PAC) and its subsequent electroanalysis. CV results show that PAC redox behavior at the copper nanoparticles modified GCE (nano-Cu/GC_{EA}) is largely enhanced. At nano-Cu/GC_{EA} electrode, the redox behavior is diffusion controlled. SWV results show that, the modified electrode (nano-Cu/GC_{EA}) is highly selective and sensitive to PAC quantification. Some likely interferents were addressed and selectivity was improved. The detection and quantification limits were calculated and found to be 0.35 and 1.05 µM, suggesting that the nano-Cu/GC_{EA} can be utilized with high sensitivity and selectivity for the PAC determination. The suggested method successfully utilized for the estimation of PAC in some PAC pharmaceutical samples where it gave recoveries ranging between 97.5 and 108.2%.

Keywords: Copper nanoparticles; Oxidized glassy carbon; Paracetamol; Electrocatalysis; Analytical determination.

1. INTRODUCTION

Paracetamol or acetaminophen, N-(4-hydroxyphenyl) acetamide, (PAC, Fig. 1) is an effective as used analgesic and antipyretic agents. It is also used to relief pain associated with numerous diseases [1,2]. Generally, it is commonly used as an alternative to aspirin [3]. Albeit of many merits of PAC when applied within the safe therapeutic limit, large doses of PAC or other drugs results in several problems including for example liver disorders and nephrotoxicity [4,5]. In addition, a trace of paracetamol in

drinking water is expected to have chronic health effects, especially with long term ingestion of these compounds [6,7]. Thus, a suitable method for easy and sensitive method for the analysis of PAC is critically important. Several techniques have been applied for paracetamol determination. These include capillary electrophoresis (CE) [8], chromatographic methods [9-12] and spectrophotometric methods [13-15]. Electrochemical methods are characterized by remarkable detection sensitivity, reproducibility, and ease of miniaturization [16-20]. Thus, they have a plenty of applications in many fields especially pharmaceutical analyses [21-28]. The sensitive determination of drugs in pharmaceuticals has a significant role in quality control and diagnosis in clinical medicine. Therefore, developing a suitable analytical procedure for the identification and quantification of drugs is essential. Voltammetric methods are also used for the determination of paracetamol as it contains oxidizable group. The voltammetric analysis have been achieved on bot bare and modified electrodes, with simple and sophisticated procedures [29-35]. Recently, nanomaterials modified electrodes have attracted a lot of attention. Those inorganic nanoparticles modified electrodes can be easily assembled on a suitable substrate using simple and electrochemical methods [36-41]. Using of inorganic nanoparticles as sensors is an exciting area in quantification of various analytes because they can differentiate the response of different analytes at relatively low concentrations [42-45]. In this correspondence, Cu nanostructures has been reported to enhance electron transfer with good peak-peak separation, reduce overpotential with increase in sensitivity and selectivity [46,47]. In this work copper nanoparticles modified pre-electroactivated glassy carbon electrode is fabricated by electrodeposition and applied for PAC analysis. Effect of loading of nano-Cu and pH of electrolyte as well as other method parameters are optimized. PAC is analyzed at the optimum conditions and a good LOD and LOQ are obtained.

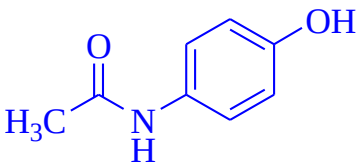


Figure 1. The structure of paracetamol (PAC)

2. EXPERIMENTAL

2.1. Materials and Reagents

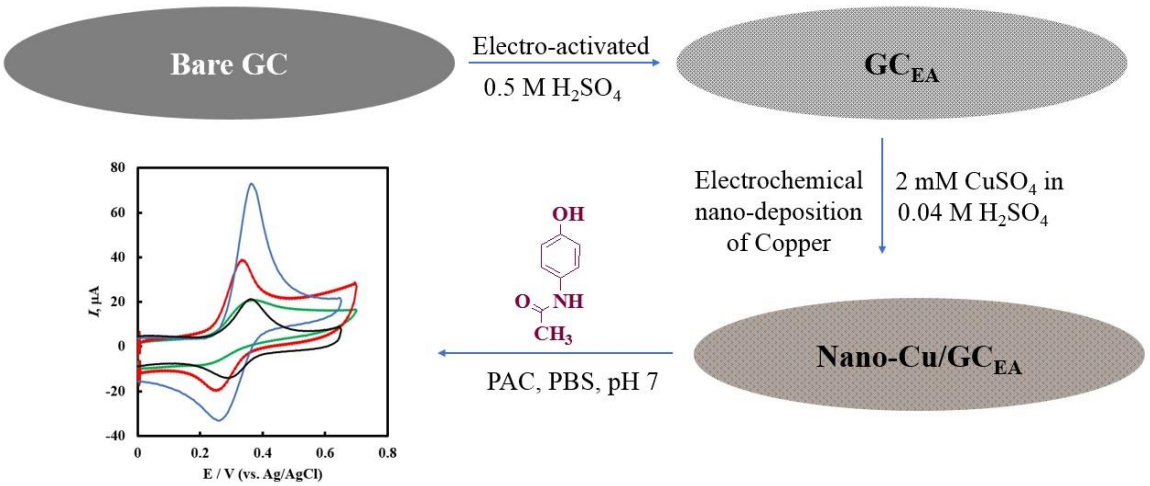
The chemicals used were of analytical quality and were utilized exactly as they were given to us. Sigma-Aldrich provided the sulfuric acid (H_2SO_4, 98 percent) and copper sulphate ($CuSO_4$, 99.9%). BDH provided sodium hydroxide (NaOH) with a purity of 99.8%. The revealed method was used to make phosphate buffer (PB) solutions of various pHs utilizing NaH_2PO_4/Na_2HPO_4 couples [48]. Amriya Pharmaceutical Industries in Egypt supplied paracetamol (PAC). By dissolving an appropriate amount of the powder in bi-distilled water, a newly stock solution of suitable concentration of PAC was created. The electrolyte solutions were de-aerated using nitrogen gas prior to electrochemical testing.

