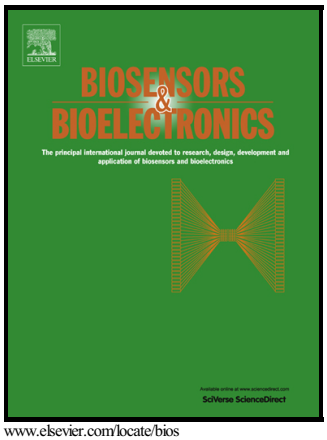

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Amplified electrochemical hydrogen peroxide reduction based on Hemin/G-quadruplex DNAzyme as electrocatalyst at gold particles modified heated copper disk electrode

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Abstract

A new gold particles modified heated copper disk electrode (Au-HCuDE) with direct current was fabricated. The hemin/G-quadruplex horseradish peroxidase-mimicking DNAzyme (HRP-DNAzyme) was self-assembled on the heated electrode and resulted in a new biosensor denoted as HRP-DNAzyme/Au-HCuDE. By controlling the temperature of the surface of the electrode, the dramatic temperature effect on the electrocatalytic reduction of H_2O_2 at HRP-DNAzyme/Au-HCuDE sensing platform was demonstrated. This electrocatalytic activity of HRP-DNAzyme was enhanced with electrode temperature elevated. This method was thus preliminarily used to develop an electrochemical biosensor for highly sensitive detection of H_2O_2. A detection limit of 1.6×10^{-7} M could be obtained (S/N = 3) with an electrode temperature of 50^{o}C, which was more than one magnitude lower than that at electrode temperature of 0^{o}C. This heated electrochemical biosensor shows many merits such as easy fabrication and simple heating equipment, low cost, high thermal stability, and high sensitivity and good reproducibility.

Keyword: Gold particles modified heated copper disk electrode; Hemin/G-quadruplex DNAzyme; Horseradish peroxidase-mimicking DNAzyme; Electrocatalysis; H_2O_2.

1. Introduction

In the early 1990s, electrically heated metal wire microelectrodes were invented (Gründler et al. 1993) and have been widely used in electroanalytical chemistry (Flechsig et al. 2005; Flechsig and Walter 2012; Gründler and Flechsig 2006; Lau et al. 2005; Wei et al. 2009) due to the enhanced convection and the accelerated redox reaction rates with elevated electrode temperature. Various heated electrodes have been designed, such as heated carbon paste electrodes (Wang 2000), heated graphite cylinder electrodes (Sun et al. 2007; Wu et al. 2007), and heated screen-printed carbon electrodes (Wei et al. 2008).

The above heated electrodes were symmetrically designed and heated by alternative current in order to eliminate the interference with the electrochemical signal from the heating current. Alternatively, indirectly electrically heated gold disk electrodes based on low temperature co-fired ceramic technology were introduced and used to enzyme-based sensors (Lau et al. 2004; Tseng et al. 2009) and DNA biosensor (Walter et al. 2013). The heating current would not interfere with the electrochemical signal because of the separation between heating and electrochemical circuits. But the fabrication of this heated electrode was complicated. Later, an indirectly heated copper microdisk electrode was fabricated (Chen et al. 2010), but this electrode was only suitable for determination of very limited kinds of substances such as polyhydroxy compounds. Likewise, indirectly heated gold disk electrode (Wu et al. 2010) and heated glassy carbon disk electrode (Zhong et al. 2010) were presented, but they were both expensive. Recently, very cheap heated pencil lead disk electrode was designed in our group (Wu et al. 2013), but it was not very suitable for DNA self-assembling.

Deoxyribozymes (DNAzymes), a kind of functional nucleic acids isolated by systematic evolution of ligands by exponential enrichment (SELEX) process (Ellington and Szostak 1990; Tuerk and Gold 1990), are single-stranded DNA that exhibit specific catalytic properties. DNAzymes have been widely used to catalyze various reactions including DNA self-modification (Li et al. 2000), and RNA cleavage (Santoro and Joyce 1997). Compared with conventional protein enzymes, DNAzymes are stable under

ambient and even elevated temperature, and easier to synthesize and modify (Willner et al. 2008). Furthermore, the convenience of encoding DNAzymes sequence into the specific recognition region enables DNAzymes ideal candidates for constructing biosensing platforms (Zhao et al. 2013).

