Int. J. Electrochem. Sci., 11 **(2016)** 7849 – 7860, doi: 10.20964/2016.09.60

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Nanostructure Electrochemical Sensor for Voltammetric Determination of Vitamin C in the Presence of Vitamin B_6: Application to Real Sample Analysis

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Received: 9 June 2016 / *Accepted:* 19 July 2016 / *Published:* 7 August 2016

A carbon paste electrode modified by using ZnO/CuO nanosheets, ionic liquids (N-hexyl-3-methylimidazolium hexafluoro phosphate) and 2-(ferrocenylethynyl)fluoren-9-one was fabricated and used for electrocatalytic oxidation of vitamin C. It has been found that, the oxidation of vitamin C at the surface of such an electrode occurs at a potential about 190 mV less positive compared to an unmodified carbon paste electrode. The oxidation peak currents show a linear dependence on the vitamin C concentrations in the range of 4.0×10^{-8} M– 1.0×10^{-3} M with a detection limit of 2.0×10^{-8} M. The diffusion coefficient ($D/cm^2\ s^{-1}=5.38\times10^{-6}$), electron transfer coefficient, ($\alpha=0.28$) and the heterogeneous rate constant, ($k/M^{-1}s^{-1}=2.3\times10^{3}$) for vitamin C were determined using electrochemical approaches. The modified electrode exhibits good resolution between the voltammetric peaks of vitamin C and vitamin B_6 that makes it suitable for the detection of vitamin C in the presence of vitamin B_6 in real samples.

Keywords: Vitamin C, Vitamin B_6, ZnO/CuO nanosheets, Ionic liquid, Food analysis

1. INTRODUCTION

Vitamins constitute a group of compounds, which are essential to human body for health, nutrition and normal growth, self maintenance and functioning of human and animal bodies. Vitamin C and vitamin B_6 belongs to the water-soluble vitamins [1, 2]. Since these biochemical active molecules can not be synthesized by the human body, small quantities are required in the diet. Leftover amounts of the vitamin leave the body through the urine. That means you need a continuous supply of such vitamins in your diet [3].

Vitamin C is a significant vitamin in the human diet [4]. These days, it is used most often for preventing and treating the common cold. Some people use it for other infections including gum disease, acne and other skin infections, bronchitis, human immunodeficiency virus (HIV) disease, stomach ulcers caused by bacteria called Helicobacter pylori, tuberculosis, dysentery (an infection of the lower intestine), and skin infections that produce boils (furunculosis) [5-7].

Vitamin B_6 (pyridoxine) is used in drug formulations such as multivitamin supplements, or in enriched foods [8]. It plays a vital role in both mental and physical health [9]. For example, vitamin B_6 is needed for more than 100 enzymes involved in protein metabolism. To make hemoglobin (which carries oxygen to tissues), one's body needs vitamin B_6 [10]. Therefore, the simultaneous determination of vitamin C and vitamin B_6 is a very important and highly valuable topic in clinic medicine.

To date, numerous analytical methods for the determination of them have been described in literature including high performance thin layer chromatography, spectroelectrochemical techniques, UV/vis, fluorescence, capillary electrophoresis, flow injection systems and electroanalytical methods [11-18].

In 1958 Adams introduced carbon paste electrode. To date, a wide variety of modifiers has been used with these versatile electrodes [19-25].

Over the recent decades, ionic liquids (ILs) have become an outstanding class of compounds in many areas of chemistry. Their distinguished physicochemical properties, render these materials promising in the frame of sustainable chemistry [26-32].

Nanocrystals have attracted much attention for various applications, such as, sensor and biosensor [37-39]. Among metal oxide nanosheets, ZnO/CuO nanosheets have recently received significant attention [40-50]. So, ZnO/CuO nanosheets deserve further investigation as an extraordinary and promising candidate for support material in the construction of the biosensors.

Based on the effective electrocatalytic activity of the carbon paste electrode modified with 2-(ferrocenylethynyl)fluoren-9-one, ZnO/CuO nanosheets and ionic liquids (2FE/ZC/IL/CPE) toward vitamin C and vitamin B_6, an electrochemical sensor is proposed for determination of these species.

2. EXPERIMENTL

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat. An Ag/AgCl/KCl (3.0 M) electrode (as reference electrode), a platinum wire (as auxiliary electrode) and 2FE/ZC/IL/CPE (as working electrode) were used.

