

## تعیین الکتروشیمیایی هیدروژن پراکسید در الکترود اصلاح شده با نانولوله‌های کربنی و نانوذرات نقره

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## Electrochemical Determination of Hydrogen Peroxide at Multi-Wall Carbon Nanotube/Silver Nanoparticle Modified Electrode

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### چکیده

در این تحقیق، یک روش جدید برای احیای کاتالیزوری هیدروژن پراکسید در الکترود کربن شیشه اصلاح شده با نانولوله‌های کربنی دوپ شده با نانوذرات نقره ارائه شده است. نانوتیوپ دوپ شده با نانوذرات نقره به عنوان حد واسط ردوکس جهت احیای کاتالیزوری هیدروژن پراکسید عمل کرد. ابتدا رفتار الکتروشیمیایی نقره در الکترود اصلاح شده مطالعه شد. نتایج واکنش کنترل شده با جذب سطحی را در سطح الکترود اصلاح شده نشان می‌دهد. سپس رفتار احیای کاتالیکی هیدروژن پراکسید در الکترود اصلاح شده مطالعه شد. مطالعات الکتروشیمیایی با روش ولتامتری چرخه‌ای انجام شد. محدوده خطی منحنی کالیبراسیون در این روش ۱/۵ میکرومولار تا ۴/۰۴ میلی‌مولار و حد تشخیص روش ۰/۱۴۲ میکرومولار محاسبه گردید. انحراف استاندارد نسبی روش براساس ده بار تکرار برای غلظت ۰/۱۵ میلی‌مولار از هیدروژن پراکسید ۲/۳۶ درصد بدست آمد. الکترود ارائه شده برای تعیین هیدروژن پراکسید در نمونه‌های حقیقی بکار رفت که نتایج بدست آمده، رضایت بخش بود.

### واژه‌های کلیدی

نانولوله‌های کربنی؛ نانوذرات نقره؛ تعیین الکتروشیمیایی؛ هیدروژن پراکسید.

### Abstract

In this work, a new method was developed for the catalytic reduction of hydrogen peroxide at glassy carbon electrode modified with silver nanoparticles and multi-wall carbon nanotubes. Silver incorporated in this modified electrode acted as catalyst to reduce hydrogen peroxide. First, the electrochemical behavior of silver, incorporated in modified electrode, was studied. The results illustrated the adsorption-controlled reaction at the modified electrode. Then, the behavior of catalytic reduction of hydrogen peroxide at the modified electrode was investigated. A linear calibration graph was obtained for hydrogen peroxide over the concentration range of  $4.04 \times 10^{-3} - 1.5 \times 10^{-6} \text{ molL}^{-1}$ . The detection limit for hydrogen peroxide was estimated  $1.42 \times 10^{-7} \text{ molL}^{-1}$ . The relative standard deviation of ten replicate measurements (performed on a single electrode at hydrogen peroxide concentration of  $1.5 \times 10^{-4} \text{ molL}^{-1}$ ) was 2.36%. The proposed electrode was used for the determination of hydrogen peroxide in real samples which led to satisfactory results.

### Keywords

Carbon Nanotubes; Silver Nanoparticles; Electrochemical Determination; Hydrogen Peroxide.

### 1. INTRODUCTION

Development of a highly selective and sensitive determination system for hydrogen peroxide is one of the topical problems in analytical chemistry, since  $\text{H}_2\text{O}_2$  is an important analytical target in the field of biochemistry, clinical chemistry, food chemistry, environmental chemistry and at high concentrations causes irritation to the eyes and skin and affects human health. Many methods have been developed for the determination of  $\text{H}_2\text{O}_2$ ,

such as spectrophotometry [1], fluorimetry [2], chromatography [3], chemiluminescence [4], titrimetry [5] and especially electrochemistry [6]. Electrochemical methods have been proved to be an inexpensive and effective way for hydrogen peroxide determination.

