

Full Paper

Ag/TiO₂ Nanocomposite Modified Carbon Paste Electrode used to Differential Pulse Voltammetric Determination of Carbamazepine

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Abstract- Ag/TiO₂ nanocomposite was used as a modifier in carbon-paste electrode (CPE) to fabricate a carbamazepine (CBZ) voltammetric sensor. The results show an efficient catalytic activity of the electrooxidation of CBZ. Electrochemical behaviour of CBZ at the sensor was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Results showed that the modified electrode exhibited a strong electrocatalytic activity toward the redox of CBZ. The effects of scan rate and pH on peak current were investigated and an optimal scan rate of 50 mV s⁻¹ and a pH 2.0, Britton-Robinson buffer solution (BR), were used. Under the optimum conditions, the catalytic peak currents of CBZ were linearly dependent on the concentrations of CBZ in the range from 2.5×10⁻⁶ to 1.0×10⁻⁴ mol L⁻¹ with a detection limit of 8.6×10⁻⁷ mol L⁻¹. This proposed method was successfully applied to determine the carbamazepin concentration in its tablet as real sample and a recovery of 95% was obtained without interference from tablet matrix.

Keywords- Carbamazepin, Ag/TiO₂ Nanocomposite, Modified Carbon Paste Electrode, Drug Samples, Differential Pulse Voltammetry

1. INTRODUCTION

Carbamazepine (CBZ), (5-H-dibenzazepine-5-carboxamide) (Fig. 1), is an anticonvulsant and mood stabilizing drug used primarily in the treatment of epilepsy and bipolar disorder, as well as trigeminal neuralgia dosage of drugs such as CBZ, which have been on the market several years [1,2], should be individually prescribed for each patient according to their age and gender [1]. CBZ is among the most widely prescribed drugs, in a variety of dosages and pharmaceutical forms [3]. Due to its high consumption rates in modern society [3] it became important to develop and establish new, fast, and accurate methodologies for the determination of this drug.

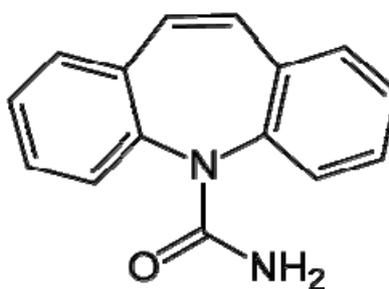


Fig. 1. Molecular structure of carbamazepine (CBZ)

Several analytical methods have been published concerning the determination of CBZ in pharmaceutical formulations, clinical, and environmental samples. Spectrofluorimetry [4], gas-liquid chromatography (GC) [5,6], Spectrophotometric [7-11], planar chromatography [12], electrokinetic chromatography [13], LC-MS tandem [14,15], and high performance liquid chromatography (HPLC) [16-21] have been used to determine CBZ. Most of the methods reported are highly sophisticated, costly, and time consuming and require special sample preparation. For these reasons, the rapid, simple and accurate method is expected to be established. Electroanalytical techniques bring with them important advantages such as, high sensitivity, low detection limits, relative simplicity, low costs and portable field based equipment. Despite the present of redox groups in the CBZ molecule, few works have reported on the use of voltammetry method to describe the electrochemical analysis of CBZ [22-27].

Carbon pastes are well known as useful material for the fabrication of various electrochemical sensors for analytical purpose [28-30]. Carbon paste electrodes are currently in widespread use in electroanalytical chemistry, because of their broad potential window, low cost, rich surface chemistry, low back ground current, ease of surface renewal, individual polarizability, and easy to apply modifications. The disadvantage of CPE is the tendency of

the organic binder to dissolve in solutions containing an appreciable fraction of organic solvent [31-33].