The hemin/G-quadruplex horseradish peroxidase-mimicking DNAzyme (HRP-DNAzyme) exhibiting peroxidase-like activity (Travascio et al. 1999; Travascio et al. 1998), one important type of DNAzymes, has received considerable attention in recent years. G-quadruplex DNA is self-assembled by G-rich DNA sequence. The HRP-DNAzyme is formed by coordination between Fe ion in hemin and π-π conjugate system in G-quadruplex DNA. Hemin is the catalytic activity center, and the G-quadruplex DNA serves as the micro-environment which is in favor of the catalytic action of hemin. HRP-DNAzyme can effectively catalyze H_2O_2-mediated oxidation of 2,2′-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) (Huang et al. 2013; Li et al. 2009), 3,3′,5,5′-tetramethylbenzidine sulfate (TMB) (Du et al. 2011; Zhu et al. 2010), luminal (Niazov et al. 2004; Pavlov et al. 2004), or thiamine (Zhang et al. 2011), accompanied by color change, chemiluminescent or fluorescent emission. So HRP-DNAzyme can be employed to construct colorimetric, chemiluminescent, or fluorescent sensing platform for detection of important biomolecules (Li et al. 2007; Xiao et al. 2004). But only recently, the bioelectrocatalytic properties of the HRP-DNAzyme were investigated (Pelossof et al. 2010), and the bioelectrocatalytic functions toward the electrochemical reduction of H_2O_2 was demonstrated. The use of HRP-DNAzyme as electrocatalytic label for the assembly of various biosensors was also introduced (Zhang et al. 2012; Zhang et al. 2013). However, the electrocatalytic properties of the HRP-DNAzyme at heated electrode have not been explored.

In this paper, a new indirectly heated gold particle modified copper disk heated electrode (Au-HCuDE) with direct current was fabricated. The HRP-DNAzyme with bioelectrocatalytic functions towards reduction of H_2O_2 was self-assembled on this heated electrode by Au-S interaction and led to a new biosensor named as HRP-DNAzyme/Au-HCuDE. By elevating the surface temperature of the electrode, the dramatic temperature effect on this electrocatalytic reduction of H_2O_2 was demonstrated. The detection limit of H_2O_2 at HRP-DNAzyme/Au-HCuDE with elevated electrode temperature was greatly lowered. This

heated electrochemical biosensor shows many merits such as easy fabrication and simple heating equipments, low cost, high thermal stability, high sensitivity and good reproducibility.

2. Experimental

2.1. Chemicals and apparatus

Cu enameled wire (100 and 600 μm in diameter). 6-mercapto-1-hexanol (MCH), hemin, 4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), hexaammineruthenium (III) chloride ($[Ru(NH_3)_6]^{3+}$, RuHex), and tris(2-carboxyethyl) phosphine hydrochloride (TCEP), Tri(Hydroxymethyl) Amino Methane Hydrochloride (Tris-HCl) were purchased from Sigma-Aldrich. Chloroauric Acid ($HAuCl_4$) was from Sinopharm Chemical Reagent Co. Ltd. The other chemicals were of analytical grade and used without further purification. All solutions were prepared with doubly distilled water (Millipore Milli-Q system, USA). The stock solution of hemin (2 mM) was prepared with dimethylsulfoxide (DMSO) and stored in the dark at − 20°C. A thiolated DNA oligonucleotide (SH-ssDNA) that includes the G-rich sequence of the HRP-mimicking DNAzyme was purchased from Sangon Inc. (Shanghai, China), and the sequence was: 5′-HS-$(CH_2)_6$-TTT-GGG-TAGGG-CGGGTTGGG-3′. The buffers involved in this work are as follows: DNA immobilization buffer solution (I-buffer, 10 mM HEPES, 1 mM TCEP, pH 7.2). Note that TCEP was employed to cleave disulfides. Buffer solution for electrochemical experiments (E-buffer, 10 mM HEPES, 50 mM KCl, pH 7.2).

