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Magnetic Core–shell Fe_3O_4@SiO_2/Graphene Nanocomposite Modified Carbon Paste Electrode for Voltammetric Determination of Ascorbic Acid in the presence of L-Cysteine

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Abstract- An ionic liquid– magnetic core–shell Fe_3O_4@SiO_2/graphene nanocomposite modified carbon paste electrode (ILFSGCPE) was used as a fast and sensitive tool for the investigation of the electrochemical oxidation of ascorbic acid using voltammetry. This modified electrode has been fabricated using hydrophilic ionic liquid (n-hexyl-3-methylimidazolium hexafluoro phosphate) as a binder. The modified electrode offers a considerable improvement in voltammetric sensitivity toward ascorbic acid, compared to the bare electrode. Using differential pulse voltammetry (DPV), the electrocatalytic oxidation peak current of ascorbic acid shows a linear calibration curve in the range of 1.0×10^{-6} to 9.0×10^{-4} M ascorbic acid. The limit of detection was equal to 2.3×10^{-7} M. The electrode was also employed to study the electrochemical oxidation of ascorbic acid in the presence of L-cysteine.

Keywords - Ascorbic acid, Magnetic core–shell Fe_3O_4@SiO_2/graphene nanocomposite, Ionic Liquids, Carbon paste electrode

1. INTRODUCTION

Ascorbic acid commonly known as vitamin-C, is synthesized from glucose in the liver of most mammalian species except humans [1]. Ascorbic acid as an essential nutrient can be found mainly in fruits and vegetables. Due to its anti-oxidant and pH regulator properties, this vitamin is present or added to a wide variety of food products and pharmaceuticals [2]. It is easily oxidized chemically and electrochemically to L-dehydro ascorbic acid. It is unstable, undergoing oxidation, especially in aerobic conditions, alkaline media, and at exposure to light. It is commonly used to prevent and treat the common cold, mental illness, infertility, cancer, photo-aging, skin disorders, and aids [3]. Therefore, detecting and determining of ascorbic acid in samples are of great importance for pharmaceutical, clinical, and food industries [2]. The determination of ascorbic acid has been established by such methods as chromatography, spectrophotometry, mass spectrometry, flow injection, chemiluminescence and electrochemical methods [4-10].

Cysteine, a non-essential amino acid, plays an important role in biological systems and has been widely used in the medicine and food chemistry [11]. It has several pharmaceutical applications; namely it is used in some antibiotics and for the treatment of skin damage and as a radio protective agent [12]. It is a sulfur containing amino acid required for tissue protein synthesis, and itself or as a component amino acid in glutathione, is capable of forming conjugates with free radicals or trace elements, thereby functioning as a detoxifying agent [13]. Therefore, measurement of cysteine in body fluids is very important from the biological and pharmacological stand points [14]. Many attempts have been applied for the determination of cysteine. Electrochemical oxidation of cysteine is comparatively simple, rapid, inexpensive and sensitive with a suitable linear range. For these reasons there are several reports on the determination of cysteine using electrocatalytic method [15-17].

Ascorbic acid and L-cysteine show high activity for oxidation at the surface of the most reported modified electrodes [18]. Thus, the simultaneous determination of ascorbic acid and L-cysteine for quality control analysis and for medical control is very important. Electrochemical methods appear to be very promising since they ensure reasonably good analytical performance characteristics with essentially no need for expensive and complicated instrumentation.

Among all the carbon electrodes, the carbon paste electrode (CPE) is an appealing and widely used electrode material in the fields of electrochemistry, electroanalysis, etc [19]. Carbon paste electrode (CPE) was introduced by Adams in 1958 [20]. Carbon paste electrodes (CPEs) have better performance and have attracted considerable attention due to their inherent advantages such as very stable electrochemical response, low Ohmic resistance, chemical inertness, easy construction, facile renewability of the surface for electron exchange, long operational lifetime, no need for significant prior pretreatment and suitability for a variety of sensing applications [21,22]. CPEs are nontoxic and environmentally friendly

electrodes [23]. The preparation of CPE usually involves the dispersion of graphite powder in a hydrophobic binder to form a homogeneous paste, followed by filling a tube with the resulting paste [24,25]. The selectivity and sensitivity of the CPEs can be improved by incorporating a selective agent (modifier) in the carbon paste. The modified electrode has good electrocatalytic activity, sensitivity, and selectivity; it has also a low detection limit compared to traditional carbon paste electrodes [26-35]. The electrochemical methods using chemically modified electrodes (CMEs) have been widely used as sensitive and selective analytical methods for the detection of the trace amounts of biologically important compounds [36-42]. One of the most important properties of CMEs has been their ability to catalyze the electrode process via significant decreasing of overpotential respect to unmodified electrode. With respect to relatively selective interaction of the electron mediator with the target analyte in a coordination fashion, these electrodes are capable to considerably enhance the selectivity in the electroanalytical methods.

