



Facile fabrication of dual-ratiometric electrochemical sensors based on a bare electrode for dual-signal sensing of analytes in electrolyte solution

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ABSTRACT

In this work, a general strategy to facilely fabricate novel dual-ratiometric (DR) electrochemical sensors (ECSs) was developed. This strategy referred to three types of substances with respective oxidation current peaks at different electric potentials, such as ferrocene (Fc) at 0.15 V, methylene blue (MB) at -0.26 V, and doxorubicin (DOX) at -0.62 V. In a conventional electrolyte solution of phosphate buffered saline (0.01 M, pH 6.5, containing 0.15 M of NaCl), Fc and MB as reference electroactive substances were added and their concentrations in electrolyte solution were fixed to 30 and $4 \mu\text{M}$, respectively. Then, DOX as the analyte was also added into the electrolyte solution to form a homogeneous electrolyte solution. Through directly using a bare glassy carbon electrode as dual-signal sensing platform, square wave voltammetry curves of various electrolyte solutions containing three components of different concentrations were measured, with the each increment of DOX concentration [DOX] from 0.01 to $6 \mu\text{M}$. Ratiometric oxidation current peak intensities ($I_{\text{DOX}}/I_{\text{Fc}}$ or $I_{\text{DOX}}/I_{\text{MB}}$) nearly linearly enhanced with the increase of [DOX], together with good linear coefficients and low limits of detection (3 nM). The DR-ECSs enabled highly selective and sensitive DOX detection in real human serum and saliva samples with high detection recoveries. These results revealed that this strategy to fabricate novel DR-ECSs was facile and flexible, which would facilitate a further development in the field of electrochemical sensing.

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1. Introduction

As one of promising analysis techniques, electrochemical sensors (ECSs) can convert chemical or biological information rapidly, ranging from the concentration of specific sample component to the total composition analysis, into an electrical signal [1–7]. During the past a few decades, ECSs have received increasing attention in Analysis Science because of their unique advantages, such as rapid operation, response and recognition performance, as well as low limit of detection (LOD), high selectivity and sensitivity to analytes [8,9]. Traditional ECSs with single electrical signal response are probably influenced by intrinsic or extrinsic factors, such as sensor concentration, instrumental efficiency and environmental condition [10–13]. By contrast, the ratiometric ECSs with dual

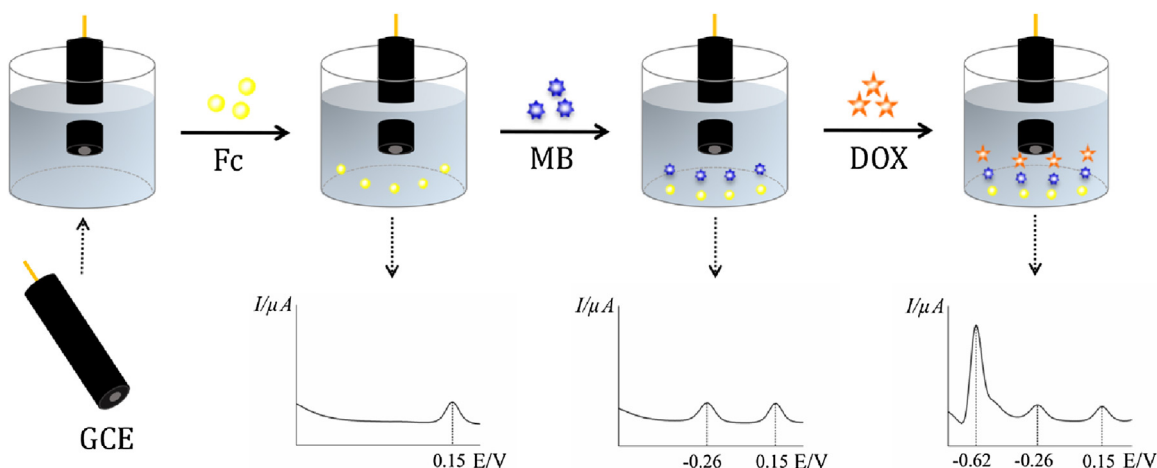
electrical signal responses are superior alternatives to the traditional ECSs. Ratiometric ECSs can detect analytes by measuring the changes of the ratio of dual oxidation current peaks at different redox potentials, and hence have attracted much attention in recent years. Theoretically, the strategy of ratiometric ECSs can provide an intrinsic built-in correction to the effect from intrinsic background electrical signals, having a significant potential to improve the accuracy and sensitivity in electrochemical sensing applications [14–16].