The heating current was provided by a direct current power supplier (Zaoxin DC Power Supply RXN-303A, Shenzhen Zaoxin Electronics Co. Ltd., China). Electrochemical experiments were performed with CHI660D (CH Instruments, Inc., USA). An electrochemical cell with conventional three-electrode system was used, a modified Au-HCuDE as working electrode, a platinum wire as counter electrode and an Ag/AgCl electrode as reference electrode. Field emission scanning electron microscopy (FSEM) measurements were carried out on a Nano SEM 232 scanning electron microscope (American FEI Company).

2.2. Preparation of Au-HCuDE

Preparation of the heated copper disk electrode (HCuDE) was similar to the heated copper microdisk electrode (HCME) (Chen et al. 2010). In brief, one Cu enameled wire (600 μm in diameter) was wound by a thinner double parallel Cu enameled wire (100 μm in diameter) as

a heater. Then the electrode was inserted into a plastic tube, which was further sealed with epoxy resin. The electrode was successively polished with 500-mesh and 2000-mesh sand papers and alumina (0.3 μm and 0.05 μm in diameter) suspensions, washed with water and ethanol, respectively, and dried with nitrogen.

Then Ni film was deposited on HCuDE by chronopotentiometry applying a current of 1.314×10^{-5} A for 600 s in $NiSO_4$ solution at 50 ~ 60 °C with a stirring speed of 1000 r min^{-1}. Finallly AuNPs were deposited on the Ni film covered HCuDE by amperometry applying a potential of − 0.6 V for 600 s in 3.0 mM $HAuCl_4$ solution. The obtained electrode was named as Au- HCuDE.

2.3. Fabrication of the HRP-DNAzyme modified Au-HCuDE

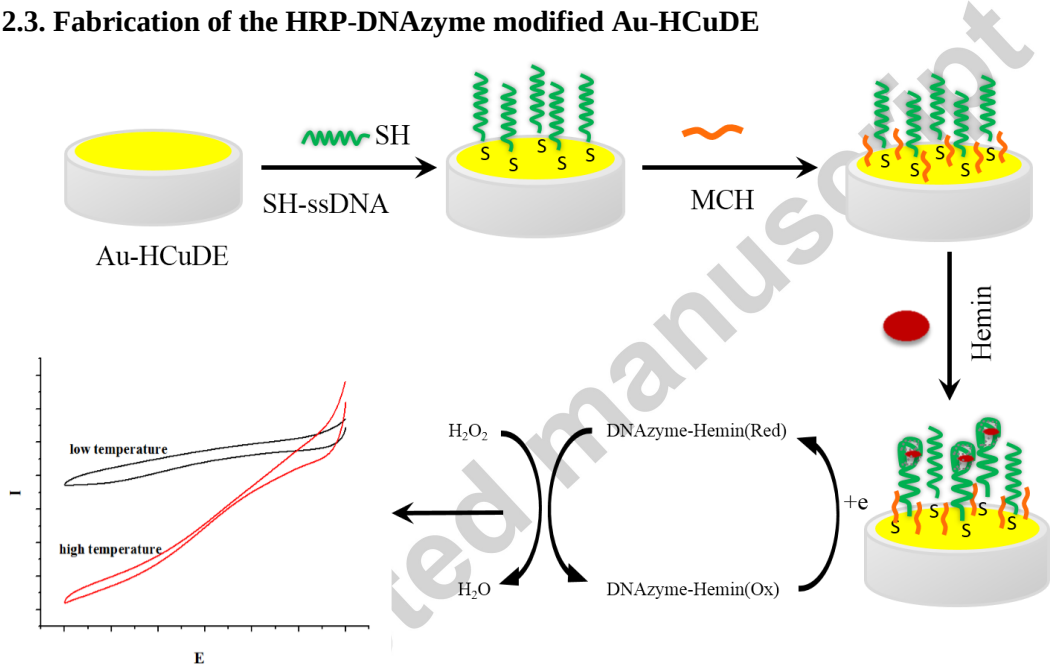

Fig.1. The scheme of constructing HRP-DNAzyme/Au-HCuDE biosensing platform for electrocatalytic reduction of H_2O_2 with elevated electrode temperature.

