



Original scientific paper

A sensitive and simple electrochemical technique for detecting ascorbic acid content in pharmaceutical and biological compounds

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Received: April 29, 2022; Accepted: June 4, 2022; Published: August 10, 2022

Abstract

In the current study, a glassy carbon electrode (GCE) modified with graphene-CoS₂ nanocomposite was investigated for electrochemical sensing of ascorbic acid. The electrochemical performance of the modified electrode was examined using differential pulse voltammetry (DPV), linear sweep voltammetry (LSV) and chronoamperometry (CHA) techniques. The electrochemical behavior of ascorbic acid at the graphene-CoS₂/GCE displayed a higher oxidation current and lower oxidation potential than bare GCE. Under the optimal experimental conditions, the sensor presented a good linear response between the current and the ascorbic acid concentration range of 0.15–245.0 μM, with a low detection limit of 0.05 μM. Finally, the graphene-CoS₂ nanocomposite-modified GCE was applied for the determination of ascorbic acid in real samples and displayed excellent recoveries.

Keywords

Glassy carbon electrode; graphene-CoS₂ nanocomposite; sensors

Introduction

Ascorbic acid, also known as vitamin C, is a natural water-soluble vitamin broadly existing in a variety of fruits and vegetables [1]. Ascorbic acid is one of the most common small biological molecules found in human blood, and it plays an integral part in the body's general physiological functioning [2]. Ascorbic acid acts as a neuro-modulator and critical nutrient for the human body, with a daily dose of 100 mg necessary for good health [3]. Ascorbic acid plays crucial role in many physiological reactions and biochemical processes, including the synthesis of collagen and wound healing as well as its redox functions [4-6]. It promotes cellular immunity by increasing the number of immune cells, including lymphocytes and neutrophils. Ascorbic acid guards against any oxidative damage to DNA, membrane lipids, and proteins, which has been implicated as a major factor in the development of chronic diseases such as cataracts, cancer, and cardiovascular diseases [7]. This vitamin is also considered an indirect antioxidant by regenerating other biologically important antioxidants such as vitamin E and glutathione to their active state [8]. Ascorbic acid is included in

the biosynthesis of collagen and acts as a co-factor in the biosynthesis of cholesterol, L-carnitine, catecholamines, amino acids, and some peptide hormones [9,10]. Ascorbic acid deficiency reduces resistance to bacterial, viral and fungal infections and is associated with symptoms of scurvy such as muscle weakness, tooth loss, rash, tiredness, and joint pain [11]. Therefore, developing an approach for the detection of ascorbic acid is an essential step. Until now, several techniques, including electrophoresis [12], spectrophotometry [13,14], chemiluminescence [15], fluorescence and chromatography [17,18] have been investigated and applied. Although these techniques are superior in accuracy and selectivity, they require sample purification steps and skilled technicians and are expensive. The alternative methods developed for the detection of ascorbic acid are required to be sensitive and precise.

At this point, the electrochemical techniques that provide highly sensitive data with precision, as well as ease of experimental setup and rapid response, attracted great attention [19-27]. Glassy carbon electrode (GCE) is a relatively pure material, highly inert to chemical attack, gas impermeable, electrically conductive, and easily modified [28].

The electron transfer efficiency and detection sensitivity of electrochemical sensors will be improved with the selection of suitable sensor surface modification materials [29-38]. Advances in nanotechnology and nanomaterials bring new perspectives to various fields [39-44]. Their unique properties, such as physical, chemical, biological, optical, and magnetic properties, nanoscale materials have high surface/volume ratios that facilitate the recognition of molecules and contribute to the enhanced signal transmission between the interface and the target molecule. Hence, many research efforts have been devoted to the modification of electrodes by nanomaterials to improve analytical performance [45-53].

Carbon-based compounds are commonly used because of their biocompatibility, good chemical stability, high surface area, unique electrical properties, good electron transfer kinetics, and low cost. Graphene is one kind of two-dimensional carbon-based nanomaterial, and it has received considerable interest since it was discovered [54]. Because of extraordinary physicochemical properties, including large surface area, excellent conductivity, and good biocompatibility, inexpensive graphene-based materials have been widely employed as electrode materials for constructing electrochemical sensors [55-60]. Furthermore, electrodes modified with integrated graphene-based materials and transition metal sulfides nanoparticles can generally retain the properties of each material, increase surface area and improve the analytical performances for analyte determination [61]. Transition metal sulfides such as cobalt sulfide and their composites have attracted considerable attention in electrochemical due to their fascinating properties, including high specific capacity, improved electric conductivity, and desirable electrochemical activity compared to their corresponding oxides [62-64]. These marvelous properties endow them with more outstanding electrochemical performance, providing the tremendous potential for a modified electrode.

