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Short Communication

Electrochemical determination of Vitamin B_6 in fruit juices using a new nanostructure voltammetric sensor

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ABSTRACT

In this study, MgO/CNTs nanocomposite was synthesized using a simple approach according to the hydrogen bonding between the oxygen atom in MgO and hydrogen atom in SWCNTs-COOH. The nanocomposite was characterized using the FESEM and EDS methods. The MgO/CNTs nanocomposite was used for amplification of the paste electrode (PE) at the presence of 1-methyl-3-buthyl imizazolonium tetrafluoroborate (MBITF) as the binder. The MgO/CNTs/MBITF/PE was used as an electroanalytical tool for electro-oxidation determination of vitamin B_6 in food samples. In comparison to PE, the oxidation signal of vitamin B_6 was improved up to 3.2 times at the surface of MgO/CNTs/MBITF/PE. At pH=6 as optimum condition, the MgO/CNTs/MBITF/PE revealed linear dynamic range of 0.1-400 μM for determination of vitamin B_6 with the detection limit of 30.0 nM. In the final step, the MgO/CNTs/MBITF/PE showed acceptable recovery data for the determination of vitamin B_6 in fruit juices samples, confirming the ability of the sensors in real sample analysis.

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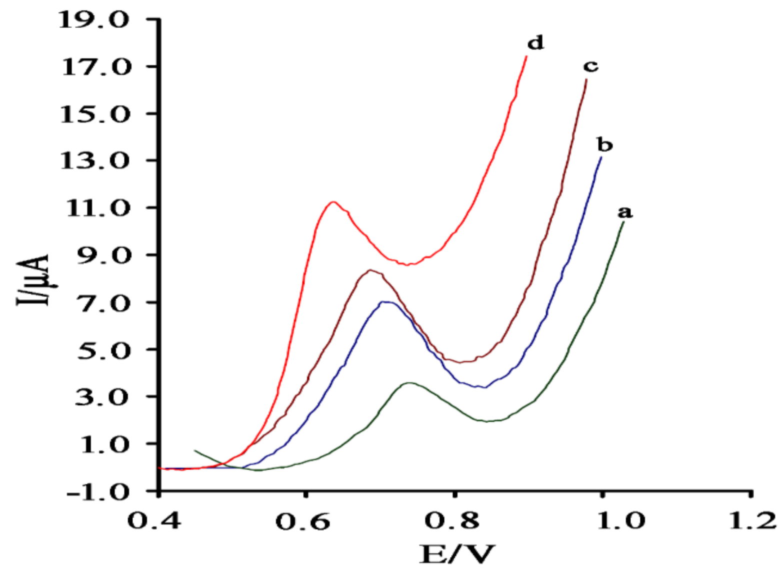
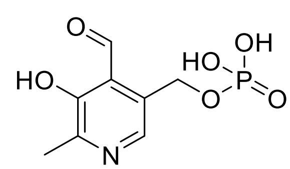
Graphical Abstract



Introduction

Vitamin B $_6$ or pyridoxine (Scheme 1) is B-type and water-soluble vitamin with many benefits for the human body and can be found in food products [1–3]. The glycosylated forms this vitamin naturally exist in vegetables, fruits, and grains that exhibit reduced bioavailability. Coenzyme forms of pyridoxine has been found in human body with many benefits for catalysts of reactions in biological samples [4–7].

The average amount of this vitamin is about 1.5 mg/day in women and 2 mg/day in men that should be provided by nutrition for the body. Multivitamin tablets and food products are the main source of pyridoxine that can supply this vitamin to the body [8–13]. Controlling food and determining the amount of vitamin B_6 in food products is necessary to evaluate a proper diet. Therefore, the measurement of vitamin B_6 in food products is interesting to many researchers. There are many different analytical methods to determine the vitamin B_6 such as the HPLC [14–17], yeast microbiological methods [18], colorimetric [19], chemometrics assisted spectroscopic [20], and electrochemical methods [21].



