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Electrochemical measurements of ascorbic acid based on graphite screen printed electrode modified with La³⁺/Co₃O₄ nanocubes transducer

Mohammad Reza Aflatoonian[1,2,✉], Somayeh Tajik[1,✉], Behnaz Aflatoonian[3], Hadi Beitollahi[4]

[1]*Research Center for Tropical and Infectious Diseases, Kerman University of Medical Sciences, Kerman, Iran*
[2]*Leishmaniasis Research Center, Kerman University of Medical Sciences, Kerman, Iran*
[3]*Neuroscience Research Center, Kerman University of Medical Sciences, Kerman, Iran*
[4]*Environment Department, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran*

Corresponding authors: ✉m.aflatoonian97@gmail.com; Tel.: +98 3426226613; Fax: +98 3426226617; ✉mTajik_s1365@yahoo.co

Abstract

Electrochemical characterization of ascorbic acid oxidation on a graphite screen printed electrode (SPE) modified with La³⁺/Co₃O₄ nanocubes is performed by applying cyclic voltammetry (CV), chronoamperometry (CHA), and differential pulse voltammetry (DPV) techniques. Synthesized La³⁺/Co₃O₄ nanocubes for SPE modification, La³⁺/Co₃O₄/SPE, enhance the ascorbic acid electrooxidation kinetics by reducing the anodic overpotential. Excellent La³⁺/Co₃O₄/SPE electrochemical properties provide sensitive ascorbic acid voltammetric determination with low detection limit, good stability and quick response towards electrooxidation of ascorbic acid as compared to bare SPE. Under optimized conditions, DPV current demonstrates a linear response for ascorbic acid over a concentration range of 1.0 to 900.0 μM with a correlation coefficient of 0.9997, and detection limit (LOD) (S/N = 3) = 0.3 μM. The proposed procedure offers a potential application for producing the sensor with good repeatability. Also, fast response of fabricated sensor can allow a real-time analysis of real samples.

Keywords

Introduction

Ascorbic acid is a water soluble vitamin (vitamin C), widely present in many biological systems, fruits and vegetables. Beyond its function in collagen formation, ascorbic acid is known to increase absorption of inorganic iron, to have essential roles in the metabolism of folic acid, some amino acid and hormones, and to act as an antioxidant [1-4]. Deficiency of ascorbic acid will cause scurvy disease [2-5]. It is administered in the treatment of many disorders, including Alzheimer's disease, atherosclerosis, cancer, and infertility [3-6]. In the light of these facts, determination of low concentrations of ascorbic acid without any interference from other biomolecules is a very important subject in pharmacology fields [5-8].

Numerous approaches such as fluorescence [9], UV spectroscopy [10], chemiluminescence [11], electrophoresis [12], and liquid chromatography [13] have been reported for the determination of ascorbic acid. These methods suffer from the lack of specificity and are prone to interferences with other reducing agents in the sample. Moreover, some complications in chromatography performances were detected, such as selecting a proper column or a mobile phase with liquid chromatographic methods, costly instruments, long response time, difficult procedure, and low detection ability. Since ascorbic acid is an electroactive compound, electrochemical techniques for its detection has received a considerable interest [14-16]. Electrochemical methods came to attention due to their high sensitivity, easy operation and low cost [17-23].

Nowadays, a variety of nanoparticles with numerous properties, such as high speed, minor size, smaller distances for electrons to travel, lower power, and lower voltages, made important advances in the field of nanotechnology. Thus, the utilization of nanomaterials such as metal nanoparticles, metal oxide nanoparticles, magnetic nanomaterials, carbon materials, quantum dots and metallophthalocyanines enhanced the electrochemical signals of biocatalytic events occurring at the electrode/electrolyte interface [24,25]. Along with nanoscience and nanotechnology development, there were numerous trials to employ innovative nanomaterials in constructing modified electrodes [26-28]. Nanostructured metal oxides were also investigated in recent years as electrochemical sensor materials, showing promising results owing to several benefits of the materials such as high surface area, workability, and increasing synthetic accessibility [29-32].

