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La³⁺-doped Co₃O₄ Nanoflowers Modified Graphite Screen Printed Electrode for Electrochemical Sensing of Vitamin B₆

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In this study, we combined the advantages of good conductivity, small size, large surface area, and the catalytic property of La^{3+}/Co_3O_4 nanoflowers to fabricate an electrochemical sensor sensitive for determination of vitamin B₆ in real samples. La^{3+}/Co_3O_4 nanoflowers were synthesized by a co-precipitation method that is a convenient, environment-friendly, and inexpensive process. The synthesized nanoflowers were characterized by SEM. A simple and sensitive sensor based on graphite screen printed electrode (GSPE) modified by La^{3+}/Co_3O_4 nanoflowers was developed for the electrochemical determination of vitamin B₆. The electrochemical behavior of vitamin B₆ was studied in 0.1 M phosphate buffer solution (PBS) using cyclic voltammetry (CV), chronoamperometry (CHA), and differential pulse voltammetry (DPV). The modified electrode ($La^{3+}/Co_3O_4NFs/GSPE$) showed excellent electrocatalytic activity and remarkable sensitivity towards the oxidation of vitamin B₆. The fabricated sensor displayed good operating characteristics including low detection limit, and a wide linear dynamic range for the detection of 0.4 μ M were obtained. Finally, reliability and accuracy of the proposed sensor were studied in real samples.

Keywords: La³⁺/Co₃O₄ Nanoflowers, Electrochemical sensor, Vitamin B₆, Real samples, Modified electrode

INTRODUCTION

Vitamins are vital components for self-conservation, normal growth and elaboration of animal and human bodies. They are divided into water and fat-soluble vitamins [1].

Vitamin B_6 (Scheme 1) belongs to water soluble B complex vitamins group, commonly called pyridoxine [2]. Vitamin B_6 is a significant vitamin that aids in the formation of healthy red blood cells and supports the more vital physiological metabolism [3,4]. Vitamin B_6 is essential for many enzymes involved in the bio-metabolism of proteins, carbohydrates, amino acids and fats [5]. Vitamin B_6 also supports nervous and immune systems functions [6]. Furthermore, a vitamin B_6 deficiency can lead to anemia that



Scheme 1. Chemical structures of vitamin B₆

resembles an iron deficiency anemia [7]. Due to its role in human body there is a need for fast, low cost and reliable analytical procedures for the selective and sensitive determination of vitamin B_{6} .

Various methods such as spectrophotometry [8], chemiluminescence [9], liquid chromatography [10], high performance liquid chromatography [11] and

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Fig. 1. XRD of La^{3+}/Co_3O_4 nanoflowers.



Fig. 2. SEM image of La^{3+}/Co_3O_4 nanoflowers.

electrochemical techniques [12-15] have been utilized to detect vitamin B_6 . Some of these methods involve complicated operations, expensive instruments, and using large amounts of toxic organic solvents or need separation processes. Electrochemical detection of biological compounds is an alternative method that has attracted lots of attention due to its simplicity, low cost, high rate, selectivity, high sensitivity and good reproducibility [16-20].

However, the voltammetric response of biological

compounds is not satisfactory at the bare electrodes for analytical applications because of slow heterogeneous electron transfer, and the direct electrochemical oxidation of biological compounds at high overpotential. Therefore, chemically modified electrodes (CMEs) are excellent approaches to reduce the overpotential and increase the sensitivity of determinations by introducing a modifier to the electrode [21-34].

Screen-printed electrodes (SPEs) have received great

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Scheme 2. The proposed mechanism for the oxidation of vitamin B₆ at the La³⁺/Co₃O₄/GSPE [49]



Fig. 3. CVs of a) $La^{3+}/Co_3O_4/SPE$ and b) SPE in the presence of 100.0 μ M vitamin B₆ at a pH 7.0. In all cases the scan rate was 50 mV s⁻¹.

attention for the on-site monitoring as well as fast speed, high efficiency, portability, low cost and small sample size. Therefore, the use of screen-printing technology in the serial production of disposable low-cost electrodes for the electrochemical determination of a wide range of substances is currently undergoing widespread growth [35-38].

Nowadays, the nanomaterials have been attracted much attention to modify the surface of electrodes for electrochemical detection of biological compounds due to their unique properties, such as large surface area, plenty active sites, high electronic conductivity and good chemical stability [39,40].

The lanthanides represent a group of elements from La to Lu that shows very similar physical and chemical properties. Lanthanum (La) is one of the most important lanthanide elements. La ions own relatively low toxicity and extraordinary catalytic properties, thus, those ions can be used to construct environment-friendly sensors [41-43].

