DETERMINATION OF TRACE OF IODIDE
AT A POLY-L-METHIONINE MODIFIED GLASSY CARBON ELECTRODE

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This work developed a highly simple and sensitive voltammetric method for accurate determination of trace iodide using poly-L-methionine modified glassy carbon electrode. The oxidation current of iodide at the modified electrode was found to be more higher than that at the bare GCE, which was attributed to the ion exchange capacity of L-methionine. The electrocatalytic oxidation response of iodide at this modified electrode has been investigated by various voltammetry methods including cyclic voltammetry, anodic stripping voltammetry and differential pulse voltammetry. Applying the optimal differential pulse voltammetry conditions, the oxidation current of iodide increased linearly from 2.50×10^{-6} to 1.00×10^{-3} mol L^{-1} with a detection limit of 8.0×10^{-7} mol L^{-1} (at an S/N of 3). In addition, other performance of the electrode including the reproducibility, stability, and anti-interference ability were excellent. Finally, the present method has been applied to quantify the iodide in table salt samples with satisfactory results.
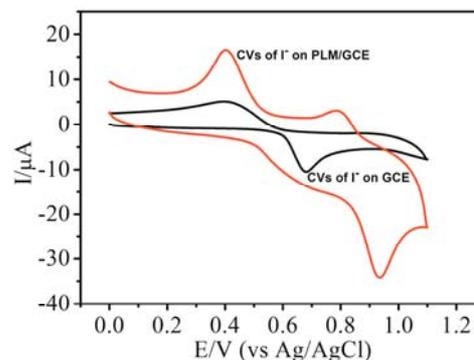
INTRODUCTION

Iodine is well known as an essential micronutrient for human body and can be found in many foods as an additive or naturally present. Deficiency of iodine can cause endemic goiter, stagnation and hypothyroidism,[1] and an excess of iodine can lead to excessive iodine goiter, chronic lymphocytic thyroiditis, iodine hyperthyroidism and hypothyroidism.[2] Thereby, accurate detection of iodine is necessary and significant. Iodine exists in various forms, such as iodine, iodide, iodate and methyl iodide. Iodine is easy to volatilize and difficult to measure. Many analytical techniques discussed in the literature including neutron activation analysis,[3] atomic fluorescence spectrometry,[4] flow injection amperometry,[5] ion chromatography,[6] capillary electrophoresis,[7] chemiluminescence,[8] inductively coupled plasma mass spectrometry,[9] and UV–vis spectrophotometry[10] have been employed for iodide determination. However, current methods meet some obstacles such as complicated sample preparation and high cost.[11] This suggests a necessity to propose an alternative technique for assay of iodide.

Electrochemical methods have been found to be more economy, oversimplified and reliable.[12-16] Since the direct electrochemical measurement own a high overpotential, modified electrodes are common used due to higher efficiency and sensitivity when compared to bare electrodes.[17] Up to now, many substances such as food additives,[18,19] biologically active compounds,[20,21] heavy metal ions,[22,23] and medicine[24,25] have achieved good detection effect through the modified electrodes. Meanwhile, many type of materials have been developed for modified

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electrodes such as reduced graphene oxide,[26,27] carbon nanotube,[28,29] and gold nanoparticles.[30-31] Different modified materials have a unique electrocatalytic property to different substances. Application of amino acids as modifier in iodide electroanalytical study offers advantages of facilitating electron transfer, decreasing overpotentials significantly, and pre-concentrating anionic compounds.[32] Methionine, is a kind of α-amino acid which contains a basic group (-NH$_2$) and an carboxyl group (-COOH) and can be protonated up to pH 3.8. It is easy to deposit onto electrode surfaces and has anion-exchange properties to accumulate iodide. As far as we know, at present it has not been used as a modifier to measure iodide.

In the development of voltammetric method to determinate iodide, the glassy carbon electrode (GCE) modified with poly-L-methionine was employed in the present work. The poly-L-methionine modified glassy carbon electrode (PLM/GCE) could be employed as an effective electrochemical tool for the analysis of iodide. Further, this proposed method has also showed a high electrochemistry activity towards iodide in real samples.