All of the other reagents were purchased from Merck (Darmstadt, Germany). Ionic liquid was purchased from Sigma Aldrich Co. Orthophosphoric acid and its salts were used to prepare buffer solutions in the pH range of 2.0-12.0. ZnO-CuO nanoplates were synthesized as reported previously [50]. Typical SEM image of ZnO-CuO nanoplates is shown in Fig. 1.

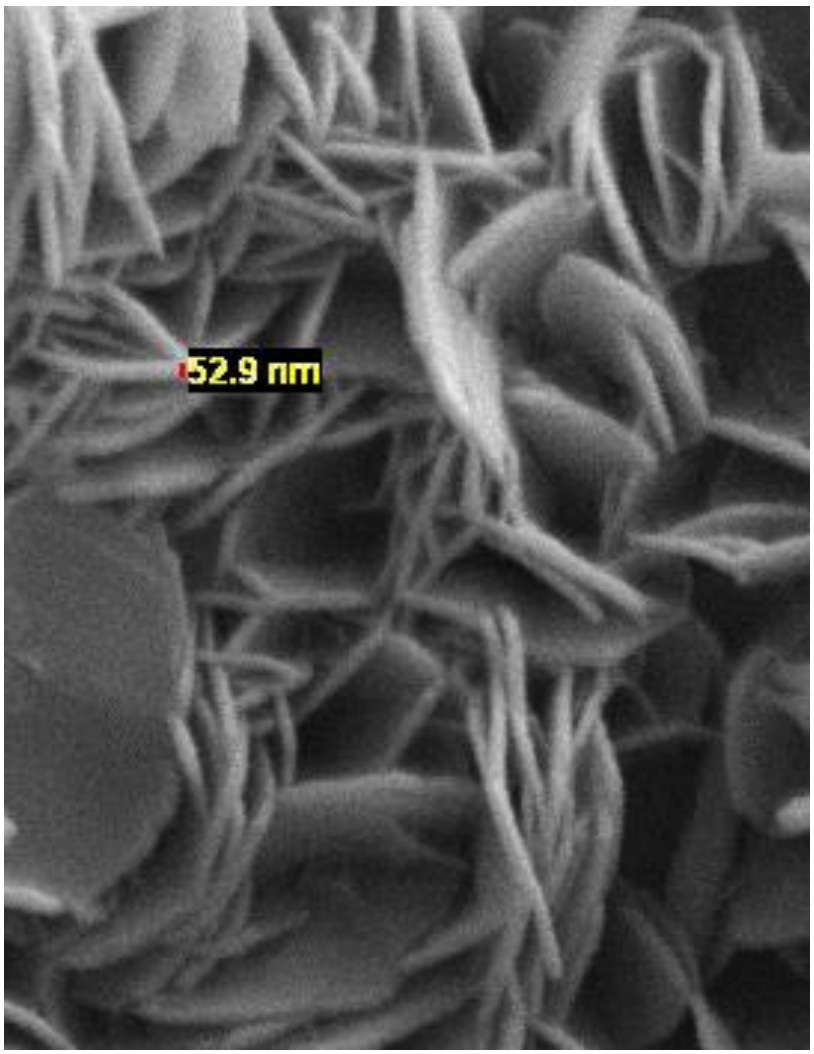

Figure 1. SEM image of ZnO-CuO nanoplates.

2.3. Synthesis of 2-(ferrocenylethynyl)fluoren-9-one

$PdCl_2(PPh_3)_2$ (29 mg) and CuI (7.6 mg) were added to a stirred solution of aryl halides (1.0 mmol, 0.26 g) and ethynylferrocene (1.2 mmol, 0.25 g) in Et_3N (5 ml) and DMF (5 ml) and the resulting mixture was stirred at reflux temperature for 3 h. The progress of the reaction was monitored by TLC. After addition of 200 mL of H_2O and stirring for 30 min, the resulting crude product was filtered. The resulting raw material was dissolved in CH_2Cl_2, then washed with diluted HCl and saturated NaCl solution. After drying with $MgSO_4$ and solvents removal, the crude products was purified by column chromatography on silica gel using hexane-CH_2Cl_2 as eluent to afford the pure product in 87 % yield.