Currently, the screen printed electrode (SPE) has become an interesting and widely applied electrode material. SPEs have already been successfully used as electrochemical sensors for various researches due to their simplicity and minimum sample preparation. In addition, the main benefit of SPE is based on its single use, after which it is discarded. However, the limitation of SPE is small surface area of the working electrode leading to the lack of sensitivity. To overcome this problem, the electrode modification is necessary [33,34].

In this study, La^{3+}/Co_3O_4 nanocubes modified SPE has been exploited for ascorbic acid sensing and the analytical performance of the suggested sensor for ascorbic acid determination in real samples is evaluated.

Experimental

Chemicals and apparatus

Electrochemical experiments were performed using an Autolab potentiostat/ galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). General purpose electrochemical system software was used to control the system. The screen printed electrode (DropSens, DRP-C110, Spain) contains three main parts which are a graphite counter electrode, a silver pseudo-reference electrode, and a graphite working electrode. The pH values were measured by a Metrohm 710 pH meter. The

morphology of the products was observed using a Philips XL30 scanning electron microscope (SEM). Prior to SEM analysis, samples were loaded on a gold film prepared by an SCD005 BAL-TEC Sputter Coater. XRD studies were conducted on a Rigaku D/max 2500 V instrument with a graphite monochromator and a Cu target. The FT-IR spectra were prepared by use of a Bruck Equinox 55 spectrophotometer and the KBr pellet of samples were used. All reagents were purchased from Merck (Darmstadt, Germany) in analytical grade. Buffer solutions within the range of 2.0–9.0 were prepared using orthophosphoric acid and its salts.

Synthesis of La^{3+}/Co_3O_4 nanocubes

In a typical synthesis, 25 mL of ammonia solution (28-30 %, Reagent Chemicals) was first mixed with ultra-pure water (1/1, v/v). Then, 0.05 g of poly(vinylpyrrolidone) (PVP; M.W. 58,000, Reagent Chemicals) was dissolved in the solution. After shaking for a few minutes, 0.364 g of cobalt nitrate hexahydrate ($Co(NO_3)_2\times6H_2O$) and 0.043 g of lanthanum nitrate hexahydrate ($La(NO_3)_2\times6H_2O$) were added into the reaction medium. After sonication, a browny transparent solution was obtained, which was then transferred into 100 mL teflon-lined stainless steel autoclave. The autoclave was kept in an electric oven at 180 °C for 6 h, after which the autoclave was taken out and cooled naturally to room temperature. After that, the black precipitate was harvested and washed with ultra-pure water several times *via* centrifugation. The product was then dried at 60 °C overnight, before being calcined at 300 °C for 2 h in air to be converted into La^{3+}/Co_3O_4 nanocubes.

Preparation of the electrode

In order to prepare the modified electrode, the surface of bare SPE was coated by a thin film of La^{3+}/Co_3O_4 nanocubes as follows: in a simple procedure, 1 mg La^{3+}/Co_3O_4 nanocubes were dispersed in 1 mL aqueous solution by ultrasonication for 15 min. Then, surface of SPE working electrode was treated with 2 µl of the prepared suspension. After drying at room temperature, the modified electrode was ready to use.

Preparation of real samples

One milliliter of a vitamin C ampoule (Darou Pakhsh Company, Iran, contained 1 mg/mL of ascorbic acid) was diluted to 10 mL with 0.1 M PBS (pH 7.0); then, different volume of the diluted solution was transferred into each of a series of 25 mL volumetric flasks and diluted to the mark with PBS. The ascorbic acid content was analyzed by the proposed method using the standard addition method.

Five vitamin C tablets (labeled 250 mg per tablet, Osvah Pharmaceutical Company, Iran) were grinding. Then, the tablet solution was prepared by dissolving 400 mg of the powder in 25 mL water by ultrasonication. After that, different volume of the diluted solution was transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The ascorbic acid content was analyzed by the proposed method using the standard addition method.

