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Chitosan/Colloid Au Modified Gold Film Microelectrode for Iodide Determination

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A simple electrochemical method for iodide detection using chitosan/colloid Au modified gold film microelectrode was developed. The modified electrode was prepared by coating chitosan/colloid Au composite on the surface of a gold film microelectrode, which was fabricated through a microfabrication procedure. In acidic conditions, -NH_2 groups on chitosan could be protonated into -NH_3^+ which has a strong electrostatic attraction with I^-. In addition, colloid Au particle could improve the response signal and electron transfer efficiency of the modified electrode. Transmission electron microscopy (TEM) was employed to investigate the colloid Au and the chitosan/colloid Au composite. Scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS) were used to characterize the bare and the chitosan/colloid Au modified gold film microelectrodes. The sensing performance of the chitosan/colloid Au modified microelectrode toward iodide was evaluated in a 0.1 $mol \cdot L^{-1}$ KH_2PO_4 (pH=2.5) solution by voltammetry and the obtained voltammetric response increased proportionally with iodide concentration in the range of 3.32×10^{-7} $mol \cdot L^{-1}$~1.57×10^{-2} $mol \cdot L^{-1}$ with a correlation coefficient of 0.9996. The detection limit was 1.20×10^{-7} $mol \cdot L^{-1}$ (3S/N). Compared with the commercial iodide selective electrode, it is more sensitive especially at low concentrations. The modified electrode also demonstrated excellent discrimination against possible interference from chloride, bromide and other potential coexistent ions. The microelectrode was also evaluated by analyzing iodide ion content in a commercial dietary supplement and satisfactory results were obtained for the real sample analysis.

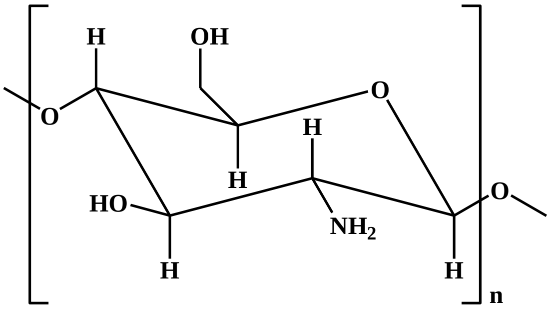
Keywords: iodide; electrochemical detection; gold microelectrode; chitosan/colloid Au; voltammetry

1. INTRODUCTION

Iodine is one of the essential elements responsible for physical and mental growth in human beings. It mainly presents in seawater and seafood in the form of iodide or iodate. Stable iodine or non-radioactive iodine is a critical nutrient that humans need in very small quantities for the thyroid gland to function properly for synthesis, storage and secretion of thyroid hormone which is fundamental for metabolism in all age groups. The latest World Health Organization (WHO) estimate is that 2 billion people are at risk of becoming iodine deficient. Iodide deficiency could cause diseases including goiter, hypothyroidism, and cretinism, and severely affect health development especially for pregnant women who need about 66% more iodine than non-pregnant women [1]. And iodide excess could also cause thyroiditis and goiter, which will cause great damage to health development too [2]. In order to ensure proper intake of iodide for different population groups, WHO recommended daily allowance of iodine are as follows ($\mu g \cdot day^{-1}$): 0-59 month: 90; 6-12-year old: 120; >12-year old: 150; pregnant and lactating women: 200. Therefore it is of special significance to monitor iodide content in food and drugs.

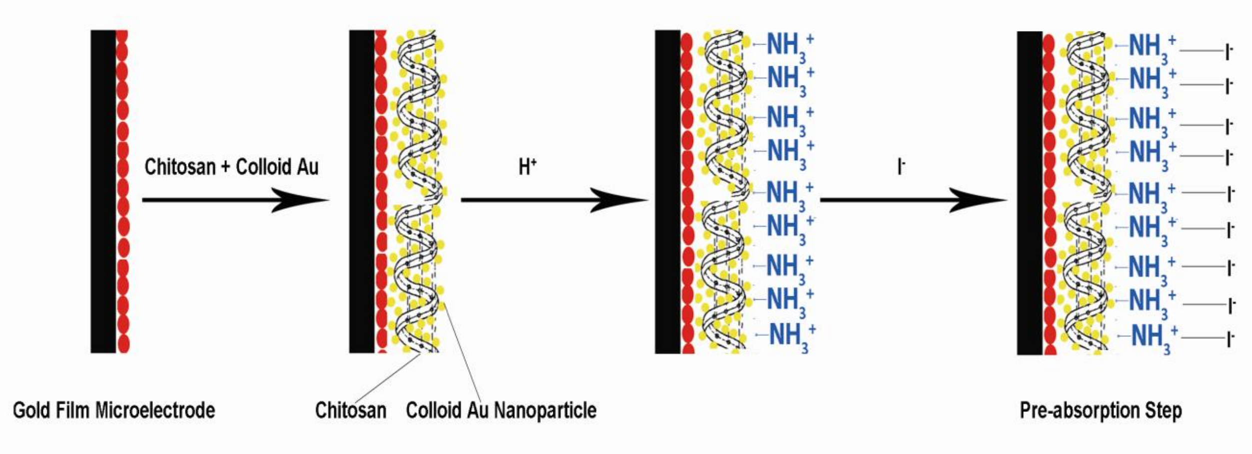
In order to achieve high sensitivity, low detection limit, and excellent selectivity, a lot of methods for iodine determination have been proposed and developed as recently reviewed by Dasgupta et. al. [3]. Particularly for iodide detection, reported methods include spectrophotometry [4], flame atomic absorption spectrometry [5], chemiluminescence [6], inductively coupled plasma mass spectrometry (ICP-MS) [7], gas chromatography-mass spectrometry (GC-MS) [8], capillary electrophoresis [9], ion-selective electrode [10], and high performance liquid chromatography (HPLC) [11]. While voltammetry provides a convenient, fast, and simple alternative with no need for expensive equipment.