Scheme 1. Structure of Vitamin B_6

Among these analytical methods, the electrochemical sensor has attracted more attention in the recent year due to its simplicity and portable feature [22–27]. Nanomaterials with uniquie properties [28] and ionic liquids introduced by electrochemical researchers as electroactive mediators for improving the sensitivity of electrochemical sensors [29–35]. CNTs with high conductivity are a major option in the design of new electrochemical sensors [36].

In this research study, the high conductive MgO/CNTs nanocomposite was synthesized using the precipitation method and utilized as a mediator for the fabrication of vitamin B_6

electrochemical sensor. Results showed that the MgO/CNTs/MBITF/PE can determine vitamin B_6 in food samples.

Experimental

Materials and Methods

Vitamin B_6, methanol, magnesium nitrate hexahydrate, sodium hydroxide and phosphoric acid , and other chemicals were purchased from the Merck and Sigma-Aldrich. Phosphate buffer solutions (PBS) with various pH values were used during the experiments. A µ-Autolab system (Netherland), which was connected to a computer, was used as the electrochemical setup and results were recorded and analyzed by NOVA software. The MgO/CNTs/MBITF/PE was used as a working electrode and signals recording according to Ag/AgCl/KCl_{sat} (Azar electrode Company) as the reference electrode.

Synthesis of MgO/CNTs

2 g SWCNTs-COOH was dispersed in 100 mL distillated water and ultrasonicated for 10 min. Then, 25.64 g magnesium nitrate hexahydrate was dissolved in the solution and stirred for 30 min. 100 mL sodium hydroxide 2 M was added to the solution and strred for 30 min. After filtering, the sample was dried at 100 °C for 16 h and calcinated at 600 °C for 4 h.

Preparation of MgO/CNTs/MBITF/PE

The MgO/CNTs/MBITF/PE was prepared by mixing of 0.06 g MgO/CNTs+0.94 g graphite powder in the presence of two drops MBITF and 10 drops of the paraffin oil as binders. The obtaining paste was added into glass tube to fabrication of MgO/CNTs/MBITF/PE.

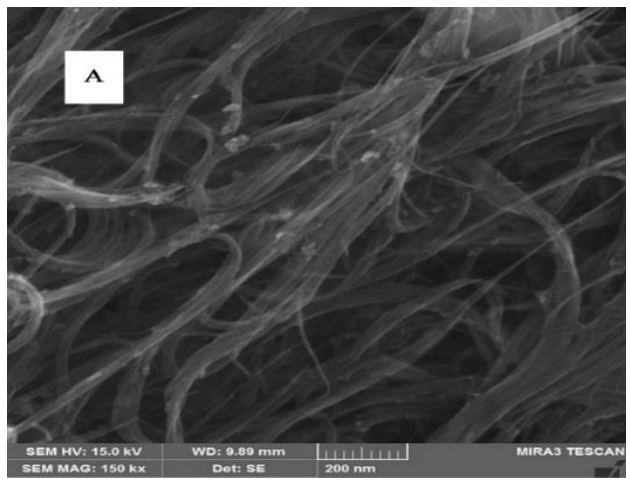
Real Sample Preparation

After purchasing fruit juices from the local market, the samples centrifuged and filtrated. Then prepared samples were used for real sample analysis by standard addition method.

Results and Discussion

Characterization of MgO/CNTs nanocomposite

The synthesized MgO/CNTs were characterized using the FESEM and EDS analysis methods and results are presence in Figure 1. The FE-SEM results showed the presence of carbon nanotubes decorated by MgO nanoparticles (Figure 1-a). EDS results in Figure 1-B confirmed the presence of Mg, O, and C elements and high purity of synthesized nanocomposite.



B

Elt	Line	Int	keV
C	Ka1	149.0	0.280
O	Ka1	326.9	0.540
Mg	Ka1	272.6	1.260

Figure 1. A) FESEM and B) EDS analysis data for MgO/CNTs

Voltammetric Investigation

At the first step, the electro-oxidation behavior of vitamin B_6 was evaluated using differential pulse voltammetric (DPV) method at different pH values (Figure 2 inset). Vitamin

B_6 is known as electro active analyte and its potential depends on pH value of the buffer solution [37]. In this respect, the electrochemical replication of vitamin B_6 at MgO/CNTs/MBITF/PE was studied at the range of 3.0-7.0. The result confirmed the presence of equal value of electron and proton in the redox mechanism of vitamin B_6 according to obtaining slope in Figure 2. In addition, due to high sensitivity in pH=6.0, this pH was selected for the next steps.

