Electronic Supplementary Material (ESI) for Analytical Methods

Electronic Supplementary Information

Electrochemistry and electrocatalysis of a nanobiocomposite film containing hematin and carbon nanotube-chitosan on poly-(acridine red) modified glassy carbon electrode

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1. The role of poly-(acridine red) and cyclic voltammogram of poly-(acridine red) in the potential window used for electropolymerisation

Repetitive cyclic voltammograms of acridine red in pH 7.4 phosphate buffer solution are shown in Fig. S1. It can be observed that the anodic and cathodic peak potentials appeared at +0.967 and −0.514 V, respectively. The anodic and cathodic peak currents increased with increasing scan number. These facts indicated that acridine red was deposited on the surface of glassy carbon electrode (GCE) by electropolymerisation method. The poly-acridine red contained more aromatic rings, in which the π bond polymer membrane structure can be formed on the GCE. The structure could enhance charge transfer and change reaction rate.

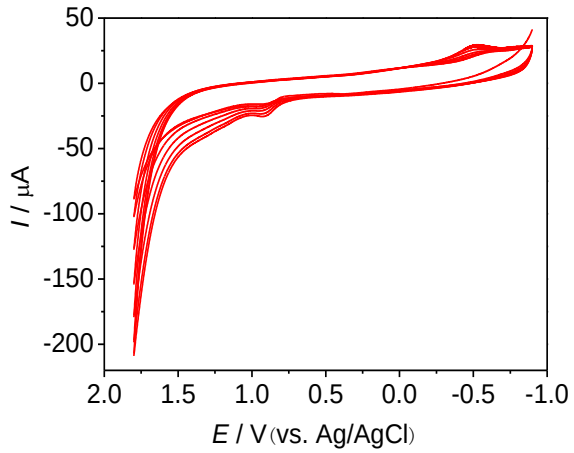

Fig. S1 Repetitive cyclic voltammograms of 1.0×10^{-2} M acridine red in pH 7.4 phosphate buffer solution. Terminal potential: +1.8 V; initial potential: –0.9 V; sensitivity: 5.0×10^{-5} A/V; scan rate: 60 mV s^{-1}; sweep circles: 7.

2. The optimum amount of hematin

The optimum amount of hematin has been investigated. In the experiment, the volume of hematin solution was served as a fixed value (0.5 mL) and the concentration of hematin was changed in the range of 1.0 to 20.0 mg mL^{-1}. It can

be seen from Fig. S2 that the peak currents increased with increasing the amount of hematin from 0.5 to 5.0 mg and then decreased from 5.0 to 10.0 mg. Therefore, 0.5 mL of 10 mg mL^{-1} of hematin solution is the optimum amount for production of the modified electrode.

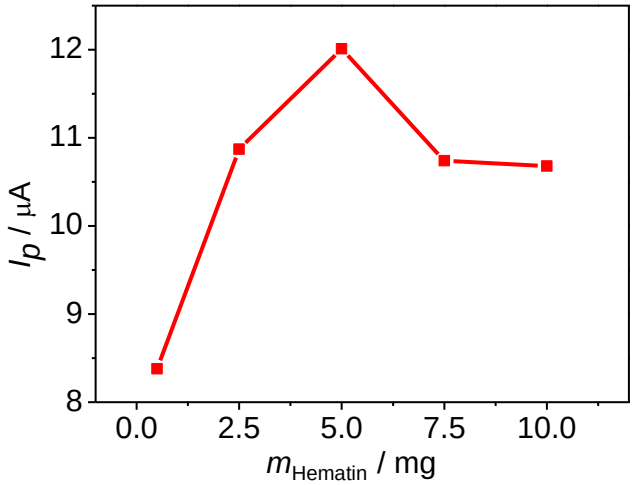

Fig. S2 The effect of different amounts of hematin on the reduction peak current at the MWCNT-CS-He/PAR-GCE in 0.1 M phosphate buffer solution (pH 7.0) containing 0.1 mM H_2O_2.

3. The ohmic resistances of different electrodes

The ohmic resistances of different electrodes are shown in Fig. S3. There was a very big semicircle domain on the bare GCE (curve a), implying very high electron transfer resistance (Ret) to the redox probe dissolved in the electrolyte solution. After poly-acridine red (PAR) was coated on the surface of the bare GCE, the semicircle domain was decreased (curve b). The semicircle domain of the He/PAR-GCE (curve c) is smaller than that of the PAR-GCE. When the MWCNT-CS-He was coated on the bare GCE, the semicircle domain was further decreased (curve d), implying very low electron transfer resistance. The semicircle of electrochemical impedance spectroscopy of the MWCNT-CS-He/PAR-GCE was smallest and nearly to zero (curve e), indicating the enhancement of the conductivity.

