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A sensitive enzymeless sensor for hydrogen peroxide based on the polynucleotide-templated silver nanoclusters/graphene modified electrode

Yalin Xia [a], Wenhua Li [a], Ming Wang [a], Zhou Nie [a,*], Chunyan Deng [b,**], Shouzhuo Yao [a]

[a] State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, PR China
[b] College of Chemistry and Chemical Engineering, Key Laboratory of Resources Chemistry of Nonferrous Metals, Central South University, Changsha 410083, PR China

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ABSTRACT

A novel, sensitive and enzymeless electrochemical sensor based on polynucleotide-templated silver nanoclusters (DNA-AgNCs)/graphene composite film was developed for the detection of hydrogen peroxide. The graphene modified glassy carbon electrode (GCE) was employed because graphene has several advantages including excellent conductivity, biocompatibility, and large surface area to volume ratio. In addition, it was found that DNA-AgNCs have remarkable electrocatalytic activity toward the reduction of hydrogen peroxide, and can be easily immobilized onto the surface of the graphene/GCE by π–π stacking. The sensor based on the (DNA-AgNCs)/graphene/GCE exhibited a rapid response (ca. 3 s), a low detection limit (3 μM), a wide linear range from 15 μM to 23 mM, high selectivity, as well as good repeatability. Moreover, the common interfering species, such as ascorbic acid, uric acid, dopamine, glutathione, and L-cysteine, did not result in any interference. This present work may expand the use of silver nanoclusters in the field of electrochemical sensor.

1. Introduction

Hydrogen peroxide is an essential intermediate product in a lot of biological and environmental circulation processes, so its accurate detection is of increasing significance in many fields such as pharmaceutical industry, clinical control, food production, and environment protection [1–4]. Up to now, various methods including spectrometry [5], titrimetry [6], chemiluminescence [7], surface plasmon resonance [8], chromatography [9] and electrochemistry [3,4] have been employed to detect hydrogen peroxide. Among these, electrochemical technique has been widely used for the detection of hydrogen peroxide because it has inherent advantages of simplicity, easy miniaturization, high sensitivity, and relatively low cost [10,11]. Therefore, various chemically modified electrodes, especially enzyme-based electrodes have been widely developed for the detection of hydrogen peroxide [1,3]. However, a common and serious problem is that the activity of enzyme can be easily affected by temperature, pH, humidity, and toxic chemicals [1,12,13]. In addition, the immobilization of the enzyme on the solid electrode by adsorption, cross-linking, entrapment, or electropolymerization is a complicated procedure [10,11,14], and this may also decrease the activity of the enzyme and have influence on the stability and reproducibility of the enzyme-based electrode. On the contrary, using an enzymeless sensor for the detection of hydrogen peroxide possesses many advantages including simplicity, low cost, improvements in stability and reproducibility. Considering these aspects, the non-enzymatic hydrogen peroxide sensor has attracted much interest. Recently, in order to enhance the sensitivity of the non-enzymatic sensor, many novel materials, especially metal nanoparticles, have been employed to modify electrodes and electrocatalyze the reduction or oxidation of hydrogen peroxide [15–17].

Metal nanoclusters (NCs) as a novel nanomaterial have excellent properties of large surface area and good electronic properties, and also hold promise for several applications, including (but not limited to) catalysis [18,19] (including fuel cell catalysts [20]), photochemistry nanoelectronics [21], chemical sensors [22] and many others. Up to now, some metal NCs have been widely used in electrocatalysis for the reduction or oxidation of some molecules. For example, Au nanoclusters (AuNCs) have been used for non-enzymatic hydrogen peroxide detection based on the electrocatalytic activity of AuNCs toward the oxidation of hydrogen peroxide [23]. Kang and coworkers have reported that CuNCs have electrocatalytic activities toward the oxidation of H_2O_2 and glucose [24]. Also, Pt nanoclusters were employed for the electrocatalytic reduction of nirite [25].