EXPERIMENTAL

1. Reagents and Materials

Potassium iodide was obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China). L-methionine was purchased from Sinopharm Chemical Reagent Co., Ltd. A dispersion of 5×10^{-3} mol L^{-1} idoxuridine was prepared by direct dissolution of the potassium iodide in doubly distilled water. Using the above dispersion, the idoxuridine standard solutions (2.50×10^{-6} – 1.00×10^{-3} mol L^{-1}) were gradually diluted with phosphate buffer solutions (PBS). The idoxuridine solution was prepared freshly before used and carefully protected from light during use. The solid L-methionine was dispersed in PBS (pH 5.5) to obtain 2.5×10^{-3} mol L^{-1} stock solution. The PBS were prepared with 0.1 mol L^{-1} Na$_2$HPO$_4$-NaH$_2$PO$_4$ solutions and the different pHs were controlled by mixing appropriate proportion of H$_3$PO$_4$ and Na$_3$PO$_4$. The doubly distilled water were used for all aqueous solutions preparation. All experiments were performed at room temperature.

2. Apparatus

Electrochemical experiments were performed on a BAS100B/W electrochemical workstation (BAS group, USA) with a conventional three-electrode configuration. The working, counter and reference electrodes were a glassy carbon electrode (GCE, 3 mm in radius) or in its modified form, a platinum wire, and a KCl-saturated Ag/AgCl respectively. A digital pH/mV meter (PHS-3C, Shanghai Leici Device Works, China) was used for all acidity measurements.

3. Preparation of Modified Electrodes

Before modification, the bare GCE (3 mm diameter) was mechanically polished to produce a mirror-like smoothness using 0.05 μm Al$_2$O$_3$ powder. Then it was placed in absolute ethanol and doubly distilled water for 1 minute ultrasonic cleaning, respectively. After rinsing with doubly distilled water, most physically adsorbed materials were removed from the electrode surface. Finally, the electrode was dried naturally in air.

The above GCE was immersed in 10 mL polymerization solution containing 5 mL 2.5×10^{-3} mol L^{-1} L-methionine stock solution and 5 mL pH 6.0 PBS. Then, electropolymerization of L-methionine was performed by potential cycling between 2.3 and −0.7 V at a pulse amplitude of 150 mV s^{-1} for 7 cycles after 15 s quiet time. After rinsed with double distilled water to remove unreacted L-methionine and dried in air, the poly-L-methionine modified GCE was acquired.

4. Electrochemical measurements

After modification, the modified GCE was electroactivated applying successive cyclic sweepings from −0.2 to 0.8 V at 180 mV s^{-1} for 1 cycle in 10 mL blank solution containing 5 mL pH 7.0 PBS and 5 mL doubly distilled water. Electrochemical measurements were subsequently conducted by cyclic voltammetry from 0.0 to 1.1 V at 200 mV s^{-1} after 15 s quiet time in 10 mL buffer solution (5 mL pH 3.5 PBS and 5 mL proper amount of idoxuridine standard solutions). In order to avoid the presence of adsorptive substances, the electrode was washed with doubly distilled water and electroactivated again as the above CV procedure prior to every measurements.

RESULTS AND DISCUSSION

Voltammetric behavior of iodide at bare GCE and PLM/GCE

The electrochemical activity of the bare GCE and the PLM/GCE for the 1.00×10^{-4} mol L^{-1} iodide oxidation were studied in pH 3.0 PBS after 15 s elapsed. As shown in Fig. 1 (curve a), at positive potential, an oxidation peak at 0.68 V was found, which correspond to the electroxidation of I$^-$ to I$_2$; at reversal potential, the corresponding reduction peak occurred at 0.39 V, which correspond to the reversible monoelectronic charge-transfer of I$_2$ to I$^-$. In curve b, the cyclic voltammogram of iodide at PLM/GCE, the oxidation peak at 0.68 V was extremely small while a remarkable oxidation peak centered at more positive potential of 0.93 V, indicating a possible further electroxidation of I$_2$ to IO$_3^-$. In the reverse scan, two reduction peaks at 0.79 V and 0.39 V were observed, which most likely correspond to the electric reduction of IO$_3^-$ to I$_2$ and I$^-$, respectively. In addition, the oxidation currents at PLM/GCE were higher than those obtained at bare