2.2. Electro-activation of glassy carbon electrode

Before the sonication treatment, the glassy carbon electrode (0.3 cm) was polished with fine alumina slurry and washed with water to eliminate alumina. Then, whichever immediately or after being electro-activated, GC was utilized. Potential cycling in the potential range of -0.2 to 2 V for varied numbers of potential cycles was used to activate the GC electrode. The anodic scan of GC within 0.5 M sulfuric acid increases the proportion of functional groups having –OH groups on the sensor surface. GC_{EA} was designated to the electrode following oxidation.

2.3. Preparation of nano-Cu/GC_{EA} electrode

The oxidized glassy carbon (GCox) is electrochemically modified with nano-copper particles through 2 mM $CuSO_4$ dissolved in 0.04 M H_2SO_4 applying three cycles over a potential from 0.7 to 0.0 V [49-51]. The obtained modified electrode is assigned as nano-Cu/GC_{EA}. The steps for modification of the under-study electrode can be illustrated as shown in the subsequent steps:



Scheme 1. Steps for modification of nano-Cu/GC_{EA} electrode

2.4. Measurements

General Purpose Electrochemical Systems (GPES) and Frequency Response Analyzer (FRA) software were used to drive a PGSTAT30 potentiostat/galvanostat (Netherlands) for electrochemical studies. For the cyclic voltammetric measurements, a conventional three-electrodes cell with an Ag/AgCl (KCl sat.) reference electrode and a Pt spiral wire auxiliary electrode was used. The volume of the cell was 20 mL. All the electrochemical experimentations were done in N_2-rich solutions. SEM images were collected using a Hitachi microscope with a 20 kV accelerating voltage. A SHIMADZU UV-VIS-NIR spectrophotometer (model UV-3600) with a slit width of 2.0 nm and 10 mm matched quartz cells was used to make the UV/Vis spectrophotometry experiments.

2.5. Application for real pharmaceutical samples

Ten tablets from three different pharmaceutical products (RELAXON, Panadol (COLD+FLU), Adol**)** obtained from local market, were grounded and an accurately weights of this powder were transferred into a 50 mL measuring flask to obtain 30 mM PAC of each product. Then, the solution was allowed to sonication for 3 min, then filtration. The obtained solutions were subjected to the procedure of the developed method at optimum conditions using the modified copper electrode.

3. RESULTS AND DISCUSSION

The microstructure of nano-Cu/GC_{EA} electrode was probed by SEM and the image is revealed in Fig. 2. The surface of bare glassy carbon electrode is modified with uniform copper nanoparticles of size ca. 20 nm. This uniform deposition was reflected on the area of the modified electrode.

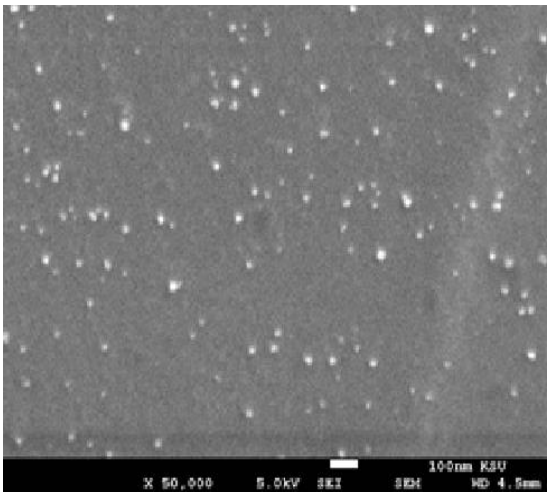


Figure 2. SEM image of nano-Cu/GC_{EA} electrode

Figure 3 displays the CVs obtained at (a) bare GC, (b,c) GC_{EA} and (d) nano-Cu/GC_{EA} electrodes in (a) PB (pH 7) containing (b-d) 6.0 mM PAC. At bare GC electrode, an oxidation peak at ca. 0.35 V is revealed (curve a). This indicates that PAC behavior is an irreversible on the bar GC electrode under the present conditions. On the other hand, a pair of distinctive redox peaks were identified. at GC_{EA} (curve b) and nano-Cu/GC_{EA} (curve d). The difference between the anodic and cathodic peak potentials (ΔE_p) is decreasing, reflects the enhanced reversibility. In addition, around four-fold anodic current enhancement at the nano-Cu/GC_{EA} electrode as compared with bare GC electrode. This points to the significant electrocatalytic activity at this electrode. At GC_{EA} electrode, the (ΔE_p (ca. 80 mV) supported by a peak current ratio at GCox is near to one, points to the reversibility of the PAC response at this electrode. At nano-Cu/GC_{EA} electrode, ΔE_p (ca. 100 mV) and peak current ratio at nano-Cu/GC_{EA} is larger than unity, and this signalizes a quasi-reversibility of the PAC redox process at nano-Cu/GC_{EA}.