The SH-ssDNA was diluted with 10 mM HEPES buffer (with 150 mM NaCl, 50 mM KCl, pH 7.2). 5 μL DNA immobilization buffer containing 1 μM SH-ssDNA was dropped on the surface of Au-HCuDE and incubated for 14 h in a humidity chamber, the SH-ssDNA was immobilized on the electrode surface via Au-S bonding. The electrode was then thoroughly rinsed with ultra pure water and dried under a stream of nitrogen gas, followed by surface blocking with MCH (2 mM) for 1 h to remove nonspecific DNA adsorption. Then, the electrode surface was again rinsed thoroughly and dried with nitrogen gas. The resulted

electrode was defined as MCH/SH-ssDNA/Au-HCuDE.

The MCH/SH-ssDNA/Au-HCuDE was incubated in 4 mL 10 mM HEPES (pH 7.2) containing 50 mM KCl for 1 h at room temperature to allow an appropriate folding structure. Subsequently, 40 μL 2 mM hemin was added to the solutions and the electrode was allowed to incubate for 1 h at room temperature. Under these conditions, hemin/G-quardruplex HRP-mimicking DNAzyme was assembled on the surface of the electrode, this electrode was defined as HRP-DNAzyme/Au-HCuDE and can be used to investigate the temperature effect of H_2O_2 electrochemical sensing. The scheme of H_2O_2 biosensor fabrication procedure based on HRP-DNAzyme/Au-HCuDE is shown in Fig. 1.

2.4. Procedure for electrochemical measurement

The resulting electrode was placed in a glass cell with 10 mL HEPES buffer solution containing 50 mM KCl, (10 mM, pH 7.2) and a specific concentration of H_2O_2 for electrochemical measurements. Before the measurements, the HEPES buffer solution was bubbled thoroughly with nitrogen for 15 min. Cyclic voltammograms (CVs) were recorded from − 0.6 to 0 V with a scan rate of 10 mV s^{-1}, and the current responses at − 0.6 V were selected as the analytical signals. Amperometric i–t curve measurement was performed by applying a potential of − 0.4 V. In the case of heated measurements, the DC was turned on during electrochemical measurement procedure.