GCE, representing a higher electrocatalytic activity of the modified electrode. This was owing to the enrichment effect of L-methionine for the iodide. On the one hand, L-methionine deposition on the electrode surface provides a larger surface area which facilitated the contact of electrolyte with the electrode; on the other hand, under this acidic conditions (pH 3.0), active group $-NH_2$ of the L-methionine molecular chain was protonated into $-NH_3^+$, which attracted I^- through electrostatic attraction.
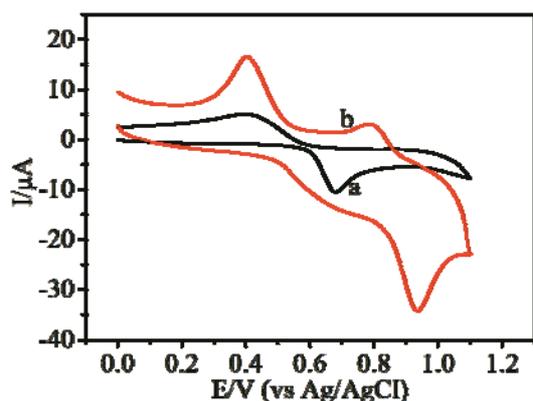

Fig. 1 – CVs of I^- on GCE (a) and PLM/GCE (b) at a scan rate of 200 mV s^{-1} in PBS (pH 3.0).

Effect of pH

The effect of pH value upon the iodide oxidation response was studied from pH 2 to 7. As indicated in Fig. 2A, the peak currents decreased with increasing pH. The weakened electrocatalytic activity of PLM/GCE towards iodide at low acidity is mainly attributed to the competitive adsorption of OH^- and I^-. Meanwhile, the peak potential

shifted negatively when increasing the pH (Fig. 2B) revealing that the oxidation of iodide at PLM/GCE is a proton transport process. The corresponding linear relationship between anodic peak potential (E_{pa}) and pH is E_{pa} = 1.1015 – 0.0499 pH, R = 0.9905. A good peak shape and large anodic peak current of iodide could be obtained at pH 3. Therefore, pH 7 was selected to be the optimal acidity for the oxidation of DA.

Effect of scan rate

The effect of scan rate on the response was investigated by means of CV in pH = 3.0 PBS containing 2.50×10^{-4} mol L^{-1} iodide as shown in Fig. 3. It was found that by applying scan rate from 20 to 400 mV s^{-1}, the anodic peak current increased gradually and the oxidation peak and reduction peak shifted positively and negatively, respectively. Accompanied by improved oxidation performance at higher scan rate, the reversibility was also deteriorated.

Fig. 4A displayed the stripping voltammetry curve at different scan rates in PH = 3.0 PBS containing 2.50×10^{-4} mol L^{-1} iodide. As scan rate more than 200 mV s^{-1} increased the signal to noise ratio making the peak type deterioration, the appropriate scan rate of 200 mV s^{-1} was considered as optimum value. In addition, the logarithm of the oxidation peak current (i) had a good linear relationship with the logarithm of the scan rate (v) shown in Fig. 4 (B). The corresponding regression equation is: lg I = 3.0418 + 1.0354 lgv, R = 0.9916. This confirmed that the behavior of iodide at PLM/GCE is adsorption-controlled.
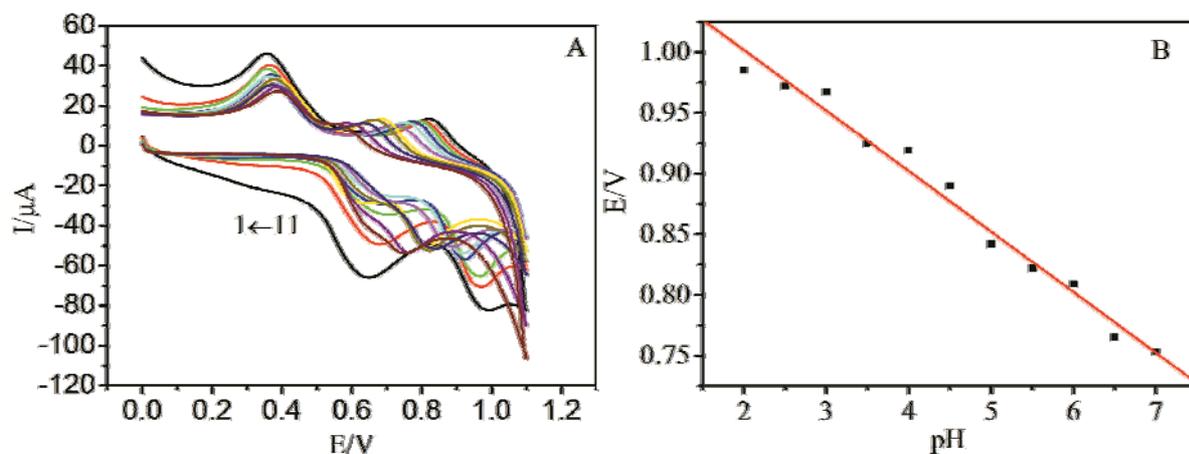