The (ΔE_p) and peak currents (i_p) obtained in the presence of 6.0 mM PAC using the studied sensors were abridged in Table 1. The cyclic voltammogram of nano-Cu/GC_{EA} in the absence of PAC shows Cu^{2+}/Cu redox couple with anodic peak potential at 0.36 V and a cathodic one at ca. 0.26 V [52,53]. While the redox couple is obtained at GC_{EA} and nano-Cu/GC_{EA} electrodes, at bare GC electrode, the cathodic peak is not revealed under the present conditions. This indicates that the modification of the electrode significantly enhances the kinetics of the PAC electrochemical response. As a criteria for the electrochemical process reversibility ΔE_p= 80 is calculated. A value of 80 mV is near to the value considered form the following equation (ΔE_p = 0.058/n), where n is the number of electrons. Regarding, I_a/Ic; the value of 1 at GC_{EA} points to stability of the oxidation product, while the value of 1.6 at nano-Cu/GC_{EA} indicate that the oxidation mechanism is different compared with that at GC_{EA} [54]

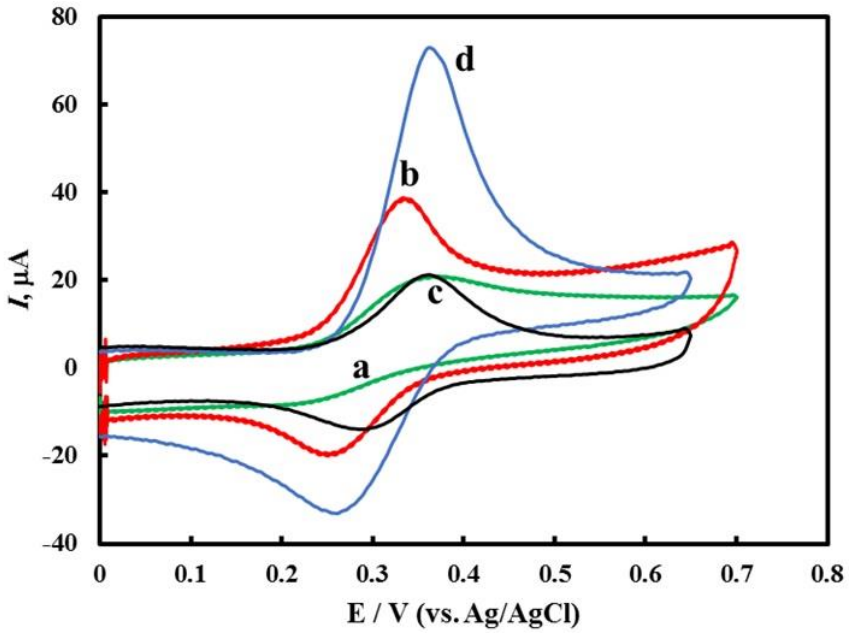


Figure 3. CV for 6.0 mM PAC on (a) bare GC, (b) oxidized GC (five oxidation cycles), (d) modified nano-Cu/GC_{EA} (three cycles Cu-loading) and (c) the modified nano-Cu/GC_{EA} without PAC in PB of pH 7 at scan rate 100 mV/sec.

The reversibility of PAC oxidation and rate determining step controlling the reaction is examined by studying the effect of scan rate on the voltammetric behavior of PAC as shown in Fig. 4. From this figure, E_p and i_p at different scan rates were extracted and plotted versus log scan rate and shown as Figs. 5 and 6, respectively. As revealed in Fig. 5, at low scan rate, the influence on the redox couple is insignificant. At a scan rate larger than 100 mV/s, the relationship of the i_p with log$v$ is linear. This change in the behavior points to the change of the process from quasi reversible at large scan rate to a reversible at lower scan rate. Moreover, the slope value (0.62) log-log plot (Fig. 6) indicates a diffusion process as a value above 0.5 is for diffusion and 1.0 is for adsorption [55].

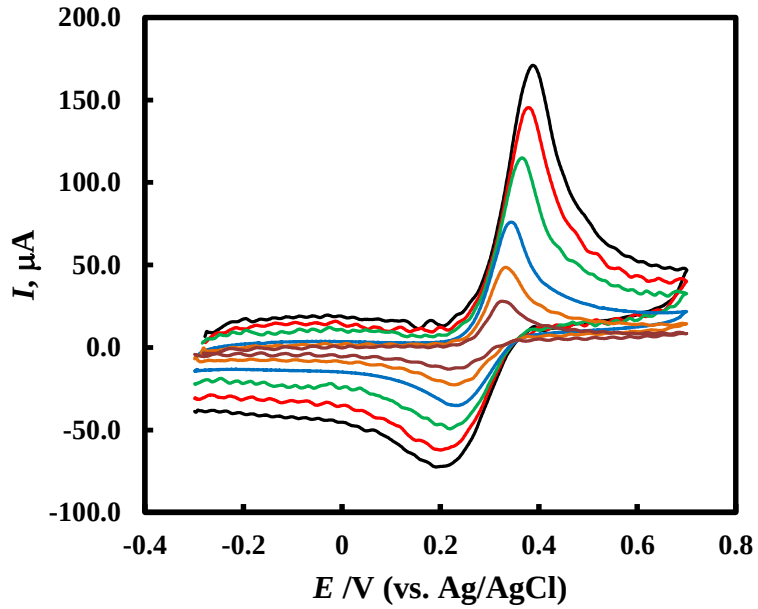


Figure 4. The impact of scan rate (20, 50, 100, 200, 300 and 400 mV/sec) on the voltammetric behavior of PAC (6.0 mM) at nano-Cu/GC_{EA}.

