Analytical Biochemistry 421 (2012) 103–107

Contents lists available at SciVerse ScienceDirect

Analytical Biochemistry

journal homepage: www.elsevier.com/locate/yabio

Enantioselective recognition of mandelic acid based on γ-globulin modified glassy carbon electrode

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ARTICLE INFO

Article history:
Received 2 July 2011
Received in revised form 1 October 2011
Accepted 11 October 2011
Available online 15 October 2011

Keywords:
Chiral recognition
Mandelic acid
Gold nanoparticles
γ-Globulin

ABSTRACT

A new chiral biosensor has been fabricated by immobilizing γ-globulin on gold nanoparticles modified glassy carbon electrodes, which could recognize and detect mandelic acid (MA) enantiomers. Differential pulse voltammetry, quartz crystal microbalance, ultraviolet–visible spectroscopy, and atomic force microscopy were used to characterize the enantioselectivity. The results exhibited that γ-globulin modified electrode could enantioselectively recognize MA enantiomers, and larger response signals were obtained from R-MA. The factors influencing the performance of the resulting biosensor were investigated. The enantiomeric composition of R- and S-MA enantiomer mixtures could be determined by measuring the current responses of the sample. The developed electrodes have the advantages of simple preparation, good stability, and rapid detection.

One distinctive biochemical signature of life is the high selectivity of chiral molecular species [1,2]. The body exhibits different physiological responses to different enantiomers. With the dramatic increase in the use of chiral drugs, chiral recognition has become a research focus in chemical, biological, and pharmaceutical sciences [3,4]. The Food and Drug Administration requires that both enantiomers of a racemate should be studied in detail and pointed out the influence on the human body [5]. Research on enantiomeric recognition of chiral compounds can provide us important information to understand the recognition process in biological systems. Although some progress in chiral discrimination has been achieved during the past decades, the selective detection of individual enantiomers is still the most difficult analytical task owing to the similar physical and chemical properties and the similar molecular configurations of chiral isomers. Therefore, it is important to develop practical and rapid available methods for the chiral recognition of enantiomers. Many methods have been used for chiral analysis [6–16]; electrochemical methods, which can be readily implemented in electronic devices, attract much attention based on simple and rapid detection.

α-Hydroxy carboxylic acids, which are the structural units of many natural products and drug molecules, represent one of the most important classes of chiral compounds in nature [17]. As one of the α-hydroxy carboxylic acids, mandelic acid (MA)[1] is a significant chiral analog of amino acids in the pharmaceutical synthetic industry [18]. It is present in certain skin care products and used as a precursor in the manufacture of certain dyes [19]. *R*-Mandelic acid (R-MA) is applied as a precursor for the synthesis of cephalosporin and penicillin [20], and as a pharmaceutical active agent it exceeds the mixture of R-MA and *S*-mandelic acid (S-MA) [21]. It is also used as a chiral resolving agent and chiral synthon for the synthesis of anti-tumor and anti-obesity agents [22]. Although many approaches have been used for recognizing MA [23–26], designing a simple and efficient system for enantioselective recognizing MA enantiomers is still a challenging task.

The proteins have the intrinsic possibility to discriminate other chiral molecules; for example, bovine serum albumin and human serum albumin have been used as chiral selectors [27,28]. However, there is little reported about γ-globulin. Hence, the enantioselective recognition of MA enantiomers using γ-globulin modified chiral interface was investigated. First, gold nanoparticles were electrodeposited on the glassy carbon electrodes (GCEs), which could provide a stable and rough surface to immobilize biomolecules favorably [29,30], and then the γ-globulin was adsorbed on gold nanoparticles modified electrodes. The resulting electrodes were employed to detect MA enantiomers, and differential pulse voltammetry

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[1] *Abbreviations used:* MA, mandelic acid; R-MA, *R*-mandelic acid; S-MA, *S*-mandelic acid; GCE, glassy carbon electrode; DPV, differential pulse voltammetry; QCM, quartz crystal microbalance; UV–Vis, ultraviolet–visible; AFM, atomic force microscopy; $HAuCl_4$, gold chloride; EIS, electrochemical impedance spectroscopy; SCE, saturated calomel electrode; CV, cyclic voltammetry; R_{et}, electron transfer resistance.