And the main effort has been laid on the development of chemically modified electrodes toward iodide detection, including forming stable compound with modified matrix [12, 13, 14], improved interaction for the modified layer with iodide [15, 16, 17, 18, 19], and signal amplification by the modified layer such as carbon nanotubes [20]. For examples, a cuprite-modified electrode [12] and a silver sulfate nanoparticle-modified carbon paste electrode [13] were developed and demonstrated good selectivity toward iodide based on the formation of stable iodide compound with the modification layer. But the limited linear response range of these electrodes hindered their application. Poly(3-Aminophenylboronic acid) (PAPBA) modified platinum disc electrode [16] showed good concentration range and excellent selectivity for iodide determination, but the material was expensive. Chai [17] used complexes of mercury (II) as the neutral carrier for a poly(vinyl chloride) (PVC) membrane iodide electrode with excellent selectivity and sensitivity but the fabrication was time-consuming and the neutral carrier based on Hg was not biological compatible because of its toxicity.



Scheme 1. Chemical structure of chitosan

In this work, chitosan/colloid Au modified gold film microelectrode was developed for iodide detection. Chitosan, 2-amino-β-1, 4-polyglucose, is the N-deacetylated derivative of chitin which is a naturally abundant mucopolysaccharide. Studies have shown that it has double helix structure and its fundamental building block is presented in Scheme 1. With a huge amount of active groups like -OH, -NH_2 and excellent properties such as biocompatibility, biodegradability, non-toxicity, adsorption prosperities, chitosan has been widely applied in pharmaceutical [21], food industry [22] and environmental protection [23]. It has been used in the determination of heavy metals because it can absorb and form ion-association complex with metal ions from aqueous solution [24]. And it can be easily obtained with low cost and could be functionalized in many different ways [25].



Scheme 2. Schematic deposition steps for the chitosan/colloid Au modified gold film microelectrode

During our study, chitosan was used as the modification layer for iodide detection. It was found that under acidic conditions, the amino groups of chitosan could be protonized into -NH_3^+ which has a strong affinity toward iodide (Scheme 2). Then the absorbed iodide could be easily detected by voltammetric method. Furthermore, colloid Au particle was used to improve electron transfer efficiency thus the response signal of the modified electrode. Results showed that the chitosan/colloid Au modified gold film microelectrode demonstrated excellent sensing performance toward iodide with a wide linear range and good selectivity.

2. EXPERIMENTAL

2.1 Fabrication of the gold film microelectrode

A gold film microelectrode (designated as the bare electrode hereafter) was fabricated by two step chemical deposition of Au nanoparticles over ultraviolet treated polystyrene (PS) (Hangzhou Baiersi Plastic Co.) following a previous work [26]. Different size and shape film electrodes could be fabricated through this procedure with excellent reproducibility.

2.2 Preparation of the chitosan/colloid Au composite

Chitosan solution (1 wt %) was prepared by dissolving 0.1 g chitosan (Sinopharm Chemical Reagent Co., Ltd) into 10 mL CH_3COOH (1%) solution.

Colloidal Au nanoparticles were prepared through reduction of $HAuCl_4$ (1 wt %) (Sinopharm Chemical Reagent Co., Ltd) with sodium citrate (1%) [27]. 1 mL sodium citrate solution was added to the boiling solution of $HAuCl_4$ with vigorous stirring, and then boiled for another 20 min. All glassware was dipped in aqua regia and washed with de-ionized and distilled water before use.