The use of nanostructured materials is one of the most promising strategies to replace macroscopic electrodes [7]. The presence of nanosized objects (e.g., nanopores, nanoparticles and

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nanorods/nanowires) in the electrochemical sensor can decrease the overpotential of many analytes and improve the sensitivity of electroanalytical method due to a large surface to volume ratio and prolonged entrapment of analyte in nanostructured electrodes. Metals, such as silver, gold, palladium, and platinum, are commonly used as nanoparticles in electrochemistry. The physical and chemical properties of nanoparticles (NPs) often differ significantly from those of the corresponding bulk material. The most important possible differences to note between nanoparticles and bulk material can be enhanced mass transport, high surface area, and their effectiveness as catalysts. High surface area can promote surface catalyzed processes, while the expression of particle crystal planes, for example, high current values or altered electronic structure, can lead to useful catalytic properties [8]. Over the last decades silver has been engineered into nanoparticles, structures from 1 to 100 nm in size.

Owing to their small size, the total surface area of the nanoparticles is maximized, leading to the highest values of the activity to weight ratio. Due to this property being distinctly different from that of the bulk metal, silver nanoparticles have attracted much attention and have found applications in diverse areas, including medicine, catalysis, textile engineering, biotechnology and bioengineering, water treatment electronics and optics. Furthermore, currently silver nanoparticles are widely used as antibacterial antifungal agents in a diverse range of consumer products.

Electrochemical technique which is also a fine detecting method has attracted much attention recently based on low cost and high sensitivity. It has been proved to be an inexpensive and effective way to examine substances [9].

Pt, Au and Pd are usually used as catalysts for electrochemical detection of  $\text{H}_2\text{O}_2$  [9-11]. Other catalytic materials such as  $\text{MnO}_2$ ,  $\text{WO}_3$  and  $\text{CuO}$  have also been investigated as possibilities. Ag nanoparticles, as a catalyst, used in the electrochemical detection of  $\text{H}_2\text{O}_2$  are much cheaper than the noble metal catalysts mentioned above.

Carbon nanotubes (CNTs) were discovered by Iijima [12] and have enormous potentials as components of nanoscale electronic devices and biosensors, as a result of their ability to promote electron transfer reactions and high thermal capacity [13-15]. Both single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) have been utilized in the detection of various kinds of biological reagents [16].

carbon nanotubes [17,18] and Ag nanoparticles [19-21] have been employed for detecting  $\text{H}_2\text{O}_2$

respectively. In order to take full advantage of the two kinds of nanomaterials, it is desirable to create novel AgNPs–MWNT hybrid, so that the unique properties of each material can be integrated, and the interactions between the two components may bring out novel properties.

In this article, by combining the advantages of carbon nanotubes and silver nanoparticles, the AgNPs–MWNT hybrid was prepared for the determination of  $\text{H}_2\text{O}_2$ . The Ag NPs with good reduction catalysis for  $\text{H}_2\text{O}_2$  would promote the ability of the electrode to eliminate the interferences from other electroactive biomolecules.

## 2. EXPERIMENTAL

### 2.1 Chemical reagents

MWCNTs (95% purity) with an average outer diameter of 3–20 nm, length of 1–10  $\mu\text{m}$ , number of walls 3–15 were obtained from Plasma Chem. (Germany). Hydrogen peroxide (30%, v/v aqueous solution), was obtained from sigma. All aqueous solutions were prepared with doubly distilled water. Phosphate-buffer (PBS) was prepared by dissolving 6.8 g of  $\text{KH}_2\text{PO}_4$  in 25 ml of doubly distilled water and adjusted to pH 7.0 by adding NaOH ( $0.1 \text{ mol L}^{-1}$ ). Then, it was diluted to 100 ml with double distilled water. All experiments were performed in PBS at room temperature, approximately  $25^\circ\text{C}$ .