Table 1. Electrochemical parameters for electrocatalytic oxidation of 6 mM PAC using the studied electrodes (Data obtained from Fig. 3)

The electrode	I_a, µA	I_c, µA	I_a/I_c	E_{pa}, mV	E_{pc}, mV	E_{pa}-E_{pc}, mV
Bare GC (a)	15	-	-	360	-	-
GC_{EA} (b)	38	20	1.1	330	250	80
Nano-Cu/GC_{EA} (d)	75	45	1.6	360	260	100

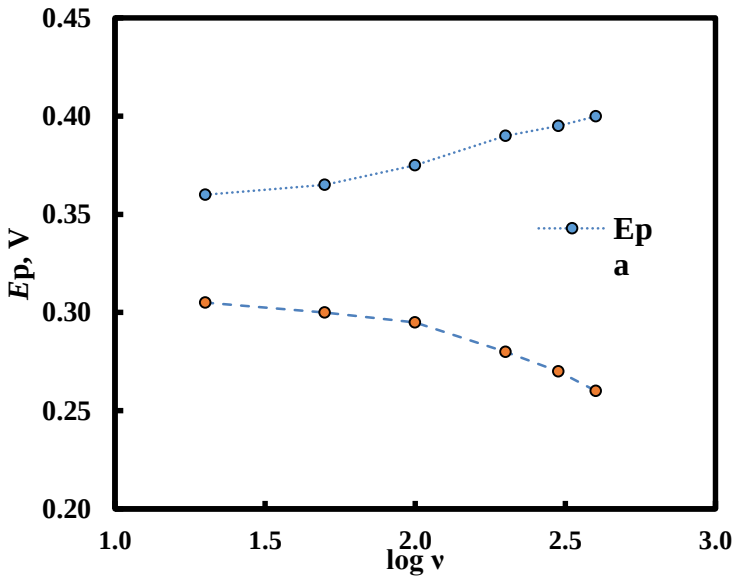


Figure 5. The Relationship among log ν and the peak potential for electrochemical behavior of 6.0 mM PAC on nano-Cu/GC_{EA} in PB pH 7.

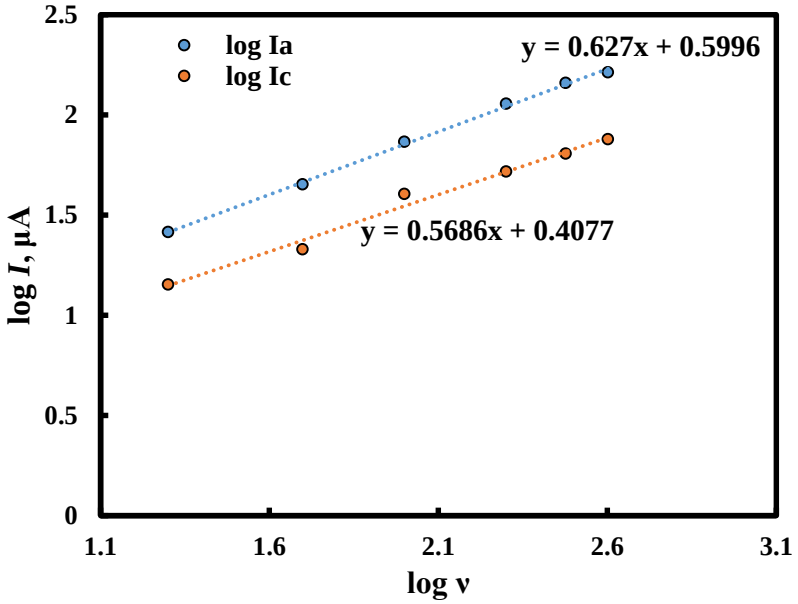


Figure 6. The relation among log *v* and log *I* for electrochemical behavior of 6.0 mM PAC on nano-Cu/GC_{EA} in PB pH 7.

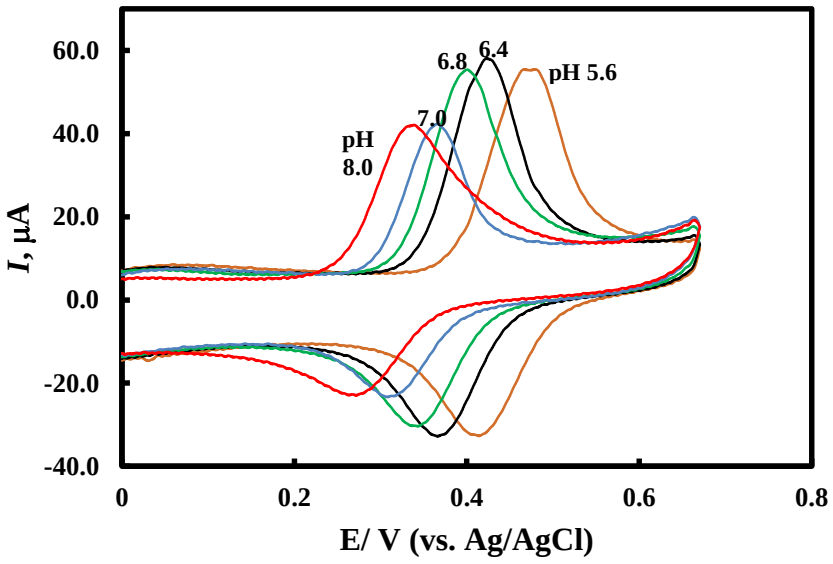
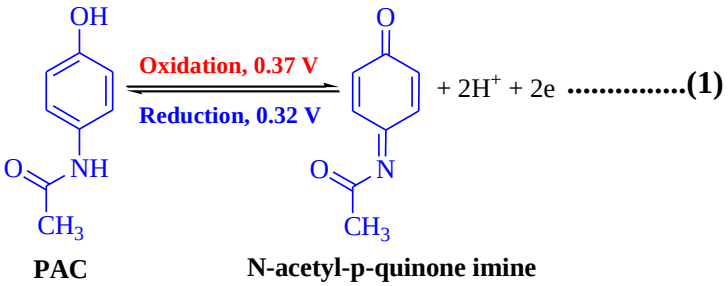


Figure 7. The influence of pH (5.6, 6.4, 6.8, 7.0, 8.0) on CV for 2.0 mM PAC obtained at nano-Cu/GC_{EA} electrode at a scan rate of 100 mV/sec.

