A new strategy for chiral recognition of amino acids

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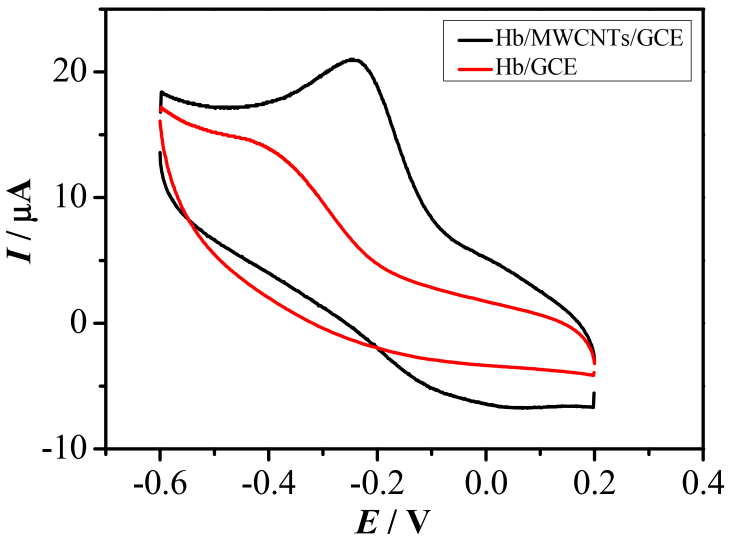
(Supplementary Material)

EXPERIMENTAL SECTION

Reagents and Materials. Hemoglobin was purchased from Aladdin. Multi-walled carbon nanotubes (MWCNTs), Chitosan (molar weight 1.0×10^6, 75-85% deacetylation), L- or D-Arginine, L- or D-glutamic acid, L- or D-aspartic acid and L- or D-serine were obtained from Sigma Chemical Co. (St. Louis, MO, USA). Dimethylformamide (DMF), Tris-HCl, $CuSO_4\cdot5H_2O$, $ZnSO_4\cdot7H_2O$, $MnSO_4\cdot H_2O$, $CoCl_2\cdot6H_2O$ were purchased from Chemical Reagent Co. (Chongqing, China). All chemicals were analytical grade and without further purification. Double distilled water was used throughout all experiments. Phosphate-buffered solution (PBS, 0.1 M) were prepared with stock standard solution of Na_2HPO_4 and KH_2PO_4. The supporting electrolyte was 0.1 M KCl. Tris-HCl buffered solution (0.1 M) were adjusted to pH 7.0.

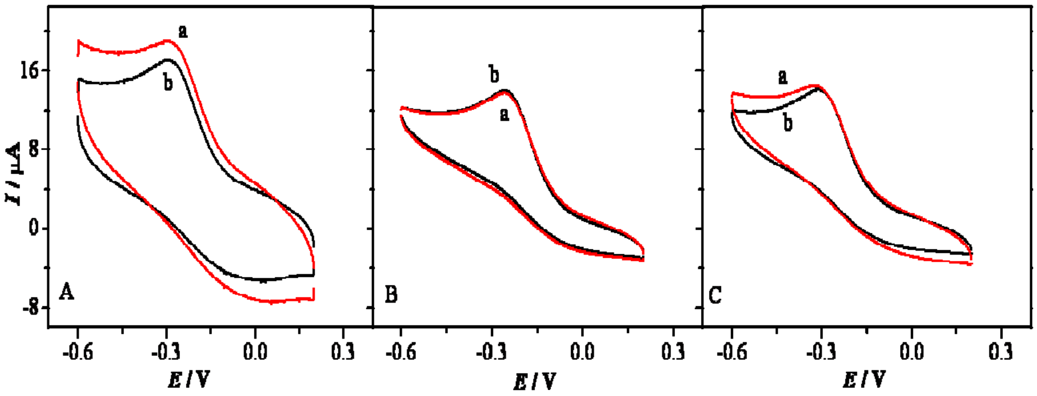
Apparatus. All electrochemical measurements were performed with a CHI660A electrochemistry workstation (Shanghai Chenhua Instruments Co., China). A three-electrode cell equipped with a modified glassy carbon electrode (GCE, $\phi = 4$ mm) as working electrode, a platinum wire as an auxiliary electrode, a saturated calomel electrode (SCE) as a reference electrode.

Electrochemical characterization of the electrode surface: Cyclic voltammetry (CV) was used to investigate the electrochemical characteristics in PBS (PH 7.0) for each assemble step. CVs of Hb/MWCNTs/GCE and Hb/GCE were compared in FigureS 1. The current peak was obviously decreased if without MWCNTs, but a large oxidation peak was clearly observed from Hb/MWCNTs/GCE, which was attributed to the fact that MWCNTs advanced the conductivity of electrons to the electrode surface.



FigureS 1. Camparison of different modified electrodes in pH 7.0 PBS containing0.1 M KCl: Hb/GCE (red line), Hb/MWCNTs/GCE (black line).

The assay for chiral recognition of Arg enantiomers in the presence of different metallic ions: In order to vertify the importance of Cu(II) in the chiral recognition, we also chose the other three metal ions as the center ion of chelation. As shown in FigureS 2, the complexes of Zn(II) with L- and D-Arg existed a difference in the PBS on Hb/MWCNTs/GCE, maybe that Hb has a higher affinity with the binary Zn(II) chelate of D-Arg than L-Arg. Zn(II) as center ions has commonly been reported in chiral ligand exchange.[1,2] No obvious difference of peak currents was observed in the presence of Mn(II) or Co(II). It also further demonstrated that the redox of Cu contributed to the enantioselectivity of Arg enantiomers on Hb/MWCNTs/GCE.



FigureS 2. Cyclic voltammograms of the modified electrode for chiral recognition in 5 mM L-Arg (a) and D-Arg (b) solution in the presence of 2.5 mM (A) Zn(II) ; (B) Mn(II); (C) Co(II);

References:

1. L. Qi, J. Qiao, G.L. Yang, Y.Cheng, *Electrophoresis*, 2009, **30**, 2266

2.Y.Z. Fu, L.L. Wang, Q. Chen, J. Zhou, *Sensor. Actuat.B-Chem.,*2011,**155**,140