Chitosan solution (1%) and colloidal Au nanoparticles were mixed with volume ratio of 1:1 to create the chitosan/colloidal Au composite. The mixture was vigorously stirred for 2 h and then kept at 4°C overnight before use. The prepared solutions were characterized by transmission electron microscopy (TEM, Philps Tecnai 10).

2.3 Fabrication of the chitosan/colloid Au modified gold film microelectrode

Whether the surface of the gold film microelectrode is clean or not has a great influence on the characteristics of the modified gold film microelectrode. The bare electrode was treated by air plasma (PDC-32G-2 plasma cleaner/sterilizer) for 8 min under the condition of high RF level and -0.1 Mpa pressure.

20 μL of the previously prepared chitosan/colloid Au composite was dropped over the surface of the bare microelectrodes. Then the electrodes were dried under room temperature and washed with deionized water thoroughly before use. For comparison purpose, chitosan modified gold film microelectrode (designated as the chitosan modified electrode hereafter) was also fabricated by coating chitosan onto the surface of the bare electrode.

Electrochemical impedance spectroscopy (EIS, Autolab PGSTAT 302N potentiostat) and cyclic voltammetry (CV, CHI-842B electrochemical analyzer) were used to investigate and compare electrochemical behavior of the bare electrode, the chitosan modified electrode and the chitosan/colloid Au modified gold film microelectrode (designated as the mixture modified electrode hereafter). EIS was conducted with a three-electrode system with Autolab PGSTAT 302N potentiostat and recorded within the frequency range of 10^{-1}-10^{5} Hz. The amplitude of the applied sine wave potential was 10 mV with the potential set at 0.25 V, and the EIS was obtained in 0.1 $mol \cdot L^{-1}$ KCl solution containing 5.0×10^{-3} $mol \cdot L^{-1}$ $K_3Fe(CN)_6$. The morphology of the microelectrodes was characterized by scanning electron microscopy (SEM, FEI Corporation SIRON).

2.4 Sensing performance

Iodide solutions were prepared from analytical grade KI (Sinopharm Chemical Reagent Co.) and high-purity water from a Millipore milliQ water purification system. Electrochemical measurements were carried out with a CHI-842B electrochemical analyzer in 0.1 $mol \cdot L^{-1}$ KH_2PO_4 to evaluate the sensing performance of the modified electrode toward iodide. A pre-absorption step was performed for the electrodes in the test solution at a potential of 0.3 V vs. a saturated Ag/AgCl reference electrode, and the detection step was from 0.3 V to 1.0 V at a scanning rate of 20 $mV\cdot s^{-1}$. Experimental conditions including pH of the test solution and absorption time were optimized. pH of the solution was measured with a Mettler Toledo Delta 320 pH meter. Real sample analysis was carried out with a potassium iodide dietary supplement manufactured by NOW FOODS, the USA.