The PAC is expected to be oxidized according to the following equation;



PAC **N-acetyl-p-quinone imine**

Thus, investigating the influence of pH on its electrochemical behavior is important from the point of view of analysis. Fig. 7 depicts the electrocatalytic oxidation of PAC (2.0 mM) studied at different pH values (5.6-8.0), at the modified nano-Cu/GC_{EA} electrode. Both the i_p and potential are significantly affected by the change in pH. The change of *E*pc and *E*pa is shown in Fig. 8. Inset shows the change of i_p with pH. The *I*p decreases with increasing pH indicating that the oxidation response of paracetamol was kinetically less promising at higher pH. The potential of both peaks shifted negatively as the pH values increased from 5.6 to 8.0.

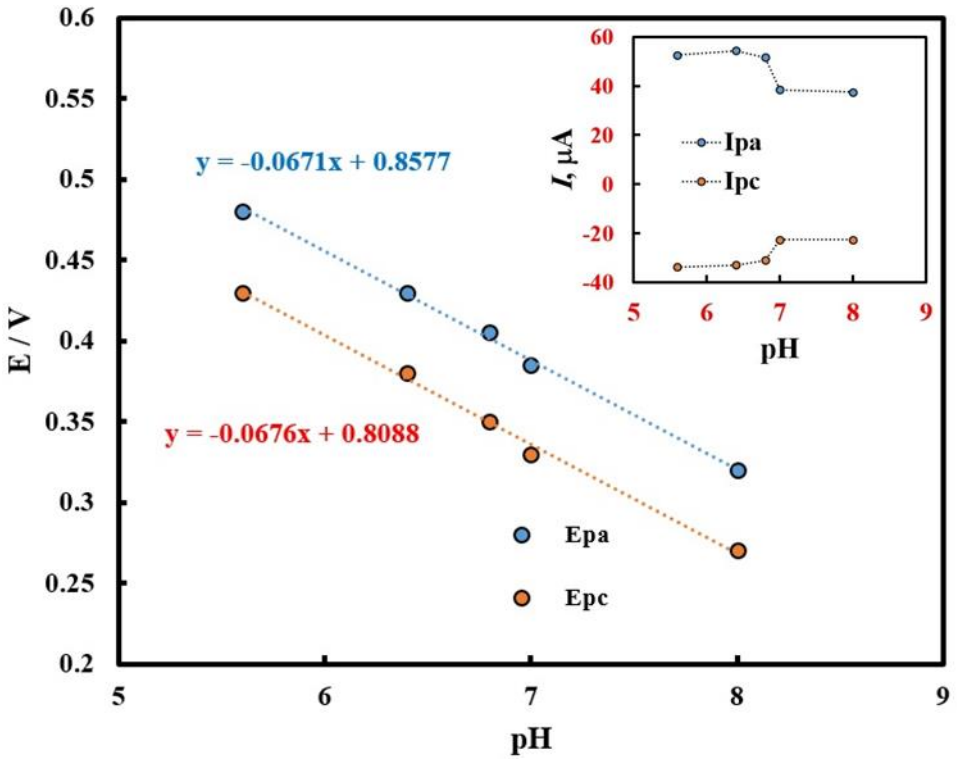


Figure 8. The relationship among pH and peak potentials for 2.0 mM PAC at scan rate 100 mV/sec (Inset: the relation between peak current and pH) using modified nano-Cu/GC_{EA} electrode.

This is attributed to that at high pH, the protons concentration is low. The linear relationship between both peaks' potential *vs*. pH values is signified through the equation $E°$ (V) = −0.067 pH + 0.8

(R^2 = 0.998). This points that an equal number of electrons (two electrons) and protons (two protons) are involved in the redox reaction as represented in Eq. 1. The anodic peak at 0.37 V is attributed to the oxidation of PAC to N-acetyl-p-quinone imine, and the reduction peak reduction at 0.32 V is ascribed to the counter reduction process. The value obtained for the slope indicates a Nernstian response, it is close to the theoretical value (−59.6 mV per pH).

