Electronic Supplementary Material (ESI) for Analytical Methods

Electronic Supplementary Information:

Electrochemical biosensing platform based on hemocyanin/ Au@QC NPs/carbon black hybrid nano-composite film

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Experimental details

1 Reagents

Hemocyanin, purchased from sigma-Aldrich, was used without further purification. The solution of hemocyanin was kept in the dark at 4℃. 1,4-hydroquinone (HQ), catechol (CC) and $HAuCl_4$ were purchased from Aladdin and used without further purification. Water-soluble quaternized cellulose (QC, M_η=7.8×10^4 g/mol) were prepared in accordance with the previous work.[S1] All other chemicals were of analytical grade. Double-distilled water was used throughout.

2 Preparation of AuNPs-QC:

Au NPs were synthesized by directly reducing $AuCl_4^-$ ions in QC aqueous solution using $NaBH_4$ as the reducing agent**.** Typically, 0.5 mL of a 0.02428 mol/L $HAuCl_4$ aqueous solution was added to 10 mL of a 3 mg/mL QC aqueous solution in a reaction vessel, followed by constant stirring. Then, 0.375 mL of 0.1 mol/L $NaBH_4$ solutions was added immediately and further stirred for 1 h. The resulting solution was then dialyzed with regenerated cellulose tubes (Mw cutoff 8000) against distilled water for 5 days. After that, the solution was diluted to 30 mL with deionized water to form a burgundy AuNPs solution.

3 Preparation of modification electrode

The glassy carbon electrode (GCE), before use, were first polished to a mirror-like with 0.3 and 0.05 μm alumina slurry on a polish cloth, and then washed with double-distilled water bath to remove any residual alumina, and dried in the air before use.

Firstly, 4 mg black carbon (CB) was mixed with 2 mL AuNPs-QC solution to obtained a 2 mg/mL Au@QC NPs-CB suspension. then a well-dispersed suspension of HC-Au@QC NPs-CB was achieve by mixing 6.6 mg/mL HC solution and 2 mg/mL Au@QC NPs-CB were mixed together according to the ratio of 1:1 (v/v) with the aid of ultrasonication agitation for about 20 min. The modified working electrode was prepared by applying a 8 μl drop of a mixed HC-Au@QC NPs-CB suspension and dry at room temperature, resulting in the HC-entrapped Au@QC NPs/CB modified GCE (Hc/Au@QC NPs/CB/GCE).

4 Apparatus and measurements

The electrochemical experiments were carried out with a CHI 830 B electrochemical workstation with a conventional three-electrode cell. A modified electrode was used as a working electrode. A AgCl/Ag electrode was employed as the reference electrode and a platinum wire was connected as the counter electrode. For the deoxygenated experiments, all solutions were purged with high purity nitrogen for at least 30 min, and were maintained nitrogen atmosphere during the electrochemical measurements. All experiments were carried out at room temperature.

Stability and reproducibility

The stability of the biosensor has been investigated. The direct electrochemical responses of the modified electrode retained constant with repeated scanning for 20 cycles at 0.05 $V \cdot s^{-1}$. After the modified electrode was stored in 4 °C for 7 days, the current retained 95% of the its initial current response. The reproducibility of the Hc/Au@QC NPs/CB film modified electrode has also been examined in phosphate buffer solution containing 5.0 μM HQ and CC. The relative standard deviation (R.S.D) for 8 times parallel detections of HQ and CC at the same modified electrode were calculated to be 2.8 % and 3.1 %, respectively. These results indicated that this biosensor has good stability and reproducibility.

References

S1 Y. B. Song, Y. X. Sun, X. Z. Zhang, J. P. Zhou and L. N. Zhang, *Biomacromolecules*, 2008, **9**, 2259.