Five effervescent tablets of vitamin C (labeled 500 mg per tablet, Hakim Pharmaceutical Company, Iran) were grinded completely. After that 500 mg of the powder was dissolved in 25 mL water using ultrasonication and different volume of the diluted solution was transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The ascorbic acid content was analyzed by the proposed method using the standard addition method.

Result and discussion

Nanostructures characterization

Figure 1 displays the FT-IR spectrum of La^{3+}/Co_3O_4 nanocubes sample in the frequency range of 400–4000 cm^{-1}. The FT-IR spectrum of La^{3+}/Co_3O_4 nanocubes showed strong vibrational bands in the lower frequency regions (about 400-600 cm^{-1}), ascribable to the vibration of metal–O. The absorption seen at ~3389 cm^{-1} is thought to be due to the symmetric vibration of the -OH groups of the absorbed H_2O molecules. The peak at ~1632 cm^{-1} corresponds to O-H groups, again related to adsorbed H_2O molecules [34].
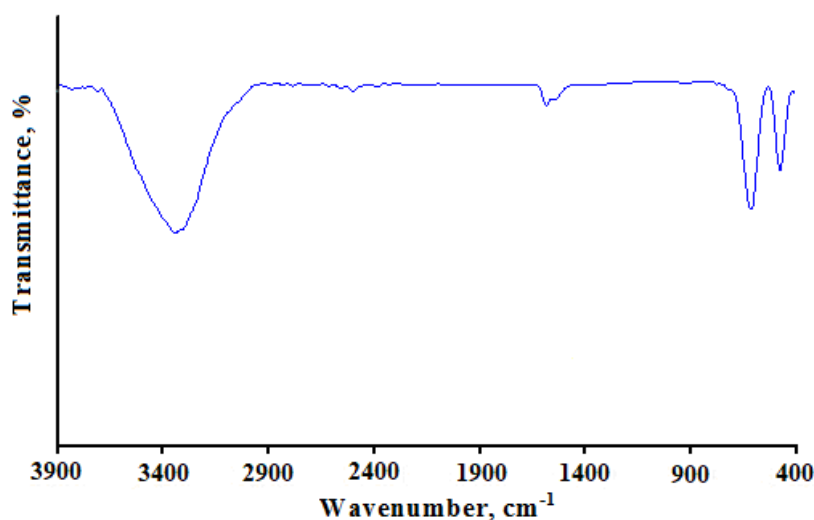

Fig. 1. *FT-IR spectrum of La^{3+}/Co_3O_4 nanocubes.*

The main characteristic diffraction peaks of La^{3+}/Co_3O_4 nanocubes are consistent with the standard patterns of Co_3O_4 (JCPDS card No. 71-0816) with cubic spinel phase, suggesting that the doping of La does not change the backbone of pristine Co_3O_4 (Figure 2). By increase of La content in Co_3O_4, the characteristic peak at 2θ =37.3° becomes weaker and slightly shifted to small-angle reflections. The introduction of La ions with f-block electronic and large atomic radiuses into the Co_3O_4 grain boundary, causes the loss of atomic degree of ordering of Co_3O_4, thereby contributing to the limited growth of the grain, grain refinement and decrease of crystallinity.
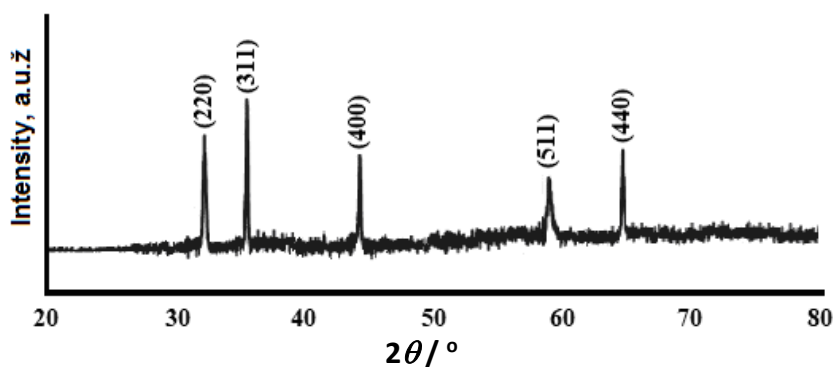

