



# Determination of H<sub>2</sub>O<sub>2</sub> in Human Serum Samples with Novel Electrochemical Sensor Based on V<sub>2</sub>O<sub>5</sub>/VO<sub>2</sub> Nanostructures

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## Abstract

**Background:** Highly selective and sensitive analysis of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 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<sub>2</sub>O<sub>5</sub>/VO<sub>2</sub> nanostructures, was introduced for measuring hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in human serum samples.

**Methods:** The characterization of the prepared V<sub>2</sub>O<sub>5</sub>/VO<sub>2</sub> 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<sub>2</sub>O<sub>5</sub>/VO<sub>2</sub> was applied for the electrochemical detection of H<sub>2</sub>O<sub>2</sub>.

**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<sub>2</sub>O<sub>2</sub> detection. The suggested method was also successfully applied for the determination of H<sub>2</sub>O<sub>2</sub> in human serum samples.

**Conclusions:** The V<sub>2</sub>O<sub>5</sub>/VO<sub>2</sub> embedded CPE offers good simplicity, sensitivity, and selectivity toward H<sub>2</sub>O<sub>2</sub> determination. In addition, the suggested assay revealed good reproducibility and anti-interference property in the measuring of H<sub>2</sub>O<sub>2</sub>.

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

## 1. Background

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

Electrochemical H<sub>2</sub>O<sub>2</sub> sensing has attracted growing attention due to the intrinsic advantages such as simple operation, cost effective, rapid response, and suitability for real-time H<sub>2</sub>O<sub>2</sub> analysis (6). In view of this, the design and fabrication of novel electrochemical sensors for H<sub>2</sub>O<sub>2</sub> determination has attracted considerable interest in recent years (7, 8).

## 2. Objectives

In this study, novel V<sub>2</sub>O<sub>5</sub>/VO<sub>2</sub> nanostructures were successfully prepared with the hydrothermal method. The V<sub>2</sub>O<sub>5</sub>/VO<sub>2</sub> 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<sub>2</sub>O<sub>5</sub>/VO<sub>2</sub>-CPE was also explored in detail. Moreover, the proposed sensor was applied for quantification of H<sub>2</sub>O<sub>2</sub> in human serum samples.

## 3. Methods

### 3.1. Materials and Apparatus

All materials including thiourea, vanadium chloride (VCl<sub>3</sub>), ethanol, ethylene glycol, paraffin oil, graphite powder, and H<sub>2</sub>O<sub>2</sub> 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  $160^\circ\text{C}$  for 12 h. The black precipitates were collected via centrifuge separation, followed by repeated washing with ethanol, and then heated at  $350^\circ\text{C}$  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  $1013\text{ cm}^{-1}$  is attributed to the stretching vibrations of V=O groups (9). The peaks at 529 and  $828\text{ cm}^{-1}$  are related to the symmetric and asymmetric stretching of the V-O-V groups, respectively (10). The peak at  $620\text{ cm}^{-1}$  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.

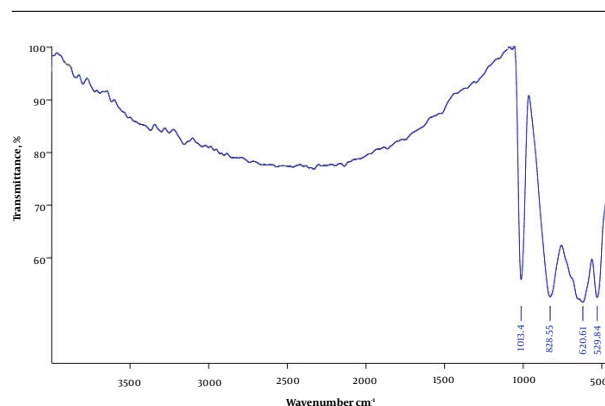


Figure 1. FT-IR spectrum of  $V_2O_5/VO_2$  material

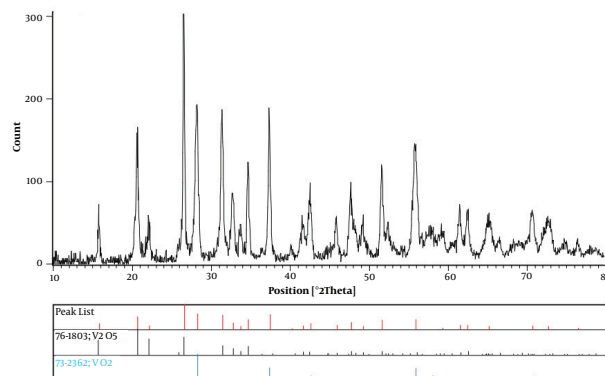


Figure 2. XRD pattern of  $V_2O_5/VO_2$  nanostructures

## 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  $100\ \mu\text{M}$  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  $-450\text{ mV}$ . 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  $215\ \mu\text{M}$  with a detection limit ( $3\sigma$ ) of  $5\ \mu\text{M}$ . 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,