Supplementary Figures

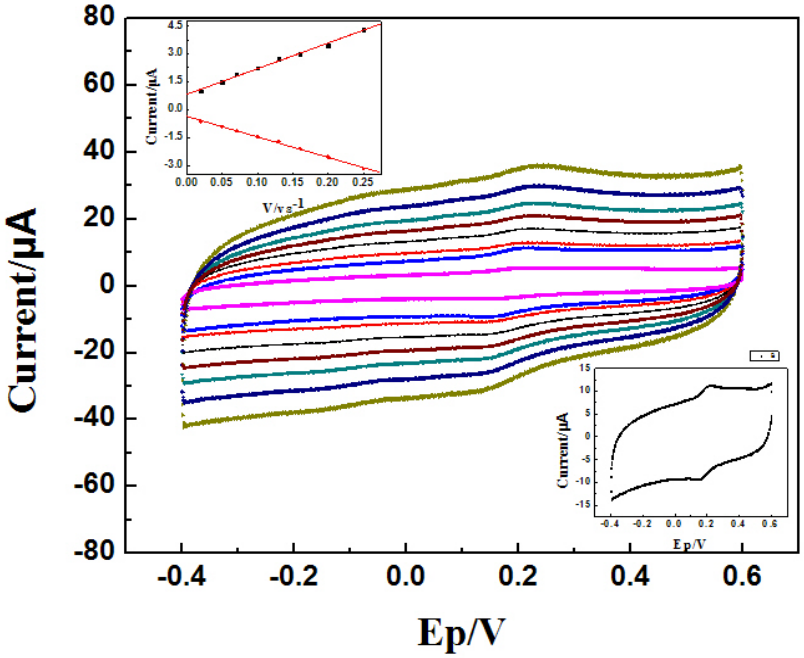

Fig.S1. Cyclic voltammograms of AuNPs-QC-BC-HC-GC electrode in PBS (PH=7.0) at different scan rates of 0.02, 0.05, 0.07, 0.1, 0.13, 0.16, 0.20, 0.25 V/s. Inset: plot of the peak current *i* against the scan rate *v*.

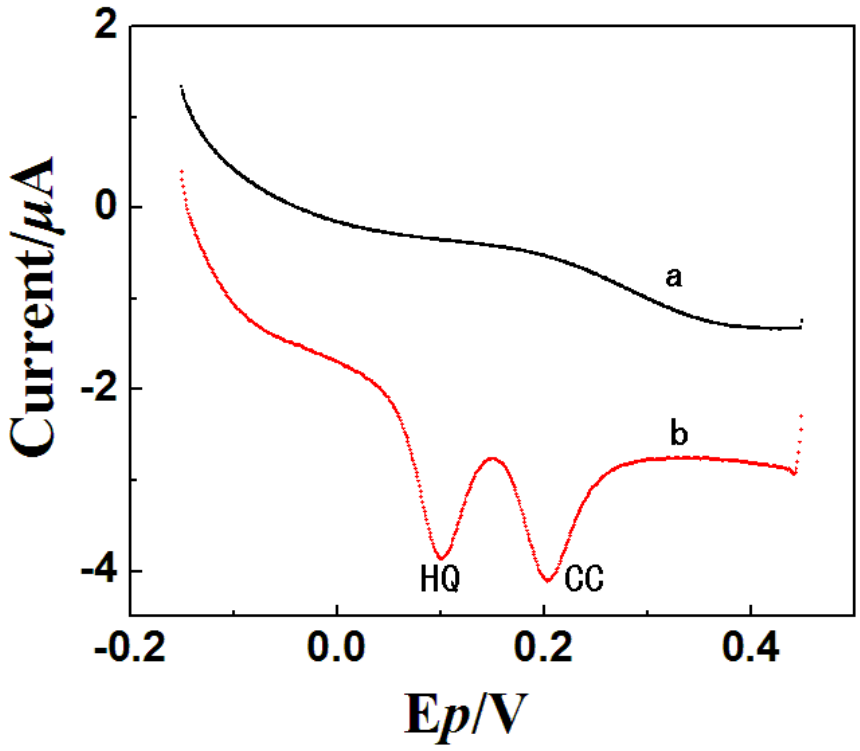

Fig. S2. LSV of 20 μM HQ and CC at bare GCE (a) and Hc/Au@QC NPs/CB film modified GCE (b) in 0.1M PBS(pH=7.0).