In recent years, polynucleotide-templated silver nanoclusters (DNA-AgNCs), made up of a few silver atoms, have been applied to different fields, such as chemical-sensing, in vitro bioassays and in vivo biological imaging [26–28], because they have unique fluorescence properties and their synthesis is very simple and

* Corresponding author.
** Corresponding author. Tel.: +86 731 8882 1626; fax: +86 731 8882 1848.
E-mail addresses: niezhou.hnu@gmail.com (Z. Nie), dengchunyan@csu.edu.cn (C. Deng).

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low-cost. In addition, it has been reported that the electrocatalytic reduction of hydrogen peroxide can be realized by the catalytic activity of Ag atoms in AgNPs [29], so it can be expected that DNA-AgNCs may also have electrocatalytic activity toward H_2O_2 reduction.

Therefore, in this work, we prepared silver nanoclusters using DNA as protection and a novel non-enzymatic hydrogen peroxide electrochemical sensor was fabricated by immobilizing DNA-AgNCs on the graphene-modified GC electrode. Just as expected, the obtained DNA-AgNCs/graphene composite film showed excellent electrocatalytic activity toward the reduction of hydrogen peroxide at relatively low overpotential, which may be ascribed to the synergic effect of DNA-AgNCs and graphene. Herein, DNA-AgNCs can electro-catalyze the reduction of hydrogen peroxide. And graphene not only has electrocatalytic activity and good biocompatibility, but also has the advantage of large surface area to volume ratio, which is useful for more DNA-AgNCs to be adsorbed on the surface of graphene-modified electrode by π–π stacking [30]. It is significant for improving the sensitivity for detection of hydrogen peroxide. Moreover, the proposed hydrogen peroxide sensor also displays other excellent attribute such as ease of fabrication, fast response, good stability, low applied potential, and low detection limit. The present work may lay a potential foundation for the use of DNA-AgNCs in the field of chemical sensor or biosensor.

2. Experimental details

2.1. Apparatus

Electrochemical measurements were carried out on a CHI660A electrochemical workstation (Chenhua Instrument Company of Shanghai, China) with a conventional three-electrode system. As a working electrode, glassy carbon electrode (GCE, 3 mm in diameter) was modified with graphene, DNA-AgNCs, and (DNA-AgNCs)/graphene, respectively. A platinum wire was used as the auxiliary electrode. The potentials mentioned in this paper were measured with respect to a saturated calomel electrode (SCE). Prior to electrochemical experiments, electrolyte solutions were deoxygenated by nitrogen for 15 min. Fluorescence measurements of DNA-AgNCs were performed on a Hitachi F-4500 fluorometer (Hitachi Co. Ltd., Japan).

2.2. Reagents

H_2O_2 (30 wt%), graphite, $AgNO_3$, $NaBH_4$, and HAc were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). NaAc was obtained from Damao chemical reagent factory in Tianjin. NaH_2PO_4, Na_2HPO_4, KCl, and DNA (5′-CCCTTAATCCCC-3′) were from Shanghai Sangon Biotechnology Co. Ltd. (Shanghai, China). All chemicals were of analytical grade and used without further purification. 0.1 M phosphate buffer solution (PBS) was used as an electrolyte solution (pH 7.0). Excepting special statement, all electrochemical experiments were performed in PBS at ambient temperature. The solution of hydrogen peroxide was prepared freshly. Double-distilled water (18.2 M Ω cm^{-1}) obtained from the Millipore Milli-Q system was used throughout.

2.3. Synthesis of graphene oxide and DNA-AgNCs

Graphene oxide (GO) was synthesized from natural graphite powder through a modified Hummers method [31]. Generally, graphite and 98% H_2SO_4 were mixed, and stirred over 24 h at ambient temperature. After that, $NaNO_3$ was added into the mixture, followed by stirring for 30 min. Subsequently, $KMnO_4$ was gradually introduced into the suspension in an ice bath. After being heated to 35–38 °C, the suspension was stirred for another 30 min. In succession, water was slowly added into the above suspension, and heated to a temperature of 98 °C for 5 min. Water and 30% H_2O_2 were injected to the suspension to terminate the reaction. The resulting suspension was washed by centrifugation three times with double-distilled water. Finally, GO was obtained after drying in vacuum.

