



Short communication

Potato starch as a highly enantioselective system for temperature-dependent electrochemical recognition of tryptophan isomers



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ABSTRACT

A simple but highly enantioselective system based on potato starch (PS) modified electrode was developed for electrochemical recognition of tryptophan (Trp) isomers. Due to favorability of host–guest interactions between PS and D-Trp, PS preferably combined with D-Trp compared with L-Trp, resulting in larger amount of L-Trp penetrating through the left-handed double helices of PS to the electrode surface than D-Trp. And therefore, successful recognition of Trp isomers was achieved at the PS-based electrode. The PS-based chiral recognition was temperature dependent, which was attributed to the significant influence of temperature on the H-bonds between PS and the guest molecules. The recognition efficiency was remarkably decreased after hydroxypropyl groups were introduced to PS, and the decreased recognition efficiency at the hydroxypropyl PS (H-PS) might be due to the extra steric hindrance.

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1. Introduction

Chiral recognition of isomers is of significant importance in the living world because the body is amazingly enantioselective, showing different physiological responses to different isomers [1]. Recent years have witnessed the development of supramolecular chemistry-based chiral recognition [2], in which the host–guest interactions are utilized for distinguishing between the left- and right-handed forms of chiral compounds. More recently, the combination of electrochemistry and supramolecular chemistry was reported by our group [3,4], which opens a new window for electrochemical enantiorecognition since it translates a chiral molecular recognition event into discernible changes in electrochemical responses.

Starch exists predominantly in two polymorphic forms (A- and B-types), in which the unit cell contains 12 glucose residues located in two left-handed, parallel-stranded double helices [5]. The double helices of A- and B-structures are arranged around a channel filled with well-localized water molecules [6]. It has been reported that the double helices structure of DNA plays a crucial key role in distinguishing chiral complexes although the mechanism has not been well explained [7,8], and thus it strongly motivates researchers to be engaged in the starch-based recognition of racemic amino acids. In fact, starch has been adopted in thin-layer chromatographic work for the enantioseparation of tryptophan (Trp) isomers [9]. Moreover, amylose-based chiral stationary

phase has also been developed for molecular enantiorecognition of omeprazole, although its function is not fully understood [10].

Another problem encountered in the starch-based chiral recognition is that due to the inferior conductivity of starch, little attention has been paid to the electrochemical enantiorecognition of chiral compounds by starch. More recently, natural polysaccharides-based electrochemistry has been realized successfully *via* self-assembly or hybridization of natural polysaccharides with electrically conductive materials such as poly(L-glutamic acid) (P-L-Glu) [11] and graphene quantum dots (GQDs) [12], which opens up new opportunities for starch-based electrochemical enantiorecognition.

Herein, we report on the electrochemical chiral recognition of Trp isomers by potato starch (PS) self-assembled on P-L-Glu. Trp is chosen as the target to be recognized owing to its great importance in most biological systems [13]. PS/P-L-Glu exhibits a higher affinity for D-Trp than L-Trp due to the favorability of intermolecular H-bonds formation between PS and D-Trp. However, the recognition efficiency is decreased when hydroxypropyl PS (H-PS) is used for the recognition instead of PS. Furthermore, the temperature-dependent feature of the proposed PS/P-L-Glu and H-PS/P-L-Glu chiral sensing systems is also investigated, and it is exciting to find that for PS/P-L-Glu, the highest recognition efficiency is obtained at 37 °C.

2. Experimental

2.1. Reagents and apparatus

Potato starch (PS) was obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China). Hydroxypropyl potato starch (H-PS) was purchased

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from Shanghai Guomin Starch Industry Co., Ltd. (China). Electrochemical experiments were conducted on a CHI-660D electrochemical workstation (Shanghai Chenhua Instruments Co., China) in a traditional three-electrode system. The working electrode was a glassy carbon electrode modified with PS or H-PS self-assembled P-L-Glu. The counter electrode was a platinum foil and the reference electrode was a saturated calomel electrode (SCE). The water contact angles of different samples were measured by a DSA25 machine (Kruss GmbH, Germany), and 2 μL of water droplet was dropped onto the surface of different samples for each measurement.

2.2. Electrodeposition of P-L-Glu and self-assembly of PS or H-PS onto P-L-Glu/GCE

Electropolymerization of L-Glu was carried out by cyclic voltammetry in 0.05 M L-Glu dissolved in 0.1 M phosphate buffer solution (PBS, pH 7.0) [14], in which the potential was set between -0.6 and 2.0 V at a scan rate of 100 mV s^{-1} for 20 cycles. Next, the P-L-Glu/GCE was immersed into 2 mg mL^{-1} PS or H-PS dissolved in 25 mL 0.1 M PBS at 8°C for 24 h, as shown in Fig. 1A.

2.3. Electrochemical chiral recognition of Trp isomers

The PS or H-PS self-assembled P-L-Glu/GCE was immersed into 25 mL 0.1 M PBS containing 0.5 mM L-Trp or D-Trp for 60 s at different temperatures. Next, the differential pulse voltammograms (DPVs) of the two inclusion complexes were measured with a step potential of 4 mV and an amplitude of 50 mV. After each measurement, the electrochemical chiral sensing system was regenerated by

cyclic voltammetry in 0.1 M PBS for 20 cycles in the potential range from 0.4 to 1.2 V.