3. RESULTS AND DISCUSSION

3.1 Characterization of the chitosan/colloid Au composite and surface of the modified gold film microelectrodes

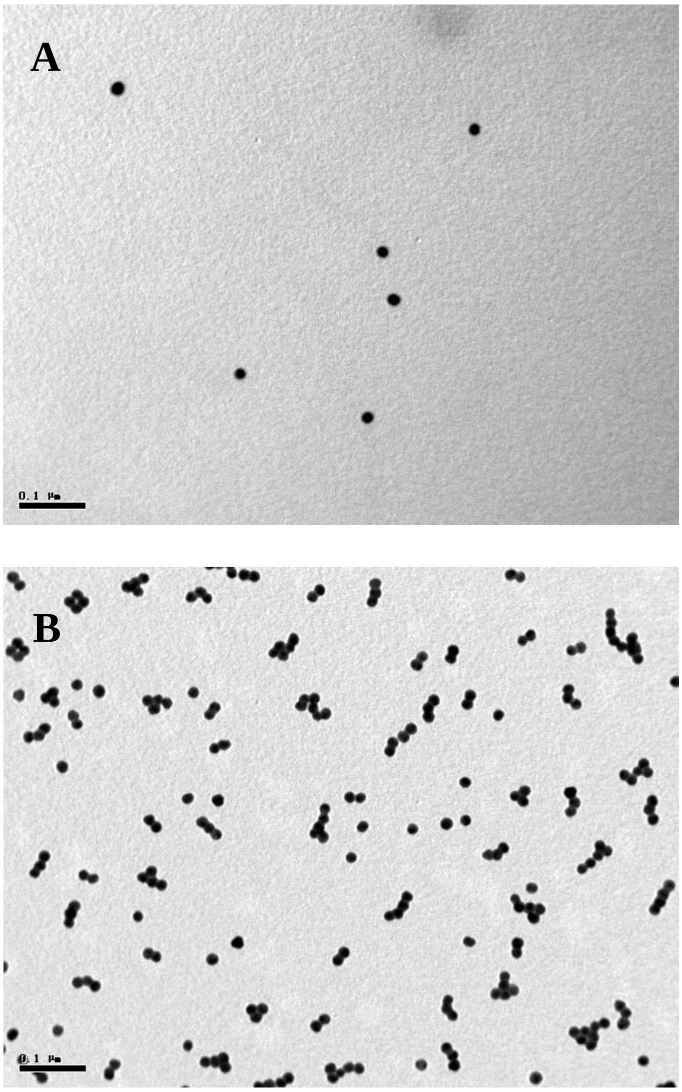


Figure 1. TEM images of (A) nano-Au colloid, (B) chitosan/colloid Au composite.

The morphology of colloid Au (Fig. 1A), and chitosan/colloid-Au composite (Fig. 1B) were characterized by TEM which is an effective method to provide information on particle size and shape.

From the TEM result of Fig. 1A, it was found that the average diameter of the colloid-Au particles was about 20 nm. The density of the colloid-Au particles increased a lot after mixed thoroughly with the chitosan solution (Fig. 1B). It also showed that the Au nanoparticles were uniformly dispersed in the chitosan solution. It is known that -NH_2 groups have great affinity toward Au nanoparticles [28], which may explain why the mixture modified microelectrode demonstrated much better charge transfer capability compared with electrode modified by chitosan alone evidenced by EIS and CV results discussed in session 3.2.

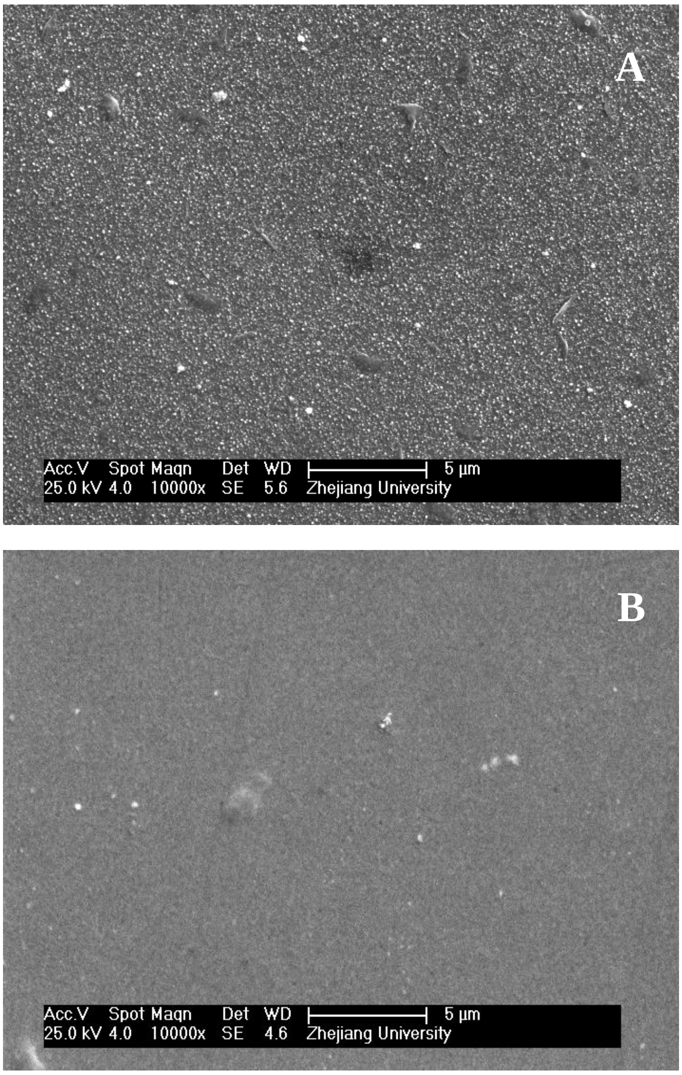


Figure 2. SEM images of the surface of (A) the bare gold microelectrode and (B) the chitosan/colloid Au modified gold microelectrode.

The morphology of the bare electrode and the mixture modified electrode was characterized by SEM, with the results shown in Fig. 2. Gold nanoparticles can be clearly seen from the bare electrode surface (Fig. 2A). The SEM result of the modified electrode (Fig. 2B) show that the surface was flat and uniform, which is significantly different from that of the bare electrode, indirectly proving that the chitosan/colloid Au composite modification step was successful.

