



Fabrication of an electrochemical sensor based on spiropyran for sensitive and selective detection of fluoride ion



Jia Tao ^{a, b, c}, Peng Zhao ^b, Yinhui Li ^{b, *}, Wenjie Zhao ^b, Yue Xiao ^b, Ronghua Yang ^{a, b, **}

^a School of Chemistry and Biological Engineering, Changsha University of Science and Technology, Changsha, 410004, China

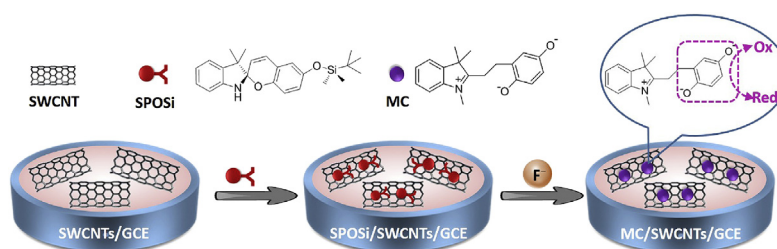
^b State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, China

^c College of Chemical Science and Engineering South China University of Technology, Guangzhou, 510641, China

HIGHLIGHTS

- Endogenous redox group in spiropyran skeleton avoids the appearance of the false positive signals.
- SWCNTs effectively amplify the electrochemical signal to improve the detection sensitivity.
- The specific reaction between F[−] and silica shows excellent anti-interference ability in urine and blood samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 December 2015

Received in revised form

7 March 2016

Accepted 14 March 2016

Available online 19 March 2016

Keywords:

Spiropyran

Fluoride ion

Electrochemical sensors

SWCNTs

ABSTRACT

In the past decades, numerous electrochemical sensors based on exogenous electroactive substance have been reported. Due to non-specific interaction between the redox mediator and the target, the instability caused by false signal may not be avoided. To address this issue, in this paper, a new electrochemical sensor based on spiropyran skeleton, namely SPOSi, was designed for specific electrochemical response to fluoride ions (F[−]). The breakage of Si–O induced by F[−] based on the specific nucleophilic substitution reaction between F[−] and silica would directly produce a hydroquinone structure for electrochemical signal generation. To improve the sensitivity, SPOSi probe was assembled on the single-walled carbon nanotubes (SWCNTs) modified glassy carbon electrode (GCE) through the π – π conjugating interaction. This electrode was successfully applied to monitor F[−] with a detection limit of 8.3×10^{-8} M. Compared with the conventional F[−] ion selected electrode (ISE) which utilized noncovalent interaction, this method displays higher stability and a comparable sensitivity in the urine samples.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Spiroprans are one of most important class of functional

organic probes called photochromic compounds [1], which undergo reversibly structural transformation between two isomers induced by light irradiation or other environmental conditions [2]. During the transformation process, chemical bond rearrangement induces changes of both electronic and geometrical structure, which can be exploited to the construction of various target-driven devices. Benefiting from this outstanding feature, a lot of spiropyran-based derivatives were designed to construct chemosensors for the detection of metal ions, anions and neutral

* Corresponding author.

** Corresponding author. School of Chemistry and Biological Engineering, Changsha University of Science and Technology, Changsha, 410004, China.

E-mail addresses: yinhui16@163.com (Y. Li), yangrh@pku.edu.cn (R. Yang).

molecules [3]. Over the last few years, our group have developed a series of spiropyran sensors using UV–vis absorption, fluorescence and electrochemistry as detection means [4–11]. However, with the development of our research, it was gradually found that there were still some problems needing to be solved such as the low accuracy and high background, and the two reasons for these problems include: i) false positivity signal may appear in the analysis results, because the structure of spiropyran was too sensitive to the environmental factors such as light and pH value; ii) the poor water-insolubility and low quantum yield also hindered the further development of optical technique based spiropyran sensors. Fortunately, the electronic arrangement during the isomerization process provides the potential to design spiropyran-based electrochemical sensor, which could overcome part of the disadvantages resulted from the optical method such as the poor water-insolubility and low quantum yield. Moreover, electrochemical strategy has captured the comprehensive interests because it allows the development of sensitive and inexpensive platforms. Therefore, spiropyran derivatives as the photoswitchable modulator have been utilized for the electrochemical sensors by regulating the electron transfer between the electrode surface and the targets [12–14], but the previous reports were limited to redox-active targets. For detections of *non*-redox targets, additional redox-active materials are needed to transduce an electrochemical signal which may lead to the appearance of instability and false signals. To address these issues, we hypothesized to construct a novel type spiropyran electrochemical sensor which was based on the change of endogenous redox signal and ruled out the effects of instability, in this paper, fluoride ion was selected as a model target.