Fig. 2. *XRD pattern of La^{3+}/Co_3O_4 nanocubes*

The broadness of diffraction peaks suggests the nano-sized nature of the product and the average crystallite size (*T*) was calculated as 67.0 nm using the Debye–Scherrer formula $T = 0.9\,\lambda\,/\,\beta\cos\theta$, where λ is the wavelength of the X-ray radiation (1.54056 Å for Cu lamp), θ is the diffraction angle and β is the full width at half-maximum (FWHM) [35].

The morphology of the product was examined by SEM. Figure 3 depicts SEM pictures of La^{3+}/Co_3O_4 nanoparticles. It can be observed from Figure 3, that nanoparticles which are nanocubes are less than 70 nm.
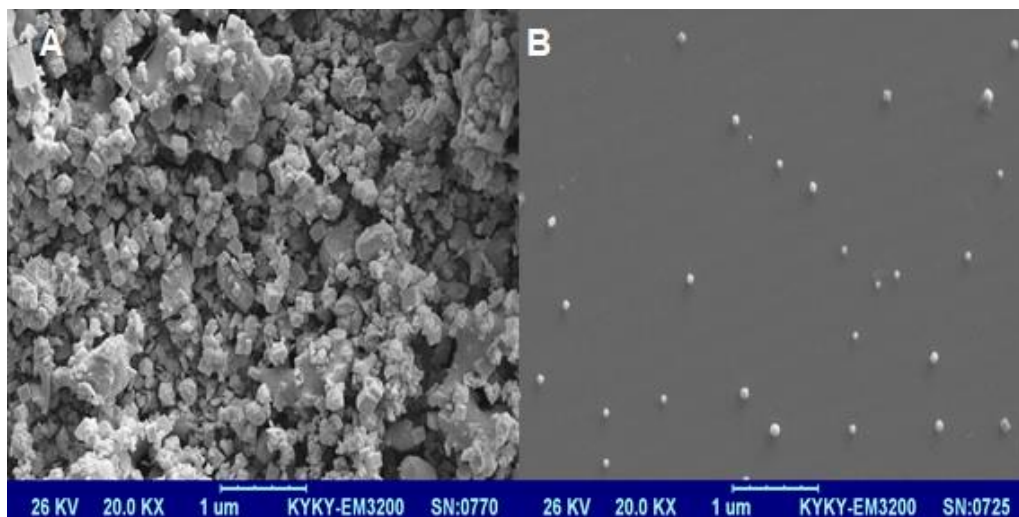

Fig. 3. *SEM images of La^{3+}-doped Co_3O_4 nanocubes for A) high concentration, B) low concentration*

Electrochemical profile of the ascorbic acid on the $La^{3+}/Co_3O_4/SPE$

In order to investigate the electrochemical behaviour of ascorbic acid and obtain the accurate results, it is essential to determine the optimized pH value since its electrooxidation is pH dependent process. For this purpose, the experiments were performed using the modified electrode at various pH values ranging from 2.0–9.0 (Figure 4).
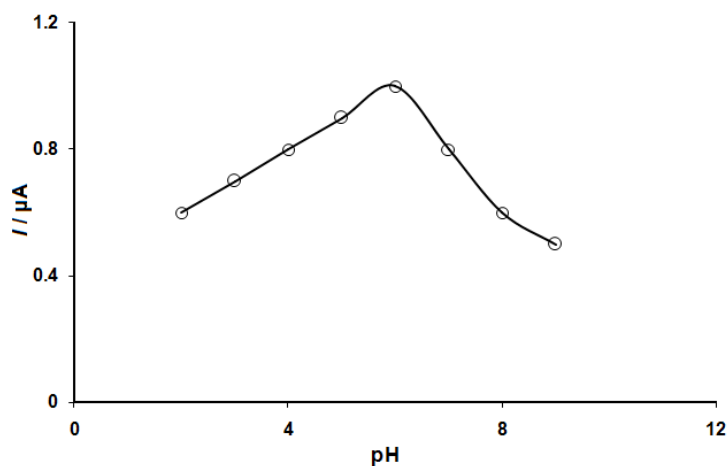