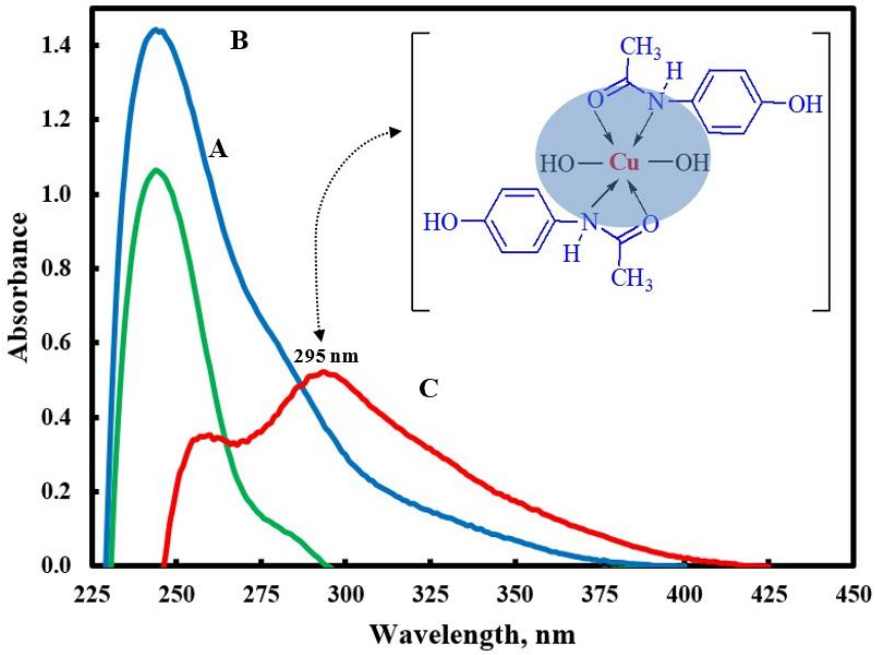


Figure 9. Absorption spectra for complex formation between 0.5x10^{-4} M PAC and 0.25x10^{-4} M Cu(II) in PBS of pH 7 where A) the absorption of PAC and buffer against buffer solution, B) the absorption of PAC, Cu(II) and buffer against buffer and C) the absorption of PAC, Cu(II) and buffer against PAC and buffer.

Why the electrochemical behavior is enhanced at modified nano-Cu/GC_{EA} electrode compared with other studied electrodes is thought to be due to the increasing of the concentration of PAC in the vicinity of the modified nano-Cu/GC_{EA} electrode. This is thought to be due to the possible complexation between copper and the PAC. This is probed by carrying out the absorption spectra for PAC and copper ion separately and in their coexistence as shown in Fig. 9 in which the absorption spectra for complex formation between 0.5 x 10^{-4} M PAC and 0.25 x 10^{-4} M Cu(II) in PBS of pH 7 where A) the absorption of PAC and buffer against buffer solution, B) the absorption of PAC, Cu(II) and buffer against buffer and C) the absorption of PAC, Cu(II) and buffer against PAC and buffer are presented. From curve A, the absorption spectrum for PAC at λ_{max} = 243 nm but after addition of copper ion, a new shoulder at wavelength about 285 nm was appeared indicating the chelation between PAC and copper ion. To eliminate the absorption spectrum of the PAC, the absorption spectra of mixture of PAC, Cu(II) and PBS of pH 7 was measured against PAC and PBS. This procedure gave peak C at λ_{max} = 295 nm. This phenomenon gave evidence for a complex formation between PAC and copper on the modified

electrode. The formed complex may be illustrated as the inset Fig. 9 [56]. This highlights the reason behind the enhancement of PAC oxidation at nano-Cu/GC_{EA} electrode.

3.1. Electroanalysis of PAC at nano-Cu/GC_{EA} electrode

Figure 10 presents the CV of various concentrations of PAC at nano-Cu/GC_{EA} electrode. Inset is the dependence of the cathodic and anodic i_p of PAC in the range 0.15-1.16 mM with correlation coefficient (R^2) of 0.9937 and 0.9952, respectively. This indicates the possible application of the nano-Cu/GC_{EA} electrode for trace level analysis of PAC.

Square voltammetry (SWV) is characterized by its highly sensitivity and resolution compared with other voltammetric techniques, and this is due to the method of assembling current. Fig. 11. Is a presentation of SWV obtained at nano-Cu/GC_{EA} electrode in the presence of different concentrations of PAC. As clear, the i_p at 0.35 V of PAC regularly increases with the increase in the PAC concentration. The linear calibration curve, obtained over the range 4.0–28.0 μM, is given as Fig. 12. It was found to be *I*pa = 1.5071[PAC] + 3.0429 with the correlation coefficient of R^2 = 0.9925. The limit of detection (LOD) is estimated to be 1.87 μM whereas the limit of quantification (LOQ) was calculated and found to be 5.62 μM. All other electrochemical parameters are presented in Table 2. The overall analytical performance of the nano-Cu/GC_{EA} modified electrode was compared with the previous literatures, see Table 3. Interestingly, the present electrode with simple fabrication exhibited a comparable sensitivity and selectivity in addition to an accurate linear response range and a low detection limit to reported modified electrodes [32,33,36,37,40-42,46]. This could be attributed to the enhancement of the electron transfer at the modified electrode. Thus, the proposed modified electrode is suggested as a suitable proper for the selective detection of PAC.