Nanomaterials exhibit many advantages such as a large ratio of surface area to volume and high activity, and are one of the most promising materials [43]. In recent days the nanostructure base ionic liquid modified electrode works very well as an electrochemical sensor for biological and pharmaceutical compound analysis [44-50].

In the present work, we describe the preparation of a new carbon paste electrode modified with an ionic liquid and magnetic core–shell Fe_3O_4@SiO_2/graphene nanocomposite (ILFSGCPE) and investigate its performance for the determination of ascorbic acid and L-cysteine in aqueous solutions.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrode cell was used at 25±1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and ILFSGCPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

Ascorbic acid, L-cysteine and all of the other reagents were of analytical grade and were obtained from Merck (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0-9.0. Ionic liquid (n-hexyl-3-methylimidazolium hexafluoro phosphate) was purchased from Sigma Aldrich Co.

2.2. Synthesis of Fe_3O4@SiO_2/GO nanocomposite

For carboxylation of GO, an aqueous suspension (50 mL) of GO was diluted by a factor of 2 to give a concentration of 2 mg mL^{-1}, and then bath sonicated for 1 h to give a clear solution. NaOH (12 g) and chloroacetic acid (Cl–CH2–COOH) (10 g) were added to the GO

suspension and bath sonicated for 2 h to convert the –OH groups to –COOH via conjugation of acetic acid moieties giving G-COOH. The resulting G-COOH solution was neutralized, and purified by repeated rinsing and filtration [51].

About 0.06 g of GO–COOH was dissolved in 42 mL of water by ultrasonic irradiation (Sono swiss SW3-H, 38 kHz, Switzerland) for 20 min. The mixture was further stirred vigorously for 30 min at 60 °C. Then 106.2 mg of $FeCl_3 \cdot 6H_2O$ was added under stirring. After the mixture was stirred vigorously for 30 min under N_2 atmosphere, 57 mg of $FeSO_4 \cdot 7H_2O$ was added and keeping it stirred under N_2 atmosphere for 30 min. At last 18 mL of 6% NH_4OH aqueous solution was added into the mixture drop by drop at 60 °C during 1 h and reacted for another 2 h. N_2 atmosphere was used during the reaction to prevent critical oxidation. The reaction mixture was then centrifuged, washed with double distilled water and dried. The obtained black precipitate was Fe_3O_4/GO nanoparticles and was ready for use. Core–shell Fe_3O_4@SiO_2/GO nanocomposites were prepared by growing silica layers onto the surface of the Fe_3O_4/GO as described by Lu et al. 15 mL of ethanol, 0.6 mL water, 0.6 mL ammonium hydroxide and 90 μL of TEOS were added in a 250 mL three neck flask in a 40 °C water bath. Fe_3O_4/GO were added to the above solution under mechanical stirring. Aliquots of the mixture were taken out after 12 h by centrifugation and washed with water and vacuum-dried at 60 °C overnight [52].

2.3. Preparation of the electrode

ILFSGCPEs were prepared by mixing 0.04 g of magnetic core–shell Fe_3O_4@SiO_2/GO nanocomposites with 0.96 g graphite powder and approximately, ~0.8 mL of ionic liquids with a mortar and pestle. The paste was then packed into the end of a glass tube (ca. 3.4 mm i.d. and 15 cm long). A copper wire inserted into the carbon paste provided the electrical contact.

For comparison, ionic liquid / carbon paste electrode in the absence of magnetic core–shell Fe_3O_4@SiO_2/GO nanocomposites (ILCPE), magnetic core–shell Fe_3O_4@SiO_2/GO nanocomposites carbon paste electrode (FSGCPE) consistent of core–shell Fe_3O_4@SiO_2/GO nanocomposites powder and paraffin oil, and bare carbon paste electrode (CPE) consisting of graphite powder and paraffin oil were also prepared in the same way.