This paper illustrates the development of an electrochemical sensor to measure ascorbic acid. The modification of GCE with graphene-CoS₂ nanocomposite provided a sensitive platform for the quantitative analysis of ascorbic acid by DPV technique.

Experimental

Apparatus and chemicals

All the electrochemical measurements were carried out on a PGSTAT302N potentiostat/galvanostat Autolab consisting of a traditional three-electrode system: a bare or modified GCE as the working electrode, an Ag/AgCl as the reference electrode and a Pt wire as a counter electrode.

Solution pH values were determined using a 713 pH meter combined with a glass electrode (Metrohm, Switzerland). Ascorbic acid and other chemicals used were analytical grade and were purchased from Merck.

Synthesis of graphene-CoS₂ nanocomposite

In the synthesis of the graphene-CoS₂ nanocomposite, 80 mg of graphene oxide powder was ultrasonically dispersed in 100 mL of deionized water to form a clear suspension. 0.2022 g CoCl₂·6H₂O and 0.1294 g thiourea were then dissolved into the above suspension. Subsequently, the prepared suspension was transferred into a Teflon-lined stainless-steel autoclave with heat at 160 °C for 12 h. Eventually, the product was obtained by centrifuging and washing with deionized water and then dried at 70 °C in vacuum. The FE-SEM image of the graphene-CoS₂ nanocomposite is shown in Fig. 1.

