Electrochimica Acta 166 (2015) 253–260

Contents lists available at ScienceDirect

Electrochimica Acta

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

Enhanced detection of saccharide using redox capacitor as an electrochemical indicator via a redox-cycling and its molecular logic behavior

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ARTICLE INFO

Article history:
Received 11 October 2014
Received in revised form 10 March 2015
Accepted 13 March 2015
Available online 16 March 2015

Keywords:
Indicator displacement assay
Redox capacitor
Saccharide
Phenylboronic acid
Logic gate

ABSTRACT

Enhanced saccharide electrochemical sensing using dopamine cross-linked chitosan film on the electrode as an indicator was achieved by coupling indicator displacement assay (IDA) with a redox cycling. The affinity of dopamine-chitosan films toward a simple receptor of 2-fluorophenylboronic acid (FPBA) was comparable to that of saccharide towards FPBA in solution. Evidence for redox-capacitor activity of the films was then studied. The electrochemical behaviors of the films binding to FPBA and the competition with saccharide were investigated by cyclic voltammetry. FPBA binding to 1,2-diols on the films blocked electron transfer of a soluble mediator mixture between electrode and the films via a redox-cycling, resulting in a decrease in amplified signal of the mediators. The increase of amplified signal was detected in proportion to the concentration of added saccharide, ascribing to the displaced 1,2-diols from the binding receptor by competition reaction. The sensing strategy was allowed detection of micromolar levels of saccharide. Based on these properties, a molecular level IMP gate with saccharide and FPBA as inputs could be successfully mimicked.

1. Introduction

Phenylboronic acid (PBA) is known to have a high reversible affinity with diol (cis 1,2- or 1,3-diols) containing compounds to form a cyclic ester in aqueous media. As a result, much attention has been paid to the development of saccharide sensors based on PBA and its derivatives as recognition components [1,2]. The artificial receptors by appending chromophores [3,4], fluorophores [5,6] and electro-active groups [7–11] covalently associated with PBA have been widely used for recognition and detection of saccharide and other biologically important agents (e.g., dopamine [12,13], sialic acid [14], NAD(P)+/NAD(P)H [15], glycoproteins [16,17], bacteria [18,19] and cell [20]).

As another popular sensing strategy, indicator displacement assay (IDA) is a competition between the indicator and the analyte for the binding receptor. The advantage of this method is that the indicator is not covalently attached to receptor, and it is possible to change receptors and indicators at will [21,22]. IDA has been used in competitive binding assays of saccharides in fluorescent and colorimetric sensing system [23–25]. A typical kind of fluorescent saccharide sensing system which is similar to an IDA has been achieved based on the formation of a ground-state complex between fluorophores such as fluorescent dye [26] or graphene quantum dots [27], and boronic acid appended bipyridinium salts. Based on this result, further design for implementation in sensor array [28] and molecular logic gate [29,30] has been reported.

Electrochemical detection is a promising read-out method for its relative technical simplicity, high sensitivity and rapid response. Recently, Alizarin Red S and dopamine containing 1,2-diols as electrochemical indicators have been combined with PBA in homogeneous phase for competitive assay of saccharides [31,32]. Based on this principle, the major requirement for an IDA is that the affinity between the indicator and the receptor be comparable to that between the analyte and the receptor [22]. Unfortunately, simple PBA shows a significantly higher affinity for these indicators than for saccharide (more than one or two order of magnitude) in solutions [24], resulting in determining millimolar levels of saccharide. Therefore, it is essential to develop a novel sensing strategy for both adjusting the affinity of indicator with PBA to be comparable with that of saccharide with PBA, and sensitive detecting the signal of displaced indicator represents a basic and critical subject for improving the sensitivity of saccharide detection. Electrochemical processes are fundamentally being heterogeneous in nature, and much more sensitive processes can

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http://dx.doi.org/10.1016/j.electacta.2015.03.096
0013-4686/

occur directly at the electrode-solution interfaces. A popular approach for electrochemical signal amplification is to employ redox-cycling reactions with redox active moieties. Payne and co-workers have reported a bio-based redox capacitor for amplifying electrochemical signal and integrating molecular logic operations [33–35].

In the current work, we investigated an IDA for detection of saccharide, using redox capacitor of dopamine-chitosan films as an indicator firstly (Scheme 1A). The affinity of the films towards a simple receptor of 2-fluorophenylboronic acid (FPBA) was comparable to that of saccharide towards FPBA in solution. Electron transfer of a soluble mediator mixture between the electrode and the films via a redox-cycling resulted in a generation of amplified signal of the mediators. FPBA binding to 1,2-diols on the films blocked the electron transfer, leading a decrease in the amplified signal. Therefore, by taking advantage of observed increase of the amplified signal, which was related to the displaced 1,2-diols through addition of saccharide (Scheme 1B), we could fabricate a novel sensing strategy for enhanced detection of saccharide. According to these properties, a molecular level logic gate corresponding to a two-input IMP function can be successfully mimicked.