3. RESULT AND DISCUSSION

3.1. Electrochemical behavior of ascorbic acid at the surface of various electrodes

Fig. 1 displays cyclic voltammetric responses from the electrochemical oxidation of 800.0 μM ascorbic acid at the surface of ILFSGCPE (curve d), ILCPE (curve c), FSGCPE (curve b) and bare CPE (curve a). The results showed that the oxidation of ascorbic acid is very weak at the surface of the bare CPE, but in the presence of ILs in CPE could enhance the peak

current and decrease the oxidation potential (decreasing the overpotential). A substantial negative shift of the currents starting from oxidation potential for ascorbic acid and dramatic increase of the current indicates the catalytic ability of ILFSGCPE (curve d) and ILCPE (curve c) to ascorbic acid oxidation. The results showed that the combination of core–shell Fe_3O_4@SiO_2/GO nanocomposites and the ionic liquid (curve d) definitely improved the characteristics of ascorbic acid oxidation. However, ILFSGCPE shows much higher anodic peak current for the oxidation of ascorbic acid compared to ILCPE, indicating that the combination of core–shell Fe_3O_4@SiO_2/GO nanocomposites and IL has significantly improved the performance of the electrode toward ascorbic acid oxidation.

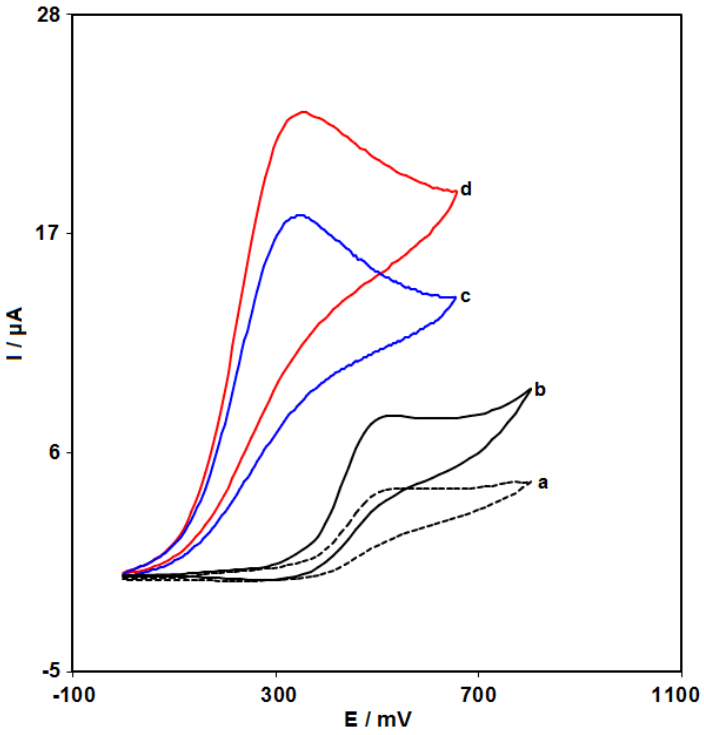

Fig. 1. CVs of a) CPE, b) FSGCPE, c) ILCPE and d) ILFSGCPE in the presence of 800.0 µM ascorbic acid at a pH 7.0, respectively. In all cases the scan rate was 50 mV s^{-1}

3.2. Effect of scan rate

The effect of potential scan rates on the oxidation current of ascorbic acid has been studied (Fig. 2). The results showed that increasing in the potential scan rate induced an increase in the peak current. In addition, the oxidation process is diffusion controlled as deduced from the linear dependence of the anodic peak current (I_p) on the square root of the potential scan rate ($v^{1/2}$) over a wide range from 25 to 500 mV s^{-1}.

Fig. 3 shows the Tafel plot for the sharp rising part of the voltammogram at the scan rate of 25 mV s^{-1}.