The operation mechanism of such chemically modified carbon paste electrodes (CMCPs) depends on the properties of the modifier used to impart selectivity towards the target species. The arrival of materials in the nanometer range has made it possible to use them as modifier in carbon paste electrodes. The use of nanoparticles in electroanalysis is an area of research which is continually expanding. Underpinning the significance of nanoparticulate materials in electroanalysis are the very specific properties which may be exhibited at the nanoscale but which are not typical of the corresponding bulk material. These include enhanced diffusion based on convergent rather than linear diffusion at the smaller NPs, high active surface area, improved selectivity, catalytic activity, and higher signal-to-noise ratio. These unique properties make nanomaterials ideally suited for electroanalytical applications. Hence, the use of nanoscale materials in electroanalysis in recent years has been extensive, particularly with respect to metallic NPs [34-40].

In the present paper, a carbon paste electrode modified with Ag/TiO₂ nanocomposite as an electrochemical sensor for CBZ is reported. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used to electrochemically study CBZ. A sensitive anodic oxidation peak of CBZ was used for quantitative determination. A good linear relationship was realized between the anodic peak current and CBZ concentration in the range of 2.5×10^{-6} to 1.0×10^{-4} mol L⁻¹. The detection limit of this method for carbamazepine was 8.5×10^{-7} mol L⁻¹.

2. EXPERIMENTAL

2.1. Apparatus

Voltammetric experiments were performed with an EN 50081-2 electrochemical workstation (Declaration of company, Netherlands). A conventional three-electrode system was used with a carbon-paste working electrode (unmodified or modified), a saturated Ag/AgCl reference electrode and a Pt wire as the counter electrode. During the measurement, the solution in the cell was not stirred and the BR buffer solution was used without un-aeration. A pH meter (Crison model GLP 22) was applied for the preparing the buffer solutions, which in turn were used as the supporting electrolyte in voltammetric experiments.

2.2. Reagents and solutions

Paraffin oil and graphite powder were obtained from Merck Company and used as received. All other chemicals were of analytical grade and used without further purification. Carbamazepine in analytical grade was prepared from Pars pharmaceutical Company

(Tehran, Iran). $1.0 \times 10^{-2} \text{ mol L}^{-1}$ stock standard solutions was prepared. Working standard solutions were prepared by appropriate dilution of the stock standard solution with BR buffer.

2.3. Preparation of Ag/TiO₂ nanocomposite

At first nano sized TiO₂ was synthesized by adding NaOH to titanium tetra chloride solution until the pH of solution was adjusted in 7 at room temperature. Then the white precipitate is washed with deionized water to remove chloride ions, the pH of the slurry was regulated at 1.5 using 1 M nitric acid. The slurry was refluxed at 343 K for 24 h, to gain a stable sol. The sol was dried at 313 K and calcined at 673 K for 3 h to obtain titanium oxide catalyst.

For synthesizing Ag/TiO₂ nanocomposite, AgNO₃ solution is added to the stable sols of TiO₂ (6/94 weight percent of Ag/Ti), then the slurry was dried at 313 K and calcined at 673 K for 3 h.

2.4. Characterization of Ag/TiO₂ nanocomposite

The morphologies of particles were investigated by SEM micrographs (PHILIPS-XLΦ-30). Fig. 2 A and B show SEM images of nanocrystalline TiO₂ and 6% silver doped sample respectively, calcined at 673 K for 3 h. The particle sizes in SEM micrographs are consistent to a good extent with the particle sizes calculated from XRD peaks by using Sheerer (around 10 nm). Furthermore, SEM images show that the synthesized nanoparticles are spherical and have homogenous morphology.

