

Voltammetric Determination of Carbidopa Using a modified Multiwall Carbon Nanotube Paste Electrode

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A modified carbon nanotubes paste electrode (MCNTPE) was used for the sensitive voltammetric determination of carbidopa (CD) in buffer solution using cyclic voltammetry (CV), square wave voltammetry (SWV) and chronoamperometry (CHA). The diffusion coefficient ($D = 2.62 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and the kinetic parameter such as the electron transfer coefficient ($\alpha=0.37$) of CD oxidation at the surface of MCNTPE was determined using electrochemical approaches. It has been found that under an optimum condition (pH 9.0), the oxidation of CD at the surface of the modified electrode occurs at a potential about 100 mV less positive than that of an unmodified carbon nanotubes paste electrode. SWV of CD at the modified electrode exhibited linear dynamic range with a detection limit (3σ) of 0.4 μM . Finally, this modified electrode was also examined for the determination of CD in urine samples.

Keywords: Carbidopa determination, Modified electrode, Carbon nanotubes, Sensor

1. INTRODUCTION

Carbidopa (Lodosyn) is a drug given to people with Parkinson's disease in order to inhibit peripheral metabolism of levodopa [1]. The combination of carbidopa/levodopa carries the brand names of Sinemet, Parcopa and Atamet; while Stalevo is a combination with entacapone, which enhances the bioavailability of carbidopa and levodopa. Therefore, determination of this drug is very important in biological sample such as urine. Different techniques have been employed for the determination of CD [2-9]. Long analysis times, the use of organic solvents and high costs are some of the drawbacks associated with these techniques. Voltammetry is considered as an important electrochemical technique utilized in electroanalytical chemistry because it provides low cost, sensitivity, precision, accuracy, simplicity and rapidity [10-12].

Carbon paste electrodes (CPEs) belong to promising electrochemical or bioelectrochemical sensors of wide applicability [13-18]. In 2008, it was exactly a half century since Ralph Norman

Adams from the University of Kansas published a short one-page report [19] in which he introduced this kind of electrode, which was originally designed as an alternative to the dropping mercury electrode. Although the concept of a dynamic renewable electrode surface was not successful, it turned out that the material with paste-like consistency could be practically employed in voltammetric analysis. Carbon pastes undoubtedly represent one of the most convenient materials for the preparation of modified electrodes [20-29].

Since the discovery of carbon nanotubes (CNTs) in 1991[30], numerous investigations were focused on the studies of their properties and applications [31–33]. Because of the special tube structure, CNTs possess several unique properties such as good electrical conductivity, high chemical stability and extremely high mechanical strength [34, 35].

In addition, the subtle electronic behavior of CNTs reveals that they have the ability to promote electron-transfer reactions and have a high electrocatalytic effect when used as electrode materials [36]. All these fascinating properties make CNTs suitable candidates for the modification of electrodes [37-45].

In this study, we used voltammetric, square wave voltammetry and chronoamperometry at pH 9.0 to demonstrate the electrochemical behavior of CD on a modified multiwall carbon nanotubes paste electrode. The proposed method has been used in the determination of CD in urine samples.

2. EXPERIMENTAL

2.1. Chemicals

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout. Carbidopa was used from Fluka.

A 1.0×10^{-2} mol L⁻¹ CD solution was prepared daily by dissolving 0.056 g carbidopa in water and the solution was diluted to 25 mL with buffer in a 25-mL volumetric flask. The solution was kept in the refrigerator at 4 °C in the dark. More dilute solutions were prepared by serial dilution with water.

Phosphate buffer (sodium dihydrogen phosphate and disodium monohydrogen phosphate plus sodium hydroxide, 0.1 mol L⁻¹) solutions with different pH values were used.

Multiwall carbon nanotubes (>90% MWCNT basis, d×l = (90–70 nm) × (5–9 μm)) from Fluka were used as the substrate for the preparation of the carbon paste electrode as a working electrode. Spectrally pure graphite powder (particle size <50 μm) from Merck and high viscose paraffin oil (density = 0.88 Kg L⁻¹) from Merck were used for the preparation of the carbon paste electrode (CPE).