3. Results and discussion

3.1. Temperature calibration and FSEM characterization of Au-HCuDE

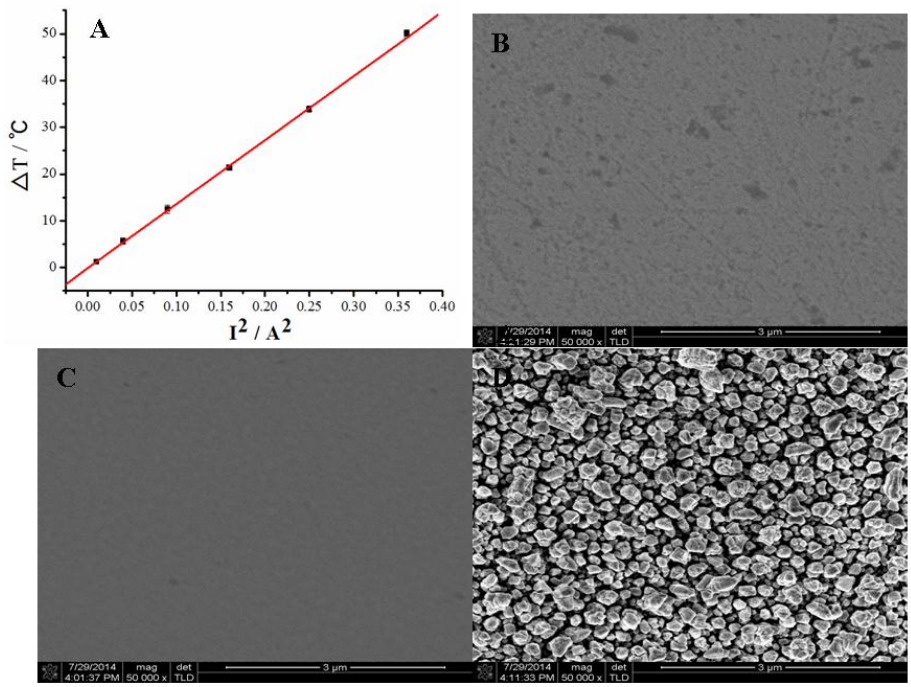

Fig.2. Relationship between the temperature rise of HCuDE and the square of heating current (A), and FSEM images of HCuDE (B), electrodeposited Ni covered HCuDE (C), and Au-HCuDE (D). Accelerating voltage, 15 kV.

Temperature calibration of the surface of the electrode was according to the previous literature (Chen et al. 2010). The results (Fig.2A) show that the temperature rise over room temperature of the electrode is linear with the square of the heating current.

The morphology of the preparation procedure for Au-HCuDE was also displayed in Fig.2 by FSEM. As can be seen, there were obvious scotches at the surface of the HCuDE after mechanical polishing (Fig.2B). However, a smooth and dense Ni layer at the surface of the electrode was observed after constant current electro-deposition of Ni onto the HCuDE surface (Fig.2C), suggesting the strong binding force between metal Ni and Cu because of their similar lattice structure. Then, after potentiostatic electro-deposition of Au on the deposited Ni modified HCuDE, the surface of the Ni layer was covered with high density of Au nanoparticles and/or microparticles (Fig.2D), indicating successful modification of Au particles onto the HCuDE due to the good metal binding ability of Ni.

3.2. Cyclic voltammetry and Chronocoulometry studies at MCH/SH-ssDNA/Au-HCuDE

In order to evaluate if the prepared Au-HCuDE can be used to effectively assemble the thiolated ss-DNA, the cyclic voltammetry and chronocoulometry experiments at SH-ssDNA and MCH mixed SAM surface (MCH/SH-ssDNA/Au-HCuDE) in 50 μM RuHex solution were performed. Before electrochemical experiments, the electrode was immersed in the solution for 1 min for adsorption equilibrium. The results were shown in Fig.S1. As can be seen from Fig.S1(A), without RuHex in 10 mM Tris-HCl buffer solution (pH 7.2) (curve a), no peak appeared. But one pair of peaks at near − 0.3 V with the peak separation being close to zero were observed (curve b), which were characteristic of a surface-confined process (Lao et al. 2005). The pair of peaks were attributed to RuHex electrostatic bound to the anionic phosphate backbones of SH-ssDNA in solutions with low ionic strength, which demonstrated that the SH-ssDNA was successfully self-assembled onto the surface of the Au-HCuDE. Furthermore, from Fig.S1(B), the surface densities of the self-assembled SH-ssDNA can then be calculated as 7.45×10^{13} molecules cm^{-2} through the redox charges of RuHex according to the chronocoulometry method firstly proposed by Tarlov group (Steel et al. 1998).

