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A novel electrochemical sensing platform for anions based on conducting polymer film modified electrodes integrated on paper-based chips

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ABSTRACT

In this paper, conducting polymer film modified electrodes were applied to fabricate paper-based chips (PCs), and different concentrations of chloride ions (Cl^-) in water can be selectively detected based on the potential response towards Cl^-. The three-electrode system was screen-printed on paper and the polypyrrole (PPy) film doped with Cl^- was electrochemically polymerized on working electrodes through cyclic voltammetry in aqueous solution. Open circuit potential-time method was used to measure the potential response. Based on such PCs, Cl^- can be selectively detected in the range of 10^{-7}–10^{-2} M. Moreover, such PCs were utilized for Cl^- analysis in real water samples and resulted in good results with recoveries between 113% and 124%. Besides, following the strategy we also employed this method to detect F^- in water to demonstrate its general applicability. In view of its novelty, simplicity, sensitivity and low price, such PCs will potentially be utilized for the monitoring of anions in the environment, and our method made a start for the application of CMEs to PCs to design electrochemical sensors.

1. Introduction

Paper-based devices have attracted more and more interests due to their advantages such as low cost, easy operation, disposability and potential to be made in mass production [1–4]. A series of paper and techniques have been employed to fabricate paper-based devices [4–9]. The commonly used paper materials, including chromatography paper, filter paper and nitrocellulose membrane, are pollution-free due to their pure cellulose component and they have appropriate thickness and hardness for manufacture and possess excellent wicking property. In addition, different methods have been developed to fabricate paper-based devices [5,10], such as photolithography [3,6,11], wax printing [4,12,13], inkjet etching [3], plasma etching [8], etc. Among these methods, photolithography is a very useful method currently available for patterning different designs on paper with well-defined and uniform boundaries [6,14,15].

Up to now, paper-based devices have shown remarkable potential applications in many areas involving determination of glucose, lactate, and uric acid in biological samples [2], immunoassay and enzyme activity screening [16], as well as monitoring the quality of water [6]. The commonly used detecting methods for these analyses were colorimetry and electrochemical detection (ECD). Colorimetry was frequently used because of its simplicity and visual analysis results [4,8]. Particularly, ECD has drawn more and more attention with the advantages of convenient quantification, good sensitivity and selectivity. In order to realize ECD with paper-based devices, electrodes were screen-printed on paper substrate, and the response of current or voltage signals towards analytes can be used as the output signals. For example, glucose, lactate, and uric acid were detected according to the reduction current of H_2O_2 generated by the reactions between analytes and their corresponding enzymes [2]. For ECD, potential signal was easy to measure because even a multimeter was enough to measure the constant potential response. However, the existing ECD for paper-based devices was mostly based on redox current signals, and only few can achieve the potential responses. In the present work, we designed a general strategy for paper-based anions sensor by measuring the potential signals, and introduced conducting polymer film, a kind of chemically modified electrodes (CMEs) into the field of paper-based devices.

CMEs have been extensively used in many fields, ranging from analytical chemistry, biology, environmental science, to material science since 1970s, and they made great contribution to the development of electrochemistry. Some special materials that had particular chemical or electrochemical properties, such as polypyrrole (PPy), were often used in CMEs. The significant advantages of CMEs-based analysis were their high selectivity and sensitivity. However, research on the application of CMEs to paper-based devices was still at an early stage and there were no reports about introducing CMEs to paper-based devices to our knowledge. In order

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to combine the superiority of both CMEs and paper-based devices, here we developed a novel paper-based device named paper-based chips (PCs) which are integrated with CMEs to achieve anions sensing. PPy was chosen as the modifying material due to its advantages of easy chemical or electrochemical polymerization, high conductivity in the doped state, high electrochemical activity, biocompatibility and environmental stability [11,17–19]. Besides, the mechanism of the electrochemical polymerization of Pyrrole (Py) has been studied thoroughly since it was first synthesized on the surface of electrodes in 1979 [20]. Moreover, when the specific anions doped PPy film was brought to a solution with the same anion, a film potential generated owing to the equilibrium distribution of anions crossing the interface formed between the hydrophobic PPy film and the aqueous solution. According to this potential response to the anions, a general strategy for the assay of various anions can be constructed.

Chloride (Cl^-) was selected as a model analyte in the current study because the detection of Cl^- was important in many fields, such as food safety [19], industrial applications [21], clinical diagnosis [22] and environmental monitoring [23]. A number of analytical methods for Cl^- have been developed such as ion chromatography [24], near-infrared spectrometry [25], light scattering [26] and turbidimetric method [27]. Compared with these protocols, the present unique paper-based Cl^--selective electrochemical sensor demonstrated its advantages. First, this sensor was small in size (15 mm × 20 mm × 0.34 mm) and the manufacture process was simple. Second, the prepared PCs can be used repeatedly to analyze a series of samples and disposable after detection with little pollution to environment. Third, the PPy film can resist solvent corrosion due to its characteristics of polymer and be stable in acidic or alkaline solution [28]. Fourthly, our method needed no complicated and expensive instruments, and even a multimeter can satisfy the need for detect of the potential response, which offered the advantages of simplicity and cost efficiency.