Recently, electrodes modified with metal oxide nanostructures have been thoroughly investigated for the electrochemical determination of several biologically important analytes because of their interesting electrocatalytic properties. Among the various metal oxide nanoparticles, Co_3O_4 nanoparticles have recently gained more interest due to their biocompability, wide availability, low cost, earth abundance, good electrochemical properties, large surface area and good ability for promoting electron transfer reactions [44-46].

In this work, the preparation of an electrochemical sensor is described for the voltammetric determination of vitamin B₆. The sensor was designed by the modification of graphite screen printed electrodes (GSPE) with La^{3+}/Co_3O_4 nanoflower. The prepared modified electrode ($La^{3+}/Co_3O_4/GSPE$) showed very high performance in the electrochemical oxidation of vitamin B₆. The linear range and detection limit of vitamin B₆ were determined. Analytical application of the prepared electrode was tested by performing the determination of vitamin B₆ in real samples.

EXPERIMENTAL

Chemicals and Apparatus

An Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was employed to perform the electrochemical experiments and the system was controlled using a general purpose electrochemical system software.

The screen-printed electrode (DropSens, DRP-110, Spain) consists of three conventional electrodes: graphite counter electrode, a silver pseudo-reference electrode, and an unmodified graphite working electrode. The pH was measured by a Metrohm 710 pH meter.

Vitamin B₆ and all other reagents were of analytical

grade, and were purchased from Merck (Darmstadt, Germany). For the preparation of buffers, the orthophosphoric acid and its salts were used to provide the pH range of 2.0-9.0.

Synthesis of La³⁺/Co₃O₄ Nanoflowers

All the chemicals used for the preparation of the nanopowders, namely cobalt acetate (Co(CH₃COO)₂.2H₂O), lanthanium nitrate (La(NO_3)_3.6H₂O), thiourea ((NH_2)₂CS) and ammonia (25% NH₃), were of analytical grade. All the precursors were dissolved in deionized water. During the preparation of the nano-powders, ammonia was used as a complexing agent. The La³⁺-doped Co₃O₄ nanostructures were prepared by dissolving 0.46 mol of cobalt acetate in 80 ml of deionized water, 0.0046 mol of lanthanium nitrate in 80 ml of deionized water, 0.18 mol of thiourea in 80 ml of deionized water and lastly by adding 19.76 ml of ammonia in 80 ml of deionized water. The amount of solutions of cobalt acetate, thiourea and ammonia was held constant at a ratio of 1:1:1. Then, the cobalt acetate solution was added in a beaker in the reaction bath, followed by adding thiourea and lanthanium nitrate solution in the same reaction bath and the mixture was stirred for a few seconds. Lastly ammonia solution was added slowly into the mixture, while continuing stirring for 5 min. The temperature of the bath was then allowed to increase up to 80 °C. After that the precipitates were formed and left overnight and filtered thereafter. The precipitates were then washed with ethanol. The obtained powders were dried at ambient conditions for several days.

Preparation of the Electrode

The bare screen-printed electrode was coated with La^{3+}/Co_3O_4 nanoflowers according to the following simple procedure. 1 mg La^{3+}/Co_3O_4 nanoflowers was dispersed in 1 ml aqueous solution within 45 min ultrasonication. Then, 5 μ l of the prepared suspension was dropped on the surface of carbon working electrodes. It remains at room temperature until becomes dry.

Preparation of Real Samples

An ampoule of 1 ml of vitamin B_6 (concentration of vitamin B_6 of 50 mg ml⁻¹) was diluted to 10 ml with 0.1 M

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Fig. 4. Cyclic voltammograms of La³⁺/Co₃O₄/SPE in 0.1 M PBS (pH 7.0) containing 700.0 μM vitamin B₆ at various scan rates; numbers 1-9 correspond to 10, 20, 30, 50, 70, 100, 200, 400 and 600 mV s⁻¹, respectively. Insets: Variation of anodic and cathodic peak currents vs. v^{1/2}.

phosphate buffer (PBS) (PH 7.0). Then, different volumes of the diluted solution were transferred into each of a series of 25 ml volumetric flasks and diluted to the mark with PBS. The vitamin B_6 content was analyzed by the developed voltammetry procedure using the standard addition method.

Urine samples were stored in a refrigerator immediately after collection. Ten milliliters of the sample were centrifuged for 15 min at 2000 rpm. The supernatant was filtered out using a 0.45 μ m filter. Then, different volumes of the solution was transferred into a 25 ml volumetric flask and diluted to the mark with PBS (pH 7.0). The diluted urine sample was spiked with different amounts of vitamin B₆.

