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An electrochemical biosensor based on single-stranded DNA modified gold electrode for acrylamide determination

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ABSTRACT

Herein, a simple and effective electrochemical biosensor for sensitive detection of acrylamide (AA) was developed by differential pulse voltammetry (DPV) approach. This biosensor was prepared by effective self-assembling process of thiol group functionalized single-stranded DNA (ssDNA) on the surface of gold electrode (GE) through specific Au—S covalent bond. The ssDNA/GE showed a single strong DPV oxidation peak, which was used as the electrochemical signal for AA sensing. The bonding interaction between AA and ssDNA was confirmed by UV–vis absorption spectrometry and DPV. AA and ssDNA formed a single complex and the binding ratio of AA with ssDNA was one AA per guanine base of ssDNA. The electrochemical oxidation of AA-ssDNA adduct on the surface of GE was an adsorption-controlled irreversible reaction and a two-electron two-proton transfer process. Under optimum conditions, ssDNA/GE exhibited excellent DPV response depending on the concentration of AA in 0.4–200 μM range. The limit of detection was 8.1 nM (3 σ/slope). This electrochemical biosensor displayed good reproducibility and high stability. This biosensor was successfully applied to the determination of AA in tap water and potato crisps. This electrochemical platform is convenient and efficient, offering great potential for construction of electrochemical biosensors toward various toxic substances.

1. Introduction

As a widely used chemical material, acrylamide (AA) is often applied in polyacrylamides production, wastewater treatment, papermaking, and tertiary oil recovery [1]. It is noteworthy that AA can generate strong neurotoxicity, genotoxicity, and potential carcinogenicity in humans [2]. High concentration of AA can be detected in high-starch foods (potato crisps, cookies, and breads) during cooking at high temperatures, since AA will be produced through Maillard reaction between asparagine and reducing sugars or reactive carbonyls at high temperatures [3]. Even a small proportion of high-starch foods still contained high levels of AA [4]. Therefore, the harmful influences of AA to human health makes its quantitative determination become an important issue. The most widely used techniques for AA determination in foodstuff are chromatography couple with mass spectrometry and capillary electrophoresis [5,6]. Elbashir et al. developed standard method for quantification of AA content in Sudanese food by using high performance liquid chromatography coupled with LTQ Orbitrap mass spectrometry instrument [5]. El-Hady and co-workers presented the simultaneous online determination of AA in food by ionic liquid micelle collapse capillary electrophoresis [6]. However, these methods suffer from the utilization of expensive instruments, high testing costs, and complicated sample pretreatment processes. For this reason, the development of simple, efficient, inexpensive and reliable strategies for rapid and precise determination of this neurotoxic and carcinogen compound in foodstuff has become of great interest.

In this context, rapid detection methods such as electrochemical biosensing with merits of simplicity and portability have obtained an increasing amount of attention and are employed for AA detection [7]. Zargar et al. determined AA by square wave voltammetry in presence of cobalt(II) ions on the hanging mercury drop electrode [8]. Mendoza and co-workers detected AA by means of its cyclic voltammetric response on carboxyl functionalized single-walled carbon nanotube modified screen printed electrodes [9]. Novel electrochemical biosensors for AA detection based on hemoglobin modified different electrodes have been developed, due to the formation of AA-hemoglobin adduct between the amino group of *N*-terminal valine of hemoglobin and AA [10–13]. Recently, Li and co-workers developed a label-free electrochemical biosensor for AA determination based on double-stranded DNA (dsDNA)

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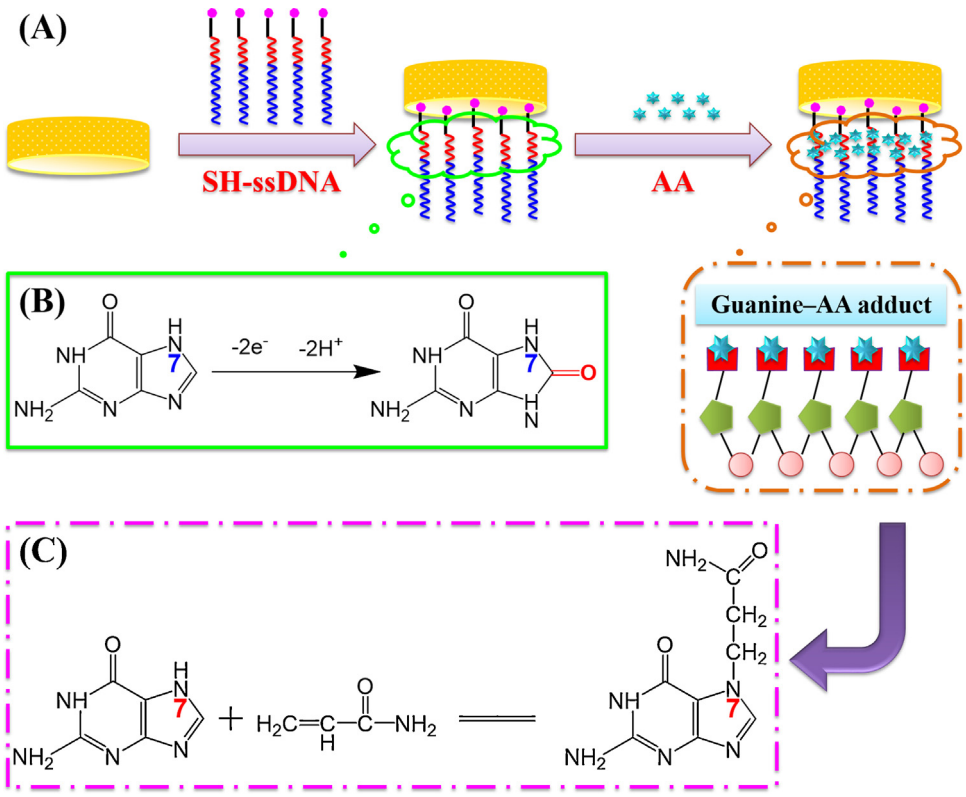