DNA-AgNCs were synthesized according to previous reports [32]. In brief, solutions of H_2O, $AgNO_3$ (1 mM, 22.5 μL) and DNA (50 μM, 55 μL) made up in phosphate buffer (40 mM, pH 7.0) were mixed at a final volume of 85 μL. After incubation in an ice bath for 15 min, Ag^+ was reduced by adding freshly prepared $NaBH_4$ (2 mM, 15 μL) under vigorous shaking. The shaking was kept for 1 min to make sure that silver ions were adequately reduced. The mixtures were then kept in the dark for 90 min at room temperature. Afterward, the obtained DNA-AgNCs were stored at 4 °C in the dark when not in use. DNA-AgNCs exhibited an excitation peak centered at 485 nm and an emission peak centered at 565 nm, as shown in Fig. 1. These obtained results are similar with those obtained by Dickson group [32], and also demonstrate that DNA-AgNCs have been successfully synthesized.

2.4. Fabrication of the (DNA-AgNCs)/graphene/GC electrode

Prior to modification, the GC electrode was successively polished to a mirror-like surface with 0.3 and 1.0 μm alumina slurry (from CH Instruments, the trace iron content is lower than 10 ppm) and then rinsed thoroughly by double-distilled water. Afterward, the electrode was washed with anhydrous ethanol and double-distilled water for 5 min in an ultrasonic bath to remove the loosely adsorbed alumina slurry. Finally, the treated electrode was dried with a stream of nitrogen.

GO suspension (1 mg mL^{-1}) was obtained by ultrasonicating (40 kHz, 480 W) GO in 0.1 M pH 5.0 acetate buffer for about 5 h. Graphene was electrodeposited onto the surface of GC electrode to obtain the graphene/GCE by electrochemical reduction of GO cycling from −1.5 to 0.5 V at 10 mV s^{-1}. The (DNA-AgNCs)/graphene/GCE was obtained by dropping 5 μL of DNA-AgNCs solution onto the surface of the well-processed graphene/GCE, and keeping for 5 min in a dark place. Finally, the prepared electrode was rinsed completely with double-distilled water to get rid of the loosely adsorbed DNA-AgNCs. For comparison, (DNA-AgNCs)/GCE, graphene/GCE, and bare GCE were also constructed using the same procedure. These modified electrodes were stored at 4 °C in PBS (40 mM, pH 7.0) when not in use.

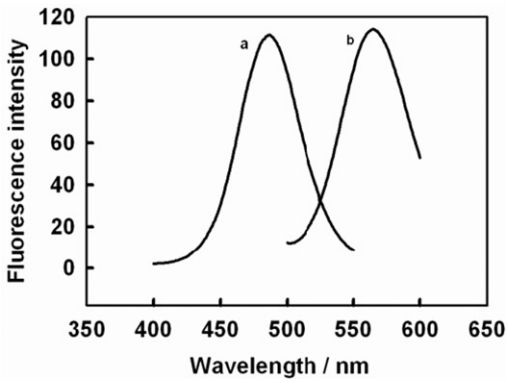

Fig. 1. The maximum excitation (a) and emission spectra (b) of the obtained DNA-Ag NCs.

