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In situ plasma sputtering synthesis of ZnO nanorods–Ag nanoparticles hybrids and their application in non-enzymatic hydrogen peroxide sensing

Dan Zhang[1,5], Yuxia Zhang[2], Chi Yang[1,5], Cunwang Ge[1], Yuanhong Wang[1], Hao Wang[1] and Hongying Liu[3,4]

[1] Department of Pharmacy & Chemistry and Chemical Engineering, Nantong University, Nantong 226001, People's Republic of China
[2] Shangqiu Medical College, Shangqiu, 476100, People's Republic of China
[3] College of Life Information Science & Instrument Engineering, Hangzhou Dianzi University, Hangzhou, 310018, People's Republic of China
[4] State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry & Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

E-mail: toyangchi@ntu.edu.cn

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Abstract

In this paper, ZnO nanorods–Ag nanoparticles hybrids were first synthesized via a facile, rapid, and *in situ* plasma sputtering method without using any silver precursor. The obtained materials were then characterized by scanning electron microscopy, high-resolution transmission electron microscopy, energy-dispersive x-ray spectroscopy, and cyclic voltammetry. Based on the electrochemical catalytic properties of the obtained nanohybrids, a non-enzymatic hydrogen peroxide biosensor was constructed by immobilizing the obtained ZnO nanorods–Ag nanoparticles hybrids on the surface of a glassy carbon electrode. Under optimal conditions, the resulting biosensor displayed a good response for H_2O_2 with a linear range of 0.2 to 12.8 mM, and a detection limit of 7.8 μM at a signal-to-noise ratio of 3. In addition, it exhibited excellent anti-interference ability and fast response. The current work provides a feasible platform to fabricate a variety of non-enzymatic biosensors.

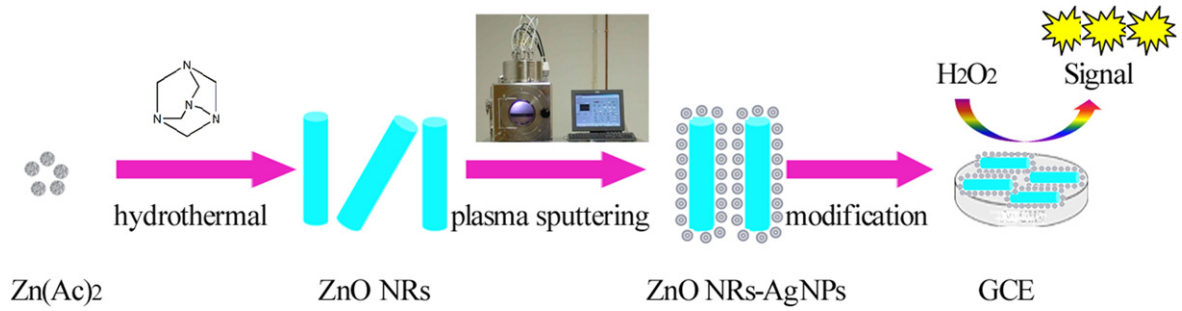
Keywords: ZnO nanorods-Ag nanoparticles hybrids, plasma sputtering method, sensor

(Some figures may appear in colour only in the online journal)

1. Introduction

Recently, hybrid materials have attracted significant interest because they present the possibility to create materials with innovative and exceptional physical chemistry properties, and thus become one of the most promising candidate materials applied in biomedicine, photocatalysis, and nanodevices that are not found in the single individual component [1–5]. Among them, the hybrid materials composed of a semiconductor and a noble metal are of great significance due to their tailored and controllable physical and chemical properties [6]. Thus, much effort has been performed on the synthesis and application of metal–semiconductor hybrids [7–9]. In particular, ZnO is one of the important metal oxide materials and can be simply obtained via a series of simple processes [10]. In addition, Ag nanoparticles (NPs) are the most developed metal NPs due to their good chemical and physical properties [11]. Therefore, it is expected that doping Ag NPs on the surface of ZnO could construct ZnO–Ag NPs hybrids with novel optical and electrical properties.

[5] Dan Zhang and Chi Yang contributed equally to this work.