The vitamin B₆ content were analyzed by the proposed

method using the standard addition method.

RESULTS AND DISCUSSION

Nanostructures Characterization

The main characteristic diffraction peaks of the La^{3+}/Co_3O_4 nanoflowers 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 will not change the backbone of pristine Co_3O_4 (Fig. 1). With increasing La in Co_3O_4 , the characteristic peak at $2\theta = 37.2^\circ$ becomes weaker and slightly shifts to small-angle reflections with the increase of La in Co_3O_4 . The

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Fig. 5. CV (at 10 mV s⁻¹) of electrode in 0.1 M PBS (pH 7.0) containing 700.0 μ M vitamin B₆. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the CV.

introduction of the La ions with f electronic and large atomic radiuses into the Co_3O_4 grain boundary causes the loss of atoms degree of order of Co_3O_4 , thereby contributing to the limited growth of the grain, grain refinement and the decrease of crystallinity [47].

The broadness of the diffraction peaks suggests the nano-sized nature of the product that its average crystallite size (t) was calculated using the Debye-Scherrer formula as 37.0 nm. 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) [48].

The morphology of the product was examined by SEM

(Fig. 2). The SEM picture of the nanoflowers shows the formation of nanoflowers with the petals in the nanorod shape, and less than 40 nm in size.

Electrochemical Profile of the Analytes on $La^{3+}/Co_3O_4/GSPE$

To study the electrochemical behaviour of vitamin B_6 that is pH-dependent (Scheme 2), the optimized pH value is required to achieve the accurate results. Using the modified electrodes at various pH values ranging from 2.0-9.0 revealed that the best results for electro-oxidation of vitamin B_6 occur at pH = 7.0. The obtained cyclic voltammograms



Fig. 6. Chronoamperograms obtained atfor La³⁺/Co₃O₄/SPE in 0.1 M PBS (pH 7.0) for different concentrations of vitamin B₆. The numbers 1-5 correspond to 0.1, 0.4, 0.7, 1.4 and 3.0 mM of vitamin B₆. Insets: (A) Plots of I vs. t^{1/2} obtained from chronoamperograms 1-5. (B) Plot of the slope of the straight lines against vitamin B₆ concentration.

in the presence of 100.0 μ M vitamin B₆ using La³⁺/Co₃O₄/GSPE the (Curve a) and bare GSPE (Curve b) are shown in Fig. 3. According to CV results, the maximum oxidation of vitamin B₆ on the La³⁺/Co₃O₄/GSPE occurs at 750 mV that is about 100 mV more negative than that of unmodified GSPE.

Effect of Potential Scan Rate on the Results

The study of the effect of potential scan rates on the oxidation currents of vitamin B_6 , shown in Fig. 4. indicates that increasing the scan rate leads to enhanced oxidation

peak current. In addition, there is a linear relationship between Ip and the square root of the potential scan rate $(v^{1/2})$ demonstrating that the oxidation procedure of analyst is in the control of diffusion. The Tafel curve of analyte was plotted applying the data from the rising sections (*i.e.* the Tafel regions) of the current-voltage curve obtained at 10 mV s⁻¹ (Fig. 5). The kinetics of electron transfer in the electrode reactions, influence on the Tafel regions of the current potential curve. The Tafel slope was obtained 0.1 V in this case. Using this slope, charge transfer coefficient of $\alpha = 0.41$ was obtained [50].



Fig. 7. DPVs of La³⁺/Co₃O₄/SPE in 0.1 M (pH 7.0) containing different concentrations of vitamin B₆. Numbers 1-10 correspond to 1.0, 5.0, 20.0, 40.0, 60.0, 80.0, 100.0, 200.0, 400.0 and 600.0 μM of vitamin B₆. Insets: A, plots of the electrocatalytic peak current as a function of vitamin B₆ concentration in the range of 1.0-600.0 μM.

Chronoamperometric Analysis

The analysis of chronoamperometry for vitamin B_6 samples was performed by the use of La³⁺/Co₃O₄/GSPE *vs*. Ag/AgCl/KCl (3.0 M) at 0.8 V. The Chronoamperometric results of different concentrations of vitamin B_6 sample in PBS (pH 7.0) are demonstrated in Fig. 6. The Cottrell equation for chronoamperometric analysis of electroactive moieties under mass transfer limited conditions is as follows [50]:

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

where D represents the diffusion coefficient $(cm^2 s^{-1})$,

and C_b is the applied bulk concentration (mol cm⁻³). Experimental results of I vs. t^{1/2} were plotted in Fig. 6A, with the best fits for different concentrations of vitamin B₆. The resulted slopes corresponding to straight lines in Fig. 6A, were then plotted against the concentration of vitamin B₆ (Fig. 6B). On the basis of the resulting slope and Cottrell equation, the mean value of D was determined to be 5.4 × 10⁻⁶ cm²/s.

