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Determination of H_2O_2 in Human Serum Samples with Novel Electrochemical Sensor Based on V_2O_5/VO_2 Nanostructures

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Abstract

Background: Highly selective and sensitive analysis of hydrogen peroxide (H_2O_2) has attracted considerable interest in the fields of clinical diagnostics, food industry, and environmental analysis.
Objectives: In the present study, an efficient electrochemical sensor, based on V_2O_5/VO_2 nanostructures, was introduced for measuring hydrogen peroxide (H_2O_2) in human serum samples.
Methods: The characterization of the prepared V_2O_5/VO_2 nanostructures was investigated by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). A carbon paste electrode (CPE) modified with V_2O_5/VO_2 was applied for the electrochemical detection of H_2O_2.
Results: The prepared sensor depicted a good linear range from 8 to 215 μM and a low detection limit of 5 μM. Moreover, the modified electrode showed notable anti-interference property and high sensitivity toward H_2O_2 detection. The suggested method was also successfully applied for the determination of H_2O_2 in human serum samples.
Conclusions: The V_2O_5/VO_2 embedded CPE offers good simplicity, sensitivity, and selectivity toward H_2O_2 determination. In addition, the suggested assay revealed good reproducibility and anti-interference property in the measuring of H_2O_2.

Keywords: Hydrogen Peroxide, Electrochemical Sensor, Vanadium Oxide, Human Serum

1. Background

H_2O_2 plays a prominent role in different areas including clinical diagnostics, food industry, pharmaceutical, and environmental protection (1). An excessive accumulation of H_2O_2 in the human body can lead to some diseases such as DNA fragmentation and tissue damage (2). Consequently, the accurate measuring of H_2O_2 in biological samples is very important. To date, various analytical methods have been developed for determination of H_2O_2, including chromatography (3), spectrophotometry (4), and chemiluminescence (5). However, above mentioned techniques are high costs, complex, and time-consuming.

Electrochemical H_2O_2 sensing has attracted growing attention due to the intrinsic advantages such as simple operation, cost effective, rapid response, and suitability for real-time H_2O_2 analysis (6). In view of this, the design and fabrication of novel electrochemical sensors for H_2O_2 determination has attracted considerable interest in recent years (7, 8).

2. Objectives

In this study, novel V_2O_5/VO_2 nanostructures were successfully prepared with the hydrothermal method. The V_2O_5/VO_2 nanostructures were utilized for modification of a simple and cheap carbon paste electrode (CPE). The main experimental factors, calibration range, and detection limit of the V_2O_5/VO_2-CPE was also explored in detail. Moreover, the proposed sensor was applied for quantification of H_2O_2 in human serum samples.

3. Methods

3.1. Materials and Apparatus

All materials including thiourea, vanadium chloride (VCl_3), ethanol, ethylene glycol, paraffin oil, graphite powder, and H_2O_2 were obtained from Merck (Darmstadt, Germany). XRD pattern was recorded via a PANalytical Empyrean X-ray diffractometer (Almelo, Netherlands). SEM image and EDX analysis were performed on a MIRA3 LM TESCAN microscope (Brno, Czech Republic). FT-IR

spectrum was measured on a Bruker Equinox 55 spectrometer (Karlsruhe, Germany). All electrochemical data were recorded on a potentiostat galvanostat impedance meter (OrigaState100, OrigaLys, Rillieux-la-Pape, France). A standard electrochemical cell including the modified CPE (working electrode), the platinum wire (counter electrode), and the Ag/AgCl (3 M KCl) electrode (reference electrode) was used for electrochemical tests.

3.2. Preparation of V_2O_5/VO_2 Nanostructures

The V_2O_5/VO_2 nanostructures were synthesized via a hydrothermal approach. Typically, 7.8 g of VCl_3 was dissolved in a mixed solution of ethanol (50 mL) and ethylene glycol (25 mL) under vigorous stirring. Afterward, 7.6 g of thiourea was added to the above mixture vigorous stirring. The mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and then heated at 160°C for 12 h. The black precipitates were collected via centrifuge separation, followed by repeated washing with ethanol, and then heated at 350°C for 3 h under air condition.

3.3. Electrode Fabrication

The modified CPE (V_2O_5/VO_2-CPE) was fabricated by mixing of graphite powder (65% w/w), V_2O_5/VO_2 (10% w/w), and paraffin oil (25% w/w). Then, a portion of the obtained paste was packed into a glass tube (3 mm in diameter) in contact with a copper wire for electrical connection.

4. Results

The FT-IR spectrum of the V_2O_5/VO_2 nanostructures is presented in Figure 1. Absorption peak appearing at 1013 cm^{-1} is attributed to the stretching vibrations of V=O groups (9). The peaks at 529 and 828 cm^{-1} are related to the symmetric and asymmetric stretching of the V-O-V groups, respectively (10). The peak at 620 cm^{-1} can also be assigned to the stretching of the V-O groups (11).