Scheme 1. The schematic illustration for the preparation of ZnO NRs–Ag NPs hybrids.

A variety of techniques have been employed to synthesize ZnO–Ag nanohybrids, such as electrochemical [12], photochemical [13], sol-gel [14], hydrothermal [15], microwave [16], laser [17], and ultrasonic spray pyrolysis [18]. However, all of the above-mentioned methods require an additional Ag source into the precursor. Therefore, it is of great interest to open a simple, rapid, one-pot method for the synthesis of ZnO–Ag nanohybrids without using any silver precursor. Plasma sputtering-based approaches in that respect are more appealing. The advantages of this technique are rapid, *in situ* simplicity and high purity of the product. However, the attention paid on the synthesis of the ZnO–Ag nanohybrid based on the *in situ* plasma sputtering method is scarce.

On the other hand, hydrogen peroxide (H_2O_2) is an essential mediator in food, medicine, environment, and industry analyses [19]. Thus, accurate and rapid determination of H_2O_2 is of practical importance and widely investigated. Until now, many strategies have been explored for this purpose, such as localized surface plasmon resonance [20], spectrometry [21], fluorescence [22], and electrochemistry [23]. Among them, the electrochemical technique has become an interesting subject due to its simple, rapid, cheap, and effective characteristics. Originally, an enzymatic electrochemical biosensor was adopted in the determination of H_2O_2 [24]. However, the poor stability and reproducibility that resulted from the intrinsic nature of the enzyme limited its development [25]. In order to circumvent these problems, non-enzymatic electrochemical sensors were selected to evaluate the H_2O_2 concentration. With the development of nanotechnology, many nanomaterials were applied in the field of enzyme-free sensors [26, 27]. Recently, Ag-based nanomaterials have been widely used as non-enzymatic H_2O_2 biosensors because of their outstanding conductivity and electroactivity. To further improve the sensitivity of sensor on Ag-based nanomaterials, hosts were used as a platform to impregnated Ag nanomaterials.

In this paper, we developed an *in situ* plasma sputtering strategy to synthesize ZnO nanorods–Ag NPs (ZnO NRs–Ag NPs) hybrids and primarily explored the structural and electrochemical properties of the nanohybrids. To the best of our knowledge, the synthesis of the ZnO NRs–Ag NPs hybrids via plasma sputtering has not been reported so far. Compared with other synthetic methods, this one is simple, rapid, *in situ*, and without using any silver precursor. Additionally, a non-enzymatic H_2O_2 biosensor was fabricated by considering the catalytic of ZnO NRs–Ag NPs hybrids.

2. Experiment

2.1. Reagents

Zinc acetate dehydrate ($Zn(Ac)_2{\cdot}2H_2O$, 98%) and hexamethylenetetramine were purchased from Sigma Aldrich (China). D-(+)-Glucose, NaH_2PO_4, Na_2HPO_4, and H_2O_2 were obtained from Sinopharm Chemical Reagent Co. Ltd (China). Nafion (Nf, 5%) was obtained from Shanghai Hesen Electric Co. Ltd (China). Phosphate buffer saline (PBS) of different pH values were prepared by mixing a stock solution of NaH_2PO_4 and Na_2HPO_4, and then adjusting the pH with 0.1 M NaOH and H_3PO_4. All the other chemicals were of analytical grade and used as received. All solutions were freshly prepared using ultrapure water ($\geqslant$18 MΩ, Milli-Q, Millipore).

2.2. Apparatus

High-resolution transmission electron microscopy (HRTEM) imaging and energy-dispersive x-ray spectroscopy (EDX) were obtained using a JEOL2010 electron microscope at an acceleration voltage of 200 kV. The scanning electron microscopy (SEM) images were obtained with a Hitachi X650. Electrochemical measurements were performed on a CHI 660B workstation (Shanghai Chenhua Apparatus Corporation, China) with a conventional three-electrode system composed of a platinum wire as the auxiliary, a saturated calomel electrode as the reference, and a nanohybrid modified or bare glassy carbon electrode (GCE) as the working electrode. The amperometric experiments were performed in a continuous stirring solution using a magnetic stirrer. A 5 mL PBS (0.05 M, pH 7.4) was employed as the supporting electrolyte solution. It was purged with high purity nitrogen for 20 min prior to experiments and blanketed with nitrogen during electrochemical experiments.