Calibration Plot and Limit of Detection

The peak current of vitamin B_6 oxidation at the surface of $La^{3+}/Co_3O_4/GSPE$ can be used for determination of vitamin B_6 in the solution (Fig. 7). Hence, differential pulse

Electrode	Modifier	Method	LDR	LOD	Ref.
			(M)	(M)	
Glassy carbon	Carbon nanotubes mixed	Voltammetry	5.0×10^{-7} - 5.0×10^{-5}	3.09×10^{-9}	[1]
electrode	with ionic liquid crystal				
	and CuO nanoparticles				
Boron-doped	-	Voltammetry	7.0×10^{-6} - 4.7×10^{-5}	3.76×10^{-6}	[2]
diamond electrode					
Glassy carbon	Silver doped	Voltammetry	1.0×10^{-5} - 3.0×10^{-3}	$5.0 imes 10^{-6}$	[6]
electrode	poly(L_arginine)				
Glassy carbon	Au-CuO/MWCNTs	Voltammetry	$7.9 \times 10^{\text{-7}}\text{-}1.84 \times 10^{\text{-5}}$	1.5×10^{-7}	[7]
electrode					
Screen	Ru nanoparticles-	Voltammetry	2.6×10^{-6} - 2.0×10^{-4}	$0.8\times 10^{\text{-}6}$	[14]
printed electrode	MWCNTs				
graphite screen	La ³⁺ /Co ₃ O ₄ Nanoflowers	Voltammetry	$1.0\times10^{\text{-6}}6.0\times10^{\text{-4}}$	4.0×10^{-7}	This
printed electrode					work

Table 1. Comparison of the Efficiency of some Modified Electrodes Reported for the Detection of Vitamin B₆

Table 2. Determination of Vitamin B ₆ in Real	Samples. Concentrations are in	$\mu M (n = 5)$
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Sample	Spiked	Found	Recovery	R.S.D.
			(%)	(%)
	0	5.0	-	3.2
Vitamin B ₆ ampoule	2.5	7.4	98.7	1.7
	5.0	10.1	101.0	2.9
	7.5	12.4	99.2	2.3
	0	-	-	-
Urine	10.0	9.8	98.0	1.6
	15.0	15.5	103.3	2.7
	20.0	20.1	100.5	3.1

voltammetry (DPV) experiments were carried out for different concentrations of vitamin B_6 . The oxidation peak currents of vitamin B_6 at the electrode surface were proportional to the concentration of the vitamin B_6 in the range of 1.0-600.0 μ M. The detection limit (3σ) of vitamin B_6 was found to be 0.4 μ M. Table 1 shows a comparison of analytical properties for the detection of vitamin B_6 at the prepared electrode in this work and various electrodes.

Interferences Study

The influence of various substances as compounds potentially interfering in determination of vitamin B₆ was studied under optimum conditions with 30.0 μ M vitamin B₆ at pH 7.0. The potentially interfering substances were chosen from the group of substances commonly found with vitamin B₆ in pharmaceuticals and/or in biological fluids. The tolerance limit was defined as the maximum concentration of interfering substance causingan error less than ±5% in determination of vitamin B₆. According to the results, glucose, sucrose, lactose, fructose, citric acid, methanol, ethanol, Mg²⁺, SO₄²⁻, Al³⁺, NH₄⁺, Fe²⁺, Fe³⁺, CO₃²⁻, Cl⁻ or F⁻, alanine, methionine, phenylalanine, glycine, folic acid (vitamin B₉), saturated starch solution, urea, dopamine, ascorbic acid, epinephrine and norepinephrine did not interfere in determination of vitamin B₆.

Analysis of Real Samples

In order to evaluate the analytical applicability of vitamin B_6 , the proposed method was also applied for determination of vitamin B_6 in vitamin B_6 ampoule and urine samples, using a standard addition method. The results for determination of the vitamin B_6 in real samples are given in Table 2. Satisfactory recoveries of the experimental results were found for vitamin B_6 . The reproducibility of the method was demonstrated by the mean relative standard deviation (R.S.D.).

CONCLUSIONS

 La^{3+}/Co_3O_4 nanoflowers were synthesized and used for modification of GSPE. The modified electrode exhibited good electrochemical sensor applications for vitamin B₆ determination. The proposed method showed good sensitivity and a low detection limit (0.4 µM) for vitamin B₆ determination. In addition, the good recovery results were applicable to the real sample analysis.

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