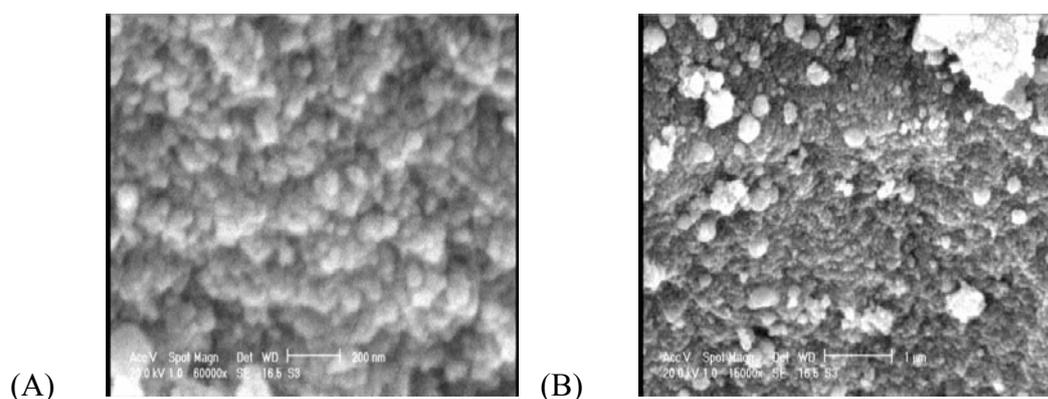


Fig. 2. SEM image of (A) nanocrystalline TiO₂, (B) nanocomposite of Ag/TiO₂

The evidences of the penetration of silver into matrix or existence in titania walls were informed by energy dispersive X-ray (EDX) analysis. The result shows that the mean weight percentage ratio of Ag/Ti in nanocomposite is equal to 6/94 (Fig. 3).

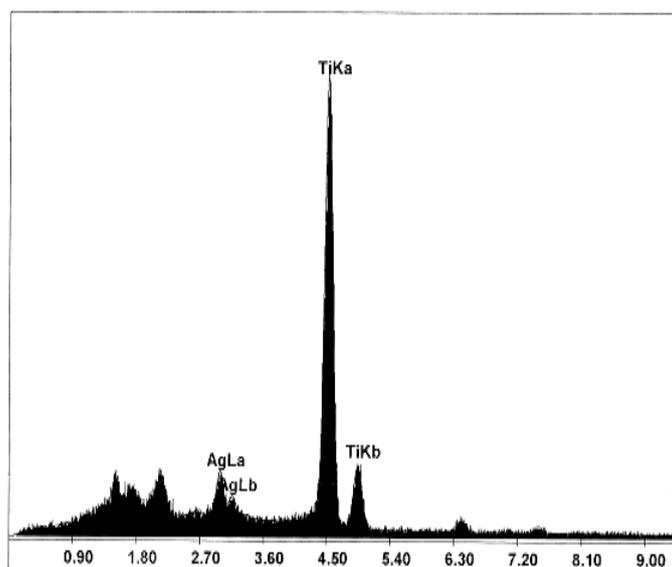


Fig. 3. EDX spectrum of nanocomposite of Ag/TiO₂

2.5. Preparation of modified electrode

The unmodified CPE was prepared by mixing 60 mg of graphite powder with 30 mg of mineral oil (paraffin) and thorough hand mixing in a mortar and pestle. The carbon paste was packed into the end of a polyethylene syringe (2.5 mm diameter), the tip of which had been cut off with a cutter. Electrical contact was made by forcing a thin copper wire down into the syringe and into the back of the composite. Ag/TiO₂ nanocomposite was used for modification of the paste. 10 mg Ag/TiO₂ nanocomposite was added to the above unmodified composite and mixed thoroughly for at least 30 min to get a homogenous paste. Then, the modified composite was packed into the end of a polyethylene syringe.

The electroactive area of the bare and Ag/TiO₂ nanocomposite modified CPE was calculated using 1 mM K₄Fe(CN)₆ as a probe at different scan rates by CV. For this, we have employed Randles-Sevcik equation as shown below:

$$i_{pa} = (2.69 \times 10^5) n^{2/3} A D_0^{1/2} \nu^{1/2} C_0^*$$

Where i_{pa} is the anodic peak current, n is the number of electrons transferred, A is the surface area of the electrode, D_0 is the diffusion coefficient, ν is the scan rate and C_0^* is the concentration of K₄Fe(CN)₆. For 1 mM K₄Fe(CN)₆ in 0.1 M KCl electrolyte, $n=1$, $D_0=7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, then from the slope of the plot of i_{pa} vs. $\nu^{1/2}$, area of the electrode was calculated.