3. Results and discussion

3.1. Electrochemical characterization of the modified electrodes

According to literature [33], graphene can be electrodeposited onto the surface of GC electrode by electrochemical reduction of GO to fabricate the graphene modified electrode, and moreover, the thickness of graphene film can be easily controlled. Herein, 10 cycles were used for graphene electrodepositon to obtain the graphene/GCE. Fig. 2 shows the current response of 5.0 mM $[Fe(CN)_6]^{3-/4-}$(1:1) at the bare GC (a), graphene/GC (b) and (DNA-AgNCs)/graphene/GC (c) electrodes. It can be seen that compared with the bare GC electrode, the current response of $[Fe(CN)_6]^{3-/4-}$ at the graphene/GC electrode was greatly enhanced and the anodic-to-cathodic peak separation (ΔE_p) of $[Fe(CN)_6]^{3-/4-}$ at the graphene/GC electrode became smaller (ca. 95 mV, data not shown), which is consistent with reports in literature [33]. This demonstrates that graphene has been successfully deposited on the GC electrode and more electroactive sites have been introduced onto the surface of graphene/GC electrode. After DNA-AgNCs were assembled onto the surface of graphene/GCE, the current response of $[Fe(CN)_6]^{3-/4-}$ decreased (Fig. 2c), which can be explained by the fact that the negatively charged phosphate backbone of DNA in DNA-AgNCs repels the $[Fe(CN)_6]^{3-/4-}$ anions from the electrode surface and thus results in an enhanced electron-transfer resistance. And this illustrates that DNA-AgNCs have been successfully assembled onto the graphene/GC electrode by $\pi-\pi$ stacking.

3.2. Electrochemical behavior of the (DNA-AgNCs)/graphene/GC electrode and its electrocatalysis toward H_2O_2

Electrochemical behavior of the (DNA-AgNCs)/graphene/GC electrode was investigated by cyclic voltammetry (CV), and the corresponding results are shown in Fig. 3. From Fig. 3, a distinct anodic peak at +0.16 V can be obviously observed, which is the characteristic oxidation peak of DNA-Ag(0)NCs. Meanwhile, a small reduction peak at a potential of −0.04 V can also be seen, which may be due to the reduction of Ag^+. This further demonstrates that DNA-AgNCs have been successfully immobilized onto the surface of graphene/GCE.

Additionally, the electrocatalytic behavior of the (DNA-AgNCs)/graphene/GC electrode toward H_2O_2 was investigated. Fig. 4 shows CVs of (A) the bare GC electrode, (B) graphene/GC electrode, (C) (DNA-AgNCs)/GC electrode and (D) (DNA-AgNCs)/graphene/GC electrode in N_2 saturated PBS (0.1 M, pH 7.0) without (a) and with (b) 2 mM H_2O_2. It can be seen that the background current of graphene/GC electrode was higher than that of

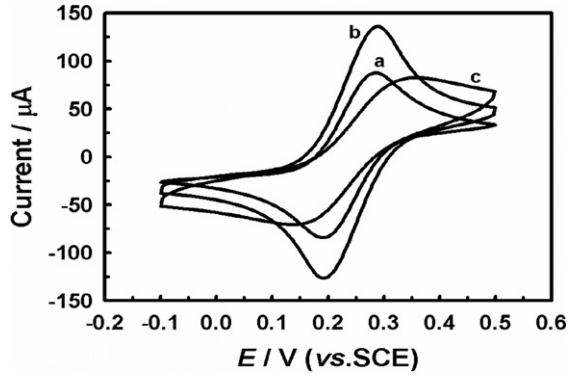

Fig. 2. Cyclic voltammograms of the bare GCE (a), graphene/GCE (b) and (DNA-AgNCs)/graphene/GCE (c) in 0.1 M KCl aqueous solution containing 5.0 mM $[Fe(CN)_6]^{3-/4-}$(1:1) at a scan rate of 50 mV s^{-1}.

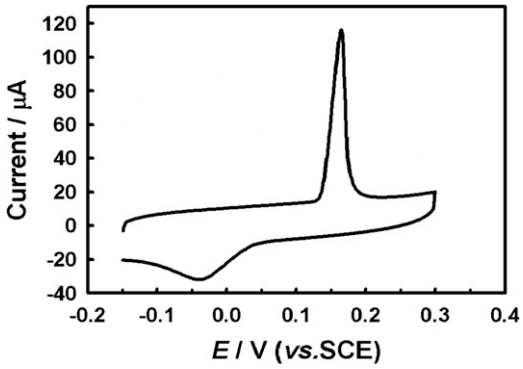

Fig. 3. Cyclic voltammogram of the (DNA-AgNCs)/graphene/GCE in PBS (0.1 M, pH=7.0) at a scan rate of 50 mV s^{-1}.