### 2.2 Apparatus

Voltammetric experiments were performed using a Metrohm electroanalyzer (Model 797 VA computrace). All voltammograms were recorded with a three electrode system consisting of an Ag/AgCl reference electrode, a platinum wire as the counter electrode, and a modified glassy carbon electrodes as a working electrode. A Metrohm 710 pH meter was used for pH adjustments. All the electrochemical experiments were carried out under pure nitrogen atmosphere at room temperature.

### 2.3 Synthesis of silver nanoparticles

Silver nanoparticles were synthesized according to the method reported in previous article [22] with slight modifications. In brief, 200  $\mu\text{L}$  of  $0.1 \text{ mol L}^{-1}$   $\text{AgNO}_3$  aqueous solution was mixed with 630  $\mu\text{L}$  of  $0.1 \text{ mol L}^{-1}$  sodium citrate aqueous solution and diluted to 19.6 mL, followed by adding 0.4 mL of  $0.1 \text{ mol L}^{-1}$   $\text{NaBH}_4$  aqueous solution drop wise. The resulted solution was stayed still for 24 h to totally decompose  $\text{NaBH}_4$ .

### 2.4 Modification of multi-wall carbon nanotubes

MWCNTs were dissolved in the mixture of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  (3:1, v/v), and then dispersed in ultrasonic bath for about 4 hours. The resulted MWCNTs were separated and washed

with distilled water by centrifugation (10.000 rpm) until the pH of the resulted MWCNTs solution became neutral.

### 2.5 Preparation of the modified electrode

2 g of prepared nanotube was added to the nano-silver solution, and the suspension was sonicated for 60 min, then the modified MWCNTs were filtered and washed with doubly distilled, deionized water and got dried at room temperature. Fig. 1 shows the typical XRD pattern of the AgNPs–MWNT hybrid. The morphology of the prepared nanocomposite was characterized by TEM and SEM (Fig. 2 and Fig. 3).

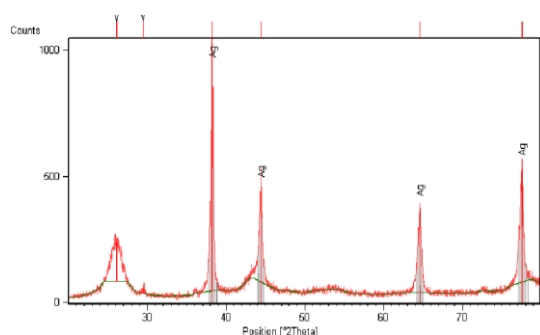


Fig. 1. XRD patterns of Ag/MWNTs.

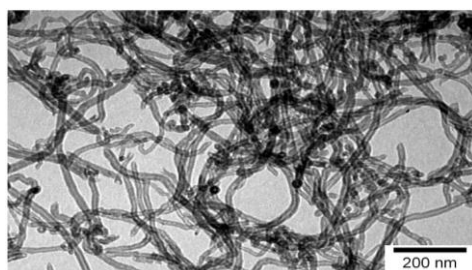


Fig. 2. TEM images of Ag/MWNTs.

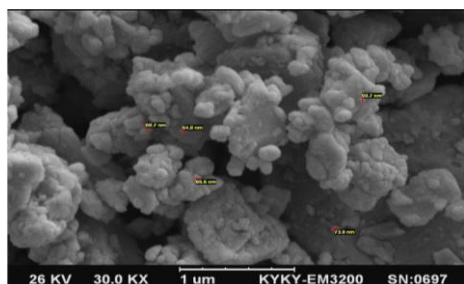


Fig. 3. SEM image of Ag/MWNTs.

