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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

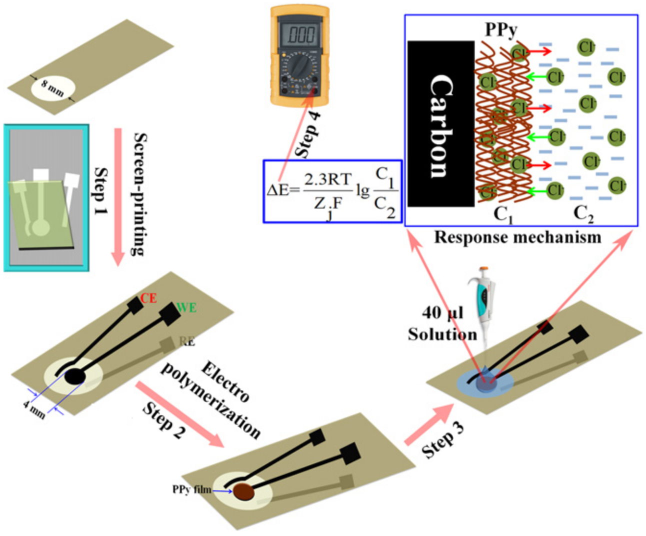
Py of reagent grade was purchased from Aldrich. Sodium chloride, sodium nitrate, sodium iodide, sodium bromide, sodium fluoride, sodium sulfate and lithium chloride were bought from Beijing Chemical Factory (Beijing, China). Whatman chromatography paper ♯1 (200 mm × 200 mm) was obtained from Whatman 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.

0.4 to 1.0 V with a scan rate of 50 mV s^{-1}. The aqueous solution was degassed by N_2 for 25 min before the polymerization and a N_2 atmosphere was kept during the experiment. Once the PPy film was prepared, it should be activated in a Cl^- solution for 6 h to achieve a stable potential response to Cl^-. After use, these prepared chips should be stored in 1 M Cl^- solution to keep the state of activation and can be used repeatedly in one week. The carbon paste will peel off from the paper substrate if the chips are immersed in solution for more than 1 week, which makes the chips unusable.

2.3. Potential response of PPy film modified PCs to Cl^-

When the PPy film modified PCs was in contact with an aqueous solution containing Cl^- (Scheme 1, step 3), a potential response will generate and it can be measured by a multimeter (Scheme 1, step 4). A halt of 30 s was kept before the measurement of potential so as to obtain a stable potential response.

3. Results and discussion

3.1. Fabrication of PCs

Whatman chromatography paper with the thickness of 0.34 mm was chosen to produce PCs due to its appropriate hardness for manufacture and excellent wicking property. As shown in Fig. 1, we first used polymerized photoresist to form hydrophobic barriers on paper, accompanied by a hydrophilic circular zone with a diameter of 8 mm. The WE, CE (carbon ink) and RE (silver conductive ink) were then screen-printed on the prepared paper substrate to fabricate PCs. For easy operation, the WE and CE were laid on one side (Fig. 1A) while the RE was laid on the other side (Fig. 1B). The whole process can be finished within 10 min, and six or more chips can be produced once a time, indicating that this design was suitable for mass production. A row of the completed chips was shown in Fig. 1.

3.2. The response principle of the anion sensor

PPy is a large, highly conjugated series of linked cations with strong hydrophobic property [29]. In the current study, we used PPy film modified electrodes to construct a novel paper-based anions sensor. Using Cl^- as a model analyte, when the Cl^- doped PPy film was in contact with a Cl^- aqueous solution, a sensing interface formed between the hydrophobic PPy film and the aqueous solution. So there will be a concentration difference between both sides of the film resulting in an equilibrium distribution of Cl^- crossing the interface to generate a film potential (Scheme 1, response mechanism). According to Eq. (1) which was transformed from the Nernst equation to adapt to our situation, the concentration difference will generate a potential response

