Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

A biomimetic enzyme modified electrode for H_2O_2 highly sensitive detection

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The reduction scheme of AuNPs by PEI

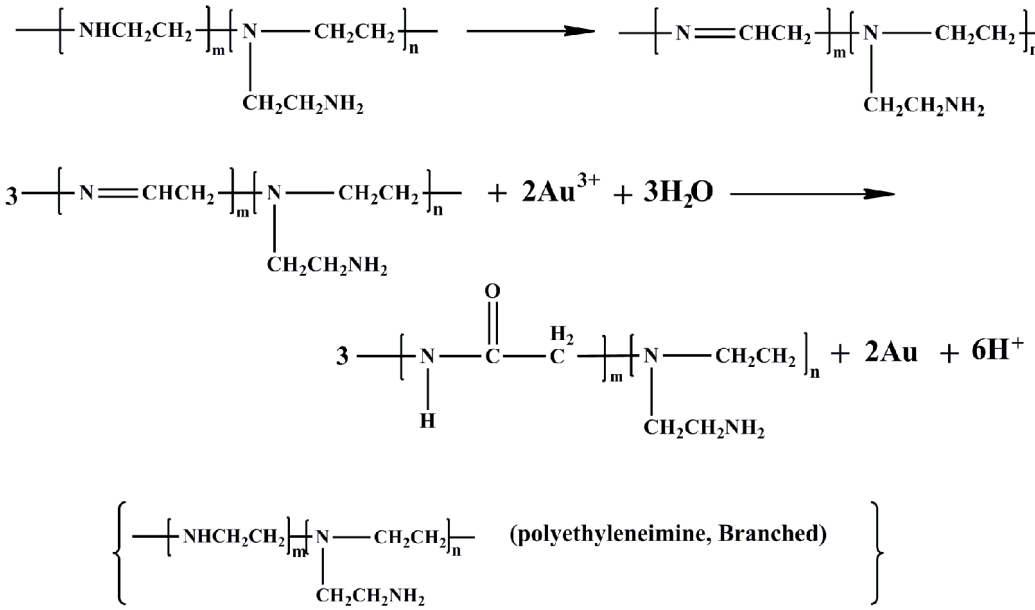

Fig. s1. Scheme of the reduction mechanism according to references.[1,2]

Synthesis of PEI-AuNPs-Hemin

The AuNPs were synthesized following the procedure described in experimental section of the article. Due to the different volume ratio of Au and $PEI_{monomer}$ (branched, 25 kDa), the particle size of synthesized AuNPs was multifarious (Table s1). At ambient temperature with stirring, 0.2-1 mL of PEI solution, was added to 5 mL of 1 mM solution of $HAuCl_4$ to achieve a mixture of Au:$PEI_{monomer}$ (volume ratio) proportions of 25:1 to 5:1. And the particle size of synthesized AuNPs was published in table s1. It showed that when Au:$PEI_{monomer}$ reached to 50:5, the diameter of AuNPs was the minimum, hence we chose the ratio of 50:5 for preparing AuNPs.

The bulk PEI-AuNPs solutions were divided into 1 mL portions, then they were mixed with various quantities of hemin, ranging from 0.5 mL to 1.5 mL of 0.1 mM hemin solutions, to obtain the desired PEI-AuNPs-Hemin nanocomposites. After 1 h of stirring, the mixture was centrifuged at 14,000 rpm for 30 min, then washed and centrifuged again in ultrapure water for further 20 min. Samples were prepared by diluting the nanocomposite in ultrapure water with the final concentration of 0.5 $mg \cdot mL^{-1}$. The best composition was identified according to the electrochemical response to H_2O_2 decomposition (refers to supporting information) from various samples tested on the electrode. The nanocomposite with an Au:$PEI_{monomer}$ ratio of 1:10 and the PEI-AuNPs-Hemin composite with an PEI-AuNPs:Hemin ratio of 1:0.12 were subjected (Fig. s2).

Table s1 Optimization of Au:$PEI_{monomer}$ ratio

Au:$PEI_{monomer}$ ratio	Average diamater
50:2	30
50:3	25
50:4	18
50:5	10
50:6	12
50:7	11
50:8	17
50:9	20

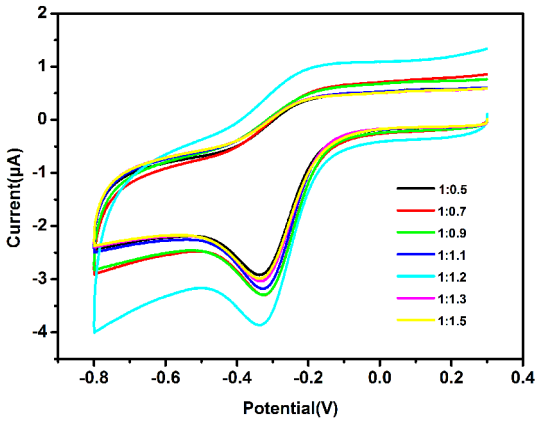

Fig. s2. Electrochemical response to H_2O_2 decomposition with different PEI-AuNPs:Hemin ratio.