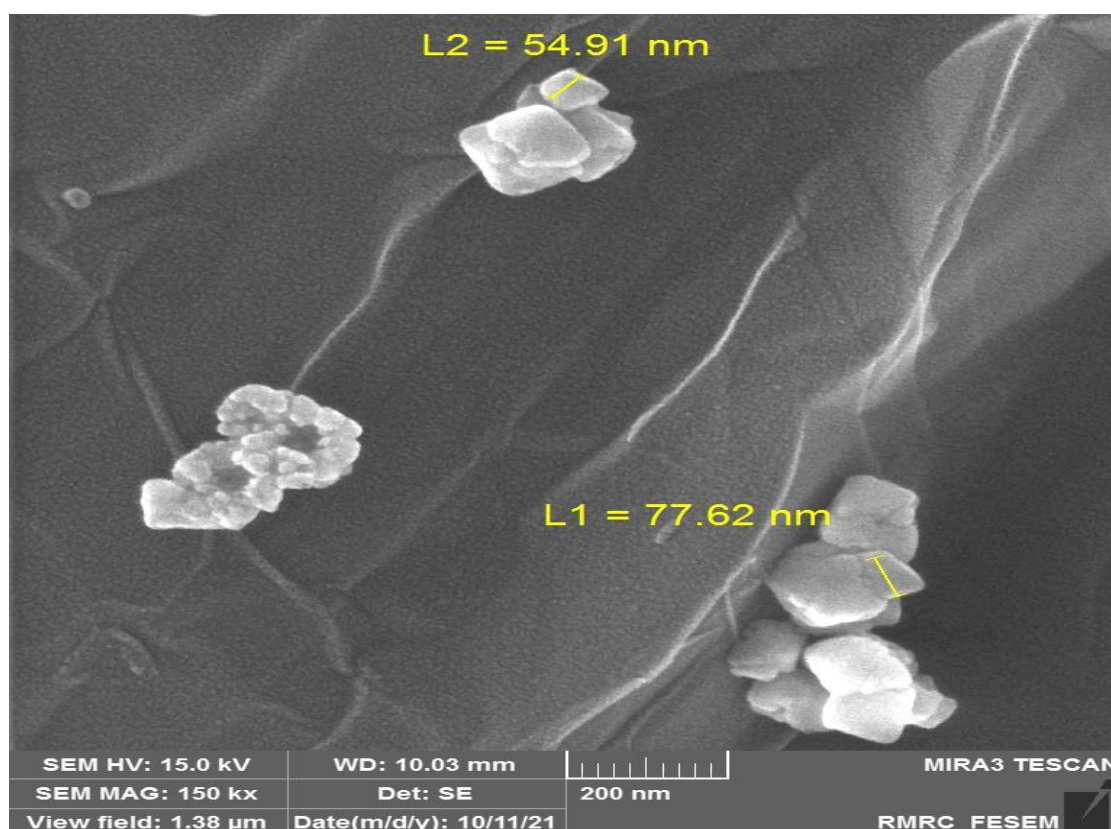


Figure 1. FE-SEM image of the graphene-CoS₂ nanocomposite

Preparation of graphene-CoS₂/GCE

Prior to modification of GCE with graphene-CoS₂ nanocomposite, a GCE was polished with alumina slurries and rinsed with acetone, ethanol, and deionized water under sonication for 2 min. Then, 1 mg graphene-CoS₂ nanocomposite was dispersed in 1 mL aqueous solution within 20 min ultrasonication. Then, 4 μL of the prepared suspension was dropped on the surface of the working electrode. It remains at room temperature until it becomes dry. The surface area of graphene-CoS₂/GCE and the bare GCE were obtained by CV using 1 mM K₃Fe(CN)₆ at different scan rates. Using the Randles-Sevcik formula for graphene-CoS₂/GCE, the electrode surface was found 0.13 cm² which was about 4.1 times greater than bare CPE.

Results and discussion

Electrochemical behavior of ascorbic acid at the surface of various electrodes

The effect of the electrolyte pH on the oxidation of 35.0 μM ascorbic acid was investigated at graphene- CoS_2/GCE using DPV measurements in the PBS in the pH range from 2.0 to 9.0. According to the results, the oxidation peak current of ascorbic acid depends on the pH value and increases with increasing pH until it reaches the maximum at pH 7.0, and then decreases with higher pH values. The optimized pH corresponding to the higher peak current was 7.0, indicating that protons are involved in the reaction of ascorbic acid oxidation.

The electrochemical behavior of ascorbic acid was investigated by DPV. The differential pulse voltammograms obtained using the bare GCE, and graphene- CoS_2/GCE in 0.1 M PBS (pH 7.0) in the presence of 100.0 μM ascorbic acid are shown in Figure 2. At the bare GCE, a weak oxidation peak current ($i_{pa} = 3.9 \mu\text{A}$) could be seen at 0.43 V. In contrast, graphene- CoS_2/GCE exhibited an enhanced sharp anodic peak current ($i_{pa} = 17 \mu\text{A}$) at a much lower overpotential $E_p = 0.32 \text{ V}$. These results confirmed that the graphene- CoS_2 nanocomposite improved the sensitivity of the modified electrode by enhancing peak current and decreasing the overpotential of the oxidation of ascorbic acid.

