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Graphene /ZnO Nanocomposite for Voltammetric Sensing of Vitamin B_6 using Modified Glassy Carbon Electrode

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Abstract- A convenient, low cost, and sensitive electrochemical method, based on a glassy carbon electrode modified with graphene/ZnO nanocomposite is described for determination of vitamin B_6. The modified electrode exhibited good electrochemical properties toward the oxidation of vitamin B_6. The diffusion coefficient ($D=1.89\times10^{-5}$ cm^2 s^{-1}), and the kinetic parameter such as the electron transfer coefficient, ($\alpha=0.53$) of vitamin B_6 oxidation at the surface of modified electrode was determined using electrochemical approaches. The anodic peak currents of vitamin B_6 were found to be linear in the concentration range of 1.0–16000.0 μM with the detection limit of 7.2×10^{-7} M.

Keywords- Vitamin B_6, Graphene /ZnO nanocomposite, Glassy carbon electrode, Voltammetry

1. INTRODUCTION

Vitamins constitute a group of compounds, which are essential constituents of food required for normal growth, self maintenance and functioning of human and animal bodies [1,2]. They are divided into water-soluble and fat-soluble vitamins. Vitamin B_6 (pyridoxine) is well-known among B group vitamins belong to the first group. Vitamin B_6 is a significant vitamin that aids in the formation of healthy red blood cells and supports the more vital physiological metabolism [3]. Vitamin B_6 also performs versatile functions in the bio-

metabolism, vitamin B_6 is necessary for enzymes involved in protein metabolism. Furthermore, vitamin B_6 plays vital role in the function of nervous and immune systems. Moreover, a vitamin B_6 deficiency can lead to anemia that resembles an iron deficiency anemia [4]. Therefore, an effective, sensitive and valid analysis method for vitamin B_6 determination is needed. Several methods have been developed to determine vitamin B_6, such as flow injection systems, high performance thin layer chromatography, and liquid chromatography with electrochemical detection [5-8]. However, these methods require sophisticated and expensive instrumentation, and the procedures used in these methods are lengthy requiring long executing times. Furthermore, they have the inability to carry out in situ measurements. Therefore, rapid determination of this component in pharmaceutical and illicit samples has been remained as a great challenge in analytical chemistry [9].

Electrochemical techniques, especially voltammetric methods, due to having more simplicity and selectivity have been widely used for individual determination of vitamins [10,11]. The use of electrochemical technique for vitamin B_6 determination has limited by low sensitivity and reproducibility, slow electron transfer reaction, low stability over a wide range of solution composition and high overpotential at which the electron transfer process occurs and some of them are not sensitive enough for real sample analysis [12,13]. The chemical modification of inert substrate electrodes with redox activated thin films offers significant advantages in design and development of electrochemical sensors [14-21]. Different modified electrodes have been used for electrooxidation of vitamin B_6 so far. Hence, it is pertinent to explore and develop a simple and reliable method to fabricate modified electrodes with new electron transfer mediators.

Wide bandgap oxides such as ZnO has declaimed to be very promising in electrochemical applications, due to its thermal stability, chemical inertness, wide direct band gap (3.37 eV at room temperature), large exciton binding energy (60 meV) and a high isoelectric point (IEP) (~9.5) and being friendly to the environment, as well as the tunable optical and electrical properties [22-27]. However, the application of ZnO nanoparticles is limited by their rigidity, and they are easily destroyed in the process of sensor preparation [28]. The structure of nanoparticles can be maintained if ZnO nanoparticles are composited with some flexible materials.

As a representative of flexible material, graphene is a 2D monolayer carbon atomic sheet with rich edge defects, large surface area, remarkable electronic conductivity, superior mechanical property, high thermal stability and so on [29-35]. Similar to graphene, graphene oxide (GO) based biosensors have also raised concerns due to simple fabrication, the abundant surface functional groups and high surface area [36]. GO/semiconductor hybrid nanostructures have attracted great attention in biosensor due to the synergistic effect of two materials and the additional functionality of the GO [37-40].

