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An interesting strategy devoted to fabrication of a novel and high-performance amperometric sodium dithionite sensor

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ABSTRACT

According to the recently rumors about abusing of sodium dithionite (SDT) in baking bread by some bakers, we motivated to plan a study to fabricate an electrochemical SDT sensor. This work reports our results on fabricating a novel and high performance electrochemical sensor based on AuPd nanoparticles (AuPd NPs)/chitin-ionic liquid (Ch-IL)/ferrocene dicarboxylic acid-carbon black-ionic liquid (FDCA-CB-IL)/glassy carbon electrode (GCE) to ultrasensitive determination of SDT in bread samples. The modifications steps were characterized with the help of cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy. After characterization of the modifications, the sensor was electroanalytically characterized by chronoamperometry and the sensor was able to detect SDT in two linear ranges of 0.001–6 and 6–200 μM with a limit of detection of 0.1 nM and a sensitivity of 21.76 $\mu A\,\mu M^{-1}$. After confirming the capability of the sensor for SDT determination in synthetic samples, it was applied to determination of SDT in three Iranian traditional bread samples and fortunately, there wasn't any SDT in the tested bread samples and to further investigation of the ability of the sensor, the real samples were spiked and good recoveries obtained which guaranteed a good performance for the fabricated sensor.

1. Introduction

Food is a substance which is consumed for providing nutritional support for an organism of a creature. Food could be obtained from plants or animals which contains vital nutrients such as fat, carbohydrate, vitamin protein, and minerals. Ingested food by an organism is assimilated by the cells to provide energy, maintaining the life and stimulating the growth [1].

Bread is a staple food which is prepared by mixing wheat-flour dough and water, culturing with yeast, allowing to arise and baking in an oven. Bread is popular around the world and is one of the oldest artificial foods which is very important in daily meals [2]. The final quality of the bread is critically depended on culturing with yeast. Baker's yeast is a general name for yeast's strains which is used as a leavening agent and is able to convert the fermentable sugars of the dough to carbon dioxide and ethanol [3]. Salt and sugar are able to inhibit the yeast growth and inhibition is more performed by salt than sugar [3]. It has been reported that somethings such as butter and eggs are able to slow down the yeast growth [3]. Fermentation is a time-consuming procedure which must be applied before baking the bread. In commercial point of view, it is better to shorten the time of fermentation and according to the recently rumors, bakeries use a substance namely sodium dithionite (SDT) to shorten the fermentation time. SDT is a white-colored crystalline powder with a sulfurous odor with industrial uses and in the body is able to inhibit the antioxidants, causing blood pressure, gastric cancer, skin disorders and respiratory disorders [4]. Therefore, determination of SDT is very important and to achieve this goal, developing efficient analytical methods is highly demanded. Among the available analytical techniques, electrochemical sensors because of their sensitivity, simplicity, selectivity, repeatability, simple construction, simple operation, reliability, rapid response, capability of real sample analysis, low-cost and reproducibility may be preferred for determination of SDT.

In fabricating electrochemical sensors, the bare glassy carbon electrode (GCE) is usually modified with different materials which can help to improve the selectivity and sensitivity of the sensor [5–17]. All the materials used in modifying the bare GCE especially carbon nanomaterials have good electronic, chemical and mechanical properties and

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high surface area. Recently, a new and low-cost nanocarbon namely carbon black (CB) with a better electroanalytical performance than nanotubes due to the more number of disordered and defective sites present within and higher surface area has been reported [18–28]. These advantages motivated us to use CB for modifying the GCE to fabricate an electrochemical SDT sensor. Ionic liquids (ILs) have obtained a broad range of application in constructing electrochemical sensors and biosensors due to their high chemical and electrochemical stability and good ionic conductivity [29]. Because of the unique properties of ILs such as wide electrochemical window, high ionic conductivity, and good thermal stability, they are applied in different electrochemical applications such as in lithium batteries, capacitors, solar cells and electrochemical sensors and biosensors [30–33]. 1,1′-Ferrocenedicarboxylic acid (FDCA) as a derivative of ferrocene is a well-known mediator due to the good stability in both oxidized and reduced forms and stability in solution, fast and independent pH response and fast electron transfer [34,35]. Chitin (Ch) is a natural biopolymer which due to its properties such as good film forming ability, nontoxicity and high mechanical strength has been frequently used in constructing electrochemical sensors and biosensors [36]. It has been previously reported that Ch is able to accumulate metallic ions via some mechanisms such as chelation, electrostatic attraction and ion exchange [36]. Combination of Ch with other materials such as ILs can improve the properties of Ch [36]. Electrochemical synthesis of nanoparticles (NPs) is a controllable and green technique where characteristics of the NPs such as size, shape and density can be controlled by instrumental parameters.

In this study, we are going to fabricate a novel electrochemical SDT sensor based on modification of the bare GCE by AuPd nanoparticles (AuPd NPs)/Ch-IL/FDCA-CB-IL/GCE for ultrasensitive determination of SDT in bread samples. After electrochemical and microscopic characterizations of the modification steps, the sensor will be electroanalytically characterized and finally, it will be applied to the analysis of real samples. Schematic representation of the steps of this study is showing in Scheme 1.