$$\Delta E = \frac{2.3RT}{Z_j F} \lg \frac{C_2}{C_1} \tag{1}$$

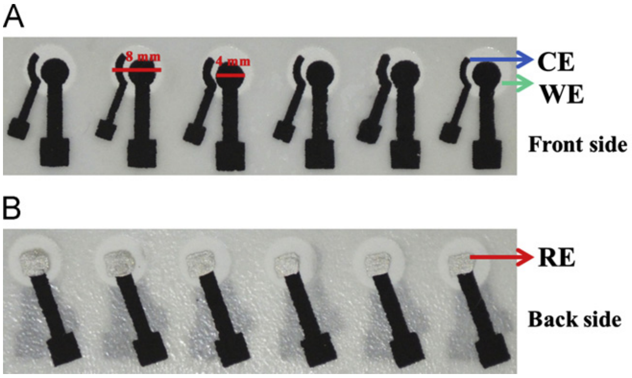


Fig. 1. Picture of PCs with integrated three-electrode system. One row contains six chips, which were screen-printed at one time. (A) Front side with working electrodes (WE) and counter electrodes (CE); (B) back side with reference electrodes (RE).

Here ΔE is the Nernst potential, the gas constant R is 8.314 J K^{-1} mol^{-1}, T is the Kelvin temperature (during our experiments, T=288.15 K), Z_j is the ionic charge (for Cl^- Z_j=1), the Faraday constant F is 96,485 C mol^{-1}, and C_1 and C_2 are the concentrations of Cl^- in two sides of the film, respectively. After replacing the letters in Eq. (1) with the known values respectively, we got a more clear equation

$$\Delta E = 0.0571 \times \lg \frac{C_1}{C_2} \tag{2}$$

We ruled randomly that C_1 was the concentration of Cl^- outside of the PPy film and C_2 represented the concentration inside of the film. So the value of C_2 was determined after activation, and the Nernst potential was linearly proportional to the logarithm of C_1 with the theoretical slope of 57.1 mV.

3.3. Proof of the electrochemical polymerization of Py

PPy film was fabricated on the above prepared PCs through electrochemical polymerization of Py in aqueous solution. The potential applied to the WE played an important role during the process of electrochemical polymerization: a low potential cannot initiate the polymerization; while the PPy film will be damaged irreversibly at an excessively positive potential. Therefore, the accuracy and stability of the RE were very important. In order to keep the demanded potential rightly applied to WE, we investigated the stability of the pseudo-RE printed with silver conductive ink and the difference between the pseudo-RE and a standard Ag/AgCl RE. As shown in Fig. S1, there was only a slight difference of about 0.03 V between these two REs and the pseudo-RE here was nearly stable during the whole process.

Besides, the thickness of PPy film was proportional to the polymerization time. Too thick membrane would increase the activation time and lower response speed. But if the film was too thin, it wouldn't give an optimal response to Cl^-. In view of these two facts, we selected 8 min (i.e. 20 CV cycles) as the polymerization time during our experiments. The CV curves of electrochemical polymerization were shown in Fig. 2. The oxidation current increased rapidly from 0.7 V (Fig. 2A) and the increased current indicated that the Py monomer was oxidized and polymerized on the surface of WE. We can also see that the current on the reverse scan was higher than that on the forward, and the two intersected at about 0.45 V to form a loop. This typical nucleation loop was also an evidence of the happening of electropolymerization. According to the previous reports, the oxidization of Py happened more easily on PPy than on the surface of electrodes, and the oxidation current increased with the circling numbers [17,30]. Fig. 2B shows the first five circles with enhanced currents and the electropolymerization in latter circle begins at a lower voltage than that in the prior cycle which was coincident with previous study.

3.4. Characterization of PPy film modified screen-printed carbon electrodes

The PPy film modified carbon electrodes were investigated using both EIS and CV. The inset in Fig. 3A showed that the circuit