2.6. Procedure for pharmaceutical analysis

The contents of 10 tablets of carbamazepine (Sobhan Darou Co., Tehran, Iran) were weighed for obtaining the average mass of each tablet, then powdered, and an amount of one tablet of drug was transferred to a 50 mL beaker and dissolved in methanol, shaken well for 10 min, then the solution filtered and diluted in a 50 mL volumetric flask to the mark with distilled water. Appropriate aliquots from the working solutions were taken for the voltammetric determination of them by DPV techniques in the standard addition mode, and diluted with buffer to obtain final concentrations in the range of calibration graph. Then solutions assayed as described under optimized proposed procedure.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of CBZ on CPE modified with Ag/TiO₂ nanocomposites

Results of previous works showed that the CPEs modified with various types of nanowires and nano particles have catalytic effects in the electro-oxidation of biologically important drugs compounds. The catalytic rule of the modifier causes lowering the anodic over potential and enhancement of the anodic peak current in the electrode process [41].

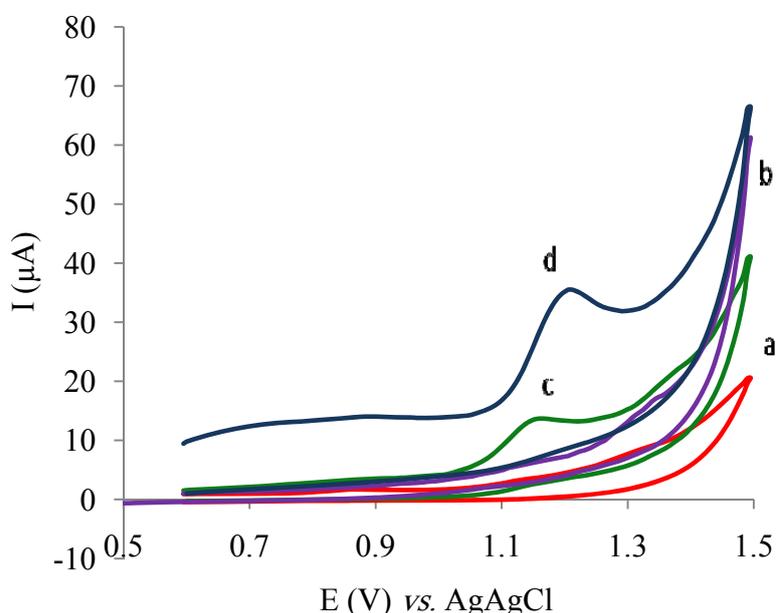


Fig. 4. (a) and (d) The blank solution at bare CPE and MCPE electrodes, (c) and (d) 4×10^{-5} mol L⁻¹ of carbamazepine at bare and Ag/TiO₂-CPE in 0.04 M BR buffer with pH 2

Preliminary electrochemical measurements were carried out in order to identify the general behavior of carbamazepine. Fig. 4 shows typical cyclic voltammograms of carbamazepine on bare CPE and modified CPE (MCPE) in 0.04 mol L⁻¹ BR buffer, for the following cases: (a) the blank solution at bare CPE, (b) the blank solution at MCPE, (c) and (d) 4×10⁻⁵ mol L⁻¹ of carbamazepine at bare and Ag/TiO₂-CPE in 0.04 M BR buffer with pH 1.8. In all cases the sweep rate was 50 mV s⁻¹. As seen, a relatively weak and broad oxidative wave for the electro-oxidation of CBZ on the unmodified electrode reveals that the electrode process is very sluggish. When the CPE modified with Ag/TiO₂ nano-composite, on the other hand, a well-defined and sharp anodic wave with a peak potential of 1.21 (±0.02)V is obtained for CBZ. However, in blank solution no peak is seen with Ag/TiO₂-CPE modified electrode. On the basis of these observations, it can be postulated that the addition of Ag/TiO₂ nano-composite to the matrix of CPE exhibits an effective catalytic fashion in the electrochemical oxidation of CBZ, leading to a remarkable enhancement of the anodic peak current. A similar behavior can be obtained in differential pulse voltammetric studies (Fig. 5). The results showed that CBZ, in the potential range of 0.5-1.5 (vs. Ag/AgCl) and all potential scan rates (from 10 to 100 mV s⁻¹), no cathodic peak was observed on the reverse sweep. This confirms an irreversible process for its oxidation on the Ag/TiO₂-CPE.