Red solid; mp: 147-148 °C; IR: υ (cm^{-1})= 750, 1602, 1712 (C=O), 2201 (C≡C); ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm)= 4.20-4.30 (*pseudo* s, 7H), 4.54 (s, 2H), 7.30-7.76 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm)= 64.62, 69.04, 70.00, 71.48, 85.03, 90.51, 120.20, 120.45, 124.36,124.88, 127.02, 129.12, 134.16, 134.27, 134.81, 137.19, 142.94, 144.07, 193.11; Anal. Found: C, 76.98; H, 3.96. Calc. for $C_{25}H_{16}FeO$: C, 77.34; H, 4.15%.

2.4. electrode Preparation

2FE/ZC/IL/CPEs were prepared by mixing 0.96 g graphite powder, 0.04 g of ZnO/CuO nanosheets nanocomposite and 0.01 g of 2-(ferrocenylethynyl)fluoren-9-one and ~ 0.8 mL of ionic liquids.

For comparison, ZC/CPE consistent of ZnO/CuO nanosheets powder and graphite powder and 2FE/IL/CPE consistent of 2-(ferrocenylethynyl)fluoren-9-one powder and ionic liquids were also prepared in the same way.

3. RESULT AND DISCUSSION

3.1. Electrochemical Properties of 2FE/ZC/IL/CPE

According to our knowledge, there is no report on a study of the electrochemical properties of 2FE/ZC/IL/CPE in aqueous media. Because 2-(ferrocenylethynyl) fluoren-9-one is insoluble in aqueous media, we prepared 2FE/ZC/IL/CPE. Then, we studied the electrochemical behavior of 2FE/ZC/IL/CPE in pure buffered aqueous solution by cyclic voltammetry. The cyclic voltammetric results show well-defined and reproducible anodic and cathodic peaks related to Fc/Fc^+ redox system (with E_{pa}=0.35 V, E_{pc}=0.250 V, $E_{1/2}$=0.3 V vs. Ag / AgCl / KCl $_{sat}$ and ΔE_p=100 mV).

The peak separation potential, ΔE_p (E_{pa}-E_{pc}), is greater than the (59/n) mV expected for a reversible system. This result suggests that Fc/Fc^+ redox couple in 2FE/ZC/IL/CPE shows a quasireversible behavior in an aqueous medium [51].

3.2. Electrochemical behavior of vitamin C at the surface of various electrodes

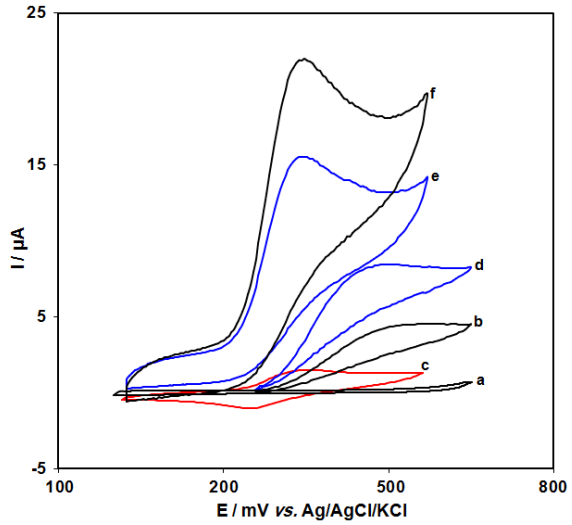

Figure 2. CVs of (a) unmodified CPE in PBS; (b) unmodified CPE in PBS including 0.45 mM vitamin C; (c) 2FE/ZC/IL/CPE in PBS; (d) ZCPE in PBS including 0.45 mM vitamin C; (e) 2FE//IL/CPE in PBS including 0.45 mM vitamin C and (f) 2FE/ZC/IL/CPE in PBS including 0.45 mM vitamin C. In all cases the scan rate was 10 mV s^{-1}.

Fig. 2 shows the CV responses for the electrochemical oxidation of 450.0 µM vitamin C at unmodified CPE (curve b), ZCPE (curve d), 2FE//IL/CPE (curve e) and 2FE/ZC/IL/CPE (curve f).

As it is seen, while the anodic peak potential for vitamin C oxidation at the ZC/CPE, and unmodified CPE are 480 and 540 mV, respectively, the corresponding potential at 2FE/ZC/IL/CPE and 2FE/IL/CPE is ~ 350 mV. These results indicate that peak potential for vitamin C oxidation at the 2FE/ZC/IL/CPE and 2FE/IL/CPE shift about ~ 130 and 190 mV toward negative values compared to ZC/CPE and unmodified CPE, respectively. 2FE/ZC/IL/CPE exhibited a redox couple reaction (Fig. 2, curve c) in PBS. However, in the presence of 450.0 µM vitamin C (curve f) there was an increase in the anodic peak current.