2.2. Apparatus

Cyclic voltammetry, chronoamperometry and square wave voltammetry were performed in an analytical system, Autolab PGSTAT 302N, potentiostat/galvanostat connected to a three electrode cell,

Metrohm Model 663 VA stand, linked with a computer (Pentium IV, 1200 MHz) and with Autolab software.

A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an Ag/AgCl (KCl_{sat}) electrode as a reference electrode was used. The working electrode was either an unmodified carbon nanotubes paste electrode (CNTPE) or a MCNTPE. The prepared electrodes with carbon nanotubes and with the modifier were characterized by scanning electron microscopy (SEM) (XLC Philips).

A pH-meter (Corning, Model 140) with a double junction glass electrode was used to check the pH of the solutions.

2.3. Preparation of the electrode

1.0 mg chloranilic acid hand mixed with 89 mg of graphite powder and 10 mg of carbon nanotubes in a mortar and pestle. Using a syringe, 0.88 g paraffin was added to the mixture and mixed well for 40 min until a uniformly-wetted paste was obtained.

The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture.

When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper. The unmodified carbon paste electrode (CPE) was prepared in the same way without adding mediator and carbon nanotubes to the mixture to be used for comparison purposes.

2.4. Preparation of real samples

The urine samples were stored in a refrigerator immediately after collection. Ten milliliters of the sample was centrifuged for 10 min at 2000 rpm. The supernatant was filtered using a 0.45 μm filter and then diluted 5 times with universal buffer pH 9.0. The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment. Standard addition method used for the determination of CD in real samples.

2.5. Recommended procedure

The multiwall carbon nanotubes paste electrode was polished with a white and clean paper. To prepare a blank solution, 10.0 mL of buffer solution (PBS, pH 9.0), was transferred into an electrochemical cell.

The initial and final potentials were adjusted to -0.2 and $+0.20$ V vs. Ag/AgCl, respectively. The SWV was recorded with frequency of 10 Hz to give the blank signal and labeled as I_{pb} . Then different amounts of CD solution were added to the cell, using a micropipette, and the SWV was recorded again to get the analytical signal (I_{ps}). Calibration curves were constructed by plotting the catalytic peak current vs. the CD concentration.

3. RESULT AND DISCUSSION

3.1. SEM characterization of the surface of the modified electrodes

Fig. 1 displays a typical morphology of MCNTPE (Fig. 1A) and CNTPE (Fig. 1B) characterized by SEM. As shown in this figure, mediator at CNTs did not change the morphology of CNTs, but made it more compact.

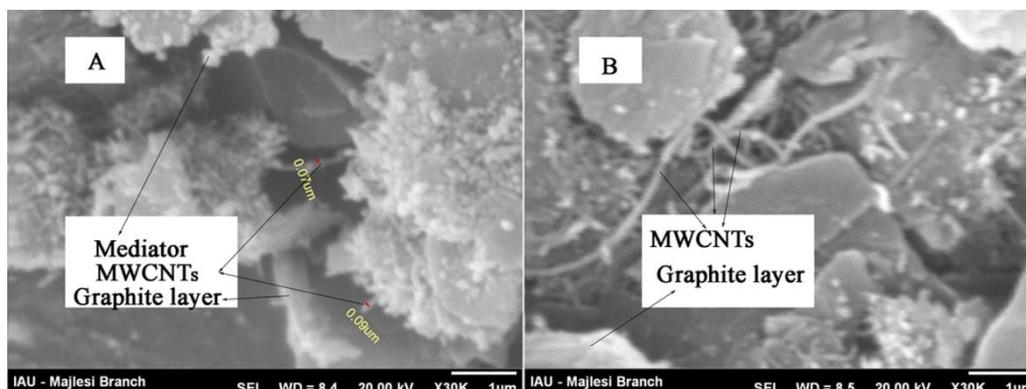


Figure 1. SEM image of A) MCNTPE and B) CNTPE.