The effect of pH on the catalysis of GCE/PEI-AuNPs-Hemin to H_2O_2.

The pH value of the electrolyte is important for the performance of the biosensor and it is related to the charges on the nanocomposite surface. Fig. s3 shows the amperometric response of GCE/PEI-AuNPs-Hemin at different pH values (pH 4.0-8.0) in the presence of the 0.1 mM of H_2O_2. The response current increased from pH 4.0 to pH 5.0 and then decreased from pH 6.0 to pH 8.0. The maximal catalysis is at pH 5.0. The lower pH in aqueous solution may help to reactivate the Fe^{3+} contained in hemin, thus enhancing the catalysis reaction on the surface of PEI-AuNPs-Hemin nanocomposite. So we choose pH 5.0 as the optimal condition of subsequent catalysis for H_2O_2.

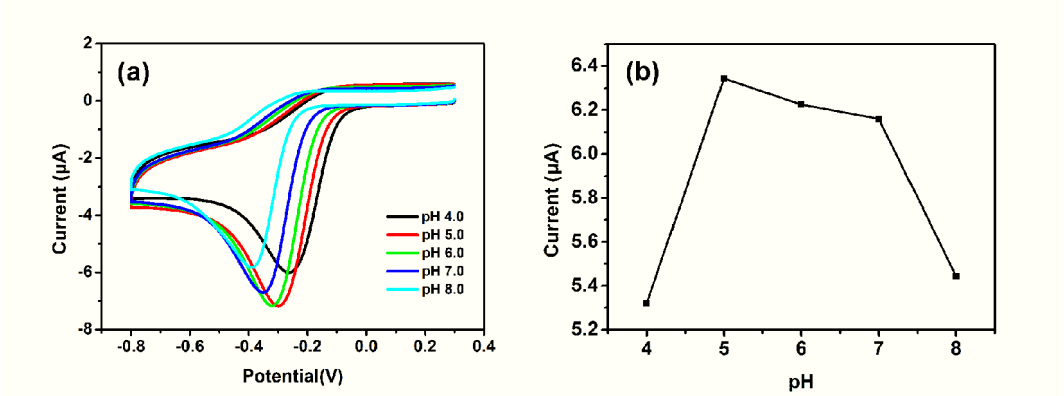

Fig. s3. (a) CVs of GCE/PEI-AuNPs-Hemin on 0.1 mM H_2O_2 in different pH of 0.1 M PBS with scan rate 100 $mV \cdot s^{-1}$; (b) The change of current with the pH.

The effect of scan rate on the electrochemical behavior of GCE/PEI-AuNPs-Hemin.

The CVs of the modified electrode at different scan rates are shown in Fig. s4. The redox peak current and the peak separation increased as a function of scan rate. The reduction peak currents increased linearly with the scan rate changing from 20 $mV \cdot s^{-1}$ to 150 $mV \cdot s^{-1}$: i=0.607+25.7v; (R^2=0.998). It is clearly that hemin was adsorbed on the surface and underwent a surface confined electron transfer.[3]

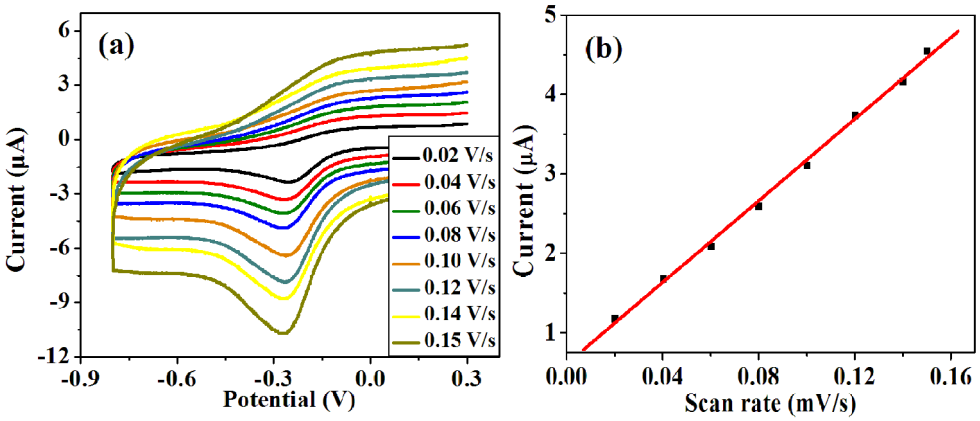

Fig. s4. (a) Cyclic voltammograms of GCE/PEI-AuNPs-Hemin in 0.1 $mol \cdot L^{-1}$ PBS (pH 5.0) containing 0.1 $mmol \cdot L^{-1}$ H_2O_2 with scan rates of 20–150 $mV \cdot s^{-1}$. (b) Plots of peak current vs scan rate.

References

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