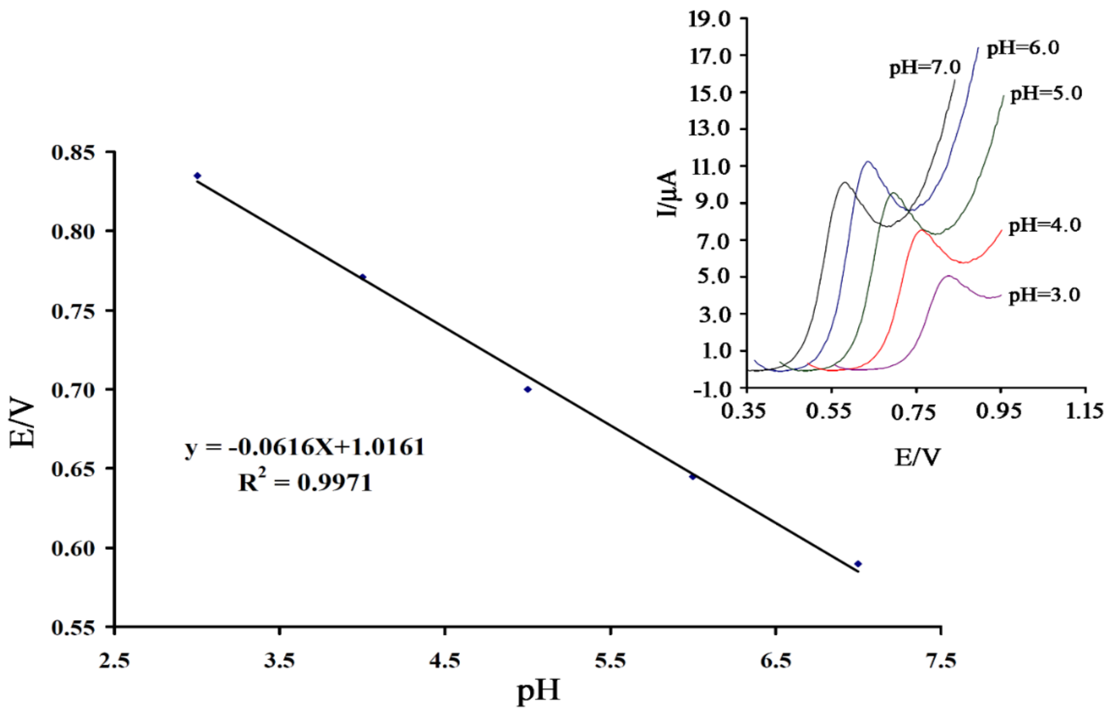


Figure 2. Plot of potential vs. pH for the electro-oxidation of 60 μM vitamin B_6 at surface MgO/CNTs/MBITF/PE. Inset: Differential pulse voltammetric response of 60 μM vitamin B_6 in $3<pH < 7$

The catalytic effect of MgO/CNTs and MBITF on oxidation signal of vitamin B_6 was investigated on the surface of CPE (Figure 3 curve a), MgO/CNTs/PE (Figure 3-b), MBITF/PE (Figure 3-c) and MgO/CNTs/MBITF/PE (Figure 3-d), respectively. Oxidation currents 3.57 μA, 6.99 μA, 8.31 μA and 11.2 μA were detected for the solution containing 60 μM vitamin B_6 at the surface of CPE, MgO/CNTs/PE, MBITF/PE and MgO/CNTs/MBITF/PE, respectively. As can be seen, oxidation of vitamin B_6 was facilitated about 3.2 times after modification of electrode with MgO/CNTs and MBITF.