2.3. Preparation of ZnO NRs–Ag NPs hybrids

The ZnO NRs–Ag NPs hybrids were synthesized by a hydrothermal method and plasma sputtering, as shown in scheme 1. First, ZnO NRs were prepared by a facile

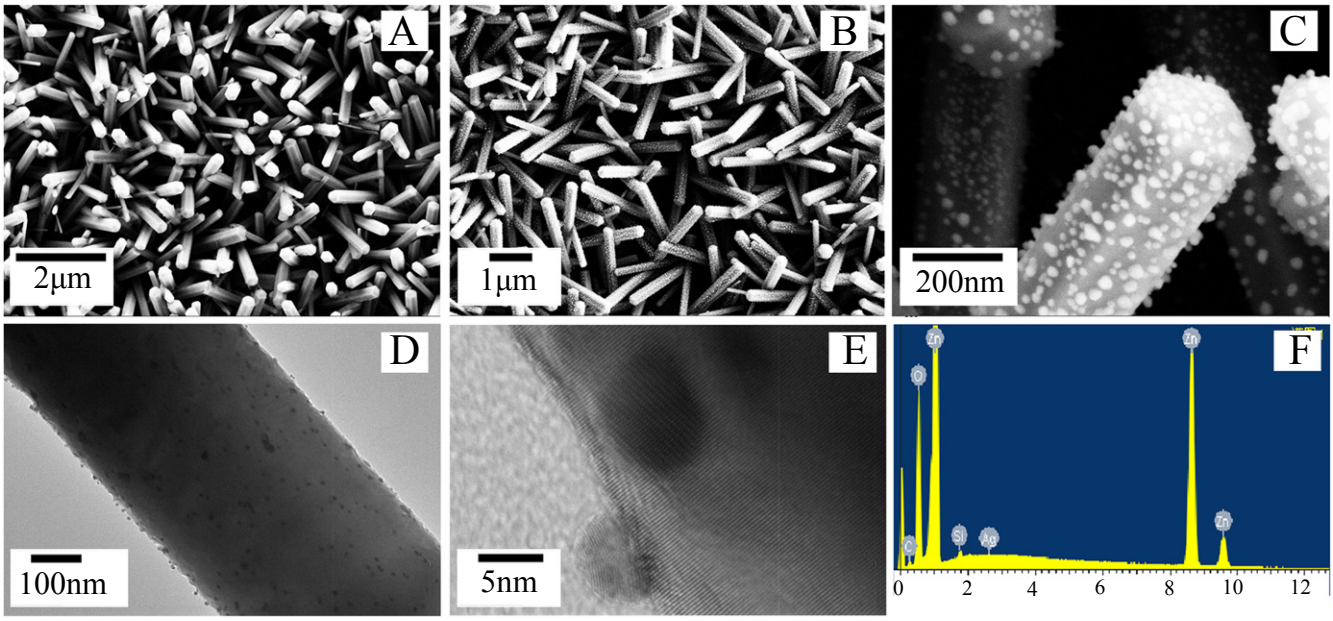


Figure 1. SEM images of ZnO NRs (a) and ZnO NRs–Ag NPs hybrids (b), (c); TEM image of ZnO NRs–Ag NPs hybrids (d); HRTEM image of ZnO NRs–Ag NPs hybrids (e); EDX analysis of ZnO NRs–Ag NPs hybrids (f).

hydrothermal route. Then, 5 mM hexamethylenetetramine and 5 mM $Zn(Ac)_2$ were dissolved in 100 mL water. The suspension was transferred into a Teflon-lined stainless steel autoclave and maintained at 90 °C for 3 h. After cooling, the product was collected, washed with absolute ethanol and deionized water, and dried in a vacuum at 60 °C for 6 h. Second, ZnO NRs–Ag NPs hybrids were obtained by the plasma sputtering method. Briefly, ZnO NRs substrates using a sputtering system (Ion Sputter Hitachi E-1010) and using 7.5 cm diameter Ag (5N) metal targets. A high purity gas of Ar at a total pressure of 40 Pa was used as the sputtering gas. The sputtering current and temperature employed during the generation of plasma were 10 mA and 200 °C, respectively. The plasma discharge time was 120 s. After being rinsed with ethanol and deionized water several times, the ZnO NRs–Ag NPs hybrids were dried in a vacuum at 60 °C for 6 h.