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doi:10.1016/j.ab.2011.10.017

(DPV), electrochemical quartz crystal microbalance (QCM), ultraviolet–visible (UV–Vis) spectroscopy, and atomic force microscopy (AFM) were used to monitor the responses. This not only provides a new method to recognize MA enantiomers, but also is expected to extend the applicability of enantioselective detection of some drugs.

Materials and methods

Chemicals

S- or R-MA, γ-globulin, and gold chloride ($HAuCl_4$) were purchased from Sigma (USA). Other chemical reagents were analytical grade, and double-distilled water was used throughout this study. Various pHs of $[Fe(CN)_6]^{4-/3-}$ solutions with 0.1 M KCl as the supporting electrolyte were prepared by 0.1 M phosphate buffer solutions.

Apparatus

DPV and electrochemical impedance spectroscopy (EIS) measurements were carried out with a CHI 660D electrochemistry workstation (Shanghai Chenhua Instruments, China). A three-electrode electrochemical cell was composed of a bare or modified GCE ($\Phi = 4$ mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode. The shift of frequency caused by adsorption of MA on γ-globulin modified quartz plates was investigated by model CHI 440A time-resolved electrochemical QCM (Shanghai Chenhua Instruments). UV–Vis absorption spectra were recorded by a UV-8500 spectrometer (Shanghai Tianmei, China). AFM images were obtained by a model SPM (Vecco, USA). All measurements were performed at room temperature.

Fabrication of γ-globulin modified chiral surface

GCEs ($\Phi = 4$ mm) were polished carefully with 1.0, 0.3, and 0.05 μm alumina slurry, respectively, sonicated in double-distilled water, ethanol, and double-distilled water each for 5 min. The cleaned electrodes were dipped into 1% $HAuCl_4$ (containing 0.1 M KNO_3) and deposited by applying a constant potential of −0.2 V for 60 s to obtain the gold nanoparticles modified electrodes (DpAu/GCEs) [31]. Next, the DpAu/GCEs were immersed in 100 μg ml^{-1} γ-globulin solution at 4 °C overnight. The γ-globulin modified chiral surface was obtained (γ-globulin/DpAu/GCE). The steps for preparing the modified electrodes are shown in Scheme 1.

Experimental measurements

The electrochemical properties of the modified electrodes were investigated using cyclic voltammetry (CV), DPV, and EIS in 5 mM $[Fe(CN)_6]^{4-/3-}$ (pH 6.5). The CV scans were done from −0.2 to 0.6 V at 100 mV s^{-1}. The enantioselective detection was based on the difference of current response ($\Delta I = I_0 - I_1$) before (I_0) and after (I_1) the modified electrodes immersed in S- or R-MA solution.

Results and discussion

Characterization of γ-globulin modified surface

EIS can be used to monitor the interfacial properties or track the modified process of modified electrodes. The impedance spectra include a linear part at low frequencies and a semicircle portion of which the diameter equals the interfacial electron transfer resistance (R_{et}) at high frequencies [32]. The bare GCE showed a very small impedance ($R_{et} = 30\ \Omega$; see Fig. 1, curve a), and after the $HAuCl_4$ was deposited on the GCE (DpAu/GCE), the impedance decreased by good electronic transmission of gold nanoparticles ($R_{et} = 10\ \Omega$; see Fig. 1, curve b). When DpAu/GCE was immersed in γ-globulin solution overnight (γ-globulin/DpAu/GCE), the impedance increased ($R_{et} = 121\ \Omega$; see Fig. 1, curve c), suggesting that the adsorbed γ-globulin hindered the electron transmission of redox probe.