In previous reports, the ratiometric ECSs were prepared through modifying at least one type of electroactive molecules on the interface of electrodes [17,18]. The specific interactions from aptamer-target [19], antigen-antibody [20] and host-guest [21] could contribute to the change of electrochemical signals because of the changed distance between the electroactive molecules and electrode surface. Although these reported methods claimed their high selectivity and sensitivity, they often suffered from time-consuming and cautious processes for electrode modification, thus restraining their extensive applications in electrochemical sens-

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Scheme 1. Schematic illustration of the fabrication process for a dual-ratiometric electrochemical sensor of DOX in electrolyte solutions.

ing. Moreover, it is also difficult to confirm whether the observed electrical signal changes are attributed to the target binding or the deterioration from sensing surface, based upon the methods from previously reported ratiometric ECSs [22]. In order to overcome these defects, the development of a simple and efficient method to fabricate highly efficient ratiometric ECSs is significant and is still a challenging research in the electrochemical sensing field.

Herein, we put forward a facile method to fabricate novel dual-ratiometric ECSs (DR-ECSs) that were directly prepared in electrolyte solution (not on electrode surface) through using a bare electrode as electric signal sensing platform. This method was inspired from fluorescence analysis methods [23,24]. The as-proposed DR-ECSs could be realized in electrolyte directly. To describe this method clearly, a specific experiment was conducted. Briefly, three types of substances with respective oxidation current peaks at different electric potentials were selected, e.g. ferrocene (Fc) at 0.15 V, methylene blue (MB) at -0.26 V, and doxorubicin (DOX) at -0.62 V. In a common electrolyte solution of phosphate buffered saline (PBS), Fc and MB as the reference electroactive substances were added into the electrolyte solution, reaching fixed concentrations of Fc and MB. Afterward, DOX as the analyte was also added in the electrolyte solution to form a homogeneous system for the dual-ratiometric electrical signal sensing of DOX. By using a bare glassy carbon electrode (GCE) as the signal sensing platform, the square wave voltammetry (SWV) curves of respective electrolyte solutions containing three components were measured, together with fixed concentrations of Fc and MB, and the increasing concentration of DOX [DOX]. Under appropriate experimental conditions, the linear relationships of ratiometric oxidation current peak intensities ($I_{\text{DOX}}/I_{\text{Fc}}$ or $I_{\text{DOX}}/I_{\text{MB}}$) versus [DOX] could be achieved.

As illustrated in Scheme 1, three well-shaped oxidation current peaks by SWV mode presented in different electric potentials without mutual interference, when the three-component system (Fc, MB and DOX) in PBS was used for electrolyte. Consequently, the oxidation current peak intensity of DOX linearly increased with the increased [DOX], by using Fc and MB as internal references. Although different analytical methods, such as liquid chromatography [25], electrophoresis [26] and spectrometry [27], have been used for DOX detection, most of them were time-consuming, expensive and low sensitive. The electrochemical methods for DOX detection have been reported, but all of them were based on the single electrical signal sensing strategies. To the best of our knowledge, so far a single- or dual-ratiometric electrochemical method for the facile and efficient detection of antitumor drugs has not been reported. Furthermore, this as-proposed method to fabricate novel

DR-ECSs has a general applicability since it can be easily extended to the efficient determination of other redox targets through properly changing specific electroactive substances in electrolyte solution. On this account, this method probably facilitates a further development in the new designs and significant applications of ECSs.

2. Experimental section

2.1. Reagents and materials

Doxorubicin hydrochloride (DOX), thrombin (Thrb), lysozyme (Lys), bovine serum album (BSA), paclitaxel (Plt), vinca alkaloids (Val), 5-fluorouracil (5-Frc) and cytarabine (Ctb) were bought from Shanghai Sangon Biotech Co., Ltd. Immunoglobulin G (IgG) and MB were obtained from Aladdin. Fc was purchased from Tianjin Zhiyuan Reagent Co., Ltd. Na_2HPO_4 , NaH_2PO_4 and NaCl were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. Other chemicals were obtained from Shanghai Reagent Co., Ltd. All chemicals are of analytical grade and can be directly used as received without any purification.

2.2. Apparatus

The electrochemical measurements were conducted through using a CHI-660C electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.). A common three-electrode system consists of GCE (3 mm in diameter) as a working electrode, platinum wire as an auxiliary electrode and saturated calomel electrode (SCE) as a reference electrode. SWV mode was used for voltammetry analysis. All potentials in this work were referred to SCE.

2.3. Pretreatment of bare GCE

Briefly, a bare GCE was polished with $0.3 \mu\text{m}$ and $0.05 \mu\text{m}$ alumina slurries separately to obtain a mirror-like surface, followed by ultrasonication treatment in deionized water and ethanol. After that, the GCE was thoroughly washed through rinsing with enough amounts of deionized water, and then it was dried under N_2 atmosphere.

2.4. Measurement procedures

Briefly, 0.01 M of PBS (containing 0.15 M of NaCl) with a certain pH value of 6.5 [28,29] was used for the electrolyte in SWV measurements. The redox substances (MB and Fc) and the target (DOX) with different concentrations were added into the electrolyte, and

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