3.2. Electrochemistry of mediator

Cyclic voltammogram of MCNTPE exhibited an anodic peak, in the potential interval of -0.20 to $+0.25$. The experimental results showed a well-defined and reproducible anodic peak related to the oxidation of chloranilic acid in MCNTPE with $E_{pa} \sim 0.10$ V. This can be used as a suitable amperometric sensor for the oxidation of some important biological compounds such as CD, characterized by a slow electron transfer [45]. The effect of potential scan rate (from 10 to 100 mVs^{-1}) on the electrochemical properties of mediator redox couple in MCNTPE was studied in the buffer solution (pH 9.0) using cyclic voltammetry. A linear correlation was obtained between the peak currents and the square root of the scan rate. This behavior indicates that the nature of the redox process is diffusion controlled.

3.3. Electrocatalytic oxidation of CD

The utility of the modified electrode for oxidation of CD was evaluated by cyclic voltammetry. The cyclic voltammetric responses of a bare carbon nanotubes paste electrode (CNTPE) in 0.1 M phosphate buffer (pH 9.0), without and with CD, are shown in Fig. 2 (curves a and b, respectively). Fig. 1c and d show cyclic voltammograms of modified electrode in the buffer solution with $400 \mu\text{M}$ of CD and without CD, respectively. The results show that the sensor produces a large anodic peak current in the presence of CD without a cathodic counterpart (Fig. 2, curve c). That the current observed is associated with CD oxidation and not the oxidation of modifier is demonstrated by

comparing the current in Fig. 2 (curve d, without CD) with the one in the presence of CD in Fig. 2 (curve c). It is apparent that the anodic current associated with the surface-attached materials is significantly less than that obtained in the solution containing CD. At the surface of a bare electrode, CD was oxidized to around 220 mV. As can be seen the electroactivity of CD on the modified electrode was significant (Fig. 2, curve c), with strongly defined peak potential, around 120 mV vs. Ag/AgCl/KCl electrode.

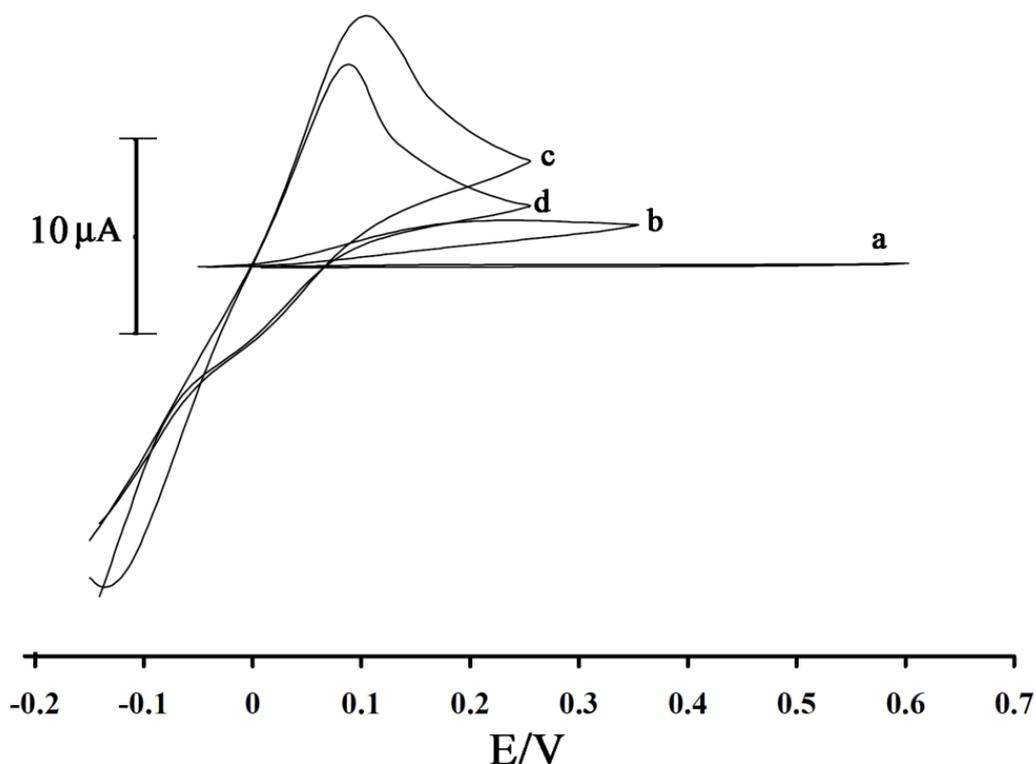


Figure 2. Cyclic voltammograms of 0.1 mol L⁻¹ PBS (pH 9.0) at a scan rate of 20 mV s⁻¹ a) in the absence; and b) in the presence of 400 μM CD, at CNTPE, respectively. c) Is as (b) at MCNTPE. d) Is as (a) at MCNTPE.