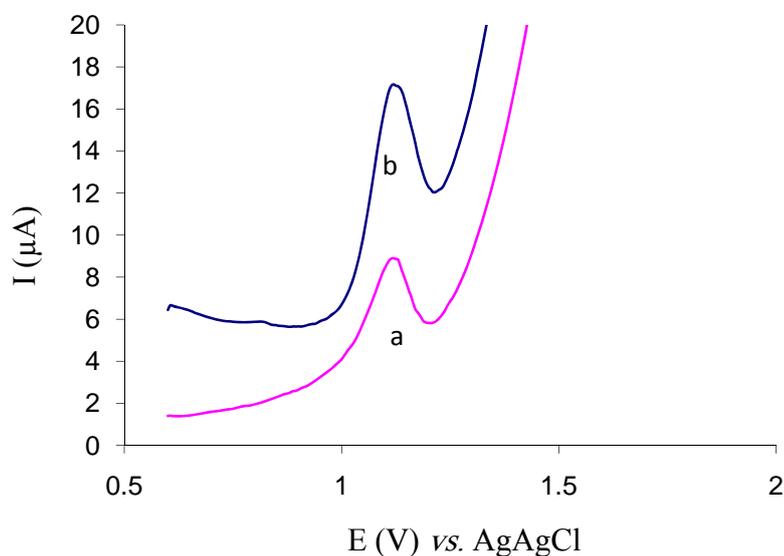


Fig. 5. Differential pulse voltammograms of 4×10⁻⁵ mol L⁻¹ carbamazepine in Britton-Robinson buffer at (a) bare carbon paste electrode and (b) modified carbon paste electrode

The effect of the potential scan rate (ν) on the electrocatalytic property of Ag/TiO₂-CPE toward electro oxidation of CBZ was studied by cyclic voltammetry (Fig. 6).