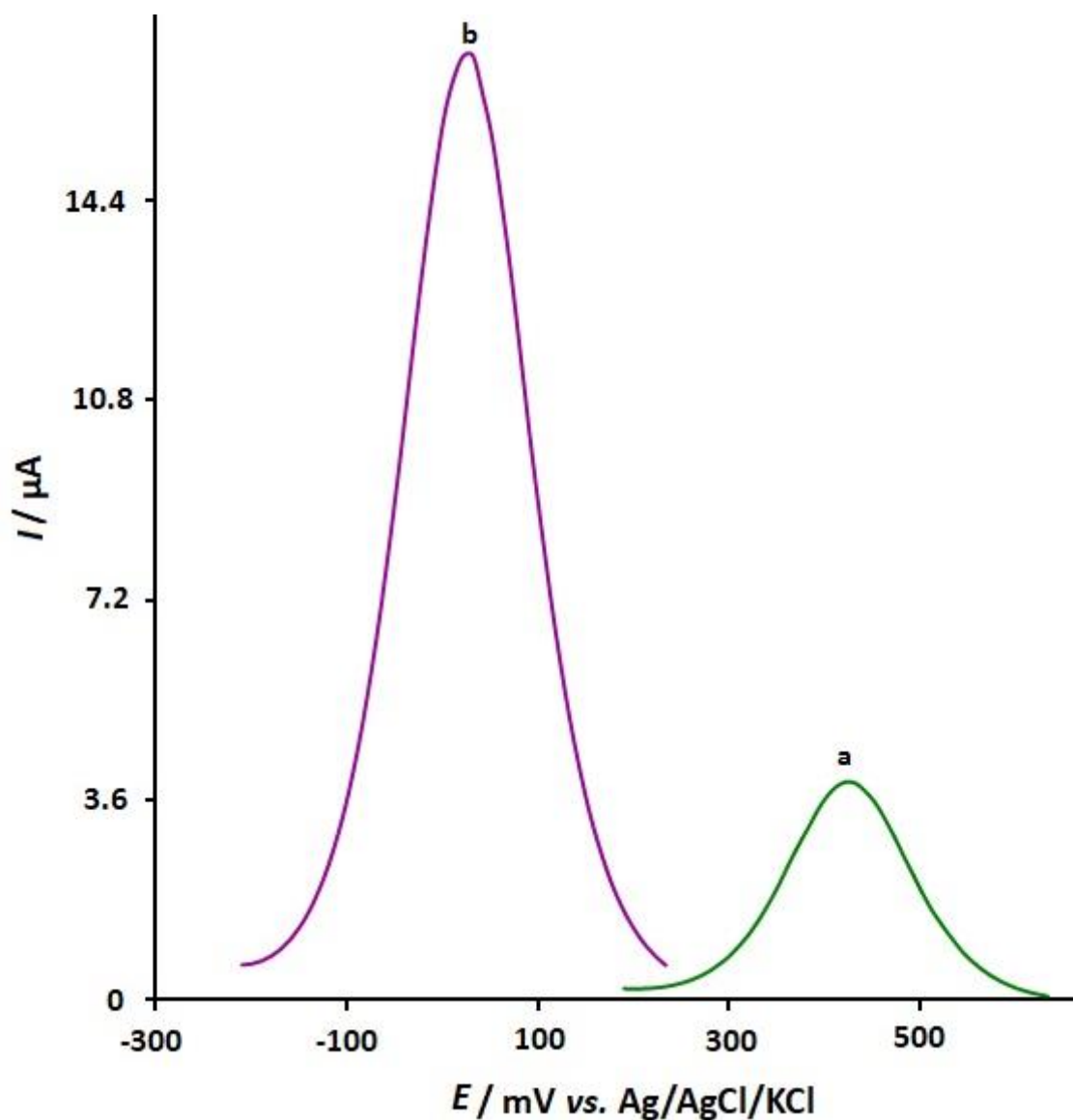


Figure 2. Differential pulse voltammograms of (a) bare GCE and (b) graphene- CoS_2/GCE in 0.1 M PBS (pH 7.0) in the presence of 100.0 μM ascorbic acid at the scan rate 50 mV s^{-1}

Effect of scan rate on the determination of ascorbic acid at graphene-CoS₂/GCE

The influence of the scan rate (ν) on the peak currents (I_{pa}) of ascorbic acid at graphene-CoS₂/GCE was investigated by LSV. Figure 3 shows the voltammetric response of 70.0 μ M ascorbic acid at graphene-CoS₂/GCE at different scan rates in the range of 10 to 600 mV s^{-1} . The oxidation peak current of ascorbic acid increases linearly with increasing scan rate. A linear regression equation was obtained from the plot I_{pa} vs. $\nu^{1/2}$ as follows; $I_{pa} = 1.7128 \nu^{1/2} - 2.0173$ ($R^2 = 0.9991$) for the oxidation process, which indicates the reaction of ascorbic acid at graphene-CoS₂/GCE is diffusion controlled.