3.2 Electrochemical characterization of the microelectrodes

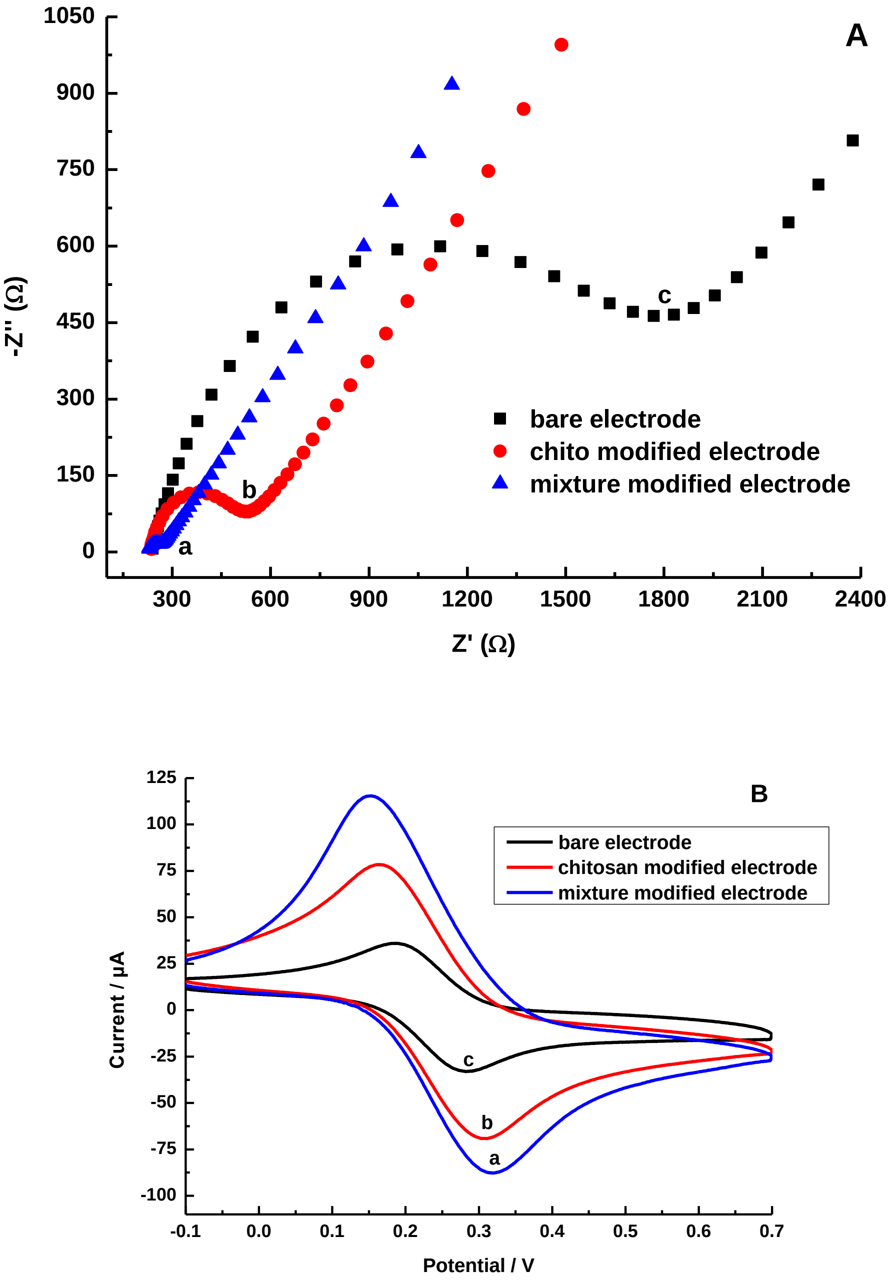


Figure 3. (A) EIS response of the mixture modified electrode (a), the chitosan modified electrode (b), and the bare electrode (c), in a 5.0×10^{-3} mol·L^{-1} $K_3[Fe(CN)_6]$ solution containing 0.1 mol·L^{-1} KCl. (B) CVs of the mixture modified electrode (a), the chitosan modified electrode (b), and the bare electrode (c), in a 5.0×10^{-3} mol·L^{-1} $K_3[Fe(CN)_6]$ solution containing 0.1 mol·L^{-1} KCl; scanning rate: 100 mV·s^{-1}.