The stability of the chiral surface was investigated by successively scanning 100 cycles in $[Fe(CN)_6]^{4-/3-}$ at 100 mV s^{-1}. Only 1.64% change of the initial peak current was observed, indicating sufficient stability of the modified electrode. The cyclic voltammograms of the modified electrode at different scan rates were investigated. The redox peak currents were proportional to the square root of scan rate from 20 to 450 mV s^{-1}, indicating a diffusion-controlled electron transfer process [33].

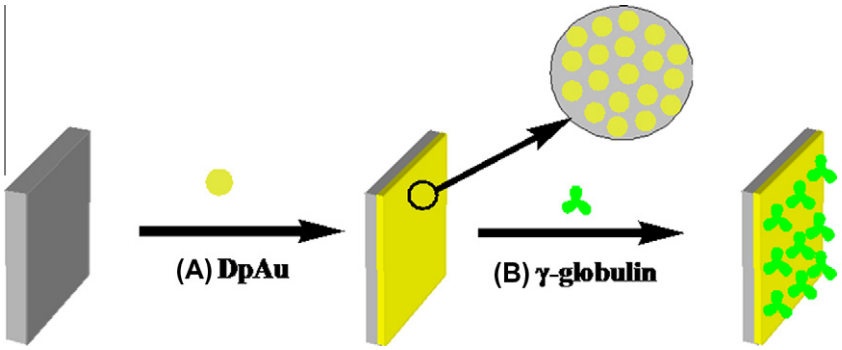
Enantioselective recognition of MA

DPV response

The electrochemical response before and after the γ-globulin modified electrode inserted into S- or R-MA solution was investigated by DPV. As shown in Fig. 2A, curve a was the DPV response of the γ-globulin modified electrode. After the modified electrode interacted with R- or S-MA, the peak current decreased and a larger decrease was obtained from R-MA (curve c) than from S-MA (curve b), suggesting that more R-MA was adsorbed on γ-globulin.

AFM measurements

The topographies before and after γ-globulin modified surface interacted with MA enantiomers were characterized by AFM. The image of γ-globulin modified Au substrate was rough and loose (Fig. 2B, image a). After γ-globulin modified surface interacted with MA enantiomers, the surface topography of γ-globulin + R-MA system was uniform and compact (Fig. 2B, image b), whereas the γ-globulin + S-MA system was irregular but thick (Fig. 2B, image c), implying that MA enantiomers exhibit different adsorption



Scheme 1. Schematic illustration of the stepwise chiral biosensor fabrication process: (A) electrodeposition of gold nanoparticles; (B) immobilization of γ-globulin.

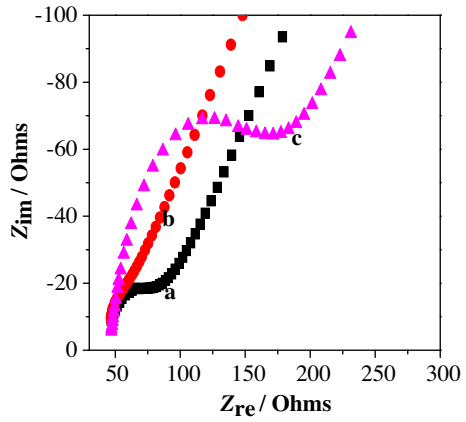


Fig.1. EIS of the different electrodes in 5 mM $[Fe(CN)_6]^{4-/3-}$ (pH 6.5): (a) bare GCE; (b) DpAu/GCE; (c) γ-globulin/DpAu/GCE.

behaviors on γ-globulin modified surface and that the adsorption quantity of S-MA on γ-globulin modified surface was less than that of R-MA.