Fig. 2 – CVs of I^- with different pH(A) and the corresponding relationship curve between the peak potential and pH(B). (pH 1~11: 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0; Scan rate of 200 mV s^{-1}).
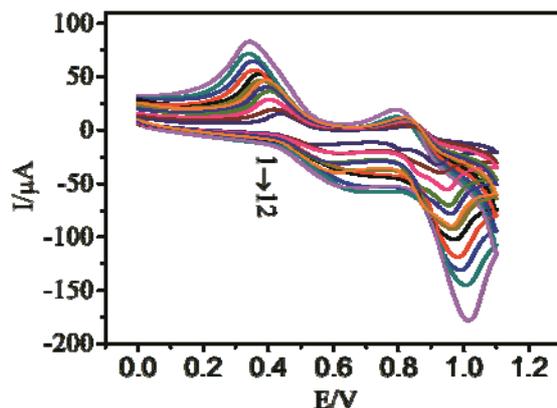
Fig. 3 – Cylic voltammograms of I⁻ at PLM/GCE with various scan rates
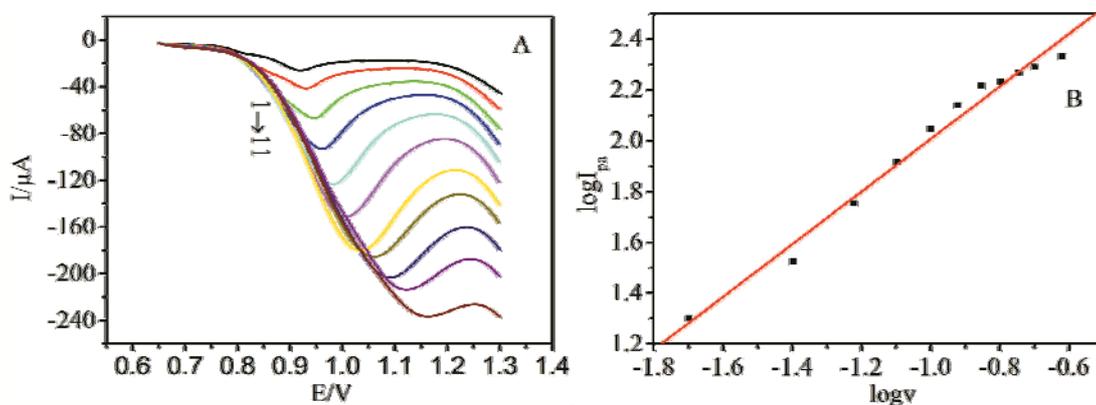(from 1 to 12: 20, 40, 80, 100, 120, 140, 180, 240, 280, 320, 360, 400 mV s⁻¹).

Fig. 4 – Stripping voltammetry curve of I⁻ at PLM/GCE with various scan rates (A)
and the corresponding relationship curve between $logI_{pa}$ and logv (B).
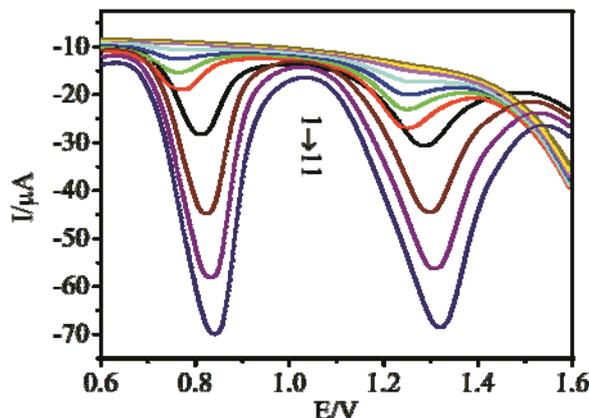(from 1 to 11: 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 240 mV s⁻¹).