Because of these unique structural and electrical properties of ZnO/graphene nanocomposites, we used graphene /ZnO nano composite glassy carbon electrode (GZGCE) as a rapid and simple sensor for electrochemical detection of vitamin B_6 without any pretreatment or separation steps. Square wave voltammetry (SWV) technique was used for detection of proposed analyte at micromolar concentration range.

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 GZGCE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

Vitamin B_6 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 2.0-12.0.

2.2. Synthesis of graphene /ZnO nano composite

The reduced graphene oxide (0.096 g) was dispersed in 40 ml water and the solution was kept in ultrasonic bath for 1h. The prepared solution was added to 40 ml of $ZnCl_2$ (0.04 M) solution. Final solution pH was set 11.7 by ammonia solution. The solution was kept at 95 ^oC for 4h. The precipitate was gathered at 15000 rpm centrifuge for 15 min. Then it was washed by distilled water three times.

2.3. Preparation of the electrode

The preparation of modified GCE was performed by mechanically polishing a glassy carbon electrode with 0.05 µm Al_2O_3 in water slurry. Then, it was electrochemically activated in a 0.1 M sodium bicarbonate solution, and pouring 4 µL of graphene /ZnO nano composite suspension (1 mg/1 mL) onto the activated GCE surface.

3. RESULT AND DISCUSSION

3.1. Electrochemical behavior of vitamin B_6 at the surface of various electrodes

Fig. 1 displays cyclic voltammetric responses from the electrochemical oxidation of 1000.0 µM vitamin B_6 at the surface of bare glassy carbon electrode (curve a) and GZGCE (curve b).

The results showed that the oxidation of vitamin B_6 is weak at the surface of the bare GCE, but the presence of graphene /ZnO nano composite at the surface of GCE 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 vitamin B_6 and dramatic increase of the current indicates the catalytic ability of GZGCE (curve b) to vitamin B_6 oxidation.

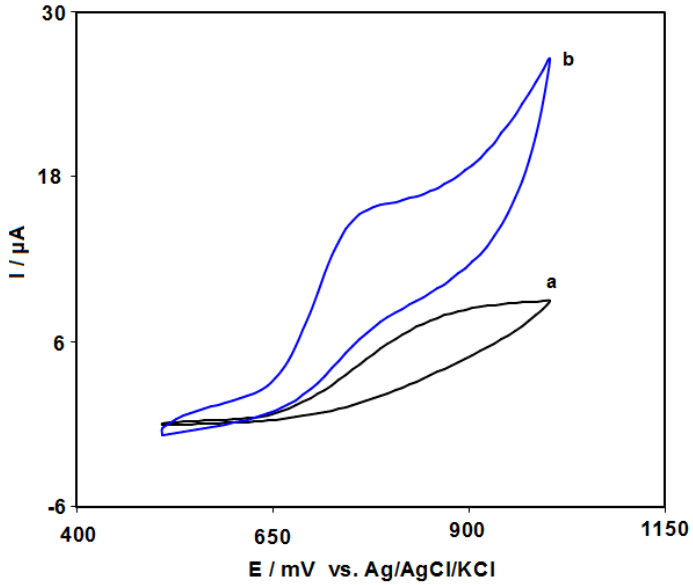

Fig. 1. CVs of a) GCE and b) GZGCE in the presence of 1000.0 µM vitamin B_6 at a pH 7.0, respectively. In all cases the scan rate was 50 mV s^{-1}

3.2. Effect of scan rate

The effect of potential scan rates on the oxidation current of vitamin B_6 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 10 to 900 mV s^{-1}.

Fig. 3 shows the Tafel plot for the sharp rising part of the voltammogram at the scan rate of 10 mV s^{-1}. If deprotonation of vitamin B_6 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 0.127 V was obtained which agrees well with the involvement of one electron in the rate determining step of the electrode process [41], assuming a charge transfer coefficient, α of 0.53.