QCM detection

It is well known that the change of substrate surface quality has a linear relationship with the shift in resonant frequency of the quartz crystals (Δ*F*) [34]. In this experiment, QCM was used to analyze the chiral recognition process. The pretreated quartz plates were immersed in 100 μg ml^{-1} γ-globulin solution at 4 °C overnight. Time-dependent frequency responses for R- and S-MA adsorbed on the γ-globulin modified quartz crystals are shown in Fig. 2C. This figure shows that the frequency responses of the modified QCM sensor to S- and R-MA were decreased and that the frequency shift tended to level off with the increase of reaction time. It also can be seen that the shift of frequency for R-MA (curve b) was larger than that for S-MA (curve a). According to the Sauerbrey equation [35], the adsorbed mass of R- and S-MA could be calculated as approximately 325.1 and 198.06 ng, respectively. That is to say, more R-MA was absorbed on the γ-globulin modified quartz crystals under the same conditions.

UV–Vis spectra

UV–Vis spectroscopy was used to further monitor the reaction between MA and γ-globulin. The optical spectrum of MA from 200 to 600 nm is showed in Fig. 2D. In the inset of this figure, curve a shows the spectrum of γ-globulin from 240 to 270 nm; there was no absorption in this scope. Curves b and c show the absorption spectra of R- and S-MA, respectively. An absorption peak was observed at around 255 nm, which was the characteristic aromatic heterocyclic $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition [36]. The absorbances of R- and S-MA were nearly the same. After γ-globulin was added to R- or S-MA solution, the absorbance of R-MA (curve e) was higher than that of S-MA (curve d). The phenomenon might be attributed to the formation of diastereoisomeric complexes between MA enantiomers and γ-globulin, which may produce different UV–Vis intensities of peak.