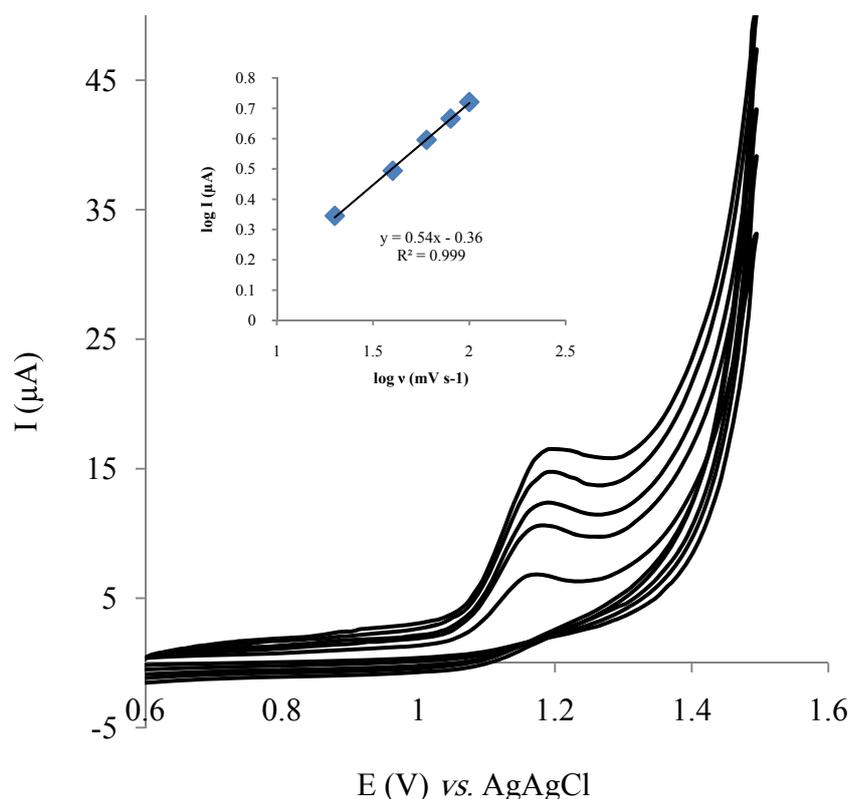


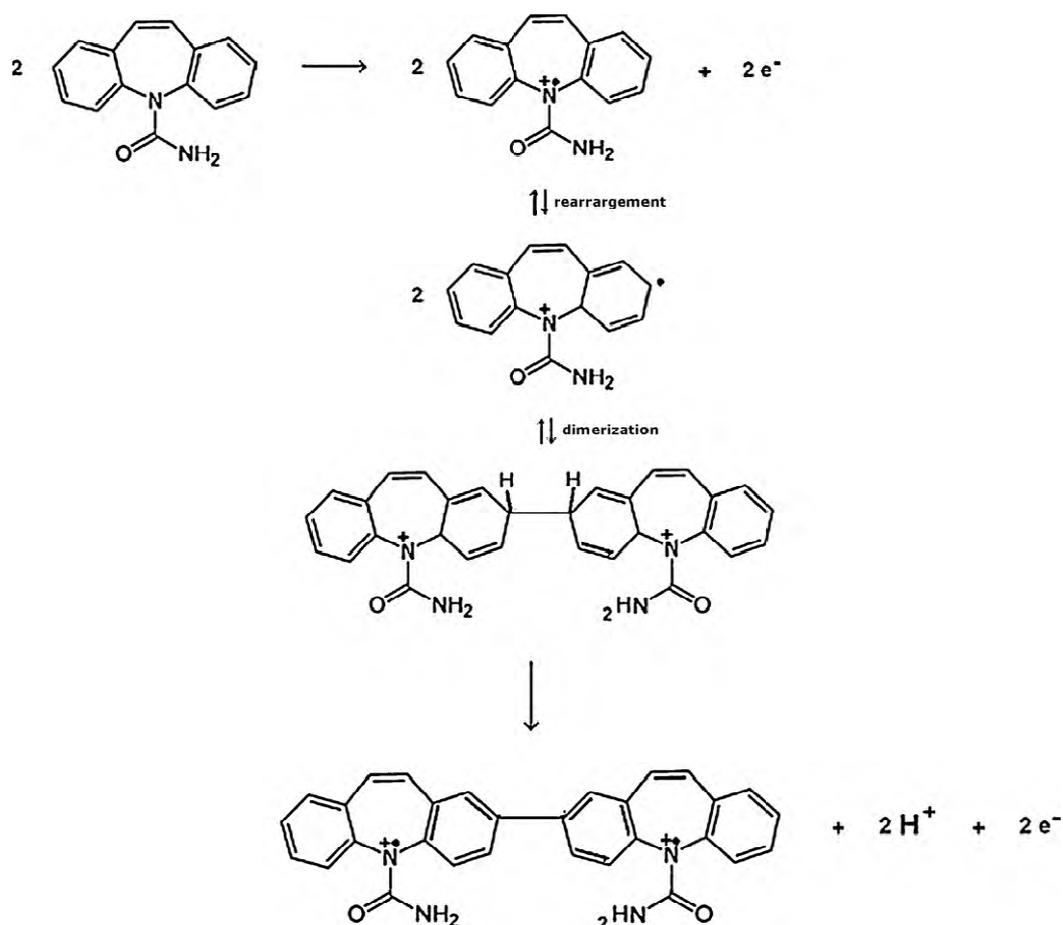
Fig. 6. Cyclic voltammogram at various scan rates and log graph of I vs. scan rate in the 0.04 mol L^{-1} Britton-Robinson buffer and $4 \times 10^{-5} \text{ mol L}^{-1}$ of carbamazepine

The slope of 0.540 for the linear variation of the log of peak current and the log of sweep rate (inset of Fig. 6) indicates a diffusion-controlled process that may be related to the diffusion of CBZ in the Ag/TiO₂-CPE. The regression equation for this relationship is:

$$\text{Log}(i_{\text{pa}}) = 0.5399 \log(v) - 0.3626 \quad (R^2 = 0.999, i_{\text{pa}}: \mu\text{A}, v: \text{mV s}^{-1})$$

On the basis of the few reports about the anodic behavior of the CBZ molecule, the electrode process under discussion can be related with the oxidation of the nitrogen atom in the central ring which results in the formation of cation radicals (Scheme 1) [26].