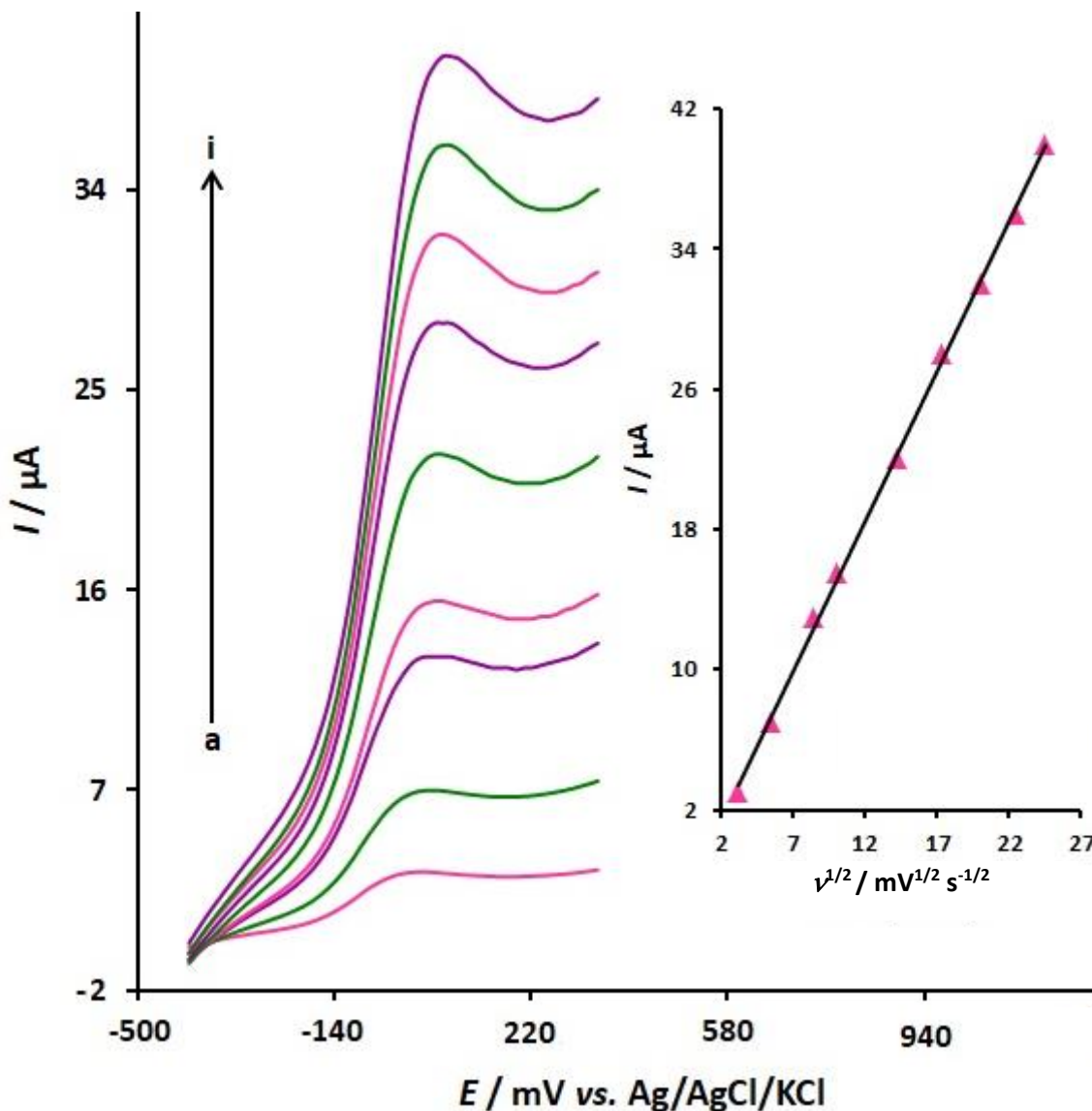


Figure 3. Linear sweep voltammograms of graphene-CoS₂/GCE in 0.1 M PBS (pH 7.0) containing 70.0 μ M ascorbic acid at various scan rates; a-i correspond to 10, 30, 70, 100, 200, 300, 400, 500, and 600 mV s^{-1} , respectively. Inset: variation of anodic peak current vs. $\nu^{1/2}$

Chronoamperometric analysis

The analysis of chronoamperometry for ascorbic acid samples was performed by use of graphene-CoS₂/GCE vs. Ag/AgCl/KCl (3.0 M) at 0.37 V. The chronoamperometric results of different concentrations of ascorbic acid in PBS (pH 7.0) are demonstrated in Figure 4. The Cottrell equation for the chronoamperometric analysis of electroactive moieties under mass transfer limited conditions is as in equation (1):

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2} \quad (1)$$

where D represents the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), and C_b is the applied bulk concentration (mol cm^{-3}). Experimental results of I vs. $t^{-1/2}$ were plotted in Figure 4A, with the best fits for different concentrations of ascorbic acid. The resulting slopes corresponding to straight lines in Figure 5A, were then plotted against the concentration of ascorbic acid (Figure 4B). The mean value of D was determined to be $9.3 \times 10^{-5} \text{ cm}^2/\text{s}$ according to the resulting slope and Cottrell equation.