Thus, a decrease in overpotential and enhancement of peak current for CD oxidation is achieved with the modified electrode. Such behavior is indicative of an EC' mechanism [46, 47]. The effect of scan rate on the electrocatalytic oxidation of 500 μM CD at the modified electrode was investigated by linear sweep voltammetry.

The oxidation peak potential shifts with increasing scan rates toward a more positive potential, confirming the kinetic limitation of the electrochemical reaction. Also, a plot of peak height (I_p) against the square root of scan rate ($v^{1/2}$), in the range 3–20 mV s⁻¹, was constructed, which was found to be linear, suggesting that at sufficient overpotential the process is diffusion rather than surface controlled (Fig. 3).

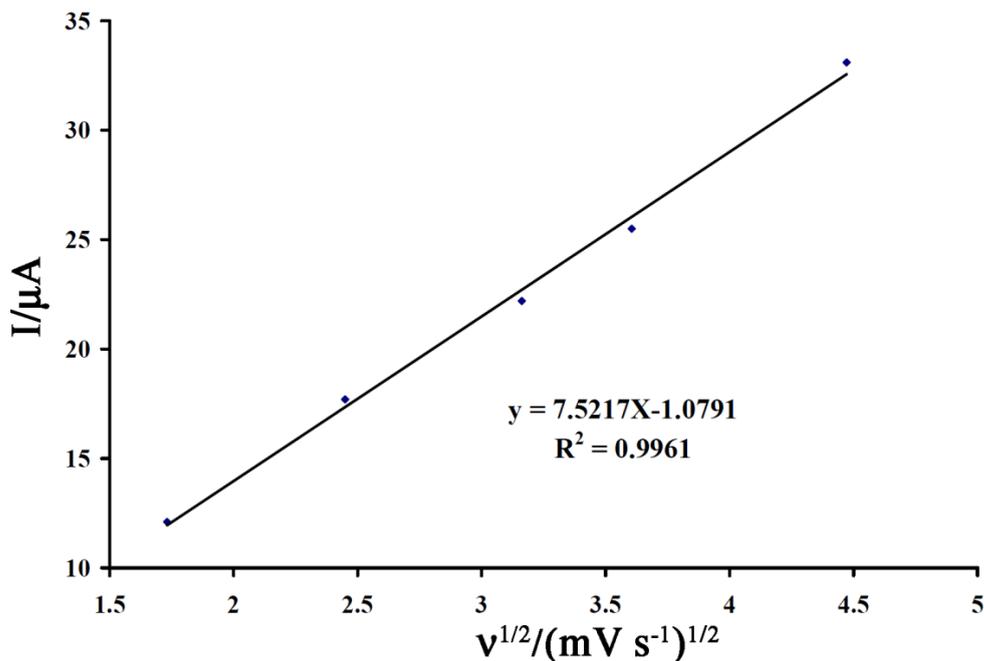


Figure 3. Plot of I_{pa} versus $v^{1/2}$ for the oxidation of CD at MCNTPE.

In order to get the information about the rate determining step, a Tafel plot was developed for MCNTPE using the data derived from the raising part of the current–voltage curve (Fig. 4). The slope of the Tafel plot is equal to $10.5930 V decade^{-1}$. Using this data gives $n_{\alpha} = 0.37$. If assuming $n = 1$, then $\alpha = 0.37$.