Fig. 4. *Plot of I_p vs. pH (2.0-9.0) in 0.1 M PBS in the presence of 900.0 µM ascorbic acid at the scan rate 50 mV s^{-1}.*

According to Figure 4, the best results for electro-oxidation of ascorbic acid are achieved at pH 7.0. Figure 5 presents cyclic voltammograms (CVs) obtained for $La^{3+}/Co_3O_4/SPE$ (curve a) and unmodified SPE (curve b) in the presence of 900.0 µM ascorbic acid. Comparing CV results of modified and bare SPE revealed that the maximum oxidation of ascorbic acid observed at 300 mV for $La^{3+}/Co_3O_4/SPE$, is about 70 mV more negative for unmodified SPE. When oxidation current peak values of ascorbic acid at $La^{3+}/Co_3O_4/SPE$ (1 µA) and bare SPE (0.5 µA) are compared, an extensive (about 100 %) enhancement for $La^{3+}/Co_3O_4/SPE$ relative to the bare SPE is observed. In other words, the results clearly indicate that La^{3+}/Co_3O_4 nanocubes improve the ascorbic acid oxidation signal.

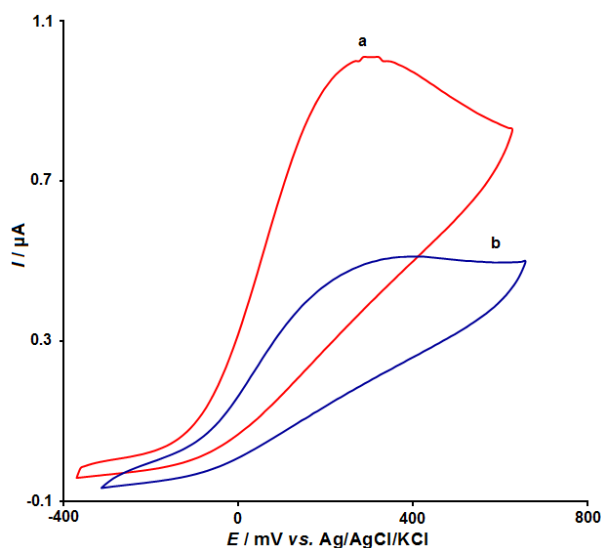**Fig. 5.** *CVs of (a) La^{3+}/Co$_3$O$_4$/SPE and (b) unmodified SPE in 0.1 M PBS (pH 7.0) in the presence of 900.0 µM ascorbic acid at the scan rate 50 mV s^{-1}.*

Effect of potential scan rate

As shown in Figure 6, investigation of the effect of potential scan rates on the oxidation currents of ascorbic acid demonstrated that increasing of the scan rate results in increased oxidation peak current values (I_p). The observed linear relation between I_p and the square root of the potential scan rate ($v^{1/2}$) indicates that oxidation of ascorbic acid is a diffusion-controlled process.
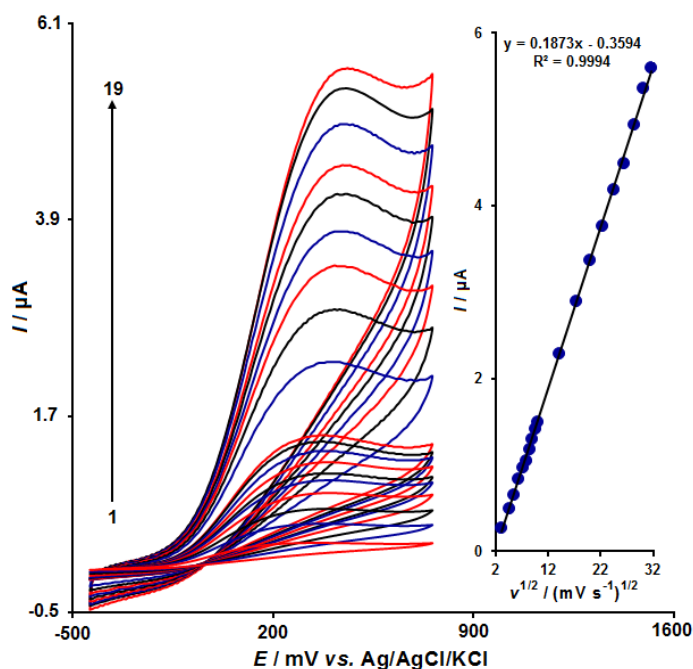