The paper-based Cl^- sensor also shows several advantages when compared with commercial Cl^- selective electrodes. First, the cost of each paper-based sensor is 0.03 US dollar, which is much cheaper than the commercial Cl^- selective electrode (Type: CS00CL02, Combination Electrode, CLEAN Co., USA) with the price of about 600 US dollars. Second, the paper-based sensor is simple in design and possesses the desired portability. The tiny size and solid Ag reference electrode make the sensor can even be laid in a wallet or a notebook. The commercial ion selective electrode involves relatively complicated configuration and liquid reference solution, which could induce extra burden to the future maintenance. Furthermore, the paper-based sensor has comparable or even better performance as commercial Cl^- selective electrode. The detection range of paper-based sensor for Cl^- is 1.0×10^{-2}–1.0×10^{-7} M while that of commercial Cl^- selective electrode is 3.55×10^{-2}–1.8×10^{-6} M. In addition, the sensitivity, response time and interference factor are almost equal. Besides, this paper-based Cl^- sensor was successfully applied to the analysis of Cl^- in real water sample and the recoveries was between 113% and 124%, demonstrating its potential in practical applications. Furthermore, this method can achieve the analysis of other anions by simply tuning the corresponding anion doped in the PPy film. Here detection of F^- was carried out to illustrate its universality.

2. Materials and methods

2.1. Reagents and instruments

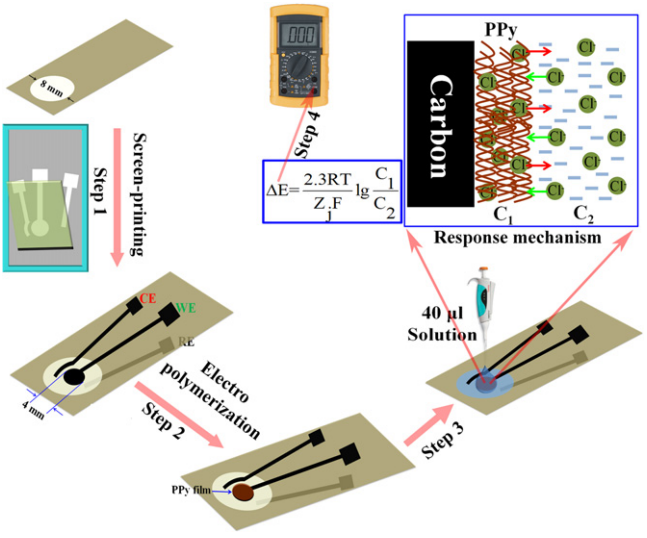
Py of reagent grade was purchased from Aldrich. Sodium chloride, sodium nitrate, sodium iodide, sodium bromide, sodium fluoride, sodium sulfate and lithium chloride were bought from Beijing Chemical Factory (Beijing, China). Whatman chromatography paper ♯1 (200 mm × 200 mm) was obtained from Whatman International Ltd. (Maidstone, England). Carbon paste and silver conductive ink were purchased from Alfa Aesar (MA, USA). All the other chemicals were of analytical reagent grade and were used as received without further purification. The water used for all experiments was purified by a Milli-Q system (18 MΩ cm). The tap water was collected without any pretreatments.

Cyclic voltammetry (CV) for the electrochemical polymerization of Py and open circuit potential-time curve were performed on a model CH Instrument 832C electrochemical workstation (Shanghai Chenhua Equipments, China). CV for the electrochemical characterizations of PPy film modified electrodes was performed on an Autolab PGSTAT30 (Utrecht, Netherlands) controlled by Software GPES4 in 5 mM $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ with the potential range from −0.2 to 0.6 V and the scan rate of 50 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was performed on the same instrument (controlled by Software Fra) under an oscillation potential of 5 mV over the frequency range of 10 kHz to 0.1 Hz. Tests on Autolab were operated in a homemade Faraday cage to decrease the stray electrical noise and all the measurements were carried out at room temperature. ABM Mask Aligner and Exposure System (CA, USA) were used to produce paper-based substrate with clear boundary between hydrophobic and hydrophilic section. The wavelength of UV light used in this experiment was 365 nm, and the energy density was 15 mJ cm^{-2}.

2.2. Fabrication and chemical modification of PCs

Paper-based substrate was fabricated by photolithography according to previously reported methods [2,6]. Briefly, a piece of Whatman chromatography paper was soaked with SU-8 3025 photoresist. After baking at 95 °C for 5 min, the paper was exposed to UV light for 6 s through a photomask. The unpolymerized photoresist was removed by soaking the paper in acetone for 1 min and rinsing the paper with acetone for three times. Then, working electrode (WE), counter electrode (CE) and reference electrode (RE) were screen-printed on it to form PCs (Scheme 1, step 1).

The electrochemical polymerization of Py was performed in an aqueous solution containing 0.1 M Py and 0.1 M LiCl using CV method (Scheme 1, step 2). The potential was set in the range from



Scheme 1. Schematic illustration of the experimental procedure for Cl^- sensing.