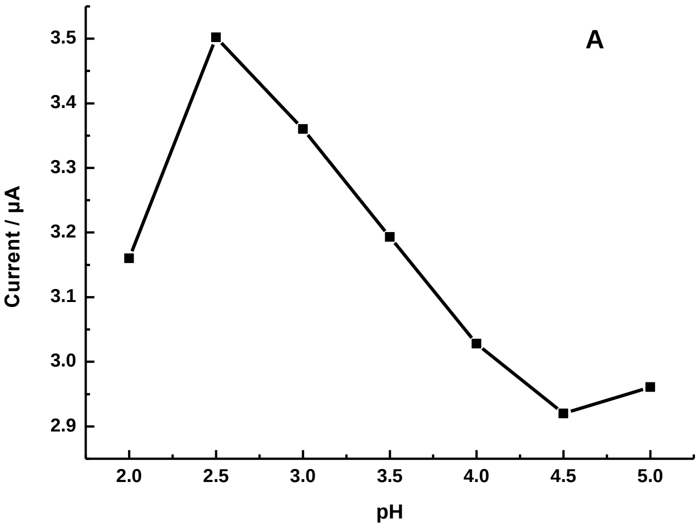
EIS is an effective tool to study interface properties of surface-modified electrodes. The electrochemical property of the mixture modified electrodes was characterized by EIS through measuring the diameter of semicircles in the spectrum and compared with that of the bare electrode and the chitosan modified electrode. Fig. 3A shows the Nyquist plot of the mixture modified electrode (a), the chitosan modified electrode (b) and the bare electrode (c). Significant difference in the impedance results can be observed for the different microelectrodes. The bare electrode exhibited a much wider semicircle compared with that of the chitosan modified electrode, while the mixture modified electrode displayed the smallest semicircle, indicating that chitosan and colloid Au particles both improved the interfacial charge transfer capability of the gold film microelectrode.

This can be further certified by the results observed with cyclic voltammetry. The CV results of the modified electrodes and the bare electrode in 0.1 mol·L^{-1} KCl solution containing 5.0×10^{-3} mol·L^{-1} $K_3[Fe(CN)_6]$ is presented in Fig. 3B. The redox-label $[Fe(CN)_6]^{3-}$ reveals a reversible CV on different electrodes while the peak current increased greatly for the mixture modified electrode (Fig. 3B (a)). It demonstrates that the modification does not affect electrical properties of the electrode but greatly increase the current response, most probably due to the addition of colloid Au in the modification layer on the surface of the electrode.

3.3 Optimization of the experimental conditions

3.3.1 pH of the test solution

The pH of the test solution dramatically affects the number of $-NH_3^+$ on the surface of the mixture modified gold microelectrode, which is critical to the absorption of I^-. Therefore the pH of the solution has a significant effect on the performance of the modified electrode. The effect of solution pH on the modified electrode behavior was investigated between pH 2 and 5 toward 5.0×10^{-4} mol·L^{-1} I^- in 0.1 mol·L^{-1} KH_2PO_4, as shown in Fig. 4A.



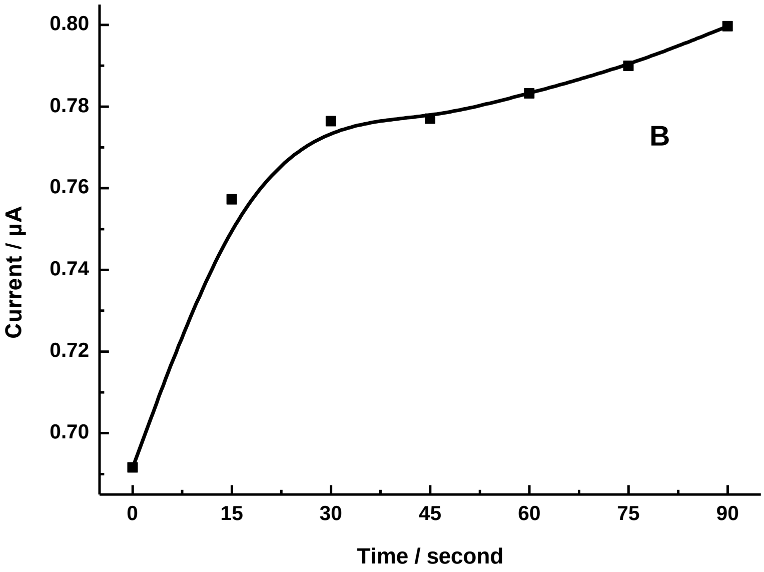


Figure 4. Optimization of the experiment conditions: (A) Influence of the test solution pH on the current response of the chitosan/colloid Au modified electrode toward 6.73×10^{-5} mol·L^{-1} I$^-$ in 0.1 mol·L^{-1} KH_2PO_4 solution; (B) The effect of absorption time on the current response of the modified electrode toward 6.73×10^{-5} mol·L^{-1} I$^-$ in 0.1 mol·L^{-1} KH_2PO_4 solution (pH 2.5).

The current response increases first with the increase of the pH, and after reaches the maximum at pH 2.5 it decreases. According to the reaction $-NH_2 + H^+ \rightarrow -NH_3^+$, lower pH of the solution could favor the formation of $-NH_3^+$, thus a larger current response for I$^-$ could be obtained. This speculation is in accordance with the pH influence resulted from Fig. 4A except for the point of pH 2.0, where the signal turns down. It is believed that the modification layer on the surface of the electrode had been partially destroyed in a strong acidic environment. From the experiment, after applied in pH 2, the electrode’s response usually decreased significantly. In later experiment, pH 2.5 was chosen through the whole study.