Fig. 6. *CVs of La^{3+}/Co$_3$O$_4$/SPE in 0.1 M PBS (pH 7.0) containing 800.0 µM ascorbic acid at various scan rates (v). Numbers 1-19 correspond to 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mV s^{-1}, respectively. Inset: Variation of anodic peak current vs. v$^{1/2}$*

Chronoamperometric analysis

The analysis of chronoamperometry (CHA) for ascorbic acid samples was performed by use of La^{3+}/Co$_3$O$_4$/SPE *vs*. Ag/AgCl/KCl (3.0 M) at 0.35 V. CHA results obtained for different concentrations of ascorbic acid samples in PBS (pH 7.0) are depicted in Figure 7. The Cottrell equation for

chronoamperometric analysis of electroactive moieties under mass transfer limited conditions is expressed as follows [36]:

$$I = nFAD^{1/2}c_b\pi^{-1/2}t^{-1/2}$$

where D is diffusion coefficient, cm^2 s^{-1}, and C_b refers to the bulk concentration, mol cm^{-3}. Experimental results of I vs. $t^{-1/2}$ are plotted in Figure 7A as the best fitted curves for different concentrations of ascorbic acid. The resulting slopes of the straight lines in Figure 7A were then plotted against the concentration of ascorbic acid in Figure 7B. Finally, regarding the resulting slope and Cottrell equation, the mean value of D was determined as 1.0×10^{-6} cm^2 s^{-1}. This value is comparable with the values reported in some previous works (2.2×10^{-6} cm^2 s^{-1} [1] and 5.66×10^{-6} cm^2 s^{-1} [37]).
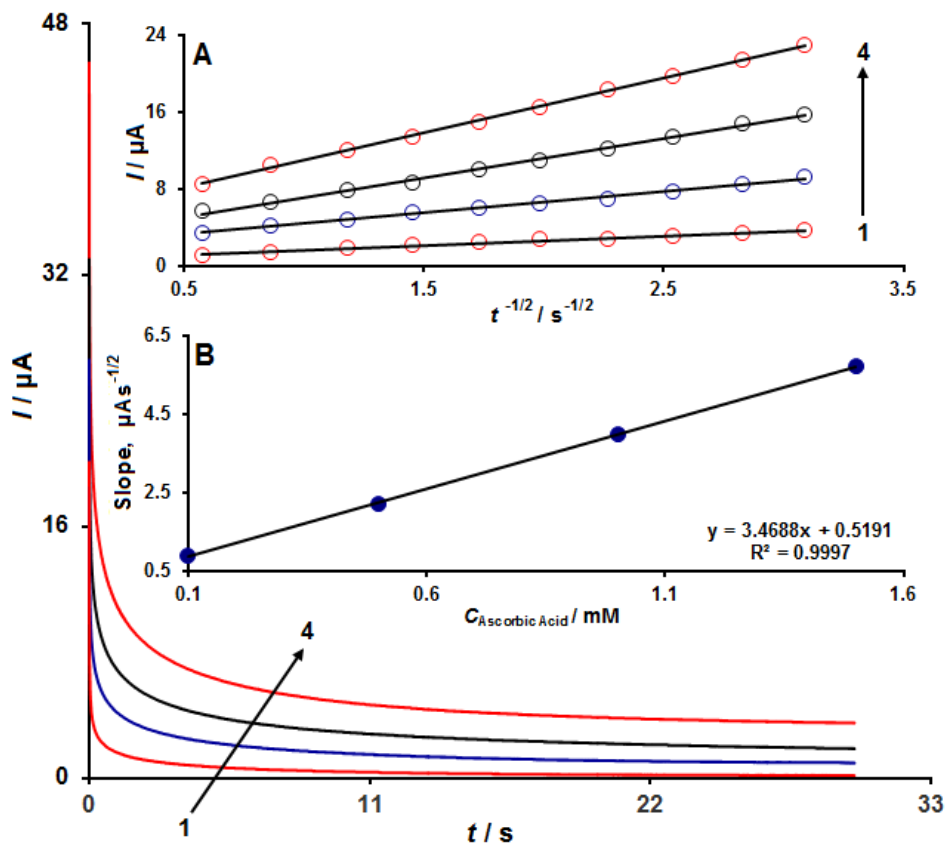