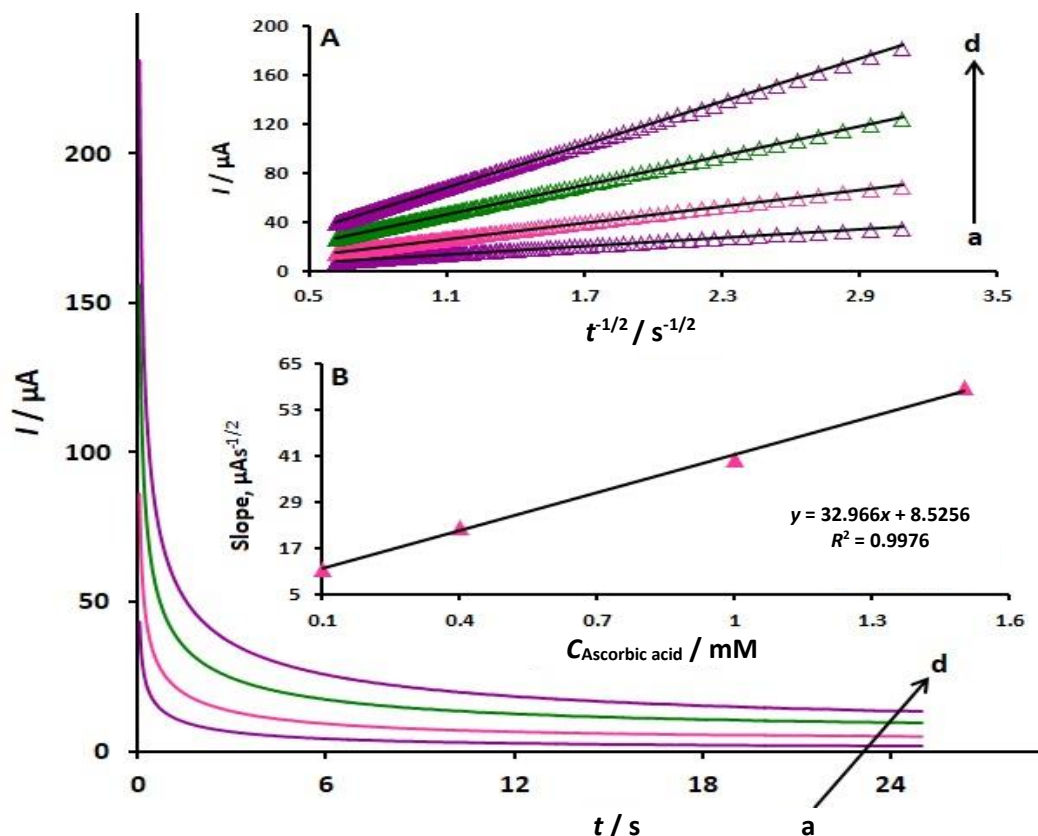


Figure 4. Chronoamperograms obtained at graphene- CoS_2/GCE in 0.1 M PBS (pH 7.0) for different concentrations of ascorbic acid; a-d correspond to 0.1, 0.4, 1.0, and 1.5 mM of ascorbic acid. Insets: (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms a-d. (B) Plot of the slope of the straight lines against ascorbic acid concentration

Calibration curve

Because DPV commonly has a higher sensitivity than the CV technology, the DPV technique was applied for the quantitative detection of ascorbic acid. Figure 5 shows the *differential pulse voltammograms* of ascorbic acid at various concentrations using graphene- CoS_2/GCE (Step potential=0.01 V and pulse amplitude=0.025 V). As seen, the oxidation peak currents of ascorbic acid enhance gradually by increasing its concentration. The oxidation peak currents (I_{pa}) show a good linear relationship with the concentrations of ascorbic acid ranging from 0.15 M to 245.0 μM . The linear equation is $I_{pa} = 0.1552C_{\text{Ascorbic acid}} + 1.1919$ ($R^2 = 0.9994$) (Figure 5 (inset)). Also, the detection limit, C_m , of ascorbic acid was obtained using the equation (2):

$$C_m = 3s_b / m \tag{2}$$

In the above equation, m is the slope of the calibration plot ($0.1552 \mu\text{A } \mu\text{M}^{-1}$) and s_b is the standard deviation of the blank response obtained from 20 replicate measurements of the blank solution. The detection limit is 0.05 μM .