Kalanur and Seetharamappa were used a GCE as working electrode for electrochemical study of CBZ and seen two oxidation peaks were noticed at potentials of 1.183 V and 1.401 V vs. Ag/AgCl in cyclic voltammogram of 0.125 mM CBZ in a phosphate buffer of pH 7.4. They were proposed the mechanism of oxidation of CBZ as shown in Scheme 1 [26]. However, in the present study we seen only one peak in all cases at pH 2 and we believe that the two steps leading to the loss of electrons, as illustrated in Scheme 1, occur simultaneously and cannot be distinguished in the voltammogram or probably in acidic media the last step cannot be done.



Scheme 1. Probable reaction mechanism for electrooxidation of CBZ at the MCPE (adapted from Ref. [26])

3.2. Influence of pH

To optimize the experimental conditions for the determination of CBZ, the effects of the composition of the buffer systems (such as Britton–Robinson, acetate or phosphate buffer) were examined. The results showed that the highest oxidation peak current for CBZ can be obtained in BR buffer. Then, the influence of pH on the electrochemical behavior of CBZ was tested at different pH values in the range of 1.5–6.0 using 0.04 mol L^{-1} B–R buffer as supporting electrolyte contain $4.0 \times 10^{-5} \text{ mol L}^{-1}$ of CBZ. Thus, an acidic solution of BR buffer (pH 2) was chosen for the determination of CBZ by DPV technique. This was agreed with the previous report on voltammetric determination of CBZ [22].

3.3. Optimization of the experimental variables

In order to establish the optimum conditions, parameters in differential pulse voltammetry were optimized. The effect of pulse amplitude, at 10 to 100 mV was studied. The results

showed that, the better signal to background current characteristic could be obtained with pulse amplitude of 70 mV.

The deposition time was investigated in the range from 0 to 100 s. The maximum peak current was obtained of 50 s, and this was the value chosen for further work. The influence of deposition potential is examined from -0.7 to +0.5 V and the best result is achieved in -0.500 V. Thus, the optimum conditions for further studies were chosen as, pulse amplitude, 70 mV, deposition time 50 s, and deposition potential -0.50 V.

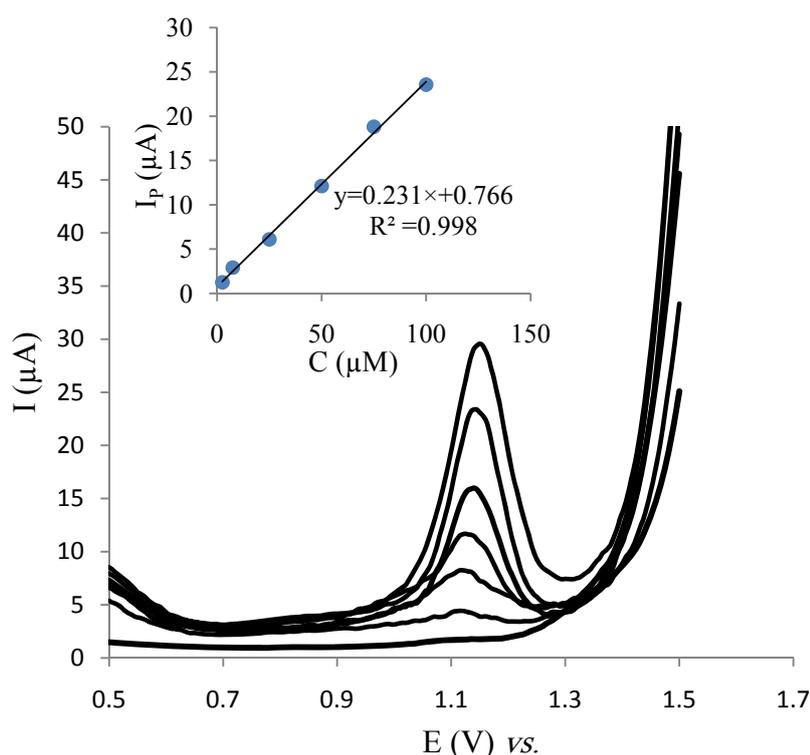


Fig. 7. Differential pulse voltammograms of solutions containing various concentrations and calibration curve of peak current versus concentration of carbamazepine. Supporting electrolyte in all measurements was 0.04 M Britton-Robinson buffer with pH 2 and pulse amplitude was 25 mV