Fluoride ion (F^-) has played a significant role in the human body and participated in various biochemical reactions [15]. Appropriate amount of intake of F^- is essential for body health and prevention of dental caries, however, excess amount of intake of F^- may induce a lot of serious illness such as ecological damage and nephrotoxic disease [16]. Therefore, it is important to develop sensitive and selective assay methods for F^- in water and biological samples. Until now, several detection strategies to F^- have been constructed, such as UV–vis absorption method [17], fluorescent method [18], and electrochemistry method [19–22]. Among them, F^- ion-selective electrode (ISE) has been regarded as a standard method by the World Health Organization (WHO) because of its high sensitivity and quick response time [23]. However, the interference cannot be ignored using ISE when there is hydroxide ion or hydrogen ion in the detection sample [19]. Moreover, compared to the molecular recognition based on specific chemical reaction, noncovalent complexation of ISE displays lower selectivity and stability. In 2001, Yamaguchi et al. reported that the Si–O bond can be specifically broken by F^- through the nucleophilic substitution reaction, making the organic probes containing Si–O bond for F^- recognition with excellent sensitivity and selectivity [24]. Recently, a number of organic probes based on desilylation induction by fluoride have been designed for F^- detection utilizing optical method [25–28]. For the first time, we assumed to develop an electrochemical probe based on the nucleophilic substitution reaction between F^- and Si–O bond, the defects suffered by electrochemical method could be addressed by rational designing a potential electrical signal group.

Herein, we present an electrochemical signal amplification strategy using self-assembly spiropyran derivative for ultrasensitive detection of F^- . Firstly, a potential redox mediator based on spiropyran skeleton, 6-(tert-butyl dimethylsilyloxy)-1',3',3'-trimethylspiro[chromene-2,2'-indoline] (namely SPOSi) was designed and synthesized. The recognition mechanism of SPOSi for F^- has been proved using the colorimetric methods in our previous study [6]. Fig. 1 shows that the fabrication of complex electrochemical

sensor and structure conversion of SPOSi on the SWCNTs modified surface of GCE triggered by F^- . The breakage of Si–O induced by F^- directly resulted in the molecular isomerization and the appearance of a redox mediator, hydroquinone-appended merocyanine (MC). This endogenous redox mediator greatly reduced the background signal and avoided the appearance of the false positive signals. Single-walled carbon nanotubes (SWCNTs) were used to construct an efficient electrode's interface of SPOSi on glass carbon electrode (GCE) and amplify the electrochemical signal, as SWCNTs have the ability to accelerate electron transfer reactions [29–31] and the strong affinity with SPOSi through π – π stacking interaction [32]. The proposed strategy would suffer less from environmental conditions as the structure changes of spiropyran were unable to output the electrochemistry signal without the desilylation induced by F^- .

2. Experimental

2.1. Materials and reagents

All chemicals were of analytical reagent grade and were supplied by Alfa Aesar or Sigma Aldrich. The carboxylated SWCNTs were purchased from Carbon Nanotechnologies, Inc., Houston, Tx. For acid-based oxidation of SWCNTs, 300 mg of SWCNTs were treated with 60 mL of 30% nitric acid solution and was ultrasonic dispersed in water bath at ambient condition for 2 h. The solutions of anions were prepared from NaF, NaCl, NaBr, NaI, $NaNO_3$, $NaHSO_4$, NaAc, NaH_2PO_4 , $NaClO_4$, respectively. They were dissolved in sterilized Milli-Q ultrapure water (18.2 M Ω) as stock solutions. SPOSi was diluted by the stock solution with Tris-HAc buffer (20 mM, pH 7.4) containing 50% CH_3CN .

2.2. Instruments

Cyclic voltammetry was performed with a three electrode cell linked to a CHI instruments model 600D electrochemical analyzer (Shanghai, China). The electrochemical cell consists of a Pt wire counter electrode, an Ag quasi-reference electrode (QRE), and a glassy carbon electrode (GCE) as working electrode (WE). Scanning electron microscopy (SEM) measurements were conducted on a JSM-6700F electron microscope. Energy-dispersive X-ray (EDX) analysis was carried out using a HITACHI S-4500 instrument. pH was measured by model 868 pH meter (Orion).

2.3. Fabrication of the SPOSi/SWCNTs/GCE

The surface of GCE was polished sequentially with 0.3 and 0.05 μm alumina powder followed by ultrasonic cleaning with ultrapure water, ethanol, and ultrapure water for 5 min each. Finally, the electrode was washed with ultrapure water and dried under a mild nitrogen stream. The GCE was held upside down, and 5 μL of SWCNTs solution (2.5 μg) was dropped onto the electrode surface. In order to make the solution evaporation, the electrode dropped with the solution was further covered under an infrared lamp. After cooling down, 5 μL SPOSi (0.1 mM) in Tris-HAc buffer solution (20 mM, pH 7.4) containing 50% CH_3CN (v/v) was dropped onto the surface of SWCNTs. Then the modified electrode was put under the infrared lamp to make the solution evaporation.

2.4. The detection of F^- in the solution

The SPOSi/SWCNTs/GCE was upside down, 5 μL varied concentrations of F^- in the 20 mM Tris-HAc buffer (pH 7.4) was dropped on the surface of SPOSi/SWCNTs/GCE for 30 min. Then, the obtained electrodes as the working electrodes were placed into a three

Download English Version:

<https://daneshyari.com/en/article/1162990>

Download Persian Version:

<https://daneshyari.com/article/1162990>

[Daneshyari.com](https://daneshyari.com)