2.4. Fabrication of the non-enzymatic H_2O_2 sensor

Prior to modification, the bare GCE ($\Phi = 3$ mm) was polished to a mirror shine using 1.0, 0.3, and 0.05 μm Al_2O_3 powder followed by sonication in acetone, ethanol, and deionized water for 1 min each, respectively. Then, 1 mg ZnO NRs–Ag NPs hybrids and 1.5 mg carbon power (C) were dispersed in 200 μL nafion solution and sonicated for 30 min in an ice water bath. Next, 4 μL ZnO NRs–Ag NPs/C/Nf solution (5 mg mL^{-1}) was cast on the surface of GCE and dried in air at room temperature to obtain ZnO NRs–Ag NPs/C/Nf modified GCE, which would be used as a non-enzymatic H_2O_2 sensor.

3. Results and discussion

3.1. Characterization of ZnO NRs–Ag NPs hybrids

A facile plasma sputtering-based synthetic route was applied to produce ZnO NRs–Ag NPs hybrids without the addition of an extra silver precursor. The morphology and structure of ZnO NRs and ZnO NRs–Ag NPs hybrids were characterized by SEM, TEM, HRTEM, and EDX, as shown in figure 1. SEM images show that the obtained ZnO NRs has the rods morphology with good dispersion (figure 1(a)). The diameter of ZnO NRs is about 300 nm with the length of 1.5–2 μm. After being treated by plasma sputtering, particles of 20 nm are observed adhering on the ZnO NRs (figures 1(b) and (c)). TEM images further confirmed the same results (figure 1(d)). Moreover, the lattice fringes of ZnO NRs–Ag NPs hybrids can be observed clearly by HRTEM (figure 1(e)). The lattice spacing is located at 0.52 nm and 0.24 nm, which corresponds to the (0001) lattice plane of wurtzite ZnO and the fcc Ag (111) plane, respectively [28]. In addition, EDX analysis displays that the nanohybrids include Zn, Ag, O, and C elements with a 0.06% Ag content (data not shown). These results confirmed that Ag NPs have been doped on the surface of ZnO NRs.

3.2. Electrochemical behavior of ZnO NRs–Ag NPs/C/Nf modified electrodes

To explore the features of the modified electrode, the electrochemical behavior of the ZnO NRs–Ag NPs/C/Nf modified electrodes was investigated by CV. No notable redox peak was observed for Nf/GCE and bare GCE, while ZnO NRs–Ag NPs/C/Nf/GCE shows a significant reduction peak. This

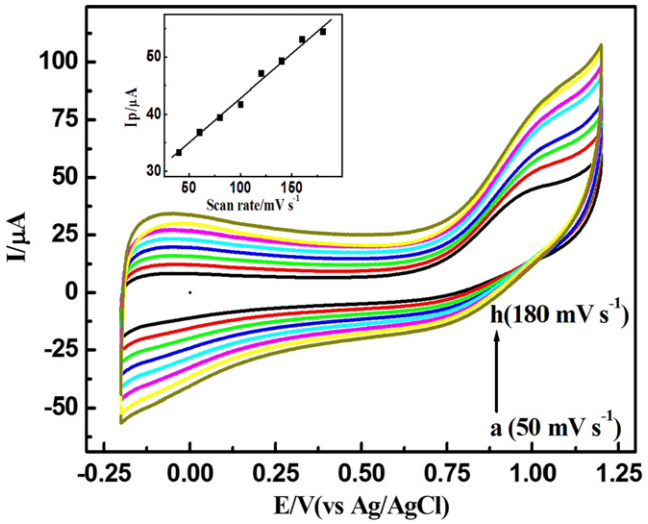


Figure 2. Cyclic voltammetries (CV) (at +0.8 V) of the ZnO NRs–Ag NPs/C/Nf/GCE in PBS (pH 7.0) at different scan rates ((a)–(h): from 50 to 180 mV s^{-1}). Inset shows the linear dependence plot of peak current with scan rate.