Prior to modification, glassy carbon electrode (GCE) was orderly polished to a mirror-like surface with 1.0, 0.3, and 0.05  $\mu\text{m}$   $\text{Al}_2\text{O}_3$ . Then, the electrode was successively ultrasonically washed with ethanol and doubly distilled water, each for 1 min. Two milligram of modified MWCNTs was dispersed with the aid of ultrasonic agitation in 0.5mL tetrahydrofuran (THF) to give a 4.0  $\text{mg mL}^{-1}$  black suspension. The AgNPs–MWNT/GC

electrode was prepared by dropping 0.5  $\mu\text{L}$  of the suspension on the clean GC electrode surface. In this way, the AgNPs–MWNT hybrids were deposited on the electrode by absorption. After drying, the modified electrode was thoroughly rinsed with distilled water and placed in the electrochemical cell as the working electrode.

## 3. RESULT AND DISCUSSION

### 3.1 Electrochemical Properties of AgNPs–MWNT/GCE

Cyclic voltammetry is one of the most common techniques used in electrochemistry to determine electroactivity. Fig. 4 show the cyclic voltammetric response obtained at the unmodified GCE and AgNPs–MWNT/GCE in the 0.1  $\text{mol L}^{-1}$  PBS (pH 7.0). At unmodified GCE (Fig.4a), no obvious redox peak was observed, but after modified with AgNPs–MWNT, Two peaks at the potential of 0.14V and 0.32V were observed (Fig.4(c) and (d)). They were attributed to the reduction and oxidation of Ag, and could prove the existence of Ag NPs.

When  $\text{H}_2\text{O}_2$  was added into the PBS solution, it can be observed (Fig. 4(b) and (d)) that response current at the potential range of  $-0.1\text{V}$  to  $-0.6\text{ V}$  indicated the reduction of  $\text{H}_2\text{O}_2$ .

As it was shown, the reduction current at AgNPs–MWNT/GCE was markedly larger than that of unmodified electrode with the presence of  $\text{H}_2\text{O}_2$  (Fig. 4b). The difference was probably engendered by the synergistic amplification effect of MWCNTs and AgNPs as well as the catalytic reduction effect of Ag toward  $\text{H}_2\text{O}_2$ . For most electrochemistry sensors, determination of  $\text{H}_2\text{O}_2$  was achieved at a relatively high potential around  $-0.6\text{ V}$ , which made it liable to interferences from electroactive compounds. In our work, we employed AgNPs which had proved to exhibit catalytic activity for the reduction of  $\text{H}_2\text{O}_2$  at lower potential to solve this problem.

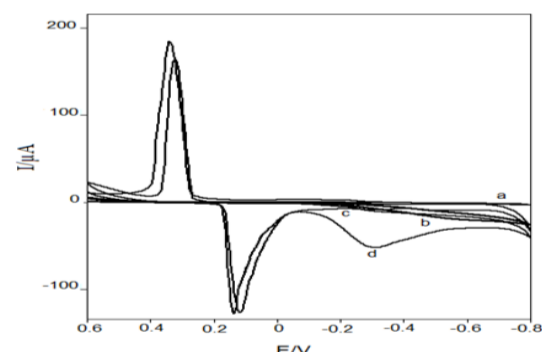
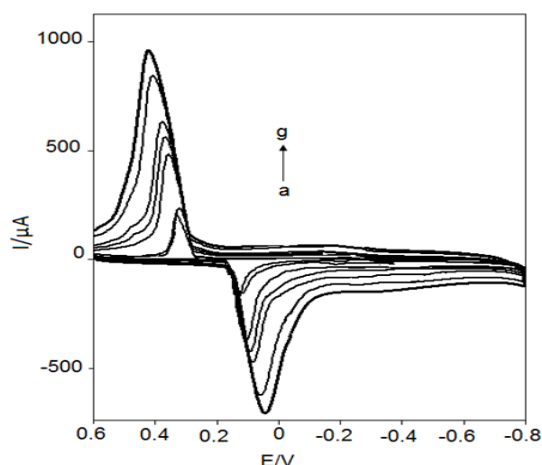