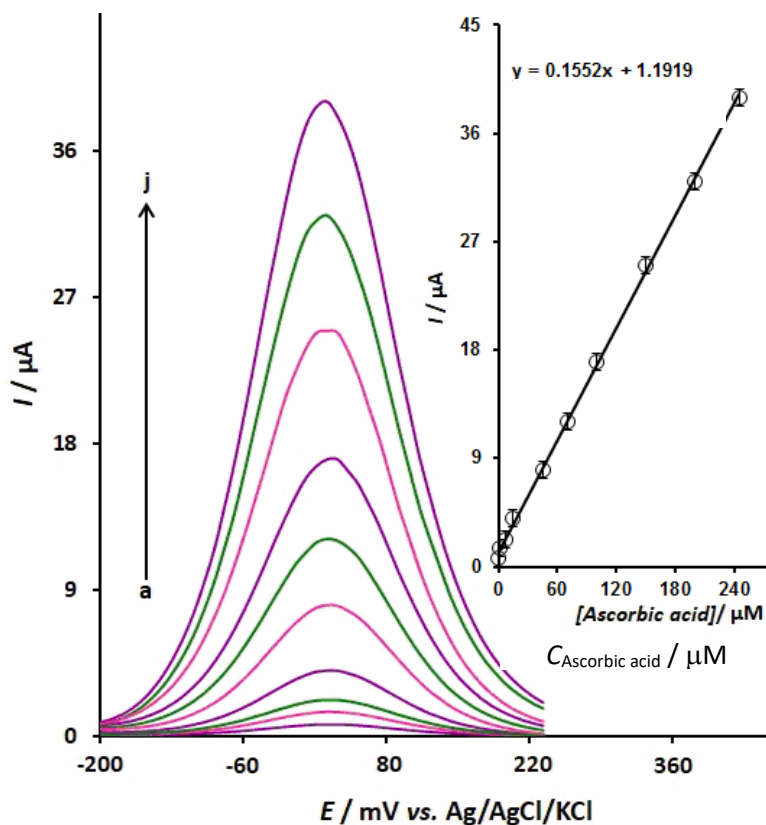


Figure 5. DPVs of graphene-CoS₂/GCE in 0.1 M (pH 7.0) containing different concentrations of ascorbic acid. Numbers 1–9 correspond to 0.15, 2.0, 7.0, 15.0, 45.0, 70.0, 100.0, 150.0, 200.0, and 245.0 μM of ascorbic acid. Inset: plot of the electrocatalytic peak current as a function of ascorbic acid concentration in the range of 0.15–245.0 μM

Analysis of real samples

The real samples for the analysis were prepared and quantified by DPV method. The developed sensor was applied to detect ascorbic acid in effervescent tablets, vitamin C ampoules and multivitamin syrup samples. The results are summarized in Table 1. Each measurement was repeated five times. The recovery and relative standard deviation (RSD) values confirmed that the graphene-CoS₂/GCE sensor has a great potential for analytical application.

Table 1. Application of graphene-CoS₂/GCE for the determination of ascorbic acid in real samples (n=5)

Sample	Concentration, μM		Recovery, %	RSD, %
	Spiked	Found		
Effervescent tablet	0	2.5	-	3.2
	2.5	4.9	98.0	1.9
	3.5	6.1	101.7	2.5
Vitamin C ampoule	0	5.0	-	1.7
	1.0	6.2	103.3	2.9
	2.0	6.9	98.6	3.3
Multivitamin syrup	0	2.0	-	2.6
	2.5	4.6	102.2	3.0
	3.5	5.4	98.2	2.1

Conclusion

In this work, the modification of a GCE with graphene-CoS₂ nanocomposite and its use as a sensor for ascorbic acid in a PBS (pH 7.0) were reported. The modified electrode exhibited good

electrochemical performance in the determination of ascorbic acid. The DPV demonstrated a linear range of ascorbic acid concentration from 0.15 to 245.0 μM , with a calculated detection limit of 0.05 μM . Also, the diffusion coefficient of ascorbic acid was obtained $9.3 \times 10^{-5} \text{ cm}^2/\text{s}$. Moreover, the practical analytical application of the graphene- CoS_2/GCE was assessed by measurement of ascorbic acid in the real samples with satisfactory results.

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