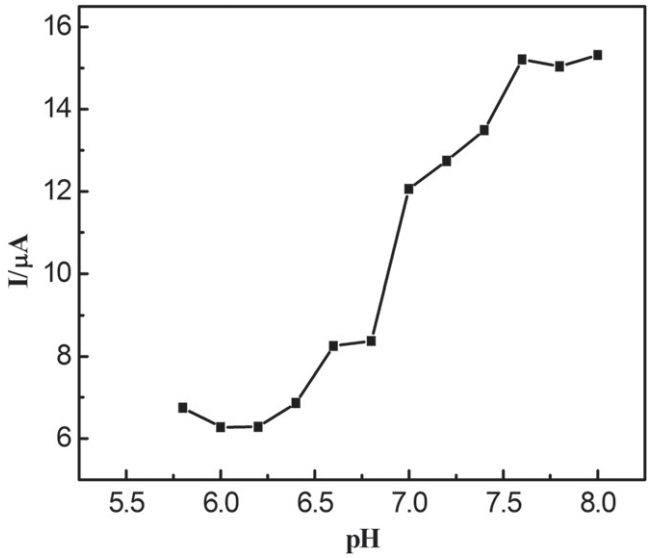


Figure 4. Effect of pH on steady-state response current of ZnO NRs–Ag NPs/C/Nf/GCE upon addition of H_2O_2 into PBS (pH 7.0).

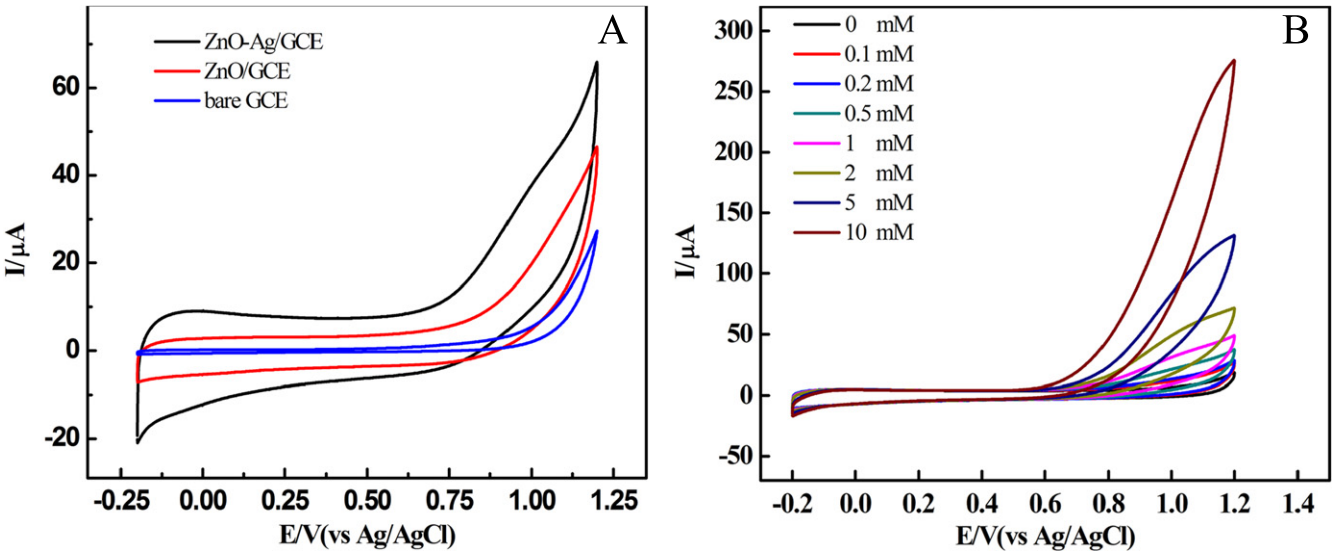


Figure 3. (a) CVs of bare GCE (blue line), ZnO/GCE (red line), ZnO NRs–Ag NPs/C/Nf/GCE (black line) in PBS (pH 7.0) containing H_2O_2; (b) CVs of the ZnO NRs–Ag NPs/C/Nf/GCE in PBS (pH 7.0) with different concentration of H_2O_2.

phenomenon indicates that ZnO NRs–Ag NPs/C/Nf/GCE had desirable electrochemical features and electron transfer ability. Furthermore, the CV of the ZnO NRs–Ag NPs/C/Nf modified electrodes in PBS at scans rates range was studied, as shown in figure 2. With increasing scan rate from 50 to 180 mV s^{-1}, the peak current increases linearly with scan rate (inset in figure 2), which indicates a typical surface-controlled electrode process.