XRD pattern of the V_2O_5/VO_2 nanostructures is shown in Figure 2. The observed characteristic reflections were matched well with the standard XRD data of V_2O_5 (vanadium pentoxide; JCPDS No 76-1803) and VO_2 (vanadium dioxide; JCPDS No 73-2362) (12).

The SEM photograph of the V_2O_5/VO_2 nanostructures is shown in Figure 3A. As can be seen, the prepared V_2O_5/VO_2 product has a nano-sized structure. Moreover, the EDX spectrum of the V_2O_5/VO_2 nanostructures (Figure 3B) shows the existence of vanadium and oxygen elements in the prepared material. According to these results, the V_2O_5/VO_2 nanostructures have been successfully prepared by hydrothermal method.

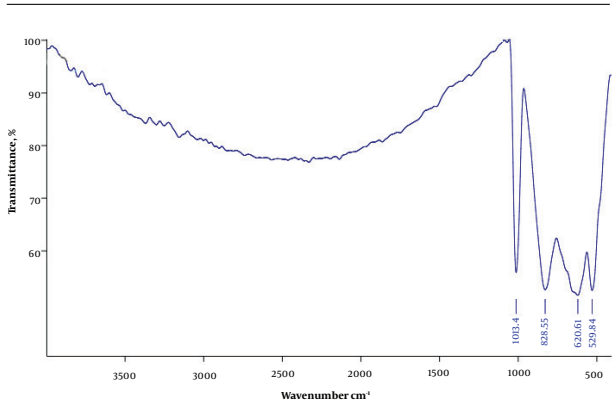

Figure 1. FT-IR spectrum of V_2O_5/VO_2 material

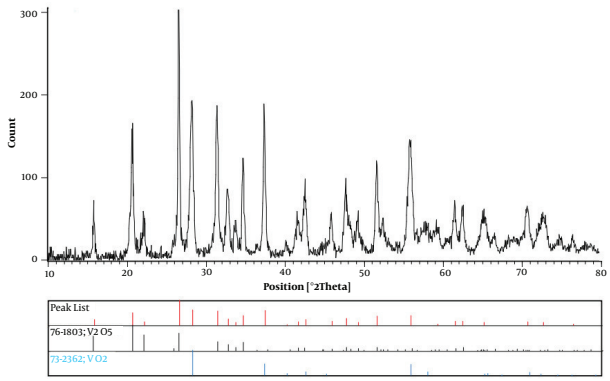

Figure 2. XRD pattern of V_2O_5/VO_2 nanostructures

5. Discussion

The ability of the V_2O_5/VO_2 nanostructures for electrochemical reduction of H_2O_2 was investigated. Figure 4 displays the cyclic voltammograms of unmodified CPE and V_2O_5/VO_2-CPE in phosphate buffer (0.1 M, pH = 7) containing 100 μM of H_2O_2. As can be seen, the V_2O_5/VO_2-CPE shows a notable reduction peak current, indicating that the reduction of H_2O_2 was improved compared to unmodified CPE.

To improve the sensitivity of the V_2O_5/VO_2-CPE toward H_2O_2 detection, amperometry method was used at applied potential of -450 mV. The amperometric responses of the V_2O_5/VO_2-CPE to the successive addition of H_2O_2 were studied as shown in Figure 5. The amperometric signal currents vary linearly with H_2O_2 concentration over the range of 8 to 215 μM with a detection limit (3σ) of 5 μM. The detection limit of the prepared sensor is lower than some reported H_2O_2 sensors (13-17), as listed in Table 1. The effect of some interfering species including glucose, uric acid, dopamine,