The effect of the scan rate on the oxidation signal of vitamin B_6 was studied over the range of 10-200 mVs^{-1} using the MgO/CNTs/MBITF/PE (Figure 4). There is a relation between the obtained peak current (i_p) and $\nu^{1/2}$ for electro-oxidation of 500 μM vitamin B_6 at the surface of MgO/CNTs/MBITF/PE which unravels that electro-oxidation of vitamin B_6 at the surface of MgO/CNTs/MBITF/PE is a diffusion-controlled process (Figure 5).

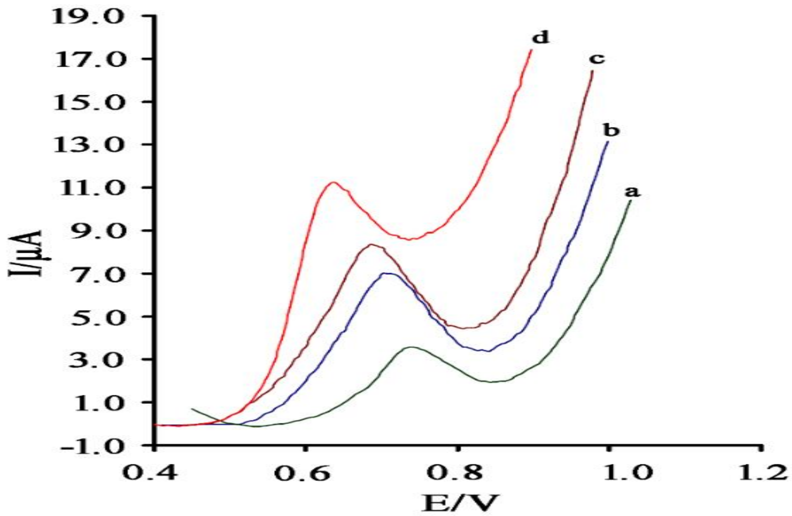


Figure 3. DP voltammograms of a) CPE, b) MgO/CNTs/PE c) MBITF/PE and d) MgO/CNTs/MBITF/PE in the presence of 60 μM vitamin B_6 at pH 6, respectively

In addition to electrochemical evaluations, chronoamperometric method was performed to determine the diffusion coefficient on the surface of MgO/CNTs/MBITF/PE with applied potential 600 mV. Using recording Cottrell plots, the value of D was calculated 4.32×10^{-5} $cm^2\ s^{-1}$.

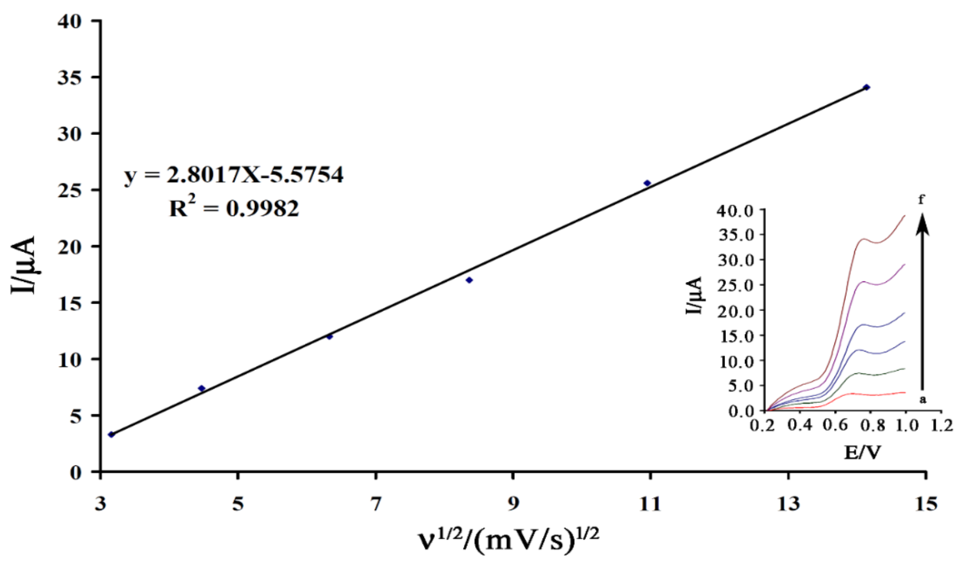


Figure 4. Plot of I_{pa} vs. $\nu^{1/2}$ for the oxidation of 500 μM vitamin B_6 at MgO/CNTs/MBITF/PE. Inset shows linear sweep voltammograms of vitamin B_6 at scan rates of a) 10.0, b) 20.0, c) 40.0, d) 70.0, e) 120, f) 200.0 mV/s