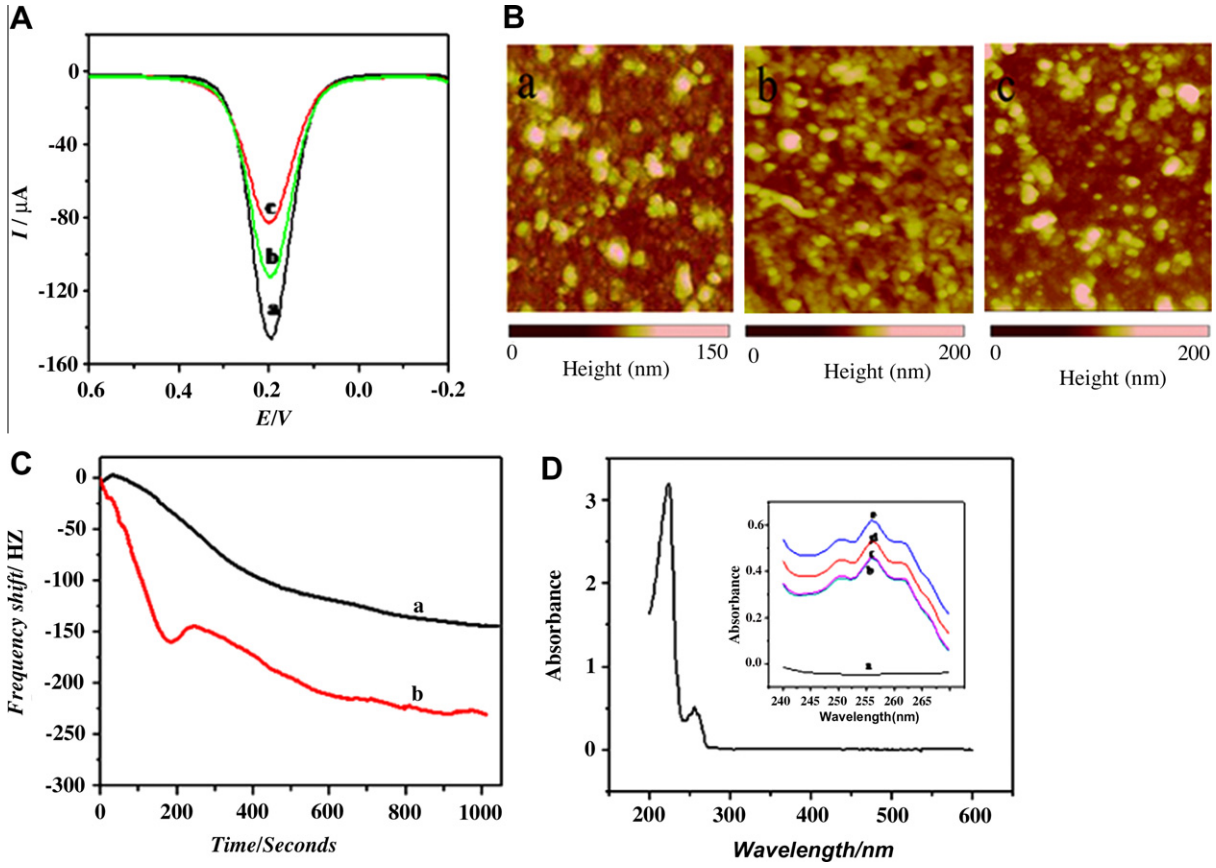


Fig.2. (A) DPV responses of (a) γ-globulin/DpAu/GCE, (b) S-MA/γ-globulin/DpAu/GCE, and (c) R-MA/γ-globulin/DpAu/GCE in 5 mM $[Fe(CN)_6]^{4-/3-}$, scan rate: 100 mV s^{-1}. (B) AFM images of (a) the γ-globulin modified surface, (b) R-MA/γ-globulin modified surface, and (c) S-MA/γ-globulin modified surface, image scales are 1 μm × 1 μm. (C) Time dependence of the QCM frequency change of the γ-globulin modified Au coated quartz-crystal resonator interaction with 1.25 mM (a) S-MA and (b) R-MA. (D) UV-Vis spectra of MA; insert: the UV spectra of (a) γ-globulin, (b) S-MA, (c) R-MA, (d) S-MA + γ-globulin, and (e) R-MA + γ-globulin.

All results indicated that larger response signals were obtained from R-MA using γ-globulin modified surface, suggesting that γ-globulin could selectivity recognize MA enantiomers. In MA enantiomers, the –COOH and –OH groups connect to the chiral carbon atoms; possessing different spatial arrangements, these could induce a different interacted mode between γ-globulin and MA enantiomers. The enantioselective recognition may be done through hydrogen bonds, hydrophobic interactions, $\pi-\pi$ actions, or other actions, which are important physical and chemical behaviors in protein. That is to say, the difference of molecular configuration of MA enantiomers may make the difference of match degree between γ-globulin and R- or S-MA. The molecular configuration of S-MA did not match with γ-globulin, resulting in a weak interaction between S-MA and γ-globulin. This study is helpful for understanding the interaction between γ-globulin and MA and is helpful for comprehending the enantioselective interaction of proteins and chiral molecular species.

Optimization of experimental conditions

Effect of pH

The pH value of the working solution is an important influencing factor for the activity of immobilized proteins. The anodic current response of the γ-globulin modified electrodes at pH values from 4.0 to 7.0 is shown in Fig. 3A. The current responses at pH values 4.0 and 6.5 both are larger than the others. Because the protein is facilitated to denature at lower pH, pH 6.5 was selected as the experimental acidity.

Influence of incubation time

The influence of incubation time on the current response was investigated in the range of 0 to 30 min. Fig. 3B shows the difference of peak currents after the modified electrode interacted with S- or R-MA for 5 min. They increased continuously with the interaction times, and the ΔI_R was larger than the ΔI_S. The current response variation decreased after the time increased to 25 min. So, 25 min was adopted as the incubation time in this work.