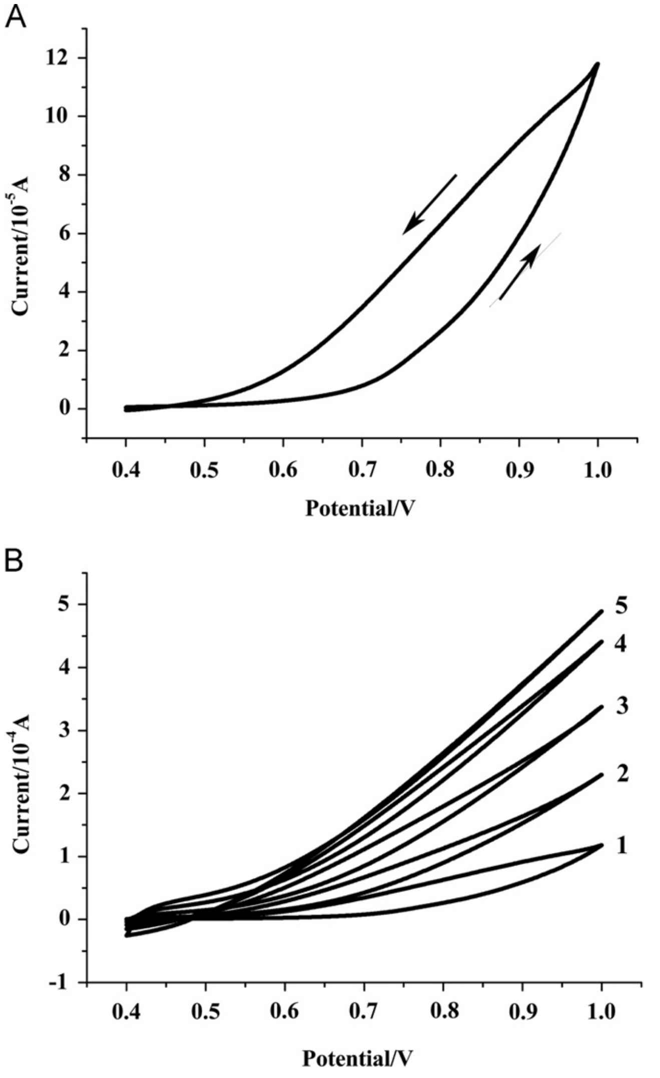


Fig. 2. Cyclic voltammetry of electrochemical polymerization of Py in a solution containing 0.1 M Py and 0.1 M LiCl. Potential range, 0.4–1.0 V; scan rate, 50 mV s^{-1}; polymerization time, 8 min (20 cycles). (A) The first cycle of CV. (B) The first five cycles of CV.

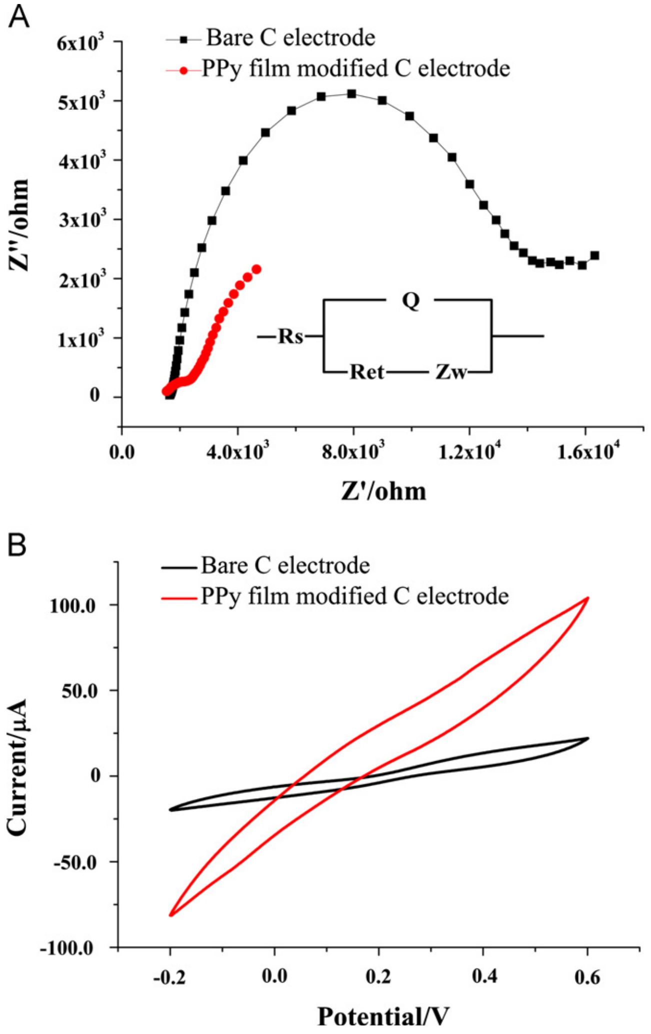


Fig. 3. (A) EIS curves of the bare carbon electrode (black line) and PPy film modified electrode (red line). Inset (A): the circuit for the EIS. (B) CV curves of the carbon electrode before (black line) and after (red line) modification. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