Fig. 5 – DPVs of different concentrations of I⁻.
(from 1 to 11: 2.50×10^{-6}, 7.50×10^{-6}, 1.00×10^{-5}, 2.50×10^{-5}, 5.00×10^{-5}, 7.50×10^{-5},
1.00×10^{-4}, 2.50×10^{-4}, 5.00×10^{-4}, 7.50×10^{-4}, 1.00×10^{-3} mol L⁻¹).

Quantitative analysis of iodide

For more sensitive determination of iodide at the PLM/GCE, DPV technique was employed. Figure 5 displays the typical DPV curves for electrocatalytic oxidation of iodide at PLM/GCE. The anodic peak current increased linearly with iodide concentration in the range of 2.50×10^{-6}-1.00×10^{-3} mol L⁻¹ and a detection limit of 8.0×10^{-7} mol L⁻¹ was estimated. The corresponding linear regression equation was: $lgI = 5.4996 + 1.2107 lg\rho$ (R = 0.9908). All these results are shown in Table 1 and show that the modified electrode is of high catalytic activity towards iodide.

Table 1

Linear ranges, regression equations, correlation coefficients and detection limits for individual determination of I^- on PLM/GCE

Analyte	Linear ranges ρ (mol L^{-1})	Linear regression eq. I (μA) ρ (mol L^{-1})	Corr. coeff.	Detection limit (mol L^{-1})
I^-	$2.50\times10^{-6} \sim 1.00\times10^{-3}$	$lg\,I = 5.4996+1.2107\,lg\rho$	0.9908	8.0×10^{-7}

Table 2

Analysis results of iodine in salt (n = 5)

Analyte	Mean Valve ρ / (mg kg^{-1})	RSD / (%)	Added ρ / (mg kg^{-1})	Found ρ / (mg kg^{-1})	Recovery / (%)
Table salt	22.1	3.14	19.0	40.6	97.4

Stability and repeatability

Reproducibility and stability of the method was determined for 2.50×10^{-4} mol L^{-1} iodide. For the stability study, the modified electrode was stored 10 days at room temperature and its oxidation peak response was monitored every day. The results showed that no significant change in response which suggests a good stability of the method. Repeatability was evaluated by measuring the response from 20 consecutive measurements. The relative standard deviation (RSD) was 3.4% revealing good repeatability of the method.

Interference Studies

The influence of some foreign substances for the detection of 1.00×10^{-4} mol L^{-1} iodide was evaluated at 95% tolerance limit. There is no interference up to 1mg of Cl^-, Br^-, ClO_4^-, BrO_3^-, K^+, Na^+, oxalic acid, glucose, folic acid. However, the presence of SCN^- and NO_2^- ($\leq$ 1 mg) could interfere in the detection of iodide ions. For NO_2^-, it can react with I^- at acidic conditions as follows: $2NO_2^-+2I^-+4H^+\rightarrow I_2+2H_2O+2NO\uparrow$. Interference from SCN was electrochemical interference.

Determination of iodine in table salt

The proposed method was applied to the determination of iodine in table salt. However, iodine is usually added as an iodate to the salt. Therefore, iodate should be reduced to iodide using ascorbic acid before determination.[33] The sample solution was prepared by dissolved 10.0000 g table salt and 0.100 g ascorbic acid in 100 mL pH 3.0 PBS, and then analyzed by this method for 5 consecutive experiments. The results of 22.1 mg kg^{-1} was in close agreement with the labeled value 22.5 mg kg^{-1}. The accuracy of this method was also verified by standard addition method and good recoveries of 97.3% and 104% were obtained, revealing the reliability of the method. All above results are listed in Table 2.

CONCLUSION

The present work has demonstrated that L-methionine modified GCE was a facile and sensitive sensor for iodide voltammetric determination. The proposed electrode showed good electrocatalytic oxidation activity toward iodide with good linearity, reproducibility, stability and low detection limit. Moreover, the good accuracy and recovery obtained in table salt samples is making it practicality in electrocatalysis of iodide in real samples.

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