Characterization of interaction between γ-globulin and MA enantiomers

The current response of γ-globulin modified electrode to R- and S-MA at various concentrations are shown in Fig. 4. The difference of current response increased with the concentration of MA from 1 to 5 mM. The differences of peak current (ΔI) were different between R-MA (curve a) and S-MA (curve b) at all concentrations, and the ΔI of R-MA was always bigger than that of S-MA, further indicating that the γ-globulin modified electrodes adsorb R-MA easily.

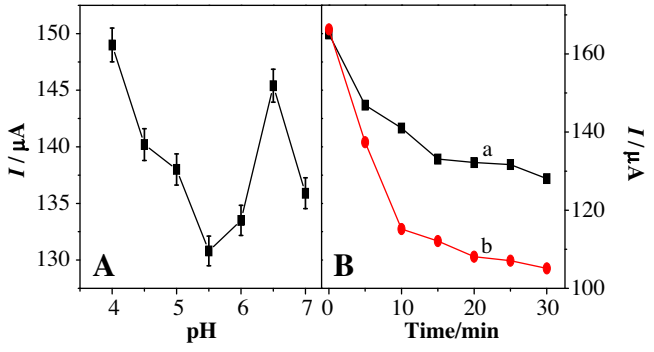


Fig.3. (A) Influence of pH value of γ-globulin/DpAu/GCE in 5 mM $[Fe(CN)_6]^{4-/3-}$. (B) Influence of incubation time on current response when the modified electrode interacts with mandelic acid: (a) S-MA; (b) R-MA.

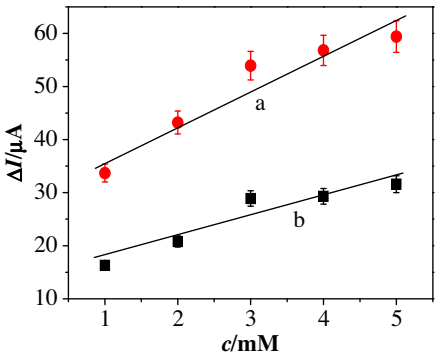


Fig.4. Difference of anodic peak currents for different concentrations of MA enantiomers on γ-globulin/DpAu/GCE: (a) R-MA; (b) S-MA.

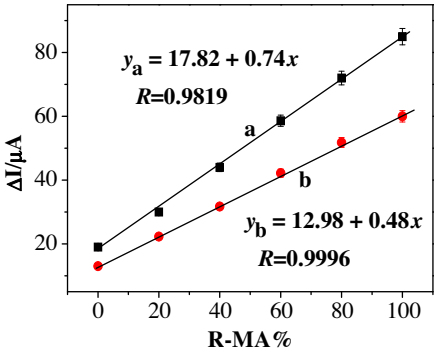


Fig.5. Current decrease of γ-globulin modified electrode with enantiomeric composition of S- and R-MA at different concentrations: (a) 5 mM; (b) 2 mM.

Application of enantioselective sensor

The modified electrode was also used to measure the current response of a series of solutions that were prepared by mixing S- and R-MA at different fixed ratios. The difference of the relative peak currents and the proportions of enantiomers are shown in Fig. 5. It is clear that the enantiomeric composition of the S- and R-MA enantiomer mixture can be determined from the calibration curves, which show good linearity.

Conclusion

An interesting phenomenon, namely that the γ-globulin modified surface could selectively adsorb MA enantiomers, was observed. All results showed that larger response signals were obtained from R-MA after the γ-globulin modified surface interacted with MA enantiomers under the same experimental conditions. The chirality-induced difference in the molecule configurations for MA enantiomers was greatly influenced by the interaction between MA and γ-globulin. The γ-globulin could bind with R-MA in the major portion through hydrogen bonds, hydrophobic interactions, or other actions, ascribing to the molecular configuration of R-MA match better with γ-globulin. This work may bring novel application insights for chiral biomolecules and drugs.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (20972128 and 20732003).

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