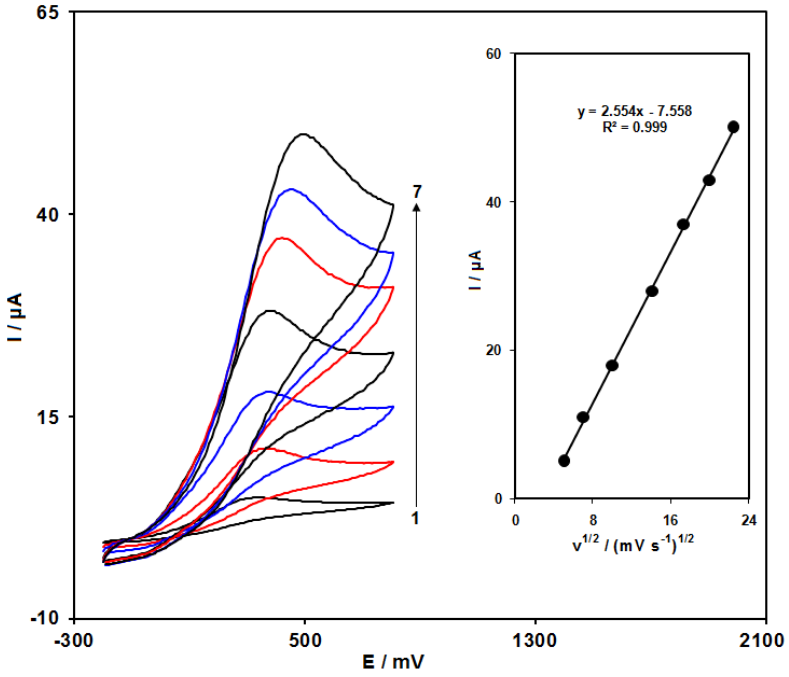

Fig. 2. CVs of ILFSGCPE in 0.1 M PBS (pH 7.0) containing 300.0 µM ascorbic acid at various scan rates; numbers 1-7 correspond to 25, 50, 100, 200, 300, 400 and 500 mV s^{-1}, respectively. Inset: Variation of anodic peak current *vs*. square root of scan rate.

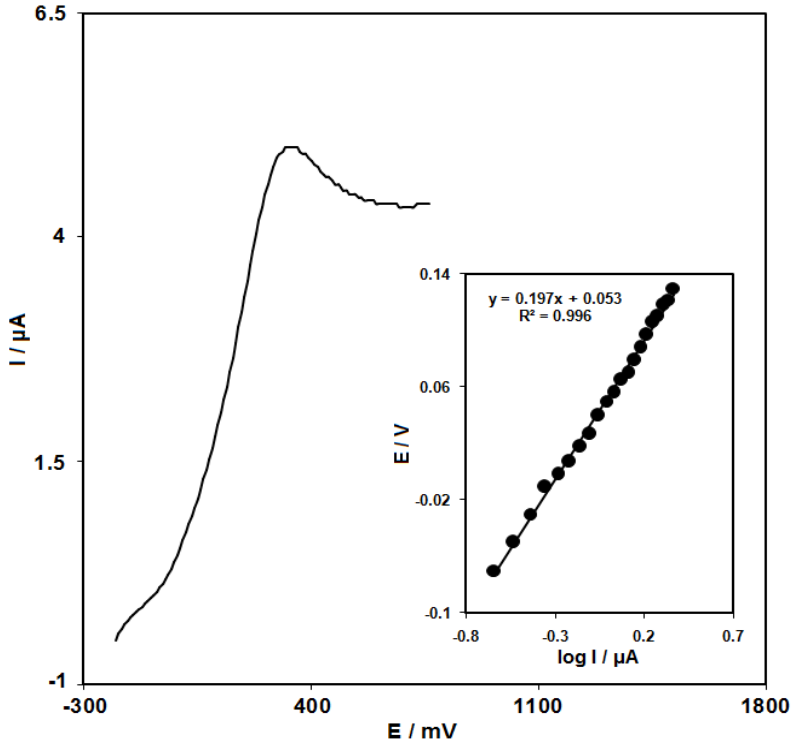

Fig. 3. LSV (at 25 mV s^{-1}) of an ILFSGCPE in 0.1 M PBS (pH 7.0) containing 300.0 µM ascorbic acid. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV

If deprotonation of ascorbic acid is a sufficiently fast step, the Tafel plot can be used to estimate the number of electrons involved in the rate determining step. A Tafel slope of 0.197 V was obtained which agrees well with the involvement of one electron in the rate determining step of the electrode process [53], assuming a charge transfer coefficient, α of 0.7.

3.3. Chronoamperometric measurements

Chronoamperometric measurements of ascorbic acid at ILFSGCPE were carried out by setting the working electrode potential at 0.4 V *vs*. Ag/AgCl/KCl (3.0 M) for the various concentrations of ascorbic acid in PBS (pH 7.0) (Fig. 4). For an electroactive material (ascorbic acid 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 [53].