Fig. 7. *CHAs of La^{3+}/Co$_3$O$_4$/SPE in 0.1 M PBS (pH 7.0) for different concentrations of ascorbic acid. Numbers 1–4 correspond to 0.1, 0.5, 1.0 and 1.5 mM of ascorbic acid. Insets: (A) Plots of* I *vs.* t$^{-1/2}$ *obtained from CHAs 1–4. (B) Plot of straight lines slope against ascorbic acid concentration*

Calibration curve

The modified electrode (La^{3+}/Co$_3$O$_4$/SPE) was applied as the working electrode in the concentration range of ascorbic acid in 0.1 M PBS and subdued to differential pulse voltammetry (DPV) since this technique in analytical applications offers advantages of enhanced sensitivity and better efficiency (Figure 8). According to the results, a linear relationship exists between the peak currents and concentrations of ascorbic acid within the concentration range of 1.0-900.0 µM with the correlation coefficient of 0.9997. The detection limit of 0.3 µM was obtained.

Interference study

The influence of various substances as compounds potentially interfering with the determination of ascorbic acid was studied in the presence of 50.0 µM ascorbic acid. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than ±5 % in the determination of ascorbic acid.
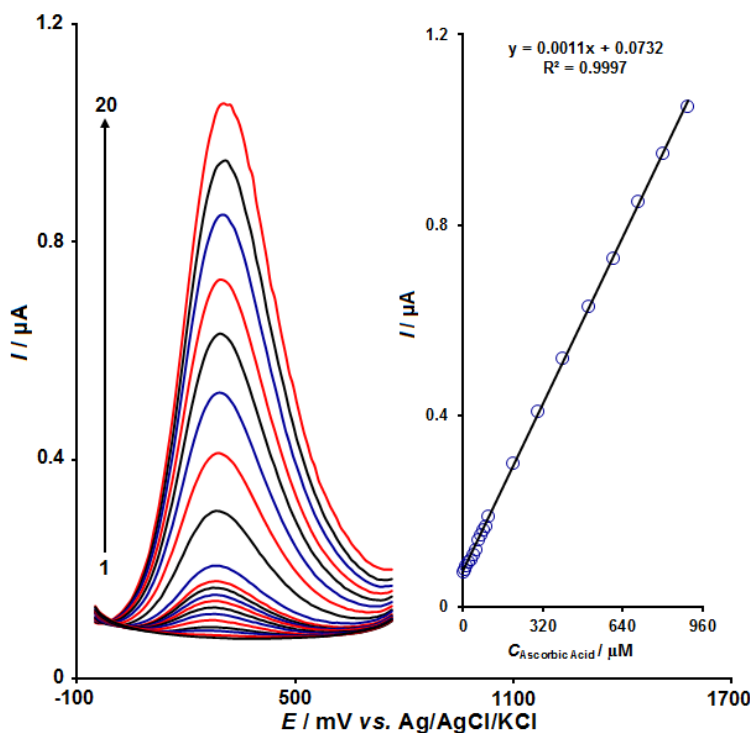
Fig. 8. *DPVs of La^{3+}/Co$_3$O$_4$/SPE in 0.1 M PBS (pH 7.0) containing different concentrations of ascorbic acid. Numbers 1-20 correspond to 1.0-900.0 μM of ascorbic acid. Inset: Plot of the peak current as a function of ascorbic acid concentration.*