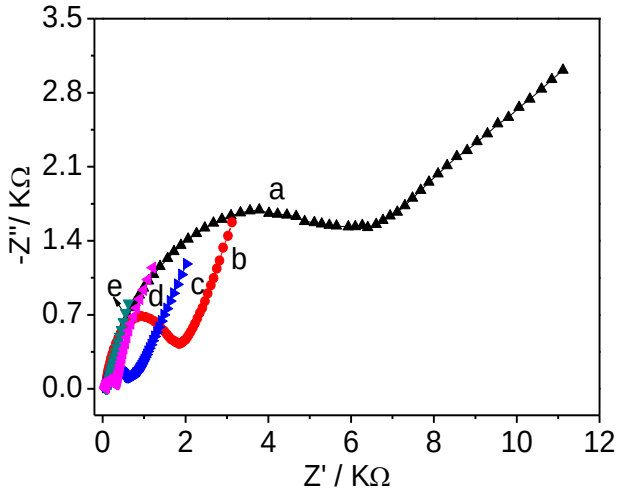

Fig. S3 The EIS measurements in 5 mM $Fe(CN)_6^{3-/4-}$ solution containing 10 mM KCl by applying an ac voltage with 5 mV amplitude in a frequency range of 0.02 to 100 kHz. (a) bare GCE, (b) PAR-GCE, (c) He/PAR-GCE , (d) MWCNT-CS-He/GCE, (e) MWCNT-CS-He/PAR-GCE

4. The effect of hydrogen peroxide for each modification step

The effect of hydrogen peroxide for each modified electrode is shown in Fig. S4. There are no obvious redox peaks at the bare GCE, PAR/GCE, and MWCNT-CS/PAR-GCE. However, obvious redox peaks can be observed at the MWCNT-CS-He/PAR-GCE. It is well known that hydrogen peroxide was reduced by the hematin Fe (III) / Fe (II) redox couple. There is no Fe (III) / Fe (II) redox couple at the bare GCE, PAR/GCE, and MWCNT-CS/PAR-GCE, illustrating that hydrogen peroxide can not be reduced at these modified electrodes. Therefore, the electrochemical response of hydrogen peroxide is due to the presence of hematin.

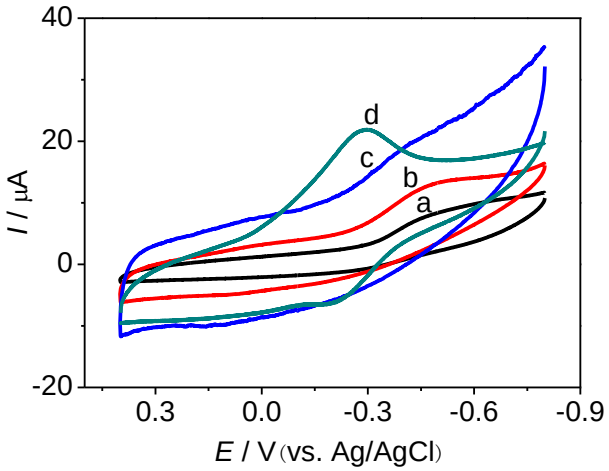

Fig. S4 Cyclic voltammograms of (a) bare GCE, (b) PAR/GCE, (c) MWNT-CS/PAR-GCE, and (d) MWCNT-CS-He/PAR-GCE in 0.1 M phosphate buffer solution (pH 7.0) containing 0.01 mM H_2O_2. Scan rate: 100 mV s^{-1}.

5. Interference studies

The interference study for this electrochemical sensor was performed with some common interfering compounds such as glucose, ascorbic acid, uric acid, and nitrite. The results are shown in Fig. S5. Addition of 5.0 μM glucose, 2.0 μM ascorbic acid, 2.0 μM uric acid, and 2.0 μM nitrite did not produce obvious change in the response current for 1.0 μM H_2O_2.

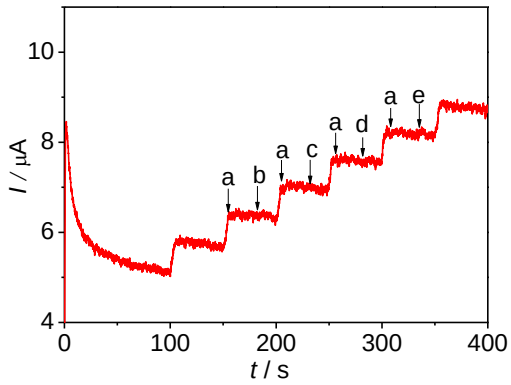

Fig. S5 Current-time curve recorded at the sensor in a 0.1 M phosphate buffer solution (pH 7.0) under stirring for the addition of 1.0 μM H_2O_2 (a), 5.0 μM glucose (b), 2.0 μM ascorbic acid (c), 2.0 μM uric acid (d), and 2.0 μM nitrite (e), respectively.

6. The internal mechanism of the redox process

According to report, in which the mechanism of catalytic reduction of hydrogen peroxide based on ferryl peroxdase was discussed [S1], we put forward a hypothesis of the redox process in this experiment as follows:

$$\text{Hematin} + H_2O_2 \rightarrow \text{Compound Ⅰ} + H_2O \quad (1)$$

$$\text{Compound Ⅰ} + e \rightarrow \text{Compound Ⅱ} \quad (2)$$

$$\text{Compound Ⅱ} + e \rightarrow \text{Hematin} \quad (3)$$

Hematin reacted with hydrogen peroxide and was firstly oxidized to a first intermediate (Compound I). Compound I obtained one electron and was reduced to the second intermediate (Compound II). At last, Compound II was reduced to hematin on the electrode surface, so the reduction current increased in the presence of H_2O_2.

Reference

S1 R. Nakajima, I. Yamazaki, *J. Biol. Chem.*, 1987, **262**, 2576−2581.