3.3.2 Pre-absorption time

With the pH value of the test solution 2.5, different time from 0 to 90 s was investigated for the pre-absorption step for the measurement. The current response toward 6.73×10^{-5} mol·L^{-1} I$^-$ in 0.1 mol·L^{-1} KH_2PO_4 of the electrodes is shown in Fig. 4B. With appropriate pH for the test solution, the maximum current response was at 30 s absorption time. The voltammetric response varied little after 45 s with increasing deposition time, indicating saturated formation of I$^-$ in the modified matrix. In later experiment, 30 s deposition time was chosen through the whole study.

3.4 Sensing performance of the modified electrodes toward iodide

3.4.1 Cyclic voltammetry of different electrodes toward iodide

CVs of different electrodes toward iodide was performed in 0.1 mol·L^{-1} containing 1.0×10^{-4} mol·L^{-1} iodide. The results are shown in Fig 5, with Fig. 5c for the bare electrode, Fig. 5b the chitosan modified electrode, and Fig. 5a the mixture modified electrode. It can be seen that compared with the bare and the chitosan modified electrode, the mixture modified electrode produces the highest signal and demonstrates excellent response toward iodide.

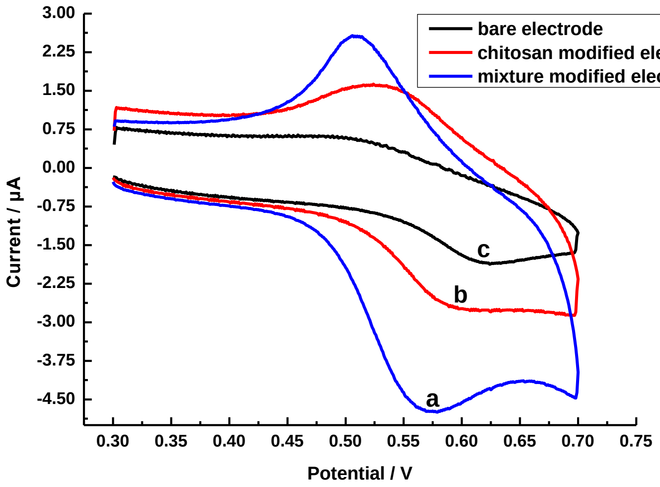


Figure 5. CVs of the mixture modified electrode (a), the chitosan modified electrode (b), and bare gold electrode (c), toward iodide in 0.1 mol·L^{-1} KH_2PO_4 (pH 2.5) containing 1.0×10^{-4} mol·L^{-1} iodide.

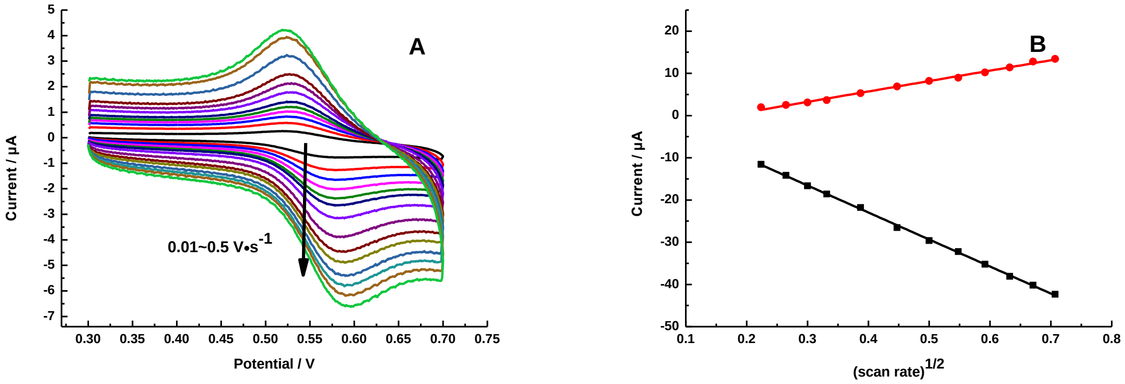


Figure 6. (A) CVs of mixture modified electrode toward iodide at different scanning rates from 0.01~0.5 V·s^{-1}. (B) The linearity between peak currents and the square root of scan rate.

Different scan rates were also investigated from 0.01 to 0.5 V·s^{-1}, with the results shown in Fig. 6A, and Fig. 6B the calibration curve. It is found that the response signal enhanced with the increase of scan rates, and they varied linearly with the square root of scan rate. This indicates that the overall process is controlled by diffusion. In order to achieve proper signal to noise level, 0.1 V·s^{-1} was chosen for later CV experiments.