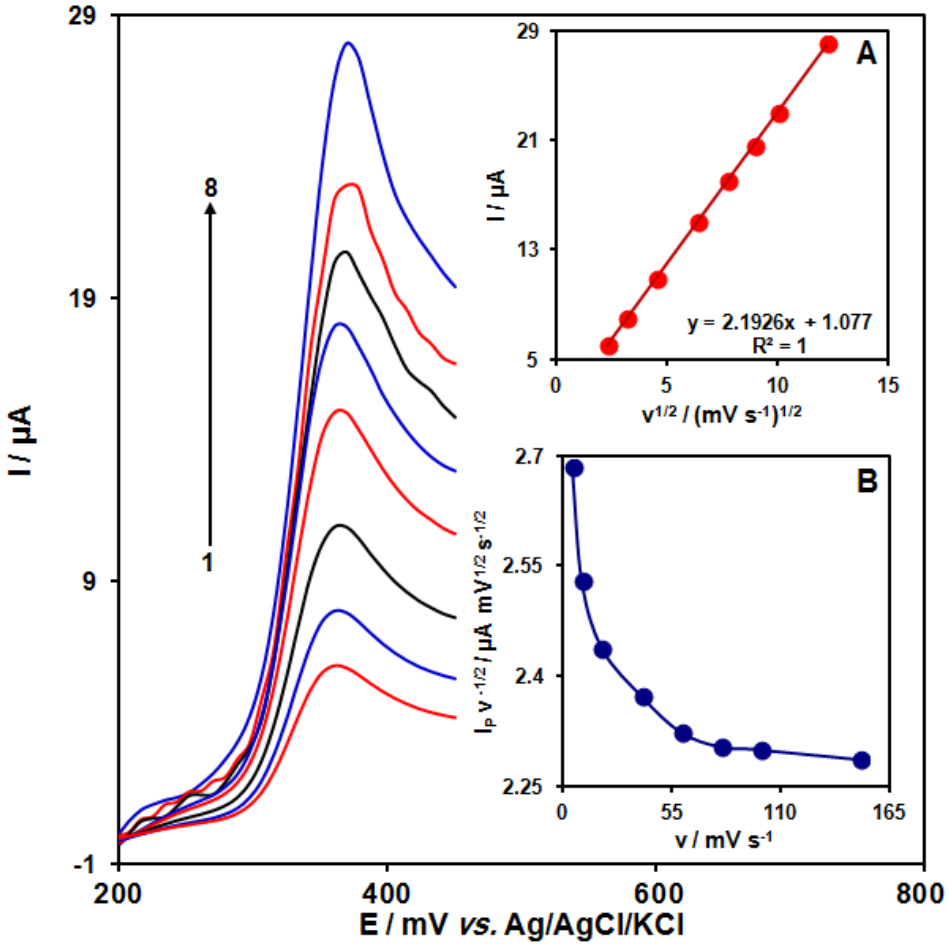

Figure 3. LSVs of 2FE/ZC/IL/CPE in PBS including 100.0 µM vitamin C at various scan rates; (5, 10, 20, 40, 60, 80, 100 and 150 mV s^{-1}). Insets: (A) Variation of anodic peak current *vs.* scan rate. (B) normalized current ($I_p/v^{1/2}$) vs. ν.

The effect of potential sweep rate on the oxidation of vitamin C at 2FE/ZC/IL/CPE was studied by LSV (Fig. 3). A plot of Ip vs. the $v^{1/2}$ was linear in the potential sweep rate range of 5-150 mV s^{-1}, suggesting that, the electrochemical process is controlled by diffusion (Fig. 3A) [51]. A plot of the scan rate-normalized current ($I_p/v^{1/2}$) vs. scan rate (Fig. 3B) shws the characteristic shape typical of an EC' process [51].