According to the results, uric acid, L-serine, L-phenylalanine, ethanol, benzoic acid, isoproterenol, methanol, serotonin, L-asparagine, acetaminophen, NADH, saccharose, urea, glucose, L-lysine, L-glycine, carbidopa, caffeine, levodopa, fructose, L-threonine, lactose, L-histidine, L-proline, S^{2-}, Mg^{2+}, SO$_4^{2-}$, NH$_4^+$, F$^-$ and Al^{3+} did not show interference in the determination of ascorbic acid.

Analysis of real samples

To assess the applicability of this modified sensor for the determination of ascorbic acid in vitamin C ampoule, vitamin C tablet and vitamin C effervescent tablet, the proposed method was tested in water samples using the described procedure. In this process, the standard addition method was employed, and the results are given in Table 1.

Table 1. *Determination of ascorbic acid in vitamin C ampoule, vitamin C tablet and vitamin C effervescent tablet*

Sample	Concentrations, μM (n=5)		Recovery, %	RSD, %
	Spiked	Found		
	0	10.0	-	3.4
	5.0	14.8	98.7	1.7
Vitamin C ampoule	10.0	20.4	102.0	2.1
	15.0	24.5	98.0	1.5
	20.0	30.9	103.0	2.9
	0	5.0	-	2.4
	10.0	15.2	101.3	1.7
Vitamin C tablet	15.0	20.1	100.5	3.4
	20.0	24.3	97.2	2.1
	25.0	30.6	102.0	3.2
	0	5.0	-	2.8
	10.0	15.3	102.0	3.1
Vitamin C effervescent tablet	15.0	19.8	99.0	2.9
	20.0	24.3	97.2	2.6
	25.0	30.5	101.7	1.6

According to the results, the recovery of ascorbic acid is satisfactory and the reproducibility of the results is approved by the mean relative standard deviation (RSD.).

The repeatability and stability of La^{3+}/Co$_3$O$_4$/SPE

The long-term stability of the La^{3+}/Co$_3$O$_4$/SPE was evaluated over 3-week period. After the modified electrode was stored for 3 weeks in atmosphere at room temperature, the experiments were performed again. According to cyclic voltammograms, the peak potential for ascorbic acid oxidation remained unchanged and a decrement of less than 2.2 % compared with initial response was observed.

The antifouling properties of the modified electrode towards ascorbic acid oxidation and its oxidation products were studied by recording CVs. Voltammograms were recorded in the presence of ascorbic acid after cycling the potential 20 times at a scan rate of 50 mV s^{-1}. Results demonstrated that peak potentials remained unchanged and the currents decreased by less than 2.1 %. According to the results, application of modified La^{3+}/Co$_3$O$_4$/SPE provides increased sensitivity and decreased fouling effect of the analyte and its oxidation product.

Conclusion

La^{3+}/Co$_3$O$_4$ nanocubes-SPE demonstrated an outstanding behavior toward ascorbic acid oxidation in the aqueous PBS (pH 7.0) solution. Our investigation exhibited that in the case of the unmodified SPE, the voltammogram of ascorbic acid displays just a small hump peak, but after modification of the electrode with La^{3+}/Co$_3$O$_4$ nanocubes, the oxidation peak currents of ascorbic acid are significantly enhanced. This technique offers a number of advantages compared to the other published electrochemical methods, such as simplicity in the preparation of the modified electrode and its high selectivity. The modified electrode represented appropriate performance in detecting ascorbic acid and revealed excellent stability and reproducibility. By DPV determination, the detection limit of ascorbic acid was estimated as 0.3 μM. Based on the electrochemical oxidation, the quantitative determination of ascorbic acid in real samples was developed by a simple, rapid, selective and sensitive DPV technique. These properties indicate that the La^{3+}/Co$_3$O$_4$ nanocubes modified electrode is a good electrochemical sensor for the ascorbic acid determination.

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