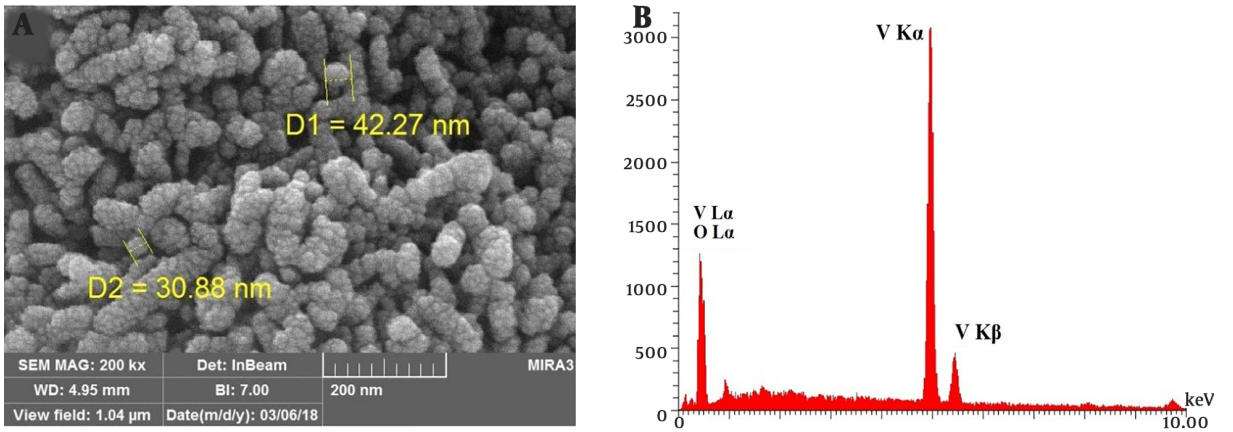

Figure 3. A, SEM image and B, EDX spectrum of V_2O_5/VO_2 nanostructures

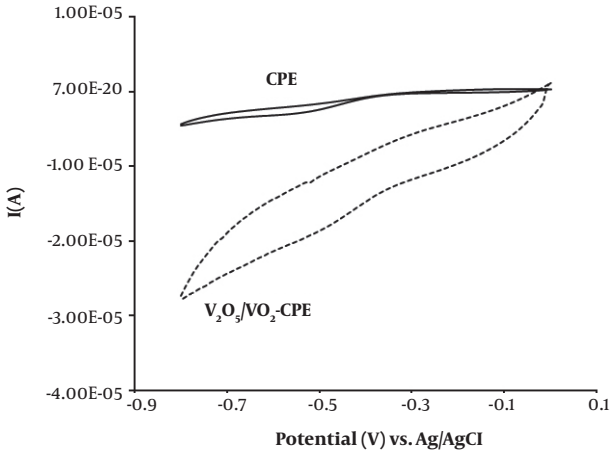

Figure 4. Cyclic voltammograms of the unmodified CPE and the V_2O_5/VO_2-CPE in phosphate buffer (0.1 M, pH = 7) containing 100 μM of H_2O_2 with scan rate of 50 mV s^{-1}

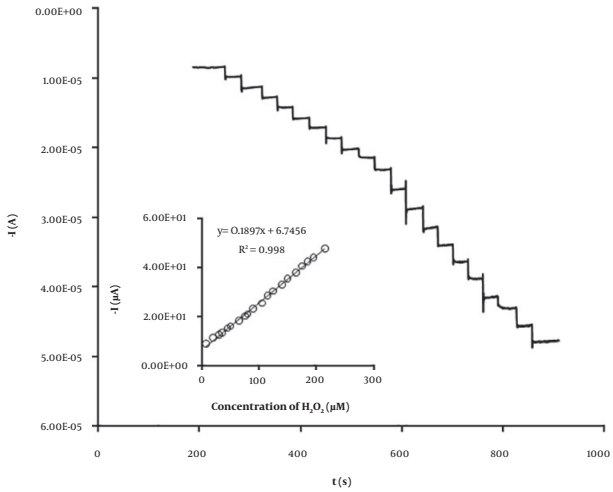

Figure 5. Amperometric responses of V_2O_5/VO_2-CPE to successive addition of H_2O_2 at the potential of -0.45 V in 0.1 M buffer solution (pH = 7.0). Inset: Calibration curve of sensor.

and ascorbic acid was also investigated. The experimental results (Table 2) show that the prepared V_2O_5/VO_2-CPE can measure H_2O_2 with recoveries more than 95% in the presence of such interfering molecules.

The suggested V_2O_5/VO_2-CPE was validated for the H_2O_2 quantification in biological samples. Human serum samples were collected from a local hospital in Kerman. Standard addition protocol was used in the recovery experiments and the obtained results are listed in Table 3.

5.1. Conclusions

In summary, a novel electrochemical sensor for determination of H_2O_2 was presented. The fabricated H_2O_2 sensor showed a wide linear range and low detection limit. The applicability of the V_2O_5/VO_2-CPE for quantification of H_2O_2 in biological samples was successfully investigated. The good simplicity and anti-interference performance of the present method indicates that the V_2O_5/VO_2-CPE has great potential working as an efficient H_2O_2 sensor for clinical applications.

Footnotes

Conflict of Interests: The author reports no conflicts of interest in this work.

Ethical Approval: Author will agree upon standard ethical behavior.

Table 1. Comparison of Some Different Electrochemical Sensors for Determination of H_2O_2

Electrode Modifier*	Linear Range, μM	Detection Limit, μM	Ref.
Cuprous oxide-reduced graphene oxide (Cu_2O-rGO) nanocomposites	30 - 12800	21.7	(13)
Poly (p-aminobenzene sulfonic acid) (PABS)	50 - 550	10	(14)
Magnetite (Fe_3O_4) nanoparticles	25 - 5000	7.4	(15)
Hematite (α-Fe_2O_3) nanoparticles	50 - 3145	22	(16)
Iodide	10 - 60000	10	(17)
V_2O_5/VO_2 nanostructures	8 - 215	5	This work

Table 2. The Effect of Interfering Species

Co-existing Molecule	Recovery, %
Glucose	96.7
Uric acid	98.5
Dopamine	98.3
Ascorbic acid	96.9

Table 3. Determination of H_2O_2 in Human Serum Samples (n = 3).

Sample	Added, μM	Found, μM	RSD	Recovery, %
Male serum				
	15	14.8	4.2	98.6
	30	29.5	3.6	98.3
	45	46.3	5.0	102.8
Female serum				
	15	15.6	4.5	104.0
	30	28.9	5.2	96.3
	45	44.2	3.9	98.2

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