2. Experimental

2.1. Chemicals and solutions

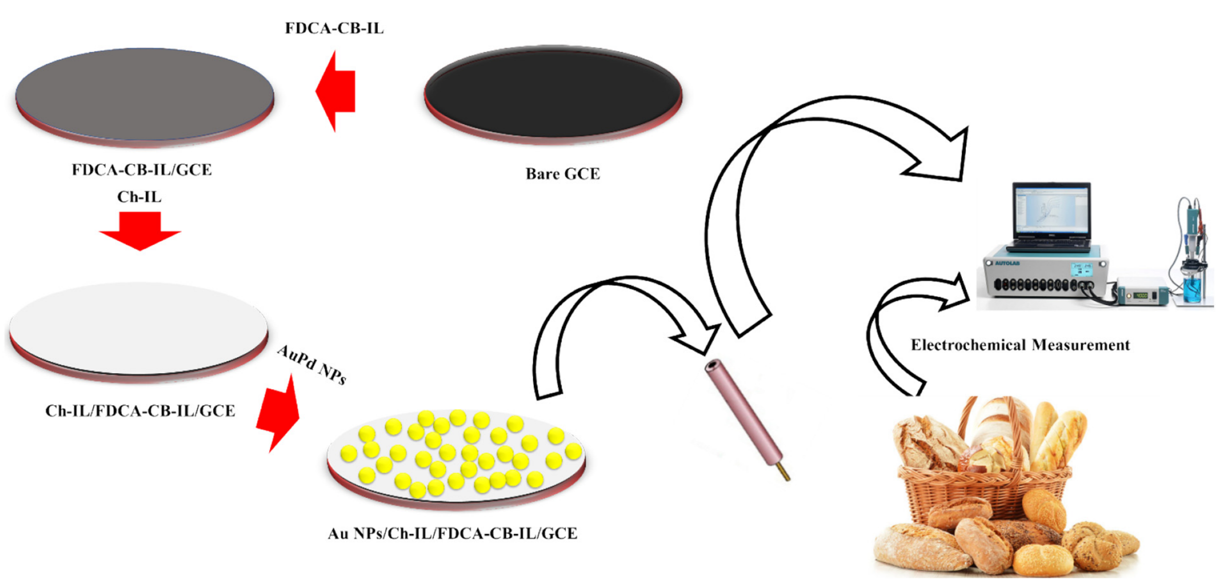
CB, Ch, SDT, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (IL), FDCA, potassium ferrocyanide, potassium ferriccyanide, gold (III) tetrachloride ($HAuCl_4$), palladium (II) chloride ($PdCl_2$), acetic acid, sodium phosphate monobasic (NaH_2PO_4), ethanol, sodium phosphate dibasic (Na_2HPO_4), phosphoric acid (H_3PO_4) and sodium hydroxide (NaOH) were purchased from Sigma. The other chemicals used in this work were purchased from regular and well-known sources and used as received. All the solutions prepared in this work were prepared by doubly distilled deionized water (DDW). A phosphate buffer solution (PBS) with a concentration level of 0.05 M was prepared by NaH_2PO_4 and Na_2HPO_4 and subsequently its pH was adjusted by H_3PO_4 and NaOH at 7.0. The redox probe solution, $[Fe(CN)_6]^{3-/4-}$, with a concentration level of 0.05 M was prepared from potassium ferrocyanide and potassium ferriccyanide by dissolution of their solid powders in 0.1 M KCl. Characterizations of the modifications applied to the bare GCE to construct the SDT sensor were performed in the redox probe solution. A stock solution of Ch (0.1% w/v) was prepared in acetic acid by ultrasonication during 40.0 min. The Ch-IL was prepared by adding 10.0 μL IL into 1000.0 μL Ch (0.1% w/v). A solution containing $HAuCl_4$ (0.5 mM) and $PdCl_2$ (0.5 mM) was prepared in Na_2SO_4 (0.1 M). To prepare the FDCA-CB-IL, 20.0 μL IL was added to 1.0 mL ethanol containing 20.0 mg CB and ultrasonicated for 40.0 min then, 10 mg FDCA was added to CB-IL and well-mixed by hand shaking. A stock solution of SDT (0.1 M) was prepared in the PBS (0.05 M, pH 7) and SDT working solutions were prepared from its stock solution by appropriate dilutions.

2.2. Instruments and softwares

All the electrochemical data reported in this study have been recorded by an Autolab PGSTAT302N-high performance controlled by the NOVA 2.1.2 software. The GCE, Pt wire and Ag/AgCl electrode which acted as working, counter and reference electrode, respectively, were purchased from Metrohm. The SEM images were captured by a KYKY-EM 3200 scanning electron microscope. Elemental analysis was performed by Energy dispersive X-ray spectroscopy (EDS). An ELMEIRON pH-meter (CP-411) was used to pH adjustments. The electrochemical data recorded in this study was transferred to MATLAB (Version 7.14, MathWorks, Inc.) environment and smoothed when necessary. All the computations were performed on a DELL XPS laptop (L502X).

2.3. Preparation of the sensor

Before fabricating the sensor, the GCE was cleaned by polishing it in on a silky pad containing alumina slurry and then, rinsed with DDW and ultrasonicated in ethanol for 30.0 min. Finally, the GCE left to be dried at room temperature. To fabricate FDCA-CB-IL/GCE, 10 μL FDCA-



Scheme 1. Schematic representation of the steps of this study.