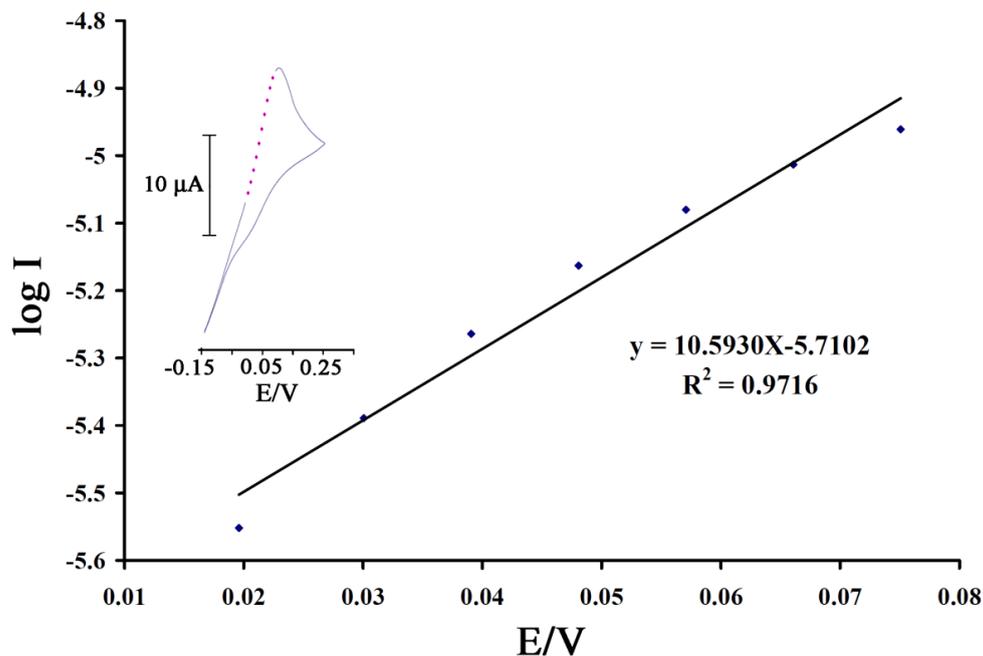


Figure 4. Tafel plot for MCNTPE in 0.1 M PBS (pH 9.0) at a scan rate of $20 mV s^{-1}$ in the presence of $400 \mu M$ CD.

3.4. Chronoamperometric study

Chronoamperometric measurements of CD at MCNTPE were carried out by setting the working electrode potential at 0.0 V (at the first potential step) and at 0.2 V (at second potential step) vs. Ag/AgCl/KCl_{sat} for the 400 μM of CD in buffered aqueous solutions (pH 9.0) (Fig. 5A). For an electroactive material (CD in this case) with a diffusion coefficient of D, the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation [48]. Experimental plot of I vs. $t^{-1/2}$ was employed, with the best fits for 400 μM of CD (Fig. 5B). The slope of the resulting straight lines was then plotted vs. CD concentration (Fig. 5B). From the resulting slope and Cottrell equation, the value of the D was found to be 2.62×10^{-5} cm²/s.

Furthermore, chronoamperometry can also be employed to evaluate the catalytic rate constant, k, for the reaction between CD and mediator at a surface of MCNTPE according to the method of Galus [49]:

$$I_C/I_L = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (kC_b t)^{1/2} \quad (1)$$

Where t is the time elapsed and C_b is the bulk concentration of CD. The above equation can be used to calculate the rate constant of the catalytic process k. Based on the slope of the I_C/I_L versus $t^{1/2}$ plot; k can be obtained for a given CD concentration. Such plots were obtained from the chronoamperograms in Fig. 5A (Fig. 5C). From the values of the slopes, an average value of k was found to be $k = 5.37 \times 10^2$ μM⁻¹s⁻¹.