included the commonly existing electrolyte resistance (R_s), constant phase element (Q), Warburg impedance (Z_w), and the electron-transfer resistance (R_{et}/R_{ct}). As PPy was positively charged, it would attract the negatively charged probe, $[Fe(CN)_6]^{4-/3-}$, resulting in an acceleration of the interfacial electron-transfer kinetics of the redox probe. Therefore, the bare carbon electrode showed a relatively large semicircle domain which represented the R_{et} (Fig. 3A, black line). However, after the modification of PPy film, the R_{et} signal decreased obviously (Fig. 3A, red line), due to the remarkably increasing electron-transfer efficiency of PPy. The CV results were consistent to the EIS measurements and the current increased obviously after the formation of PPy film on bare carbon electrode (Fig. 3B).

3.5. *Potential response to Cl^-*

Comparing with the response time of several minutes for other previous developed ion-selective electrodes, this sensor had a more fast response speed and a halt of 30 s was enough to obtain a stable potential response. The stability of potential response towards Cl^- was shown in Fig. S2 and it can be seen that the potential was almost constant within 150 s. We integrated the potential value within 150 s to eliminate the interference caused by tiny fluctuations during the process of potential measurements.

The plot of potential as a function of the minus logarithm of the concentration was shown in Fig. 4A. A linear correlation ($R^2=0.98$) existed between the value of potential and the logarithm of the concentration of Cl^- over the range of 10^{-7}—10^{-2} M. The slope of the fitting line was 59.0 mV which was close to the theoretical value in Nernst equation.

We next investigated the specificity of PPy film modified PCs towards Cl^- (10^{-5} M) relative to other anions (each 10^{-5} M), including I^-, Br^-, F^-, NO_3^- and SO_4^{2-}. These five anions have the most close hydrated ion radius to Cl^- and usually coexist with Cl^- in environment. As shown in Table S1, NO_3^-, I^- and Br^- caused severe interference, while F^- and SO_4^{2-} showed slight interference. It was believed that the potential response came from an ion association between the positively charged PPy cations and the negatively charged Cl^-. If there were other anions which had the close hydrated ion radius to that of Cl^-, these anions will also have the ability to associate with PPy cations and brought in some undesired influence. Based on this response mechanism, it was reasonable that the PPy film modified electrodes can also response to the other anions (such as NO_3^-, I^- and