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

where D and C_b are the diffusion coefficient ($cm^2\ s^{-1}$) and the bulk concentration (mol cm^{-3}), respectively. Experimental plots of I *vs*. $t^{-1/2}$ were employed, with the best fits for different concentrations of ascorbic acid (Fig. 4A). The slopes of the resulting straight lines were then plotted vs. ascorbic acid concentration (Fig. 4B). From the resulting slope and Cottrell equation the mean value of the D was found to be 1.03×10^{-5} cm^2/s.

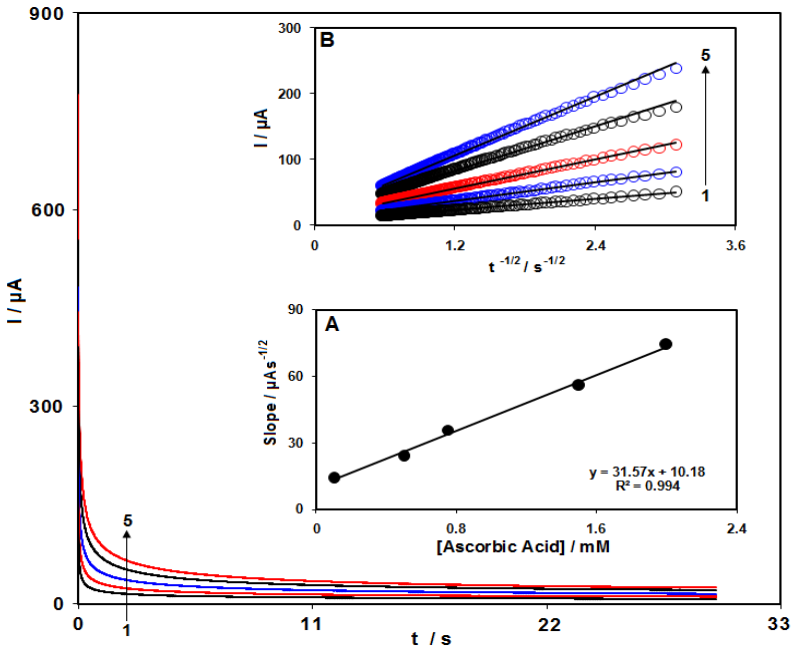

Fig. 4. Chronoamperograms obtained at ILFSGCPE in 0.1 M PBS (pH 7.0) for different concentration of ascorbic acid. The numbers 1–5 correspond to 0.1, 0.5, 0.75, 1.5 and 2.0 mM of ascorbic acid. Insets: (A) Plots of I *vs*. $t^{-1/2}$ obtained from chronoamperograms 1–5. (B) Plot of the slope of the straight lines against ascorbic acid concentrations.

3.4. Calibration plot and limit of detection

The peak current of ascorbic acid oxidation at the surface of the modified electrode can be used for determination of ascorbic acid in solution. Therefore, DPV experiments were done for different concentrations of ascorbic acid (Fig. 5). The oxidation peak currents of ascorbic acid at the surface of a modified electrode were proportional to the concentration of the ascorbic acid within the ranges 1.0×10^{-6} to 9.0×10^{-4} M with detection limit (3σ) of 2.3×10^{-7} M.