3.3. The effect of electrode temperature on the electrocatalytic reduction of H_2O_2 at HRP-DNAzyme/Au-HCuDE

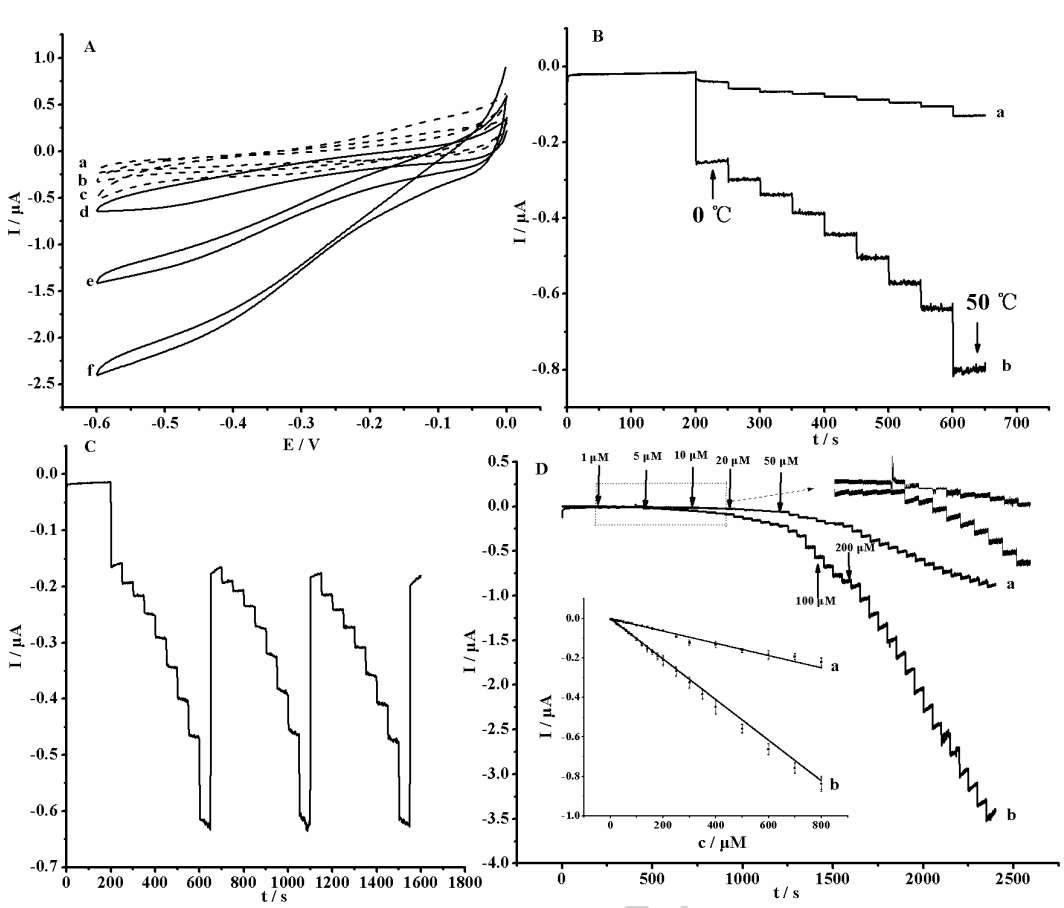

Fig.3. (A) CVs with a scan rate of 10 mV s^{-1} in 10 mM HEPES buffer solution containing 50 mM KCl (pH 7.2) in the absence (a-c) and presence (d-f) of 1 mM H_2O_2 at HRP-DNAzyme/Au-HCuDE with different electrode temperature, (a) and (d) 0 ^oC, (b) and (e) 30 ^oC, (c) and (f) 50 ^oC. (B) The amperometric i-t curves by applying a potential of − 0.4 V in HEPES buffer solution with 0.5 mM H_2O_2 at MCH/SH-ssDNA/Au-HCuDE (a) and HRP-DNAzyme/Au-HCuDE (b) with electrode temperature as 0, 10, 15, 20, 25, 30, 35, 40, and 50 ^oC, respectively. H_2O_2 was injected each 50 s. (C) The amperometric curve for consecutive three cycling in HEPES buffer solution containing 0.5 mM H_2O_2 at HRP-DNAzyme/Au-HCuDE with electrode temperature increasingly rise from 0^oC to 50^oC as in (B). (D) The typical steady-state electrocatalytic reduction current vs. time response at HRP-DNAzyme/Au-HCuDE with electrode temperature of 0^oC (a) and 50^oC (b) by successive addition specific concentration of H_2O_2 into magnetically stirred 10 mM HEPES buffer solution (50 mM KCl, pH 7.2) with an applied potential of – 0.4 V. Inset: The corresponding calibration plots.