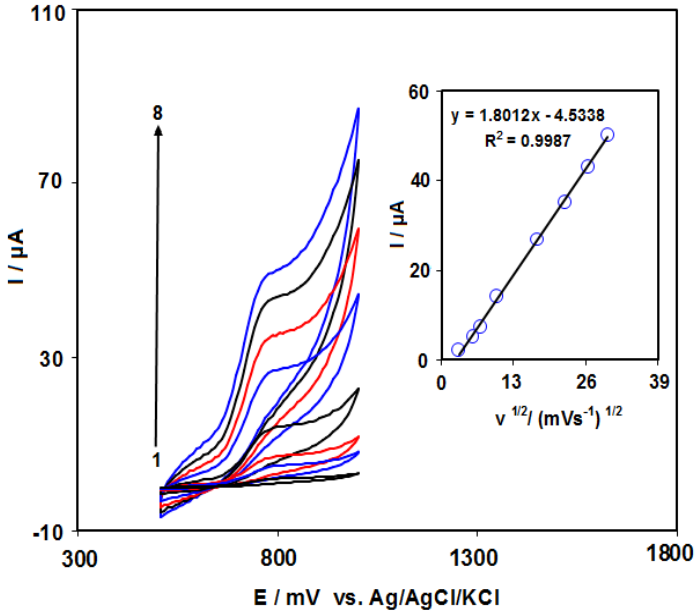

Fig. 2. CVs of GZGCE in 0.1 M PBS (pH 7.0) containing 400.0 µM vitamin B_6 at various scan rates; numbers 1-8 correspond to 10, 30, 50, 100, 300, 500, 700 and 900 mV s^{-1}, respectively. Inset: Variation of anodic peak current *vs*. square root of scan rate.

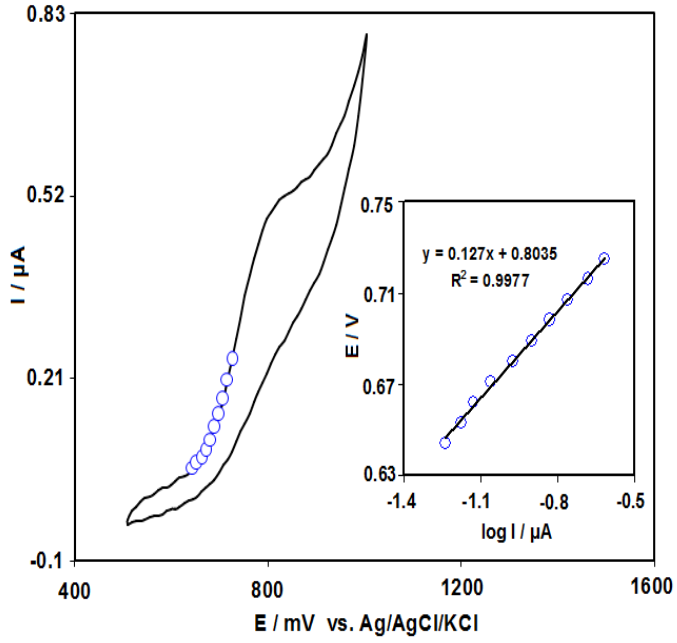

Fig. 3. CV (at 10 mV s^{-1}) of an GZGCE in 0.1 M PBS (pH 7.0) containing 100.0 µM vitamin B_6. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the CV

3.3. Chronoamperometric measurements

Chronoamperometric measurements of vitamin B_6 at GZGCE were carried out by setting the working electrode potential at 0.85 V *vs.* Ag/AgCl/KCl (3.0 M) for the various concentrations of vitamin B_6 in PBS (pH 7.0) (Fig. 4). For an electroactive material (vitamin B_6 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 [41].

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

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 vitamin B_6 (Fig. 4A). The slopes of the resulting straight lines were then plotted *vs.* vitamin B_6 concentration (Fig. 4B). From the resulting slope and Cottrell equation the mean value of the D was found to be 1.85×10^{-5} cm^2/s.