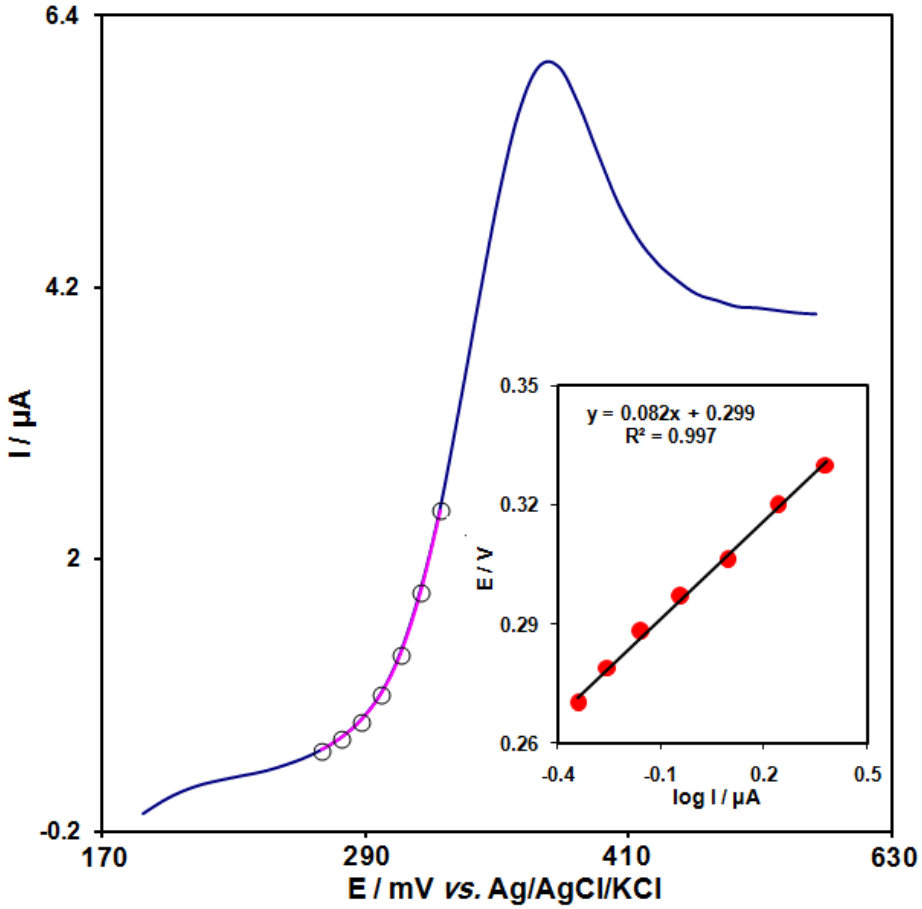

Figure 4. LSV (at 5 mV s^{-1}) of 2FE/ZC/IL/CPE in PBS including 100.0 µM vitamin C. The inset shows the Tafel plot.

Fig. 4 shows the LSV of 100.0 µM vitamin C at 2FE/ZC/IL/CPE, with a potential scan rate of 5 mV s^{-1}. The points show the Tafel region, which is affected by the electron transfer kinetics between 2FE/ZC/IL/CPE and vitamin C. The inset of Fig. 4 shows a Tafel plot with slope of 0.082 V, and a charge transfer coefficient of α=0.28 was obtained.

3.3. Chronoamperometric studies

Chronoamperometric studies of vitamin C at 2FE/ZC/IL/CPE were carried out for the various concentrations of vitamin C in PBS (pH 7.0) by setting the working electrode potential at 0.5 V vs. Ag/AgCl/KCl (3.0 M) (Fig. 5).