3.3. Electrochemical performance of ZnO NRs–Ag NPs/C/Nf modified electrodes toward H_2O_2

In order to evaluate the potential application of ZnO NRs–Ag NPs hybrids, electrochemical sensors for H_2O_2 detection are fabricated by dropping the dispersion solution with the same amount of ZnO NRs or ZnO NRs–Ag NPs hybrid on surface of GCE. Figure 3(a) shows the CVs of bare GCE (blue line), ZnO/GCE (red line), and ZnO NRs–Ag NPs/GCE (black line) in PBS containing the same concentration of H_2O_2. It was clearly observed that the peak current of bare GCE and ZnO/GCE are lower than that of ZnO NRs–Ag NPs/GCE. Moreover, the reduction peak current was increased with increasing the concentration of H_2O_2 (figure 3(B)). According to [29], the Ag NPs modified electrode exhibits a few e toward the reduction of H_2O_2. The above results clearly indicate that the introduction of Ag can improve the conductivity of the hybrids, and increase electrode surface area. This may be ascribed to synergistic effects of the good conductivity, the largee surface area, and the catalytic effect of ZnO NRs

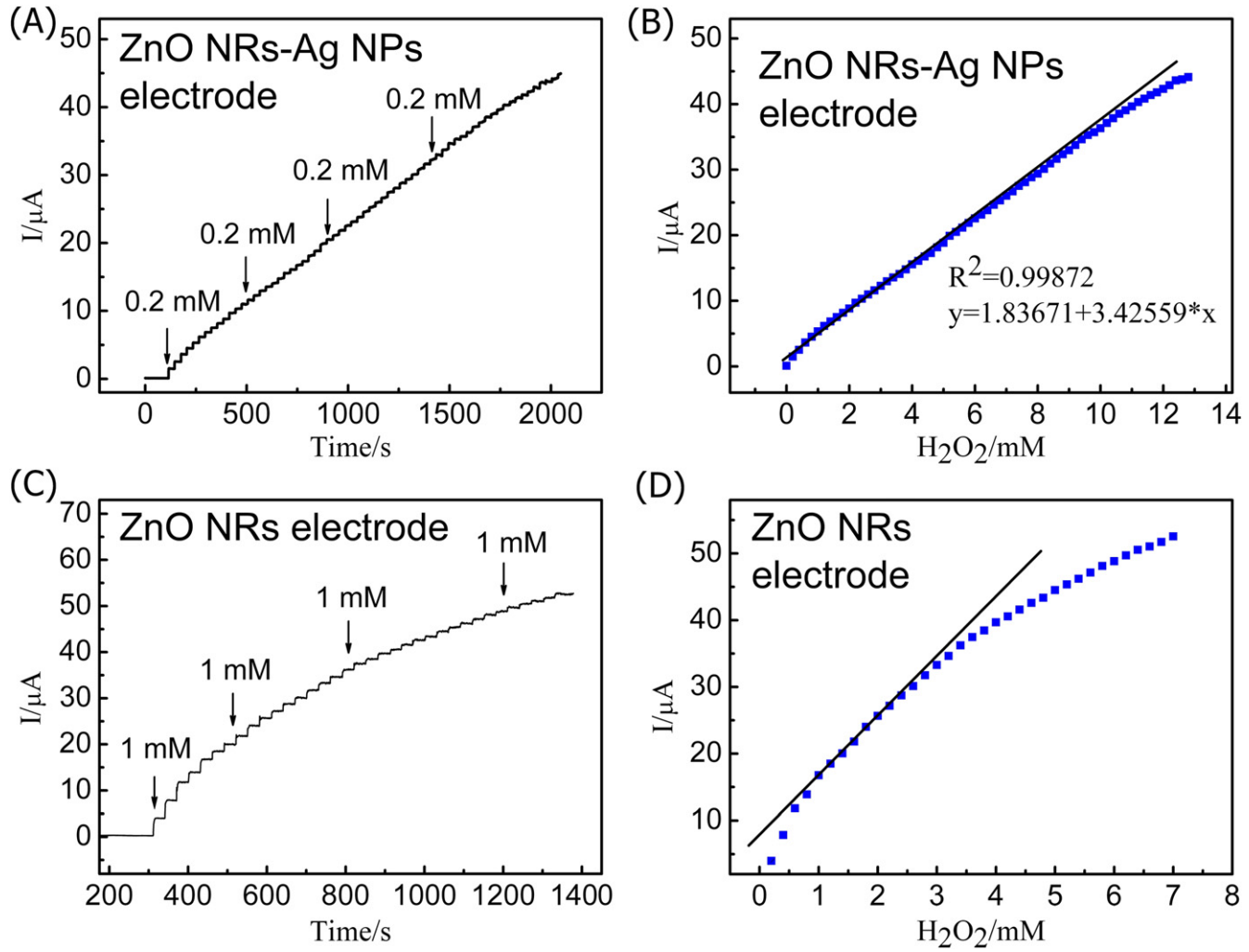


Figure 5. (a) Typical amperometric responses of the ZnO NRs–Ag NPs/C/Nf/GCE sensor to successive injection of H_2O_2 into PBS at 0.8 V; (b) the corresponding linear relationships between the catalytic current and the concentration of H_2O_2; (c) typical amperometric responses of the ZnO NRs/C/Nf/GCE sensor to successive injection of H_2O_2 into PBS at 0.8 V; (d) the corresponding linear relationships between the catalytic current and the concentration of H_2O_2.