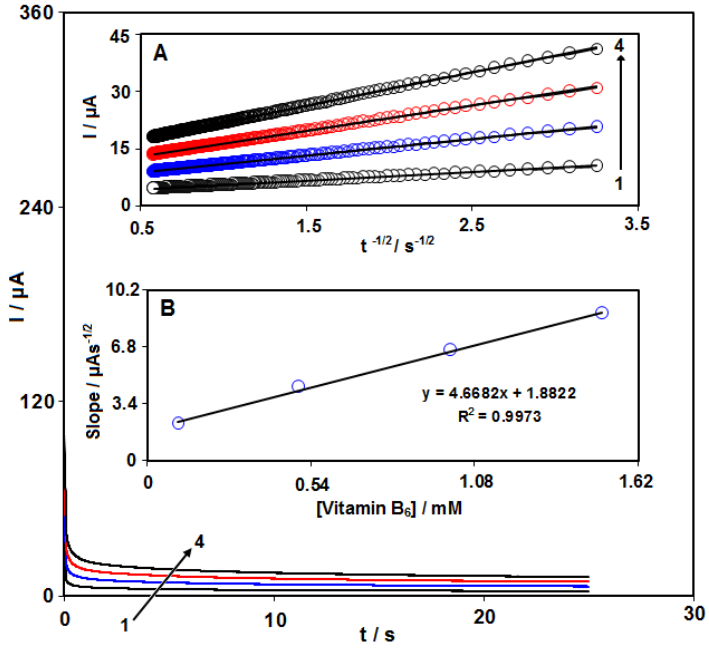

Fig. 4. Chronoamperograms obtained at GZGCE in 0.1 M PBS (pH 7.0) for different concentration of vitamin B_6. The numbers 1–4 correspond to 0.1, 0.5, 1.0 and 1.5 mM of vitamin B_6. Insets: (A) Plots of I *vs.* $t^{-1/2}$ obtained from chronoamperograms 1–4; (B) Plot of the slope of the straight lines against vitamin B_6 concentration.

3.4. Calibration plot and limit of detection

The peak current of vitamin B_6 oxidation at the surface of the modified electrode can be used for determination of vitamin B_6 in solution. Therefore, SWV experiments were done for different concentrations of vitamin B_6 (Fig. 5). The oxidation peak currents of vitamin B_6 at

the surface of a modified electrode were proportional to the concentration of the vitamin B_6 within the ranges 1.0×10^{-6} to 1.6×10^{-3} M with detection limit (3σ) of 7.2×10^{-7} M.

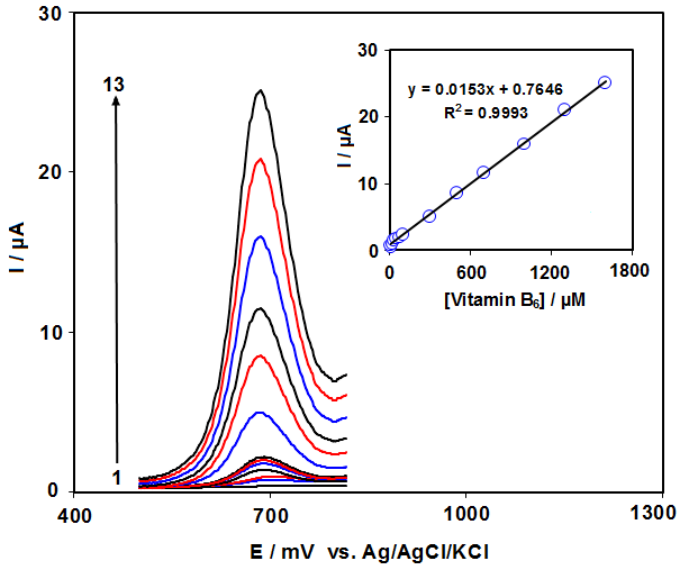

Fig. 5. SWVs of GZGCE in 0.1 M PBS (pH 7.0) containing different concentrations of vitamin B_6; the numbers 1–13 correspond to 1.0, 5.0, 10.0, 30.0, 50.0, 70.0, 100.0, 300.0, 500.0, 700.0, 1000.0, 1300.0 and 1600.0 µM of vitamin B_6. Inset shows the plots of the peak current as a function of vitamin B_6 concentration in the range of 1.0-1600.0 µM.

4. CONCLUSION

In this work, employing graphene/ZnO nanocomposite as modifiers in GCE, a novel sensor has been developed that provides an extremely sensitive and selective method for the determination of vitamin B_6. The proposed protocol demonstrated herein a novel, simple, portable, inexpensive, disposable and easy-to-use fabrication method for the measurement of vitamin B_6 concentration with good analytical performance. Due to the unique properties of graphene/ZnO nanocomposite, the sensor exhibited remarkable electrochemical activity toward the oxidation of vitamin B_6.

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