the bare GC electrode and (DNA-AgNCs)/GC electrode, which is due to the large specific area and the remaining oxygen-related defects of the graphene film [33,34]. On the other hand, at the bare GC electrode and graphene/GC electrode, the reduction current signal of H_2O_2 is very low. However, an obvious current response of H_2O_2 at the (DNA-AgNCs)/GC electrode can be observed at −1.0 V (Fig. 4C-b), which demonstrates that DNA-AgNCs can electrocatalyze the reduction of H_2O_2. By referring to the literature [29], the corresponding mechanism for electrocatalytic behavior of DNA-AgNCs toward H_2O_2 can be deduced as follows:

$$2\ \text{DNA-Ag(0)NCs} + H_2O_2 \rightarrow 2\ \text{DNA-[Ag(1)-OH)]NCs} \quad (1)$$

$$2\ \text{DNA-[Ag(1)-OH)]NCs} + 2e^- + 2H^+ \rightarrow 2\ \text{DNA-Ag(0)NCs} + H_2O \quad (2)$$

where in, DNA-Ag(0)NCs reacts with H_2O_2 (step 1) to produce argentous hydroxide existing in DNA-[Ag(1)-OH)]NCs. Subsequently, DNA-[Ag(1)-OH)]NCs are electrochemically reduced in step 2 to regenerate DNA-Ag(0)NCs.

The electrocatalysis of (DNA-AgNCs)/graphene/GC electrode toward H_2O_2 was investigated, as shown in Fig. 4D. It can be noted that the reduction peak potential of H_2O_2 shifted positively to −0.6 V and the reduction current of H_2O_2 greatly increased. This elucidates that the obtained DNA-AgNCs/graphene composite film has excellent electrocatalytic activity toward the reduction of hydrogen peroxide. This can be ascribed to not only the electrocatalytic activity of graphene, but also to the fact that more DNA-AgNCs can be easily immobilized on the surface of graphene-modified electrode by π–π stacking because graphene has the advantage of large surface area to volume ratio. Therefore, it can be concluded that the higher electrocatalytic activity of the DNA-AgNCs/graphene composite film is due to the synergic effect of graphene and DNA-AgNCs. DNA-AgNCs/graphene composite film was chosen to fabricate the modified electrode, and used for the sensitive electrochemical detection of hydrogen peroxide.

3.3. Optimization of pH and applied potential

The (DNA-AgNCs)/graphene/GC electrode was used to determinate H_2O_2, and pH value of buffer solution and applied potential were optimized. Fig. 5A shows that the effect of pH on the voltammetric behaviors of H_2O_2 reduction at (DNA-AgNCs)/graphene/GC electrode in 0.1 M N_2 saturated PBS in the presence of 2 mM H_2O_2. It was noted that the reduction currents of H_2O_2 gradually increased with pH values increasing from 4.0 to 7.0. When the pH value was higher than 7.0, the reduction currents decreased. This may be ascribed to the fact that when AgNCs were synthesized by using DNA as template, cytosine in DNA would be partially protonated at the lower pH value [35], leading to