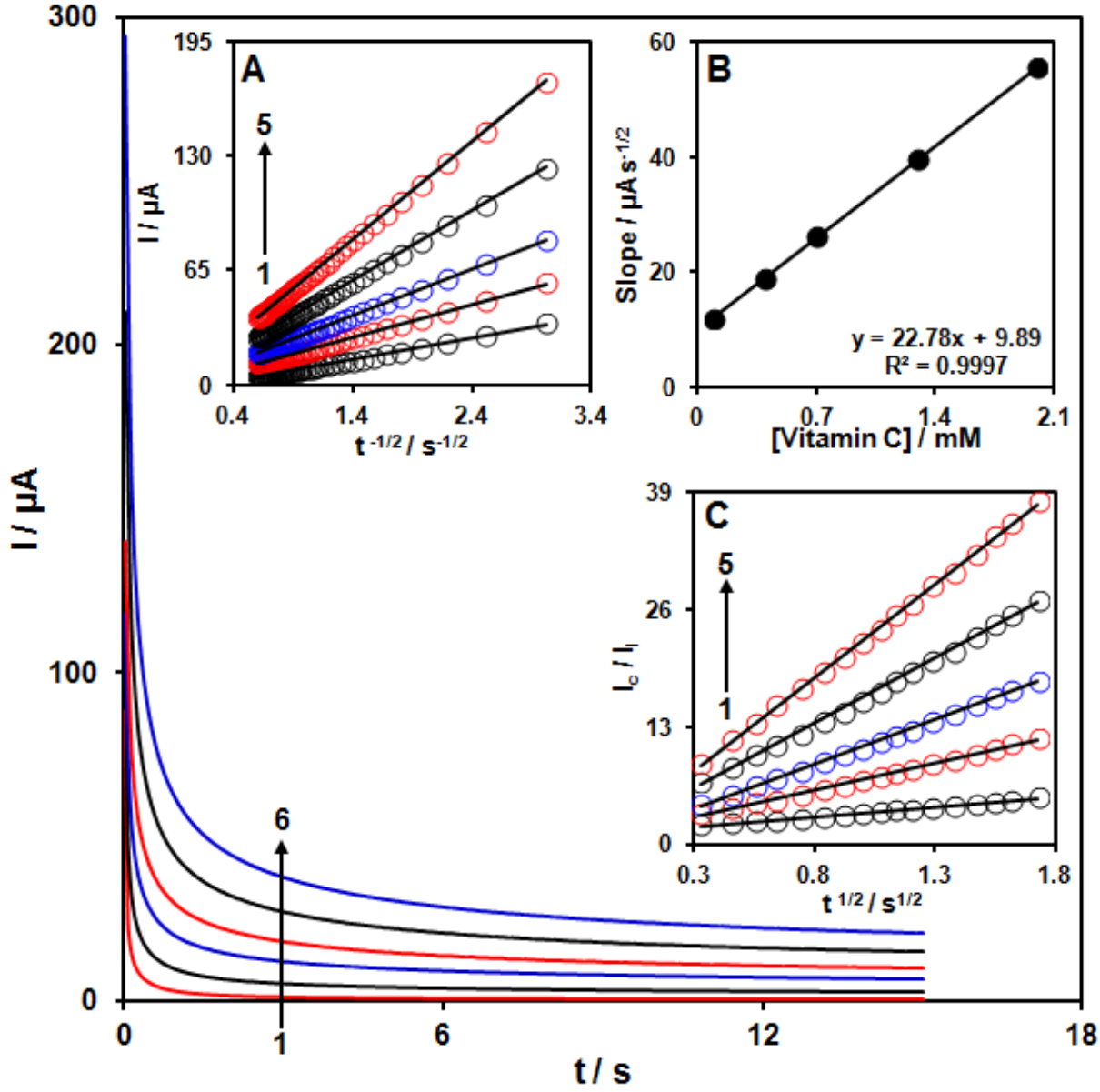

Figure 5. Chronoamperograms of 2FE/ZC/IL/CPE in PBS (pH 7.0) for different concentrations of vitamin C (0, 0.1, 0.4, 0.7, 1.3 and 2.0 mM). Insets: (A) Plots of I vs. $t^{-1/2}$ for chronoamperograms 2-6. (B) Plot of the slopes of the straight lines against vitamin C concentrations for chronoamperograms 2-6. (C) Dependence of I_{cat}/I_l on $t^{1/2}$ for chronoamperograms 1-6.

In chronoamperometric studies, we have determined the diffusion coefficient of vitamin C for a 2FE/ZC/IL/CPE. Inset A Fig. 5, shows the experimental plots of I vs. $t^{-1/2}$. The slopes of the resulting straight lines were then plotted versus the vitamin C concentration (Fig. 5, inset B). From their slope and using the Cottrell equation [51] a diffusion coefficient of 5.38×10^{-6} cm^2/s for vitamin C was calculated.

Catalytic rate constant, k, can be calculated according to the method described by Galus [52]. The average value of k was found to be 2.3×10^{3} M^{-1} s^{-1} from the values of the slopes (Fig. 5C),

3.4. Calibration plot

SWV studies were done for different concentrations of vitamin C. Within the range 4.0×10^{-8} to 1.0×10^{-3} M, the currents were proportional to the concentration of the vitamin C and detection limit (3σ) of 20.0 nM was obtained.

In the case of vitamin B_6 electro-oxidation peak currents of vitamin B_6 at the surface of modified electrode were linearly dependent on the vitamin B_6 concentrations, in the range of 1.0×10^{-6}–1.2×10^{-3} M and the detection limit (3σ) was obtained 8.0×10^{-7} M. These values are comparable with values reported by other research groups for electro-oxidation of vitamin C and vitamin B_6 at the surface of chemically modified electrodes (Table 1).