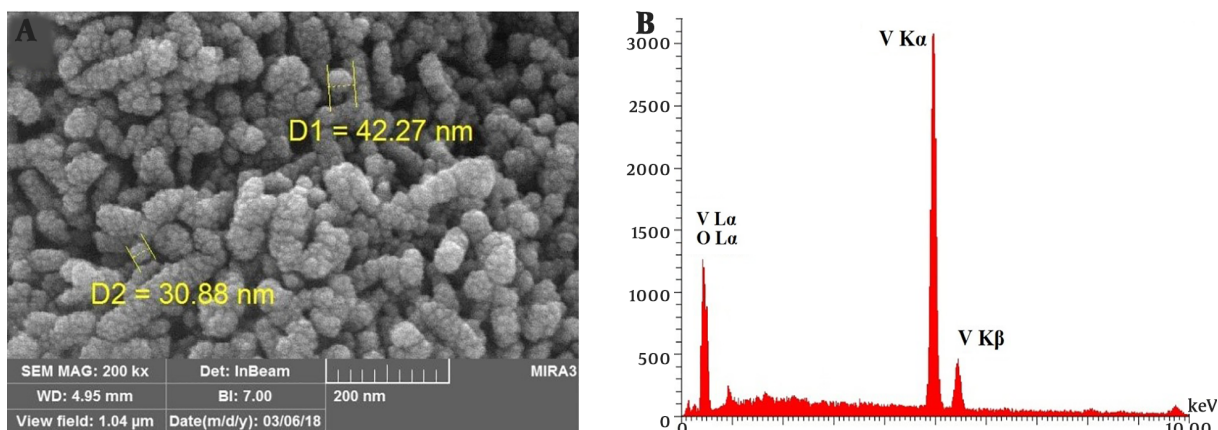


Figure 3. A, SEM image and B, EDX spectrum of  $V_2O_5/VO_2$  nanostructures

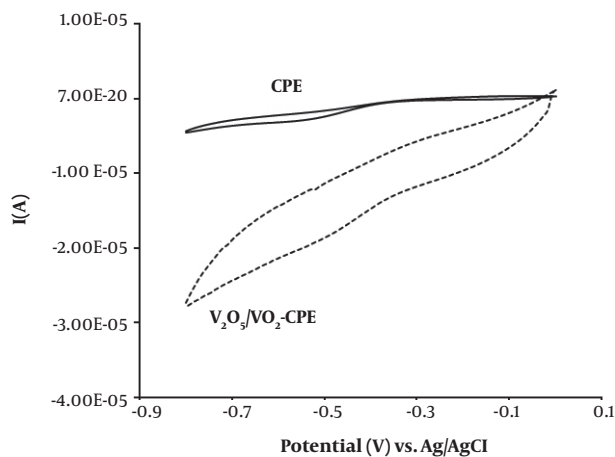


Figure 4. Cyclic voltammograms of the unmodified CPE and the  $V_2O_5/VO_2$ -CPE in phosphate buffer (0.1 M, pH = 7) containing  $100 \mu M$  of  $H_2O_2$  with scan rate of  $50 mV s^{-1}$

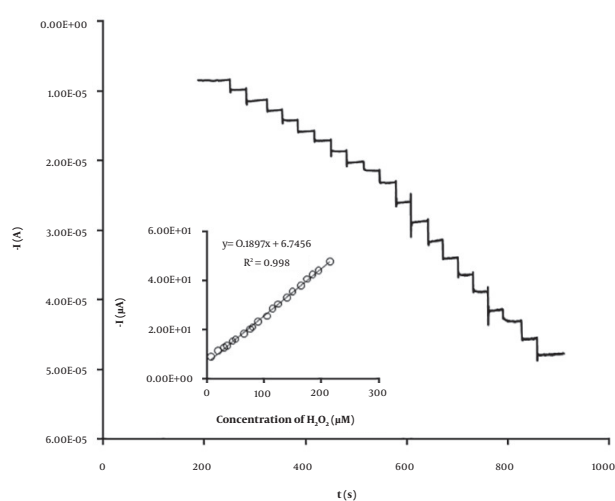


Figure 5. Amperometric responses of  $V_2O_5/VO_2$ -CPE to successive addition of  $H_2O_2$  at the potential of  $-0.45 V$  in 0.1 M buffer solution (pH = 7.0). Inset: Calibration curve of sensor.

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<sub>2</sub>O<sub>2</sub>

Electrode Modifier*	Linear Range, $\mu\text{M}$	Detection Limit, $\mu\text{M}$	Ref.
Cuprous oxide-reduced graphene oxide (Cu <sub>2</sub> O-rGO) nanocomposites	30 - 12800	21.7	(13)
Poly (p-aminobenzene sulfonic acid) (PABS)	50 - 550	10	(14)
Magnetite (Fe <sub>3</sub> O <sub>4</sub> ) nanoparticles	25 - 5000	7.4	(15)
Hematite ( $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> ) nanoparticles	50 - 3145	22	(16)
Iodide	10 - 60000	10	(17)
V <sub>2</sub> O <sub>5</sub> /VO <sub>2</sub> 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<sub>2</sub>O<sub>2</sub> in Human Serum Samples (n = 3).

Sample	Added, $\mu\text{M}$	Found, $\mu\text{M}$	RSD	Recovery, %
<b>Male serum</b>				
	15	14.8	4.2	98.6
	30	29.5	3.6	98.3
	45	46.3	5.0	102.8
<b>Female serum</b>				
	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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