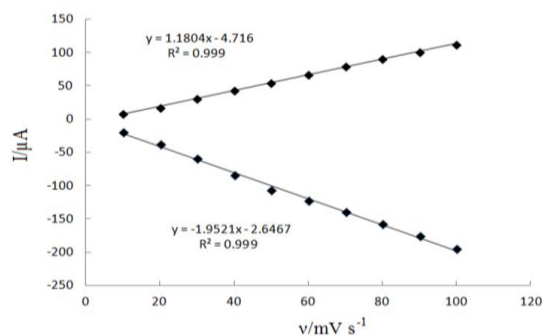
Fig. 4. CV response on the surface of the unmodified electrode in the PBS solution (a); The unmodified GCE in the presence of  $1.5 \times 10^{-4} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$  (b); The modified electrode in PBS solution(c); The modified electrode in the presence of  $1.5 \times 10^{-4} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$  (d). Conditions: supporting electrolyte: Phosphate buffer solution ( $0.10 \text{ mol L}^{-1}$ ) pH =7, scan rate =  $30 \text{ mVs}^{-1}$ .

### 3.2 Voltammetric response of the AgNPs–MWNT/GCE

Fig. 5 shows the cyclic voltammograms of the AgNPs–MWNT/GCE in 0.1 molL<sup>-1</sup> PBS (pH 7.0) obtained by scanning the potential from -0.8 to +0.6 V at various scan rates. The peak currents have a linear relationship with scan rates, indicating an adsorption-controlled reaction (Fig. 6).



**Fig. 5.** Cyclic voltammograms of a AgNPs–MWNT/GCE in the PBS solution at various scan rates: (a) 30, (b) 40, (c) 50, (d) 60, (e) 70, (f) 90, (g) 100 mV s<sup>-1</sup>.



**Fig. 6.** The plot of anodic and cathodic peak currents of the AgNPs–MWNT/GCE vs. the scan rates.

The AgNPs–MWNT/GCE was successfully applied for the determination of H<sub>2</sub>O<sub>2</sub>, the results of which are presented in the following sections.

### 3.3 Influence of pH

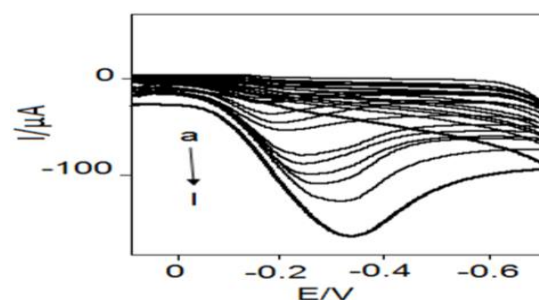
The variation of cyclic voltammograms with the solution pH was studied. When the pH changed from 4.0 to 10.0, the peak potential shifted to the negative direction. There was a linear relationship between the anodic peak potential and the pH value. The maximum anodic peak current appeared at pH 7.0 for H<sub>2</sub>O<sub>2</sub>. Therefore, considering the sensitivity, 0.1 molL<sup>-1</sup> PBS (pH 7.0) was selected as the supporting electrolyte for the determination of H<sub>2</sub>O<sub>2</sub> in this study.

### 3.4 Effect of scan rate on the response of H<sub>2</sub>O<sub>2</sub>

The CVs of 1.5×10<sup>-4</sup> molL<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> at the AgNPs–MWNT/GCE at various scan rates were recorded in the range of 10–100 mV s<sup>-1</sup>, the peak currents enhanced gradually along with the increase of the scan rate. The plot of peak current as an effect of scan rate for H<sub>2</sub>O<sub>2</sub> was also studied. The linear relationship of the peak currents and the scan rates (v) was corresponding to a regression equation:  $I_p = -1.952 v - 2.6467$  ( $I_p$ : μA,  $v$ : mVs<sup>-1</sup>,  $r = 0.997$ ), which implied that the system presented features corresponding to an adsorption-controlled process for H<sub>2</sub>O<sub>2</sub>.