3.5. Simultaneous determination of vitamin C and vitamin B_6

To our knowledge, there is no report for simultaneous determination of vitamin C and vitamin B_6 using the 2FE/ZC/IL/CPE. Voltammetric determination of vitamin C using bare electrodes suffers from interference by vitamin B_6, because the anodic oxidation potential for vitamin B_6 is fairly close to the oxidation potential of vitamin C. Therefore, we used 2FE/ZC/IL/CPE to separate their oxidation peaks from each other.

The voltammetric results using 2FE/ZC/IL/CPE showed anodic peaks at potentials of 440 and 750 mV, corresponding to the oxidation of vitamin C and vitamin B_6 as shown in Fig. 6.

Table 1. Comparison of the efficiency of some modified electrodes used in the determination of vitamin C and vitamin B_6.

Electrode	Modifier	Method	Analyte	LOD (M)	LDR (M)	Ref.
Carbon paste	5-Amino-3´,4´-dimethyl-biphenyl-2-ol	Voltammetry	Vitamin C	3.0×10^{-7}	6.0×10^{-7} – 1.0×10^{-3}	5
Glassy carbon	Manganese (IV) oxide (MnO_2) nanoparticle	Voltammetry	Vitamin C	8.0×10^{-7}	2.64×10^{-6}- 1.5×10^{-3}	6
Carbon paste	Vanadyl(IV)–Salen complex	Voltammetry	Vitamin B_6	4.25×10^{-5}	4.5×10^{-4}- 3.3×10^{-3}	8
Glassy carbon	Au-CuO/MWCNTs	Voltammetry	Vitamin B_6	1.5×10^{-7}	7.9×10^{-7}-1.84×10^{-5}	9
Carbon paste	ZnO/CuO nanosheets, ionic liquids and 2-(ferrocenylethynyl)fluoren-9-one	Voltammetry	Vitamin C	2.0×10^{-8}	4.0×10^{-8}-1.0×10^{-3}	This Work
			Vitamin B_6	8.0×10^{-7}	1.0×10^{-6}-1.2×10^{-3}	