3.4. Calibration and detection limit

The relationship between the oxidation peak current and the concentration of CBZ was examined by DPV on the surface of Ag/TiO₂-CPE and the results are shown in Fig. 7. Under the optimum conditions, the oxidation peak currents were proportional to CBZ concentrations over range of 2.5×10^{-6} to 1.0×10^{-4} mol L⁻¹ in 0.04 mol L⁻¹ B-R buffer solution (pH 2) (inset of Fig. 7). The linear regression equation for this region was:

$$I_p = 0.231 C (\mu\text{mol L}^{-1}) + 0.766 \quad R^2 = 0.998$$

Using this calibration plot, the detection limit ($S/N=3$) of 8.56×10^{-7} mol L⁻¹ is obtained for CBZ.

3.5. Repeatability, stability and reproducibility of the modified electrode

The repeatability of Ag/TiO₂ modified electrode was investigated by repetitive recording at a fixed CBZ concentration of 4.0×10^{-5} mol L⁻¹. The RSD for the peak currents in CVs based on five replicates was 2.7%, indicating excellent repeatability of the response of the modified electrode. Also, on using the Ag/TiO₂-CPE daily and storing under ambient conditions over a period of 2 weeks, the electrode retained 97.3% of its initial peak current response for a CBZ concentration of 4.0×10^{-5} mol L⁻¹, which shows long-term stability of the paste. As well the fabrication reproducibility was evaluated by preparing five modified electrodes independently. The RSD for the peak current determinations with five prepared electrodes on 4.0×10^{-5} mol L⁻¹ CBZ was calculated to be 3.4%. The results indicate that the modified electrode has a good repeatability and reproducibility in both preparation procedure and voltammetric determinations with good long-term stability.

3.6. Determination of carbamazepine in a pharmaceutical product

To assess the applicability of the proposed modified CPE, the electrode was used to determination of CBZ in “carbamazepine” tablets as a real pharmaceutical sample by applying DPV method. Following the procedure described previously (section 2.5); the determination of carbamazepine was performed by using the standard addition method in order to minimize the matrix effect. The linear dynamic range and the slopes of the calibration curves of the standard addition method were utilized to the evaluation of the recovery of the presented procedure. Although the accuracy was calculated on the recovery of known amounts of the standard CBZ solution spiked in tablet solution. Spiked samples were prepared at three levels. The results are demonstrated in Table 1, and the recoveries were in the range from 98.6% to 101.3%. Using this standard addition method, the CBZ content was obtained to be 196.3 (± 3.4) mg/tablet, which is very close to the labeled amount 200 mg/tablet.

Table 1. Determination and recovery of carbamazepine in pharmaceutical of its drug

Sample	Labeled claim (mg/tablet)	Added (mg)	Found	Recovery (%)
Carbamazepine tablet	200	-	197.3 \pm 3.4 ^a	98.6
"	-	118	321.2 \pm 3.2	101.0
"	-	175	372.5 \pm 3.7	99.3
"	-	236	441.5 \pm 3.0	101.3

^a Average of 5 determination

4. CONCLUSIONS

In the present study, electrochemical determination of carbamazepine was investigated by using a modified carbon- paste electrode with Ag/TiO₂ nanocomposite. The catalytic activity on nanosized titanium dioxide doped with Ag nanoparticles was caused enhancement in electrochemical response in CV and DPV voltammograms. The developed methodology of this study was simple, fast, sensitive and cheap especially in comparison with sophisticated techniques such as chromatography. Finally, the modified electrode has been applied successfully in determination of CBZ in real samples.

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