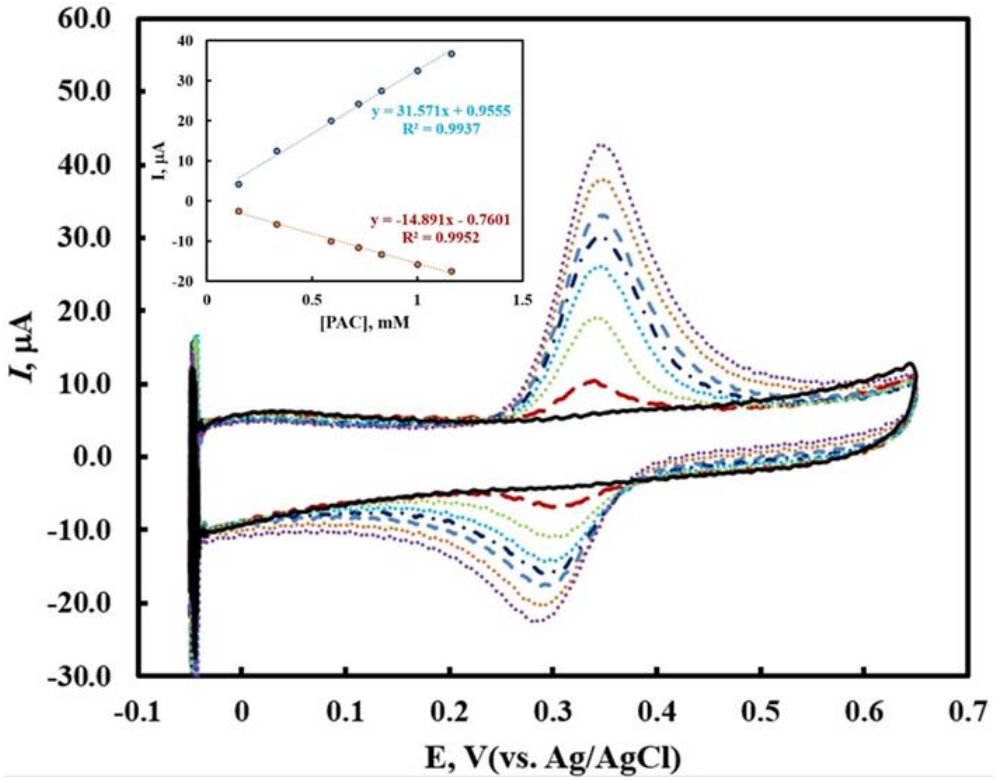


Figure 10. Effect of increasing concentration of PAC in CV of modified nano-Cu/GC_{EA} in PB of pH 7 at scan rate of 100 mV/s (0.15-1.16 mM)

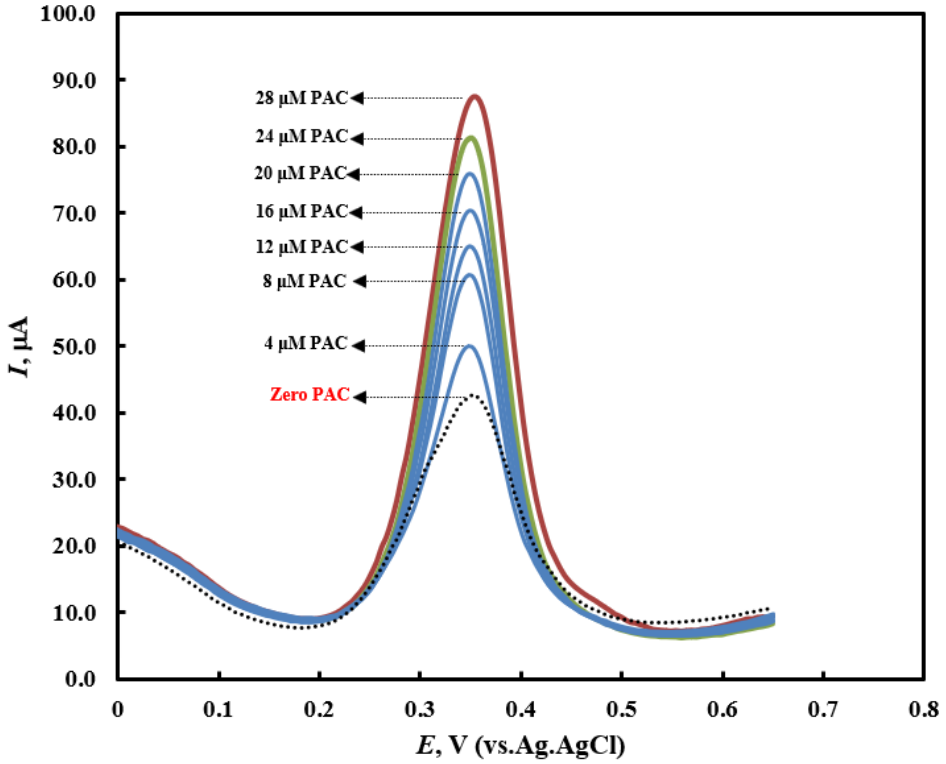


Figure 11. Square wave voltammograms obtained for determination of PAC (4, 8, 12, 16, 20, 24 and 28 µM) at modified nano-Cu/GC_{EA} in PB of pH 7 at a scan rate of 100 mV/s