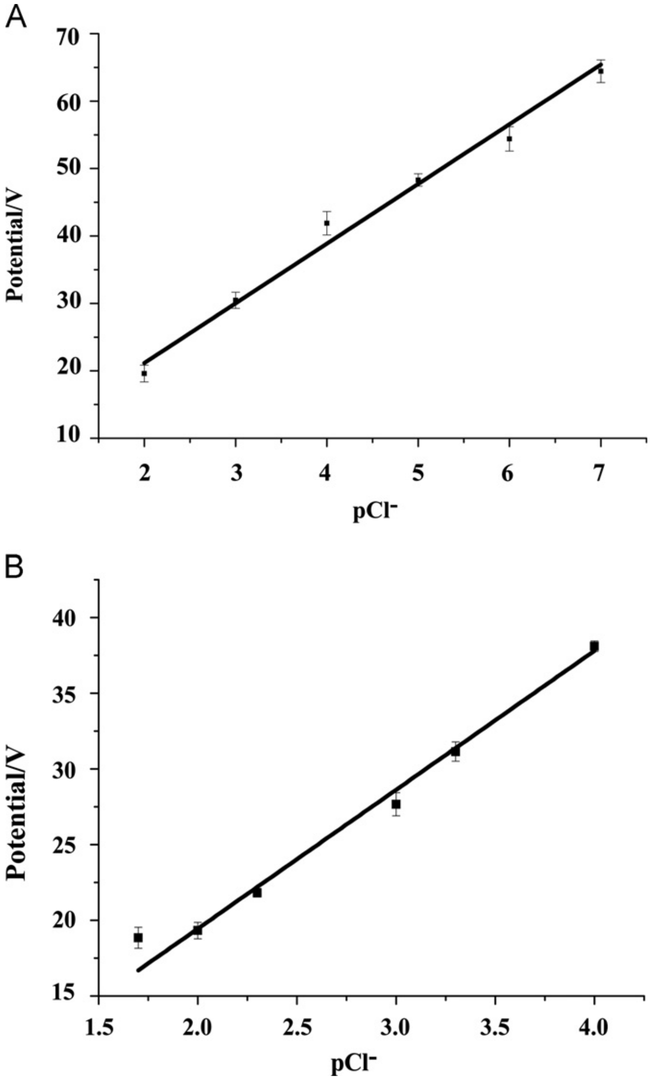


Fig. 4. (A) The calibration plot of potentials vs. the minus logarithms of the concentrations of Cl^- ($R^2=0.987$, $n=3$). (B) The linear response of the PPy film modified PCs to Cl^- from 0.1 to 20 mM ($R^2=0.989$, $n=3$). All the potential values were integrals of the transient potential for 150 s.

Br^-) whose hydrated ion radius are close to Cl^- (Table S1). However, the concentrations of interfering anions in real samples (such as blood plasma, tap water) are much lower than Cl^- and our method is still feasible in real sample analysis.

The stability of PPy film in acidic and alkaline solution was also proved by experiments. We compared the responses of the chip to 10^{-3} M Cl^- in pure water, 0.1 M NaOH and 0.05 M H_2SO_4 solutions (Figs. S2–S4) and the potential responses were 200.1, 201.3, 200.8 mV respectively. So there was no obvious influence on the potential responses caused by alkaline or acidic solutions. From the figures we can also see that the potential responses to 10^{-3} M Cl^- in alkaline or acidic solutions are as stable as in pure water. Therefore, we believe that the PPy film is stable in alkaline and acidic solutions. We select H_2SO_4 as the acidic experimental object, because there is a big difference between the hydrated ion radius of SO_4^{2-} and Cl^-, and it will not interfere the potential response to Cl^- in solution.

3.6. Application of the PCs in real sample analysis

In order to evaluate the practicability of this PCs system, it was utilized to determinate the concentration of Cl^- in tap water. For the purpose of getting a more precise result, a narrow linear range from 0.1 to 20 mM was obtained (Fig. 4B) and a standard equation was fitted accordingly: $E=-9.18lgC+1.09$. The analysis results in real samples were shown in Table 1 with the recoveries between 113% and 124%. Titrimetric analysis results showed that the concentration of Cl^- in tap water is 1.54 mM. There was a deviation of about 25% between our method and the traditional titrimetric analysis. From these results we can see that other anions did not cause significant deviation because their concentrations in tap water were much lower than Cl^-. We supposed that the deviation of 25% mostly came from NO_3^- because its concentration in tap water was the biggest among all the anions which may cause severe interference towards Cl^-.

Table 1
The analysis results of the real samples.

Sample	Analysis results (mM)	Recovery (%)
Tap water	1.93	–
Tap water added 5 mM Cl^-	8.59	124
Tap water added 10 mM Cl^-	13.48	113
Tap water added 15 mM Cl^-	19.87	117

3.7. General applicability for other anions

To demonstrate the general applicability of our method, PPy film doped with F^- was electrochemically polymerized under the same condition except that 0.1 M LiCl was displaced by 0.1 M NaF in PPy solution. Here we selected F^- mostly because this method can certainly response to other anions which caused severe interfere in Cl^- detection while F^- only caused a slight interference. Besides, there is a need for the quantification of F^- in water, because the excess quantity of F^- does great harm to people's health. The potential response to different concentrations of F^- was shown in Fig. S3 and this method can detect F^- in water from the range of 10^{-6} M to 10^{-3} M. This result suggested that our method was suitable for detecting other anions by doping each of them separately in PPy film in advance.

4. Conclusion

Herein, we demonstrated the combination of conducting polymer film modified electrodes and PCs to detect Cl^- in water for the first time. Since this chip was constructed with paper, this method was very cheap and the completed chips were portable, disposable and easy-to-use. This method did not require complicated instruments for detecting the quick and stable potential response. Besides, we analyzed Cl^- in the real water sample and got an accurate result. This method can also be utilized for detection of other anions. Such PCs will potentially be utilized for the monitoring of anions in environment. We believed that other sensing interfaces which have been constructed on glassy carbon electrodes can also be fabricated on this kind of PCs and there was a potential for employing CMEs to PCs to design electrochemical sensors.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.11.062.

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