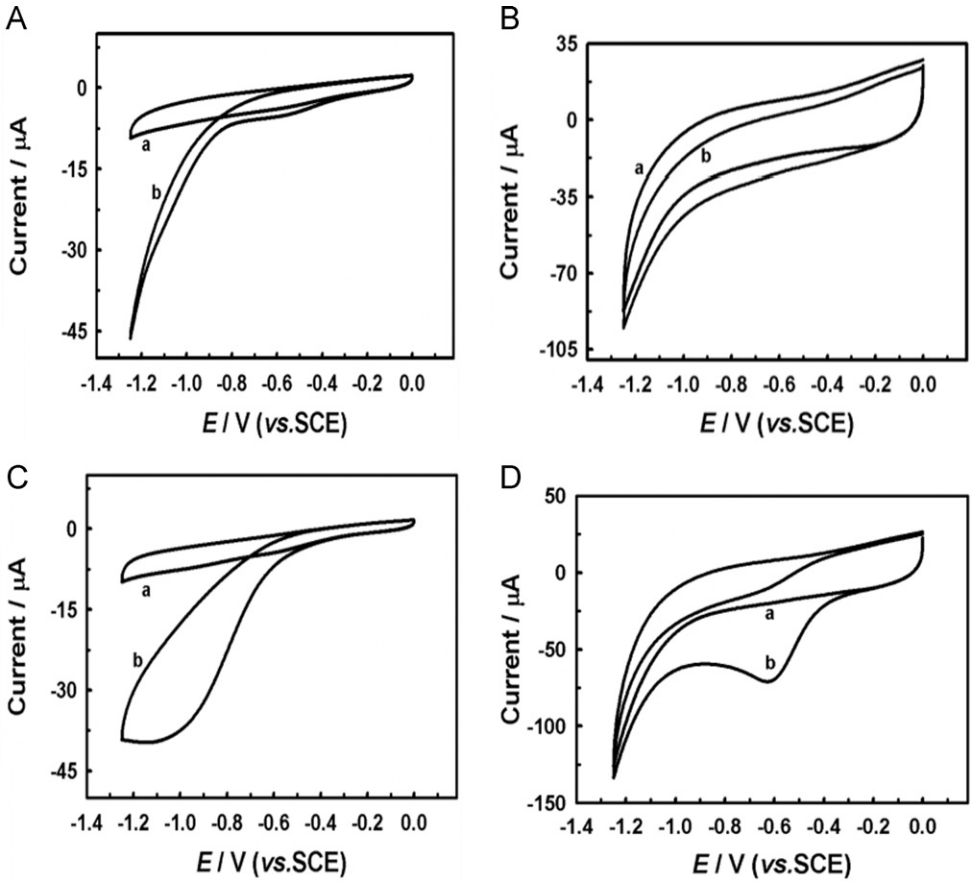

Fig. 4. Cyclic voltammograms of the bare GCE (A), graphene/GCE (B), (DNA-AgNCs)/GCE (C) and (DNA-AgNCs)/graphene/GCE (D) in N_2 saturated PBS (0.1 M, pH=7.0) without (a) and with (b) 2 mM H_2O_2. Scan rate: 50 mV s^{-1}.

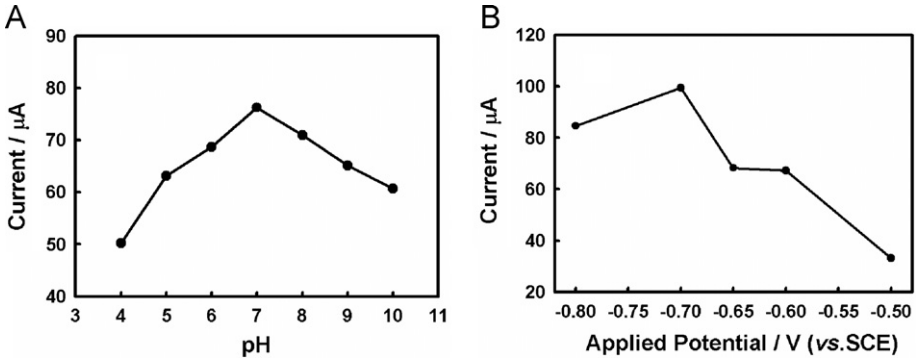

Fig. 5. Effect of pH (A) and applied potential (B) on the electrocatalytic reduction peak current of 2.0 mM H_2O_2 in N_2 saturated PBS (0.1 M, pH=7.0). Scan rate: 50 mV s^{-1}.

unstable DNA-AgNCs. Therefore, pH 7.0 was selected as the optimal pH value for the detection of H_2O_2.