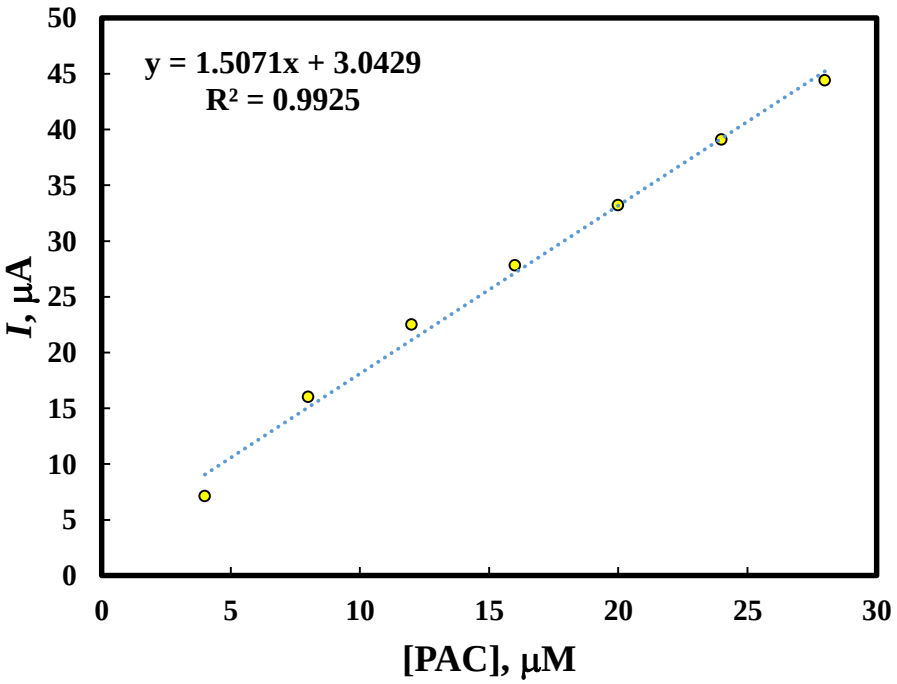


Figure 12. Calibration curve, extracted from Fig. GG, for PAC determination using modified nano-Cu/GC_{EA} electrode.

The selectivity issue is critical in electroanalytical determination of any analyte, Obviously, experiments showed that, the CV response obtained in a solution containing 1.0 mM PAC + 20 fold higher concentrations of other interferents at nano-Cu/GC_{EA} electrode presents a high selectivity of PAC with the co-existence of some interfering species as glucose, sucrose and fructose. Interestingly, the effect of adding interfering species on i_p response of PAC is negligible. This authenticate that the nano-Cu/GC_{EA} sensor is a suitable sensor for the eclectic analysis of PAC in some real samples.

For the electrochemical determination of PAC, the reproducibility of the modified sensor is critical. It was evaluated by conducting six successive SWV in N_2-saturated PB containing 16 μM PAC. The modified electrode is characterized by an acceptable repeatability with a relative standard deviation (RSD) of 1.78%. Furthermore, the reproducibility of the modified electrode was checked by conducting CV at five independent nano-Cu/GC_{EA} electrodes under the optimum conditions. In this case the relative standard deviation (RSD) of 2.2% points to the high reproducibility of the present method.

Also, the stability of the nano-Cu/GCox electrode was examined by conducting CV for the same modified electrode every day regularly, taking in consideration that the electrode was stored in a refrigerator when it is was not in use. Notably, 95% of the initial i_{pa} was retained after continuous use of the electrode for 20 days. This indicates the stability of the nano-Cu/GCox electrode. The practicability of the modified sensor for real sample applications towards the determination of PAC was acquired by the standard addition method and the subsequent calculation of the recovery. A satisfactory recovery range of (97.5-108.2) % obtained, see Table 4. As clear in this table, the developed modified electrode can be used as a candidate for selective determination of PAC in three real pharmaceutical samples.

Table 2. The optimum electroanalytical conditions for determination of PAC using modified nano Cu/GC_{EA} electrode using SWV

Parameter	**Value**
The media	Phosphate buffer solution
pH	7.0
Scan rate, mV/s	100
Number of Cu loading cycles	3 cycles
Regression equation	
Slope	1.51
Intercept	3.04
Relative standard deviation (RSD), %	1.78
SD of slope	0.042
SD of intercept	0.16
LOD, μM	0.35
LOQ, μM	1.05
Linear range, μM	4-28
Correlation coefficient, R^2	0.9925

Table 3. Comparison between the studied nano Cu/GC_{EA} electrode and previous methods for determination of PAC

The technique used	The electrode used	Linear range, µM	LOD, µM	Ref.
SWV[a]	Au	200-1500	120	[37]
SWV	Pt/GCE	0.05-90	0.008	[32]
SWV	Chitosan/CPE	400-1000	0.51	[33]
Amperometry	Au/CPE	0.66-530	0.33	[36]
AdsSV[b]	MWCNT/BPPGE	0.1-25	0.05	[40]
SWV	CPE	0.4-900	0.2	[41]
CV[c]	Polymer/GCE	5-1000	3.5	[42]
DPV[d]	FMWCNT/GCE	3-300	0.6	[46]
SWV	nano-Cu/GC_{EA}	4-28	0.35	This work

[a] Square wave voltammetry
[b] Adsorptive stripping voltammetry
[c] Cyclic voltammetry
[d] Differential pulse voltammetry

Table 4. Electroanalytical determination of PAC using nano Cu/GC_{EA} electrode in some pharmaceutical formulations.

Sample	Concentration of PAC, µm		Recovery, %	RSD, % (n=4)
	Labeled	found		
RELAXON	10	9.78	97.8	1.02
	12	12.9	107.5	2.21
	18	17.8	98.9	1.72
Panadol (COLD+FLU)	7	7.01	100.1	3.32
	14	13.88	99.14	2.77
	21	20.47	97.5	1.91
Adol	10	10.82	108.2	1.21
	14	13.91	99.4	1.08
	18	17.88	99.3	2.41

4. CONCLUSIONS

Herein, a simple strategy for the fabrication of copper nanoparticles modified glassy carbon electrode (nano-Cu/GC_{EA}) by using cyclic voltammetry is presented. Nano-Cu/GC_{EA} enhanced the electrochemical i_{pa} of PAC remarkably due to the enhanced electrocatalytic properties of nano-Cu/GC_{EA} electrode. The nano-Cu based sensor achieved high sensitivity and selectivity for the analysis of PAC with large rectilinear range and low detection limit, as achieved by square wave voltammetry. The practicability of the nano-Cu/GC_{EA} electrode was also demonstrated by estimation of PAC in some real samples.

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