2. Experimental

2.1. Materials

Chitosan flake (Medium molecular weight, 75-85% deacetylation) was purchased from Sigma–Aldrich Chemicals. Dopamine hydrochloride (DA, 98%) was purchased from Aladdin Chemistry Co., Ltd. 2-fluorophenylboronic acid (FPBA) was purchased from Adamas Reagent Co., Ltd. (98%, Basel, Switzerland). Glutaraldehyde and $NaBH_4$ was obtained from Xi'an Wolsen Bio-technology Co., Ltd. (Xi'an, China). Hexaammineruthenium(III) chloride (97.5%, Ru^{3+}), Ferrocenecarboxylic acid (98%, Fc), Methyl-α-D-glucopyranoside and N-Acetylneuraminic acid (Sialic acid) were purchased from J&K Scientific Inc. (Beijing, China). D-glucose, D-mannose and D-fructose were purchased from Xi'an Wolsen Bio-technology Co., Ltd. (99%, Xi'an, China). The 0.1 mol/L phosphate buffer solution (PBS, pH = 7.4) was used as the supporting electrolyte and prepared from KCl and Na_2HPO_4 and KH_2PO_4. All other reagents were analytical reagent grade and double distilled water was used throughout the experiment.

2.2. Instrumentation

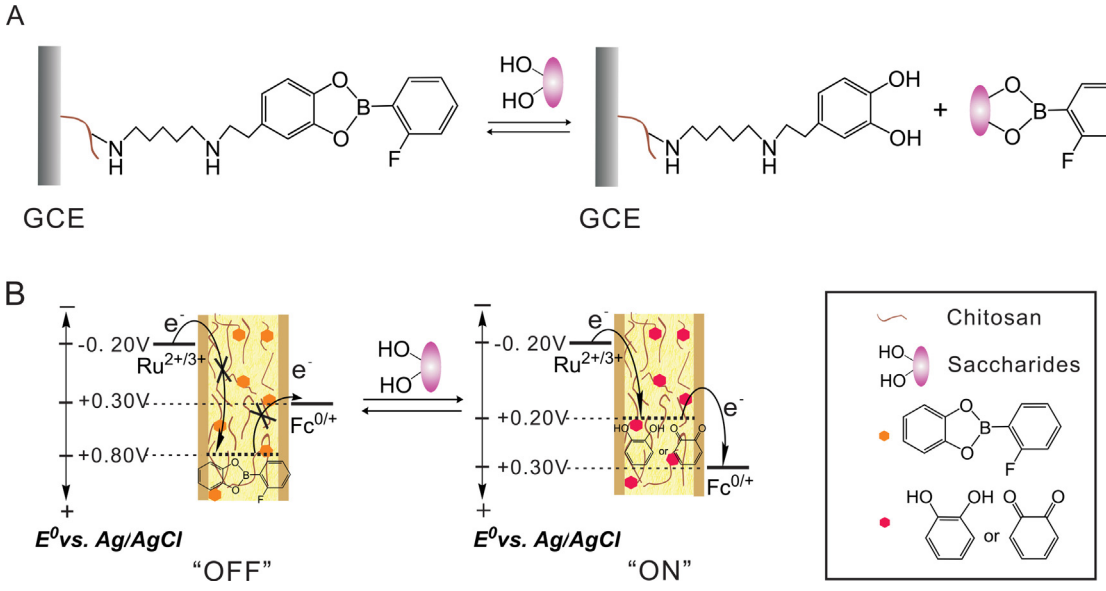
Electrochemical experiments were recorded using a three electrode system controlled by CHI 660 electrochemical workstation (Shanghai, China), with a glassy carbon electrode (GCE, 3 mm in diameter) as a working electrode, an Ag/AgCl (3 mol/L KCl) reference electrode and a platinum counter electrode. A Leici PHS-25 digital pH meter (Shanghai, China) was used to measure the pH values of the aqueous solutions. Infrared spectrum (IR) was performed on a TENSOR 27 IR spectrometer (Bruker Optics Inc., Germany). The surfaces of modified electrodes were characterized by environmental scanning electron microscope (Quanta 200, FEI Inc.,)

2.3. Electrodeposition of chitosan film on a glassy carbon electrode.

Chitosan solutions (1%, pH 5.6, W/W) were prepared by dissolving chitosan flakes in double distilled water and incrementally adding small amounts of HCl to the solution to maintain the pH near 3, then using NaOH (1 mol/L) to adjust and achieve a final pH of 5-6. The glassy carbon electrode was polished with 1.0, 0.3, and 0.05 μm alumina powders consecutively to get a mirror like surface and then sonicated in distilled water for 5 min. A constant cathodic current of 0.03 mA was applied to the pretreated glassy carbon electrode in the above chitosan solutions for 45 s. After the electrochemical deposition, the modified electrode was rinsed with distilled water, PBS and dried at room temperature.

2.4. Fabrication of dopamine-chitosan films modified electrode

The chitosan film modified electrode was put into the mixed solution containing 1% (v/v) glutaraldehyde and 5 mmol/L dopamine for 2 h at room temperature. Then, a reduction reaction was accomplished by immersing the modified electrode in alkalescent



Scheme 1. (A) Schematic representation of an IDA for saccharide sensing based on dopamine-chitosan films as indicator and FPBA as receptor. (B) Thermodynamic profile for electron transfer of a soluble mediator mixture in process of the IDA.