DPV technique was used to determine the linear dynamic range of MgO/CNTs/MBITF/PE for detection of vitamin B_6 (Figure 5). The linear dynamic ranges were obtained between 0.1-400 μM. Using the linear dynamic range data, the detection limit of vitamin B_6 was calculated about 30.0 nM ($Y_{LOD} = Y_B + 3\sigma$).

For study applicability of MgO/CNTs/MBITF/PE as an analytical tool for determination of vitamin B_6, it was used to determine the vitamin B_6 in different types of real samples such as apple and orange juices. The analysis data of real sample are demonstraed in Table 1 and recovery data confirmed high performance ability of MgO/CNTs/MBITF/PE as new vitamin B_6 sensor in real sample analysis.

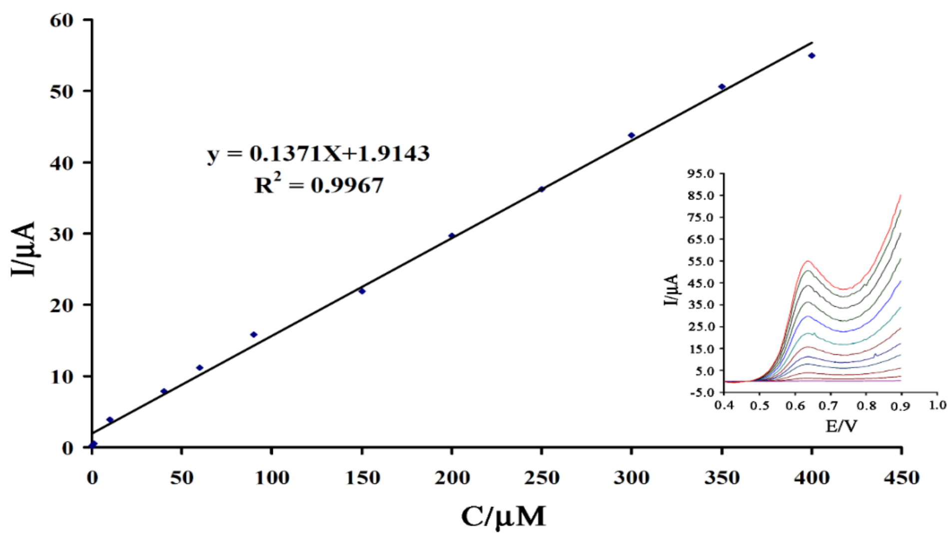


Figure 5. Plot of current-concentration for vitamin B_6 recorded at surface of MgO/CNTs/MBITF/PE. Inset) DP voltammograms of vitamin B6 recorded at surface of MgO/CNTs/MBITF/PE (Bottom-up); 0.01; 1.0; 10.0; 40.0; 60.0; 90.0; 150.0; 200.0; 250.0; 300.0; 350.0 and 400.0 µM

Table 1. Determination of B_6 in food samples (n=5).

Samples	Added vitamin B_6	Expected vitamin B_6	Found vitamin B_6	Recovery value for vitamin B_6
Orange juice	---	---	<LOD	---
	5.00	5.00	4.93±0.34	98.6
	10.00	10.00	10.27±0.82	102.7
Apple juice	-	-	<LOD	-
	10.00	10.00	10.33±0.44	103.3
	20.00	20.00	19.86±0.55	99.3

Conclusions

A new nanostructure sensor and highly sensitive analytical tool were fabricated to determine the vitamin B_6 in this research study. MgO/CNTs nanocomposite was synthesized using the chemical precipitation methods. The MgO/CNTs/MBITF/PE was successfully used to determine the vitamin B_6 in fruit juices samples. In addition, the MgO/CNTs/MBITF/PE could be used to determine the vitamin B_6 with linear dynamic range of 0.1-400 µM and in nano-molar level with detection limit 30.0 nM.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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