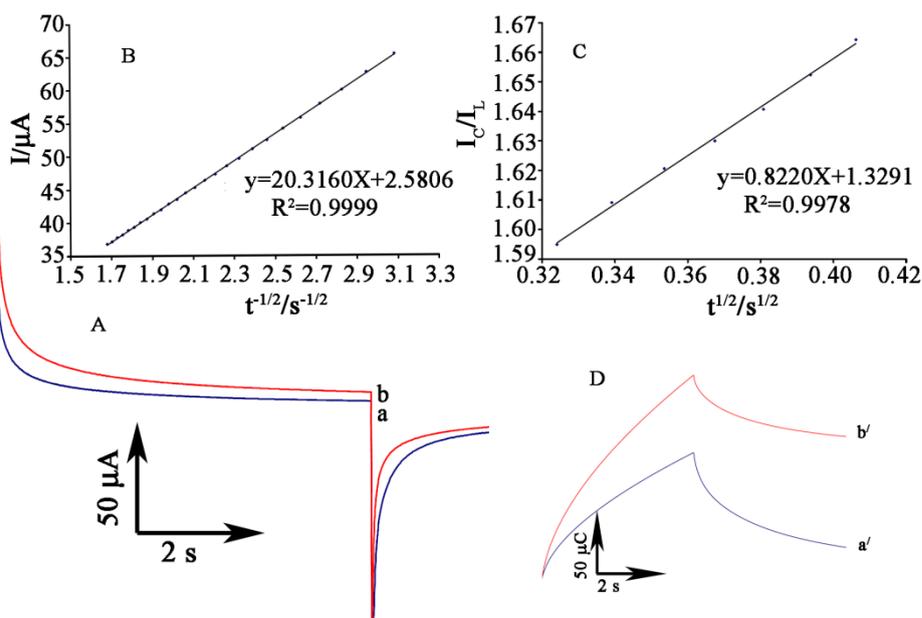


Figure 5. A) Chronoamperograms obtained at MCNTPE a) in the absence, and in the presence of b) 400 μM CD at pH 9.0. B) Cottrell's plot for the data from the chronoamperograms. C) Dependence of I_C/I_L on $t^{1/2}$ derived from the chronoamperogram data. D) The charge-time curves a') for curve (a) and b') for curve (b).

Fig. 5D shows the double-potential step chronocolougrams for the mediator in the absence and presence of 400 μM CD at a surface of MCNTPE.

The results show that forward and backward potential step chronocoloumetry in a blank buffer solution yields very symmetrical chronocolougrams.

These had about an equal charge consumed for both oxidation and reduction of the redox system in the mediator at a surface of MCNTPE. However, in the presence of CD, the charge value associated with forward chronocoloumetry was significantly greater than that observed for backward chronocoloumetry. This behavior is typically expected for electrocatalysis at chemically modified electrodes [50].

3.5. Calibration plot and limit of detection

Square wave voltammetry was used to determine the concentration of CD. Responses were linear with CD concentrations ranging from 0.6 to 100 μM and a current sensitivity of 0.0632 $\mu\text{A}/\mu\text{M}$. The detection limit (3σ) was 0.4 μM .

3.6. Determination of CD real sample

To evaluate the applicability of the proposed method to real samples, it was applied to the determination of CD in urine sample.

The CD contents were measured after sample preparation using the standard addition method. The results are given in Table 1.

Table 1. Determination of CD in urine (n=3)

Sample No.	Added (μM)	Expected (μM)	Found (μM)	Recovery (%)
1	0.0	—	<LOD	—
2	10.0	10.0	10.21 \pm 0.31	102.1
3	10.0	20.0	19.88 \pm 0.42	99.4
4	30.0	50.0	50.64 \pm 0.70	101.3

3.7. Interference studies

The influence of various substances as potential interference compounds on the determination of CD under the optimum conditions with 1.0 μM CD at pH 9.0 was studied. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than 5% for the determination of CD.

The results are given in Table 2 and show that the peak current of CD is not significantly affected by all conventional cations, anions, and organic substances.

Table 2. Interference study for the determination of 1.0 μM CD under the optimized conditions.

Species	Tolerance limits (W/W)
Glucose, Sucrose, Lactose, Fructose, Methanol, Ethanol, K^+ , Na^+ , Cl^- , Ca^{2+} , Mg^{2+} , SO_4^{2-}	1000*
Alanine, Phenylalanine, Methionine, Glycine, Tryptophan	500
Starch	Saturated
Urea, Thiourea	200

* Maximum concentration of species tested

4. CONCLUSION

In this study, the suitability of a modified carbon nanotubes paste electrode was investigated for the electrocatalytic determination of CD in an aqueous solution. The electrochemical behavior of CD at the surface of MCNTPE showed that CD electrooxidation is catalyzed at pH 9.0. Finally, the modified electrode was also examined as a selective, simple, and precise new electrochemical sensor for the determination of CD in urine sample.

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