An electrode temperature dependent biosensing platform based on hemin/G-quadruplex HRP-Mimicking DNAzyme for electrocatalytic reduction of H_2O_2

was developed. The procedure was in detail displayed in Fig.1. A thiolated nucleic acid (SH-ssDNA) that includes the G-rich sequence of the HRP-Mimicking DNAzyme was self-assembled on the surface of the Au-HCuDE. MCH was used to displace the unspecific adsorbed SH-ssDNA. The HRP-Mimicking DNAzyme was formed on the electrode surface in the presence of hemin. The active center Hemin (Red) in the HRP-DNAzyme could reduce H_2O_2 to produce H_2O, at the same time Hemin (Red) was oxidized to Hemin (Ox), which then was reduced to Hemin (Red) electrochemically.The electrocatalytic reduction current of H_2O_2 at the resulting heated electrode HRP-DNAzyme/Au-HCuDE was dependent on the temperature of the electrode surface.

The dramatic temperature effect on the electrocatalytic reduction of H_2O_2 by HRP-Mimicking DNAzyme at HRP-DNAzyme/Au-HCuDE was investigated in detail, the results were shown in Fig.3. Fig. 3A displays the CVs in HEPES buffer in the absence (a-c) and presence (d-f) of 1 mM H_2O_2 at HRP-DNAzyme/Au-HCuDE with different electrode temperature. With an electrode temperature of 0 ^oC , an obvious electrocatalytic reductive current for H_2O_2 was observed in the presence of 1 mM H_2O_2 (d) compared with that without H_2O_2 (a), indicating the catalytic activity of the HRP-DNAzyme immobilized at Au-HCuDE. The catalytic reductive signal for H_2O_2 was significantly enhanced with increasing the temperature of the electrode surface from 0 ^oC (d) to 30 ^oC (e) and 50 ^oC (f), while the background signal (without H_2O_2) was increased little with rising the electrode temperature from 0 ^oC (a) to 30 ^oC (b) and 50 ^oC (c). This demonstrated the positive temperature effect on the electrocatalytic reduction of H_2O_2. This was perhaps mainly contributed to the fact that the catalytic activity of the HRP-DNAzyme was closely related to the temperature. In a suitable temperature range, the catalytic activity of the HRP-DNAzyme was promoted with increasing the temperature of the surface of the electrode.

Furthermore, this temperature effect was also verified by using amperometric technique. Fig.3B shows the amperometric response curves in HEPES buffer solution containing 0.5 mM H_2O_2 with elevating the electrode temperature increasingly from 0 to 50 ^oC at MCH/SH-ssDNA/Au-HCuDE (a) and HRP-DNAzyme/Au-HCuDE (b). As can be seen, the catalytic reduction current response of H_2O_2 at HRP-DNAzyme/Au-HCuDE was

significantly increased with electrode temperature rise (b). However, without hemin, the HRP-Mimicking DNAzyme could not be formed at the electrode surface, so the reductive current of H_2O_2 was increased much weakly with the same temperature rise (a).

In addition, the stability and reproducibility of the temperature effect on the electrocatalytic reduction of H_2O_2 by HRP-Mimicking DNAzyme at HRP-DNAzyme/Au-HCuDE was tested. Fig.3C displays the amperometric curve in 0.5 mM H_2O_2 solution with electrode temperature rise from 0 to 50 ^oC as in Fig.3B for consecutive three cycling at HRP-DNAzyme/Au-HCuDE. As can be seen, the thermal stability and reproducibility of HRP-DNAzyme/Au-HCuDE for H_2O_2 sensing are excellent. Actually, from 0 to 50°C, the RSD is 5.09, 4.49, 6.7, 4.9, 5.5, 5.0, 2.51, 1.23, and 0.98 %, respectively. But the electrode would be unstable and even destroyed if the temperature surpasses 50°C due to the limitation of electrode fabrication technique at present, so an electrode temperature of 50°C was selected as the highest temperature in this work.