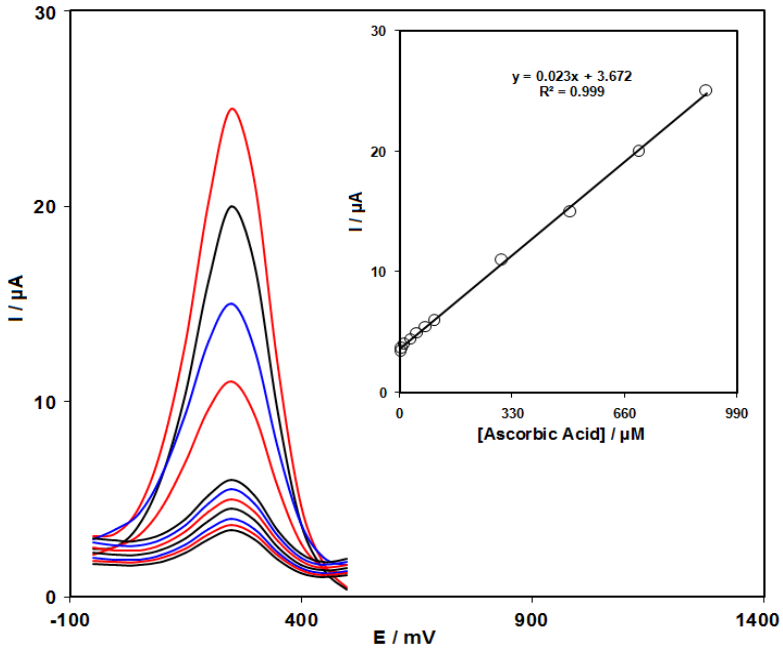

Fig. 5. DPVs of ILFSGCPE in 0.1 M PBS (pH 7.0) containing different concentrations of ascorbic acid (1.0, 5.0, 10.0, 30.0, 50.0, 75.0, 100.0, 300.0, 500.0, 700.0 and 900.0 µM). Inset shows the plots of the peak current as a function of ascorbic acid concentration in the range of 1.0-900.0 µM

3.5. Simultaneous determination of ascorbic acid and L-cysteine

To our knowledge, no paper has used the ILFSGCPE for simultaneous determination of ascorbic acid and L-cysteine and this is the first report for simultaneous determination of ascorbic acid and L-cysteine using ILFSGCPE. The electrochemical determination of ascorbic acid using bare electrodes suffers from interference by L-cysteine. Determination of two compounds was performed by simultaneously changing the concentrations of ascorbic acid and L-cysteine, and recording the SWVs (Fig. 6). The voltammetric results showed well-defined anodic peaks at potentials of 270 and 660 mV, corresponding to the oxidation of ascorbic acid and L-cysteine, respectively, indicating that simultaneous determination of these compounds is feasible at the ILFSGCPE as shown in Fig. 6.

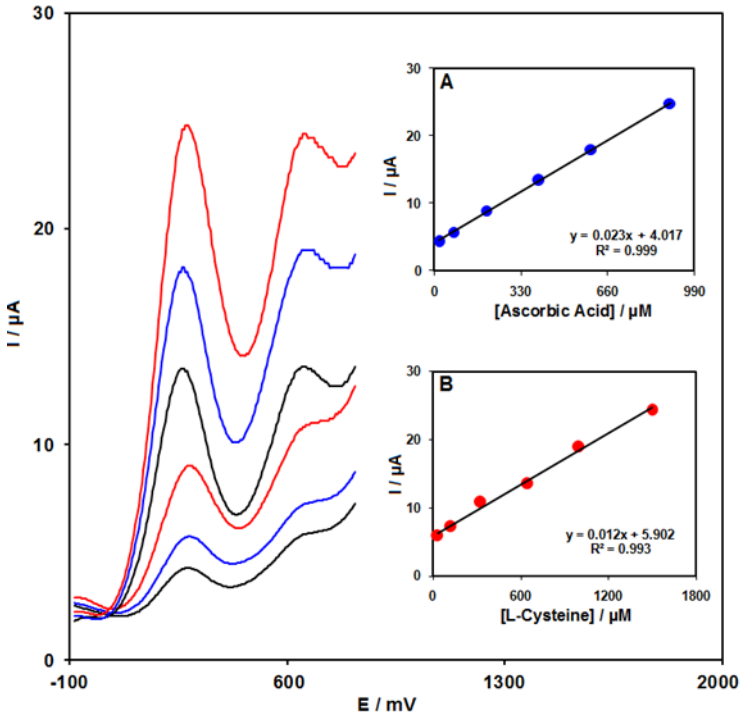

Fig. 6. SWVs of ILFSGCPE in 0.1 M PBS (pH 7.0) containing different concentrations of ascorbic acid and L-cysteine in µM, from inner to outer: 20.0+35.0, 75.0+125.0, 200.0+325.0, 400.0+650.0, 600.0+1000.0 and 900.0+1500.0 respectively. Insets (A) plots of Ip *vs*. ascorbic acid concentration and (B) plot of Ip *vs*. L-cysteine concentrations

4. CONCLUSION

This work describes the ability of the modified ionic liquids– magnetic core–shell Fe_3O_4@SiO_2/graphene nanocomposite carbon paste electrode for determination of ascorbic acid. The voltammetric investigation demonstrates that electrooxidation of ascorbic acid at the surface of ILFSGCPE showed very distinct characteristics due to the presence of magnetic core–shell Fe_3O_4@SiO_2/graphene nanocomposite and ionic liquid layer on the surface of electrode. In addition, a selective voltammetric sensor for the determination of ascorbic acid with simple, sensitive, and rapid characteristics was developed. The proposed modified electrode presented a low detection limit and good linear range and reproducibility which make it a suitable ascorbic acid sensor for practical applications.

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