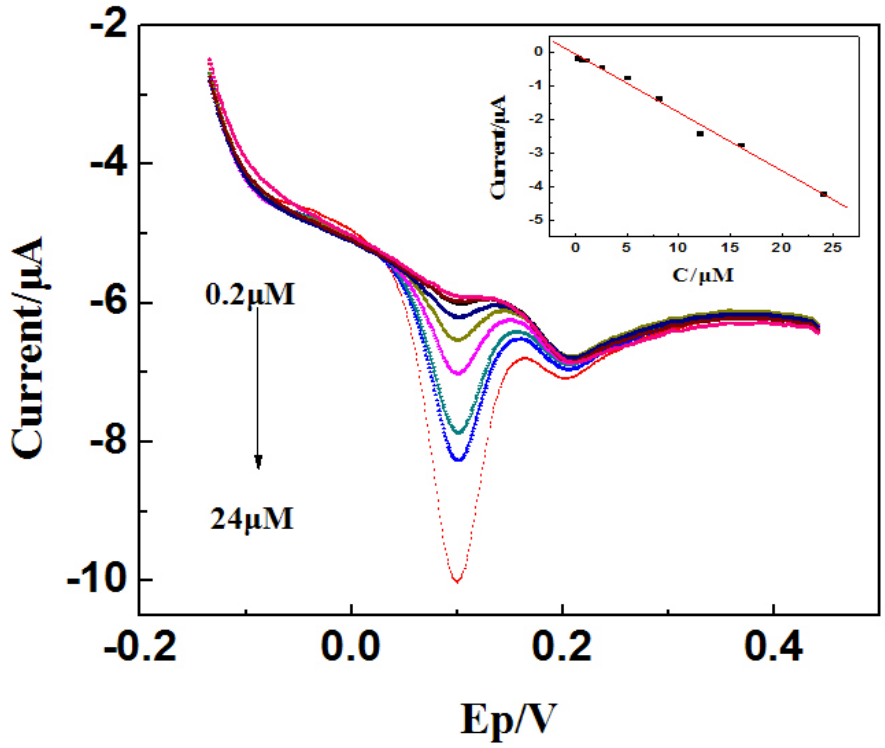

Fig. S3 LSV of different concentrations of HQ in the presence of 5μM CC.

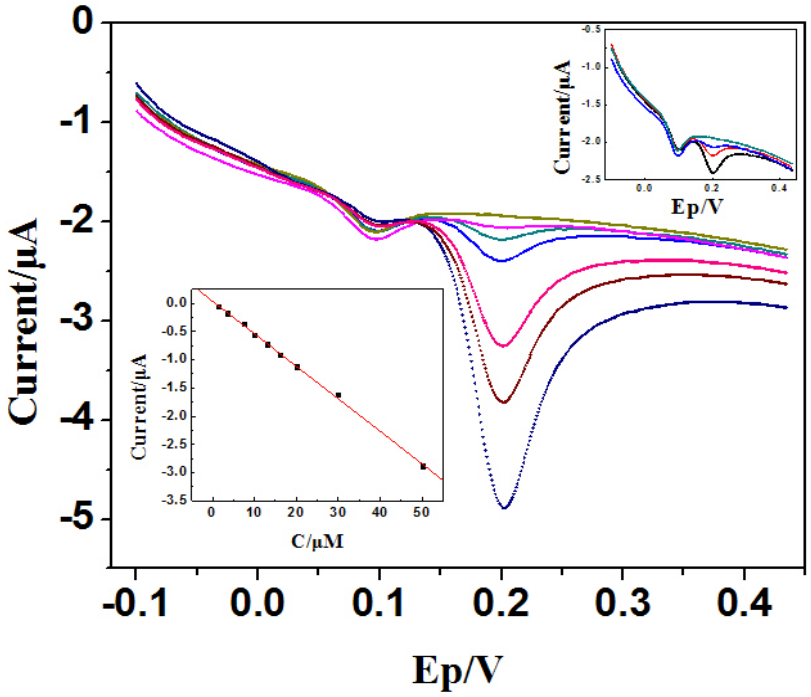

Fig. S4 LSV of different concentrations of CC in the presence of 5 μM HQ.