and Ag NPs. The ZnO NRs–Ag NPs served as a suitable supporting component of the biosensor, which promoted the electron transfer. Furthermore, spinodal decomposition may exist in our preparation material [30, 31], which can improve the catalytic performance of materials [32, 33]. Thus, the hybrid formed by ZnO NRs and Ag NPs has excellent electrocatalytic activity to H_2O_2, and then the ZnO NRs–Ag NPs/GCE could be applied in the non-enzymatic hydrogen peroxide sensing.

3.4. Optimization of the experimental parameter

In order to obtain the supreme sensitivity of the proposed electrode, some important parameters were optimized. Considering the fact that protons take part in the catalytic reaction of H_2O_2, pH is the most important factor to improve electrochemical signal. Thus, the relationship between the electrochemical signals and pH were investigated. As shown in figure 4, a significant increase of peak current was observed between 5.8 and 7.6, while no obvious difference was obtained for a higher pH value. Considering the physical environment, 7.4 was selected as the optimal pH.

3.5. Amperometric response of ZnO NRs–Ag NPs/C/Nf modified electrodes to H_2O_2

As well known, the amperometric method is more desirable than the voltammetric one in practical applications [34]. Therefore, the amperometric response of the ZnO NRs–Ag NPs/C/Nf modified electrodes toward H_2O_2 was investigated. Figure 5(a) displays the typical steady-state catalytic current-time curve of the sensor in PBS under the optimized conditions with a successive addition of H_2O_2. As H_2O_2 was injected, the ZnO NRs–Ag NPs/C/Nf/GCE achieved the stable steady-state response in 3 s, indicating a rapid amperometric response. A linear relationship between the amperometric current and the concentration of H_2O_2 was obtained. In figure 5(b), it displayed a linear range from 0.2 to 12.8 mM, and the detection limit was estimated to be 7.8 μM (S/N = 3).

Table 1. Material properties of ZnO (Voigt notation is used).