### 3.5 Calibration curve

CVs of different concentrations of H<sub>2</sub>O<sub>2</sub> at the AgNPs–MWNT/GCE were recorded (Fig. 7). The experimental results showed that the peak current ( $I_p$ ) was linear with the concentration of H<sub>2</sub>O<sub>2</sub> in the range of 4.04×10<sup>-3</sup> – 1.5×10<sup>-6</sup> molL<sup>-1</sup>. The regression equations were:  $I_p$  (μA) = 57.09 (μmolL<sup>-1</sup>) + 10.85 ( $r = 0.999$ ). The lowest detectable concentration of H<sub>2</sub>O<sub>2</sub> was 1.42×10<sup>-7</sup> molL<sup>-1</sup>. The repeatability and stability are the vital properties for the modified electrode, which should be studied for analytical measurement. The same AgNPs–MWNT/GCE was used for 10 time successive measurement, and the relative standard deviation (RSD) of the peak current was 2.36% for 1.5×10<sup>-4</sup> molL<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>.



**Fig. 7.** Cyclic voltammograms of H<sub>2</sub>O<sub>2</sub> at a various concentrations. From a to i correspond to a) 1.5×10<sup>-6</sup>, b) 5.0×10<sup>-6</sup>, c) 1.0×10<sup>-5</sup>, d) 5.0×10<sup>-5</sup>, e) 1.0×10<sup>-4</sup>, f) 5.0×10<sup>-4</sup>, g) 8.0×10<sup>-4</sup>, h) 1.0×10<sup>-3</sup>, i) 4.04×10<sup>-3</sup> molL<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub>.

### 3.6 Analytical Application of the AgNPs–MWNT/GCE

The accuracy of the AgNPs–MWNT/GCE was evaluated by determining the recoveries of hydrogen peroxide in a disinfectant using a standard addition method. Corresponding experiments were carried out with the titration method and the results displayed good consistent and precision between the two methods, as listed in Table 1. As it can be seen in Table 1, the results obtained by the AgNPs–MWNT/GCE are satisfactory, with the recovery ranging from 98.1% to 107.7%.

**Table 1.** Recovery determination results.

| Sample Number | Added H <sub>2</sub> O <sub>2</sub> (mmol L <sup>-1</sup> ) | <sup>a</sup> Found H <sub>2</sub> O <sub>2</sub> by the present sensor (mmol L <sup>-1</sup> ) | Recovery by the present sensor (%) | <sup>a</sup> Found H <sub>2</sub> O <sub>2</sub> by the titration | Recovery by the titration method (%) |
|---------------|-------------------------------------------------------------|------------------------------------------------------------------------------------------------|------------------------------------|-------------------------------------------------------------------|--------------------------------------|
| 1             | 0.2                                                         | 0.201                                                                                          | 100.5                              | 0.192                                                             | 96.0                                 |
| 2             | 0.6                                                         | 0.646                                                                                          | 107.7                              | 0.637                                                             | 106.3                                |
| 3             | 1.2                                                         | 1.177                                                                                          | 98.1                               | 1.205                                                             | 100.4                                |

<sup>a</sup> The average of five measurements.

## CONCLUSIONS

The main feature of this work was to propose a new H<sub>2</sub>O<sub>2</sub> sensor based on AgNPs–MWNT, which was realized in a very fast and simple method. In particular, experimental results indicated that AgNPs were able to catalyse the reduction of H<sub>2</sub>O<sub>2</sub>. When AgNPs were used to modify MWCNTs, the two kinds of nanomaterials had a synergistic amplification effect, which could enhance the catalytic properties of the sensor. There was an obvious difference in response current between the electrode modified with AgNPs–MWNT hybrids and the unmodified electrode. When the two kinds of nanomaterials were used at one time the sensitivity enhanced 60 times than the unmodified electrode. The resulted sensor exhibited good ability of anti-interference to electroactive biomolecules, which was attributed to the relatively lower potential at about -0.3 V.

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