3. Results and discussion

3.1. Electrochemical characterization of PS and H-PS self-assembled P-L-Glu/GCE

Fig. 1B shows the cyclic voltammograms (CVs) of the electrodes obtained at different stages in 25 mL 0.1 M KCl containing 5 mM $\text{Fe}(\text{CN})_6^{4-/3-}$, and a pair of well-defined redox peaks is observed at the bare GCE (curve a). After P-L-Glu is electrodeposited onto GCE, the peak current (I_p) is increased (curve b). The improved electrochemical reversibility is attributed to the introduced P-L-Glu films, which can accelerate the charge transfer and facilitate the transition between the redox probe couple [15]. After PS and H-PS are self-assembled onto P-L-Glu/GCE, the I_p is declined significantly, especially for PS, due to the inferior conductivity of PS and H-PS (curves c and d). Considering the chemical structures of PS and H-PS (Fig. 1C), it is no doubt that the hydroxypropyl groups on H-PS hamper the formation of H-bonds between H-PS and P-L-Glu, resulting in decreased amount of H-PS deposited onto P-L-Glu and relatively larger I_p compared with PS.

3.2. Electrochemical enantio recognition of Trp isomers

Fig. 2 shows the DPVs of L-Trp and D-Trp at different electrodes at 37°C . The completely overlapped (Fig. 2A) and almost completely overlapped DPVs (Fig. 2B) of the Trp isomers demonstrate that bare GCE and P-L-Glu/GCE exhibit no recognition ability toward Trp isomers due to the absence of chiral sites. Surprisingly, discernable differences in the

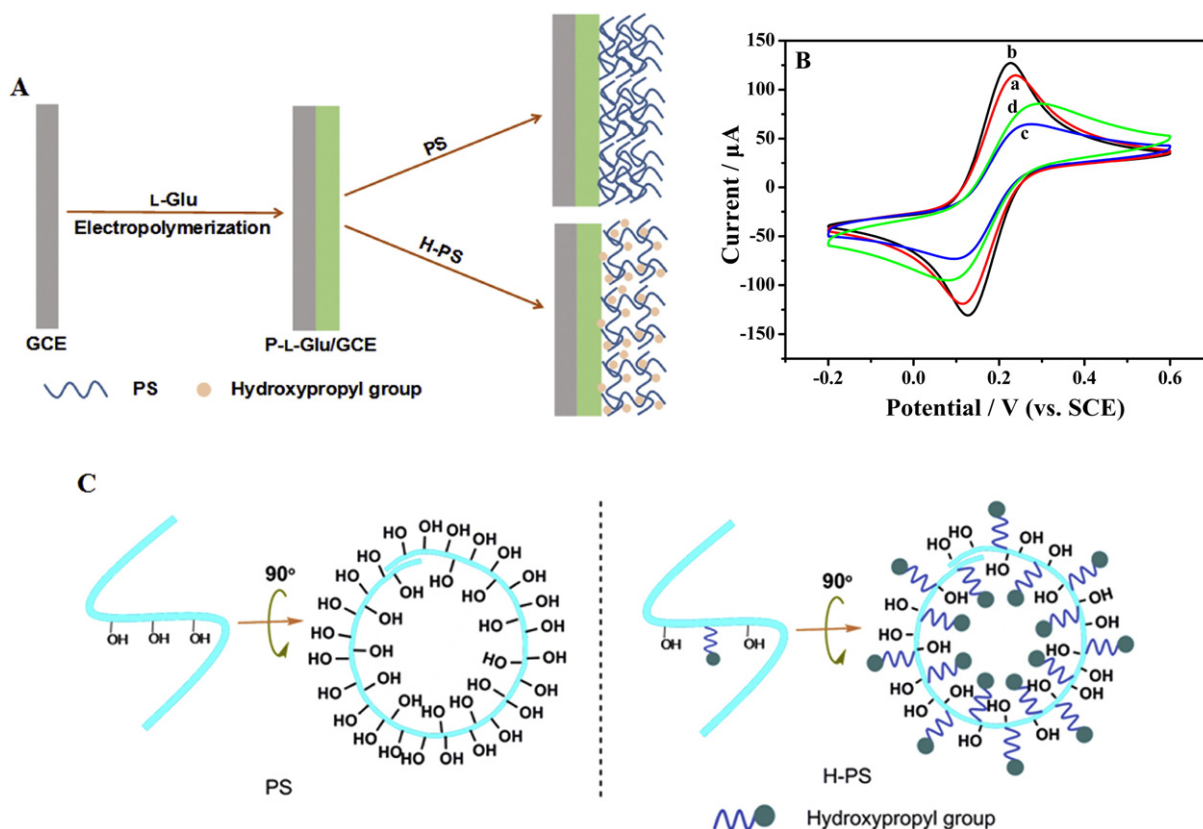


Fig. 1. (A) Schematic illustration showing the electrodeposition of P-L-Glu and self-assembly of PS and H-PS onto P-L-Glu/GCE. (B) Cyclic voltammograms of 5 mM $\text{Fe}(\text{CN})_6^{4-/3-}$ at bare GCE (a), P-L-Glu/GCE (b), PS (c), and H-PS (d) self-assembled P-L-Glu/GCE. (C) Section views of PS and H-PS.

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