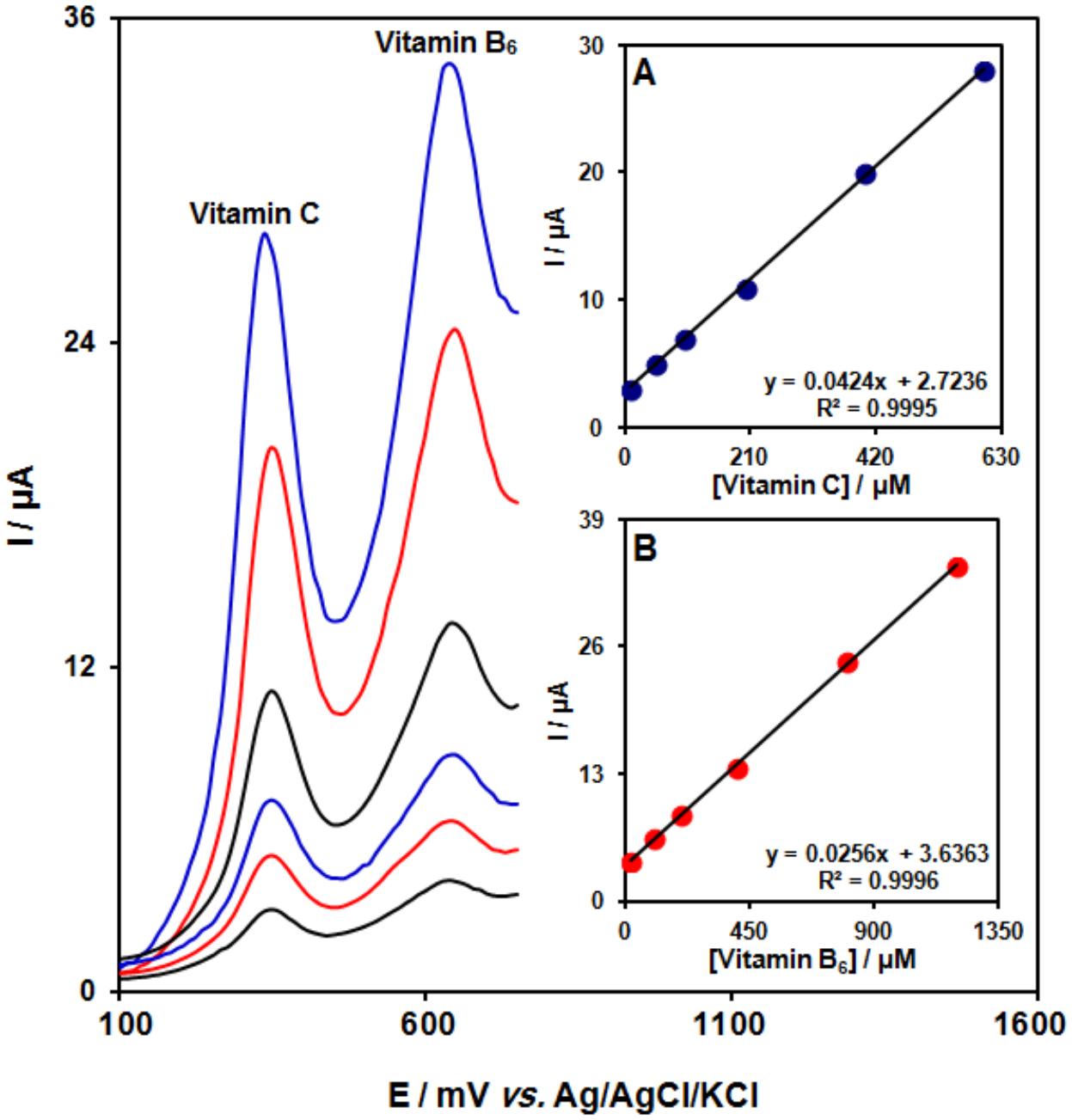

Figure 6. SWVs of 2FE/ZC/IL/CPE in PBS including different concentrations of vitamin C and vitamin B_6 in µM, (10.0+20.0, 50.0+100.0, 100.0+200.0, 200.0+400.0, 400.0+800.0 and 600.0+1200). Insets: (A) plots of current vs. vitamin C concentration and (B) plot of current vs. vitamin B_6 concentration.

3.6. Real sample studies

Proposed method was used to the determination of vitamin C and vitamin B_6 in vitamin C injection, effervescent C tablets, multivitamin syrup and urine samples (Table 2).

Table 2. Determination of vitamin C and vitamin B_6 in real samples. Concentrations are in μM (n=5).

Sample	Spiked		Found		Recovery (%)		R.S.D. (%)	
	Vitamin C	Vitamin B_6	Vitamin C	Vitamin B_6	Vitamin C	Vitamin B_6	Vitamin C	Vitamin B_6
vitamin C injection	0	0	15.0	ND	-	-	3.2	-
	5.0	30.0	19.8	31.1	99.0	103.7	1.7	3.3
	10.0	40.0	25.7	39.8	102.8	99.5	1.9	2.7
	15.0	50.0	29.1	50.5	97.0	101.0	2.8	1.6
Effervescent C tablets	0	0	20.0	ND	-	-	2.1	-
	5.0	25.0	25.2	24.5	100.8	98.0	2.7	3.4
	10.0	35.0	29.3	35.6	97.7	101.7	3.2	2.1
	15.0	45.0	34.8	46.5	99.4	103.3	1.8	2.9
,Multivitamin syrup	0	0	20.0	10.0	-	-	1.9	3.1
	7.5	35.0	27.9	44.2	101.4	98.2	1.7	2.4
	12.5	45.0	31.8	56.1	97.8	102.0	3.1	2.7
	17.5	55.0	38.4	64.6	102.4	99.4	2.2	2.3
Urine	0	0	-	-	-	-	-	-
	5.0	7.5	4.9	7.7	98.0	102.7	3.2	2.9
	10.0	12.5	10.3	12.4	103.0	99.2	2.1	2.2
	15.0	17.5	14.9	17.9	99.3	102.3	2.8	3.3

ND: Not detected

4. CONCLUSION

An electrochemical method has been developed and successfully applied for the simultaneous determination of vitamin C and vitamin B_6 using the 2FE/ZC/IL/CPE. The modified electrode greatly enhanced the electrooxidation reactions of vitamin C and vitamin B_6, and in optimized conditions well-separated voltammetric peaks for sensitive and selective determination of vitamin C and vitamin B_6 appeared using the SWV technique. The proposed method could be applied to the determination of vitamin C and vitamin B_6 in real samples.

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