Materials	Linear range (mM)	Detection limit (μM)	Ref
CoOOH NSs	0.1–1.6	40	[35]
Ag NPs-mesoporous silica	5.3–124.5	—	[36]
MWCNT-PEDOT/GCE	0.1–9.8	50	[37]
PTH/DNA/CPE	0.99–8.26	160	[38]
Ag NPs-NFs/GCE	0.1–80	62	[39]
Urchin-like core-shell CuO	0.001–5.55	10	[40]
ZnO NRs–Ag NPs hybrids	0.2–12.8	7.8	This work

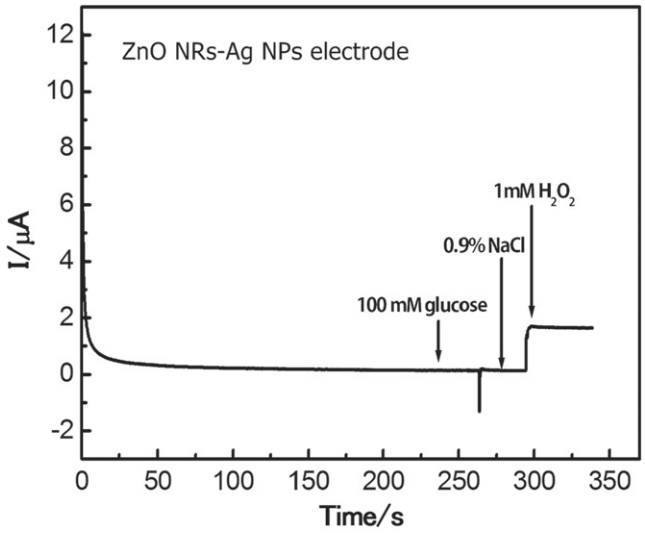


Figure 6. Interference experiment of ZnO NRs–Ag NPs/C/Nf/GCE with 100 mM glucose, 0.9% NaCl, and 1 mM H_2O_2.

Furthermore, in order to validate the enhanced sensitivity of the ZnO NRs–Ag NPs hybrids, comparative experiments involving ZnO NRs as the electrode modifier were performed (figure 5(c)). Compared to ZnO NRs–Ag NPs hybrids, the detection limit with ZnO NRs showed a 7.3 times lower response (figure 5(d)). The results showed that the enhanced sensitivity came from the introduction of Ag NPs and the combination with ZnO NRs. In addition, the analytical performance of the proposed ZnO NRs–Ag NPs/C/Nf/GCE was compared with other reported H_2O_2 sensors, as summarized in table 1. It revealed that the proposed sensor has wider linear range, a lower detection limit, and higher sensitivity.

3.6. Interference study

It is known that other electroactive species influence the sensor response. Thus, the response of the proposed sensor toward 100 mM glucose was investigated. As shown in figure 6, the glucose did not interfere with determining H_2O_2. Moreover, the tolerance of the proposed sensor to chloride was monitored by the addition of 0.9% NaCl to PBS. The result reveals that it did not affect the determination of H_2O_2, indicating excellent chloride tolerance of the proposed sensor (figure 6). However, the anodic currents of ascorbic acid (AA), uric acid (UA), and dopamine (DA) were obtained (data not shown), indicating that the AA, UA, and DA interferes with the response of the sensor to H_2O_2. Fortunately, they have different oxidation potentials and can be distinguished from the oxidation potential of H_2O_2. These results convincingly indicated that the present NRs-Ag NPs/C/Nf/GCE electrode showed high selectivity for typical glucose, and other biological species at the 0.8 V detection.

4. Conclusions

In summary, novel ZnO NRs–Ag NPs hybrids were successfully synthesized via a convenient *in situ* plasma sputtering method without the addition of an extra Ag precursor. The morphology and properties of materials were investigated by TEM, SEM, EDX, and CV. In addition, the obtained hybrids were evidenced to own excellent catalytic activity toward reduction of H_2O_2 because of the outstanding electroactive performance of Ag NPs and the significant characteristics of ZnO NRs. Our findings provide a platform to fabricate a non-enzymatic biosensor to determine H_2O_2 for a large field of applications. Compared with the ZnO NRs modified electrode, the proposed biosensor exhibits high sensitivity, good linear response, and low detection limit. This kind of ZnO NRs–Ag NPs hybrid project has promising potential and can open a new way for the development of non-enzymatic biosensors.

Acknowledgments

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