3.4 Analytical performance for H_2O_2 measurement at HRP-DNAzyme/Au-HCuDE

The HRP-DNAzyme/Au-HCuDE was further evaluated for amperometric detection of H_2O_2. Fig. 3D displays the typical steady-state electrocatalytic reduction current of H_2O_2 vs. time response at HRP-DNAzyme/Au-HCuDE with an electrode temperature of 0 ^oC (a) and 50 ^oC (b) by successive addition of H_2O_2 into a magnetically stirred 10 mM HEPES buffer solution (50 mM KCl, pH 7.2) with an applied potential of – 0.4 V. As shown, upon successive injection of H_2O_2, a well-defined response was observed. The catalytic current was promptly increased for each addition of H_2O_2 within a response time less than 2 s. These demonstrated the efficient and stable catalytic ability of the HRP-DNAzyme/Au-HCuDE. As can be seen from the calibration plot (See Method S1 for how to obtain it) in the inset of Fig.3D, with electrode temperature 0 ^oC, the catalytic current was found to be proportional to H_2O_2 concentration in the range of 5.0×10^{-6} to 8.0×10^{-4} M, the regression equation was I (μA) = 0.0003 c (μM) – 0.0027 with $r^2 = 0.9983$, the limit of detection was 3.8×10^{-6} mol L^{-1} (S/N = 3). While with electrode temperature 50^{o}C, there was a linear relationship when the H_2O_2 concentration was changed from 1.0×10^{-6} to 8×10^{-4} M, the regression equation was I (μA) = 0.0011 c (μM) + 0.0007 with $r^2 = 0.9989$, the limit of detection was 1.6×10^{-7} mol L^{-1}

(S/N = 3). With electrode temperature 50 ^{o}C, the sensitivity was obvious enhanced and the detection limit was more than one magnitude lower than that with electrode temperature 0 ^{o}C.

The reproducibility of the biosensor was examined. The electrode could be regenerated by polishing and suitable washing. With five different electrodes fabricated independently by the same procedure, a relative standard deviation (RSD) of 4.7 % toward amperometric measurements of 50 μM H_2O_2 could be obtained. With a single electrode, a set of seven different amperometric measurements for 50 μM H_2O_2 yielded RSD of 2.3 %. These indicate the good reproducibility of the biosensors.

3.5 Selectivity and water sample analysis

The interferential study of the biosensor was realized by comparing the amperometric responses of 0.5 mM H_2O_2 solution before and after adding 1 mM potential interferential substances at HRP-DNAzyme/Au-HCuDE with electrode temperature 35 ^{o}C. The results show that glucose, sucrose, uric acid and L-tyrosine did not interfere with the determination of H_2O_2 (the value of the current change below 5%, data not shown), suggesting good selectivity.

The proposed method was evaluated by analyzing real tap water samples in order to further demonstrate its practicality. The water samples were treated with 0.45 μm filter and standard addition method was applied to determine H_2O_2. The results are displayed in Table S1. The average recovery of 102.9 % revealed that this method was precise and accurate.

4. Conclusion

In this work, a new gold particles modified heated copper disk electrode (Au-HCuDE) was developed. For the first time, the dramatic temperature effect of the electrocatalytic activity of HRP-DNAzyme for H_2O_2 reduction was demonstrated by using this heated electrode platform. Because such HRP-DNAzyme can be used as electrocatalytic signal labels for biosensors, based on this, various temperature-controllable electrochemical biosensors such as DNA sensors and aptasensors will be promisingly developed. The relative research are carrying out in our lab.

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Highlights

- A new indirectly heated gold nanoparticles modified heated copper disk electrode (Au-HCuDE) with direct current was fabricated.
- The hemin/G-quadruplex horseradish peroxidase-mimicking DNAzyme was for the first time self-assembled on heated electrode and resulted in a new temperature-controllable electrochemical biosensor denoted as HRP-DNAzyme/Au-HCuDE.
- By elevating the temperature of the surface of the electrode, the dramatic temperature effect on enhanced electrocatalytic reduction of H_2O_2 was demonstrated at HRP-DNAzyme/Au-HCuDE.
- This method was used to highly sensitive detection of H_2O_2 with detection limit lowered more than one magnitude with electrode temperature rise 50 ^{o}C.
- Using HRP-DNAzyme as electrocatalytic label, this method is promising to construct other biosensors such as DNA sensors and aptasensors based on heated electrode.