Scheme 1. Schematic of the fabrication process of ssDNA/GE and its application for sensitive detection of AA.

immobilized graphene oxide-modified glassy carbon electrode [14]. Since AA could form single and stable adduct mainly with guanine bases of dsDNA at N-7 position [15–17], and the electrochemical signal of dsDNA was mainly attributed to the electrochemical oxidation of guanine bases [18,19], such electrochemical biosensors exhibited high sensitivity and strong specificity for AA determination.

Inspired by these facts, we demonstrated a convenient and sensitive electrochemical biosensor for direct determination of AA based on thiol group functionalized single-stranded DNA (ssDNA) with partial guanine bases modified gold electrode (GE). To the best of our knowledge, there has been no report on the application of ssDNA for fabrication of AA biosensor that is expected to improve the analytical performance of biosensor. These thiol group functionalized ssDNA with partial guanine bases are effectively immobilized on the surface of GE through the specific Au—S covalent bond. Due to the sensitive and specific electrochemical oxidation of guanine bases, the fabricated ssDNA/GE exhibits an enhanced differential pulse voltammogram (DPV) oxidation peak [14,18]. The idea of this electrochemical biosensor relays on the formation of AA-ssDNA adduct through the strong bonding interaction between AA and guanine base of ssDNA at N-7 position, which subsequently inhibits the electroactivity of ssDNA (Scheme 1). As a consequence, DPV peak current of ssDNA/GE decreases in parallel with an increase of AA-ssDNA adduct concentration at the electrode surface (Scheme 1), and the decrease of DPV peak current can be utilized for selective and sensitive determination of AA. Under optimum conditions, the signal of this electrochemical biosensor depended on the concentration of AA in 0.4–200 μM range, which revealed that the fabricated ssDNA/GE exhibited wider response range and lower detection limit. Importantly, the practical application of this electrochemical biosensor was demonstrated to assay AA in tap water and potato crisps. Additionally, the bonding interaction between AA and ssDNA was deduced thoroughly. This method demonstrated simple, highly sensitive, and strong selective for practical determination of AA in foodstuff.

2. Materials and methods

2.1. Reagents

All ssDNAs were purchased from Shanghai Sangon Biological Engineering Technological Co. Ltd. (http://www.sangon.com/) and purified by HPLC. Their base sequences were list as below:

S1 ssDNA: 5′-SH-$(CH_2)_6$-GGG GGT TTT TTT TTT-3′;
S2 ssDNA: 5′-SH-$(CH_2)_6$-TTT TTG GGG GTT TTT-3′;
S3 ssDNA: 5′-SH-$(CH_2)_6$-TTT TTT TTT TGG GGG-3′;
S4 ssDNA: 5′-AAA AAA AAA ACC CCC-3′.

These ssDNAs were dissolved in 0.1 M phosphate buffer (PB, pH 7.0) and stored in refrigerator at 4 °C. All other reagents were of analytical reagent grade and used as received without any further purification. Ultrapure water with resistivity of 18.2 MΩ cm was produced by passing through RiOs 8 unit followed by Millipore-Q Academic purification set (Millipore, Bedford, MA, USA).

2.2. Apparatus

Electrochemical experiments were performed on CHI-760E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China). A three-electrode cell was employed and GE or modified GE was used as working electrode. Ag/AgCl electrode was served as the reference electrode and platinum wire was employed as the counter electrode. UV–vis absorption spectra were recorded on Cary 100 UV–vis spectrophotometer (Agilent Technologies, Inc., Australia). All pH measurements were made with a basic pH meter PB-10 (Sartorius Scientific Instruments Co., Ltd., China).