To get a high sensitivity for H_2O_2 detection and prevent interference from other electrochemical interfering species, the choice of applied potentials is very important. Fig. 5B depicts the influence of different applied potential on the amperometric response of (DNA-AgNCs)/graphene/GC electrode toward 2 mM H_2O_2 in N_2 saturated PBS (0.1 M, pH 7.0). It is clear that the current response of H_2O_2 is very obvious at the potential of −0.7 V. In addition, in real samples, ascorbic acid (AA), uric acid (UA), dopamine (DA), glutathione (GSH), and L-cysteine (Cys) often coexist and affect the current response of H_2O_2. Therefore, the influence of coexisting species on the detection of H_2O_2 at the applied potential of –0.7 V was investigated, as depicted in Fig. 6. An obvious current response can be observed upon the addition of 0.05 mM H_2O_2, whereas negligible interferences can be seen after injection of 0.1 mM AA, UA, DA, GSH, and L-Cys. Therefore, it further demonstrates that it is reasonable to choose −0.7 V as the applied potential for the selective and sensitive detection of hydrogen peroxide at the (DNA-AgNCs)/graphene/GC electrode.

3.4. Amperometric detection of H_2O_2 at the (DNA-AgNCs)/graphene/GC electrode

Under optimal conditions, the typical amperometric responses to successive additions of H_2O_2 at the bare GC electrode (a), graphene/GC electrode (b), and (DNA-AgNCs)/graphene/GC electrode (c) were studied and the corresponding results were shown in Fig. 7A. There is no obvious current signal after injection of H_2O_2 at the bare GCE and graphene/GCE. From Fig. 7A(c), it can be

seen that the current response of H_2O_2 at the (DNA-AgNCs)/graphene/GCE increased obviously and the maximum current response was obtained within 3 s, which demonstrates that DNA-AgNCs/graphene composite film has higher catalytic ability towards H_2O_2 reduction and the response time is very short. These results are consistent with those in Fig. 4.

Fig. 7B is the corresponding calibration curve of the (DNA-AgNCs)/graphene/GCE for sensing H_2O_2. The linear detection range can be obtained from 15 μM to 23 mM, and the regession equation is $i\,(\mu A) = -11.7864\,(\mu A) - 40.4576c\,(\mu A\ mM^{-1})$ with a correlation coefficient of 0.9983, and the detection limit is estimated to be 3 μM ($S/N=3$). This demonstrates that the sensor for hydrogen peroxide possesses higher sensitivity. Moreover, the relative standard deviation (RSD) of the current–time response to 1 mM H_2O_2 is 3.27% for seven successive determinations, which suggests that the repeatability of the DNA-AgNCs/graphene composite modified electrode is excellent. The electrochemical performance of this sensor for H_2O_2 is comparable or better than those sensors based on AgNPs or electrodes modified with other materials , as shown in Table 1. Therefore, it can be concluded that the sensor based on DNA-AgNCs/graphene modified electrode has many merits, such as higher sensitivity, wider linear range, lower detection limit, and lower applied potential.

3.5. Real sample analysis

The real analytical application of the (DNA-AgNCs)/graphene/GCE was evaluated by detecting H_2O_2 added in water samples (from Xiangjiang River). The recovery is evaluated by comparing the analytical responses of H_2O_2 obtained from the spiked water sample with those of the standard solution of same concentration, as shown in Table 2. The values obtained by amperometric technique are very close to those concentrations of H_2O_2 that are practically added, which suggests that the enzymeless hydrogen peroxide sensor based on DNA-AgNCs/graphene modified electrode can be used to detect H_2O_2 in real samples.

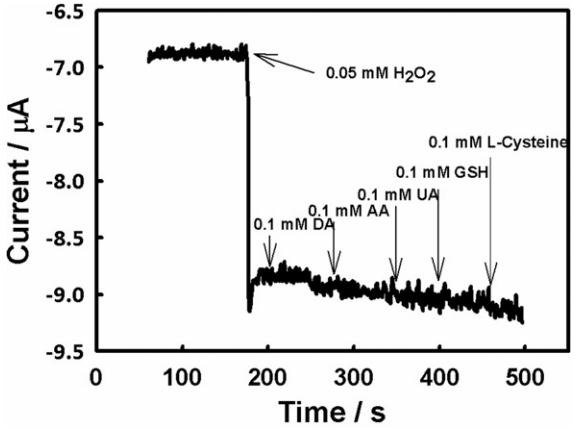

Fig. 6. Amperometric response plot at (DNA-AgNCs)/graphene/GCE in N_2 saturated PBS (0.1 M, pH=7.0) with the addition of 0.05 mM H_2O_2, 0.1 mM AA, 0.1 mM UA, 0.1 mM DA, 0.1 mM GSH, and 0.1 mM L-Cys.

4. Conclusion

In this work, a novel, simple and enzymeless electrochemical hydrogen peroxide sensor has been constructed by immobilizing DNA-AgNCs on the surface of graphene/GCE through π–π conjugation. It was found that the (DNA-AgNCs)/graphene/GCE showed enhanced electro-catalysis toward hydrogen peroxide. This ascribed to the synergic effect of DNA-AgNCs and graphene composite film, which is the remarkable electrocatalytic activity of DNA-AgNCs toward H_2O_2, and the higher conductivity, more edge plane sites and large surface area to volume ratio of graphene. Furthermore, the present sensor for hydrogen peroxide

Table 1
Comparison of the sensor based on DNA-AgNCs/graphene modified electrode in our work with the reported sensors based on AgNPs or electrode modified with other materials.

Type of electrode	Detection limit (μM)	Linear range (mM)	Reference
AgNPs–A/F–SiO_2/GO[a]–GCE	4	0.1–260	[15]
n-Ag/GCE	27	0.05–6.5	[36]
PVP[b]–AgNWs	2.3	0.02–3.6	[16]
PBNPs[c]/Nafion	1	2.1×10^{-3}–0.14	[37]
{PAH[d]/PB@Au[e]}$_5$	–	0.01–6.0	[38]
(DNA-AgNCs)/graphene/GCE	3	0.015–23	This work

[a] Adsorption/functional-SiO_2/graphene oxide.
[b] Poly pyrrolidone.
[c] Prussian blue nanoparticle.
[d] Poly(allylamine hydrochloride).
[e] The Prussian blue shell/Au core hybrid composite.

Table 2
Experimental results for the detection of H_2O_2 in water sample.

Water sample	H_2O_2 added (mM)	Found (mM)	Recovery (%)
1	2.0	1.93	96.5
2	3.0	3.05	101.7
3	4.5	4.61	102.4

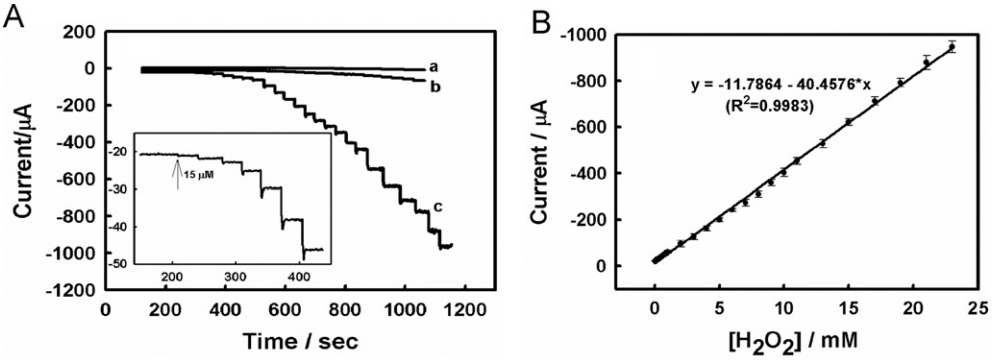

Fig. 7. (A) Amperometric response to different concentrations of H_2O_2 at the bare GCE (a), graphene/GCE (b), and (DNA-AgNCs)/graphene/GCE (c) in N_2 saturated PBS (0.1 M, pH=7.0). (B) Calibration plot obtained from A(c).

displayed a wide linear range, a fast current response, a low detection limit, excellent sensitivity with satisfactory repeatability and exhibited good resistance to interference. These excellent performances indicate that the (DNA-AgNCs)/graphene/GC electrode has a potential application for detecting H_2O_2 in biological systems or food processing systems.

Acknowledgment

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