3.4.2 Voltammetric response

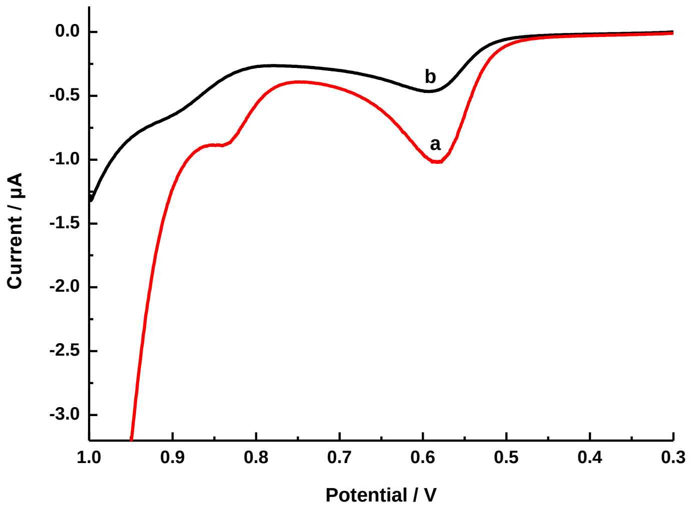


Figure 7. Comparison of voltammetric response of (a) the mixture modified electrode and (b) the bare electrode for iodide detection. The measurement was carried out from 0.3 V to 1.0 V at a scanning rate of 20 mV·s^{-1} toward 6.73×10^{-5} mol·L^{-1} I^{-} in 0.1 mol·L^{-1} KH$_2$PO$_4$ (pH 2.5) solution with a pre-absorption step of 30 s.

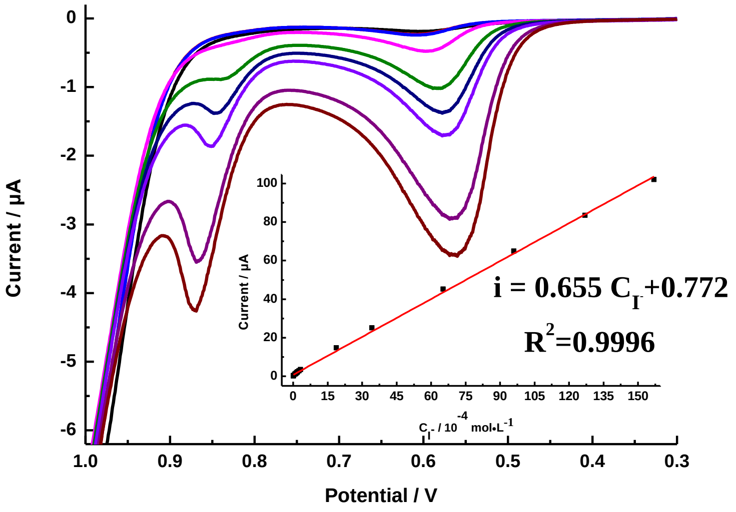


Figure 8. Voltammetric response of the mixture modified electrode toward different concentrations of iodide. The measurements were carried out from 0.3 V to 1.0 V at a scanning rate of 20 mV·s^{-1}. The inset is the calibration curve.

Under the optimized experimental conditions of pH 2.5 for the test solution and pre-absorption time of 30 s, the mixture modified electrode was used to detect iodide in 0.1 mol·L^{-1} KH_2PO_4 solution, from 0.3 V to 1.0 V at a scanning rate of 20 mV·s^{-1}. The sensing performance of the electrode toward 6.73×10^{-5} mol·L^{-1} iodide was evaluated and compared with that of the bare electrode. Fig. 7a and 7b are the current response for the mixture modified electrode and the bare electrode respectively. The peak potential changed very little for the two electrodes but the signal is much more sensitive for the electrode than that for the bare electrode. The potential of about 0.58 V at maximum current is in accordance with the electrode potential of the redox reaction $I_2 + 2e^- \rightleftarrows 2I^-$. The current response obtained increased proportionally with iodide concentration in the range of 3.32×10^{-7} mol·L^{-1}~1.57×10^{-2} mol·L^{-1} with a correlation coefficient of 0.9996 (Fig. 8, with the calibration curve presented in the inset). The detection limit (3S/N) was 1.20×10^{-7} mol·L^{-1}. In this work, lower detection limit and wider linear range with higher sensitivity was obtained for iodide determination comparing to previous work (Table 1).

Table 1. Sensing performance of various electrodes toward iodide

Electrode	Analytical Method	Linear range (mol·L^{-1})	Detection limit (mol·L^{-1})	Reference
cuprite-modified carbon paste electrode	voltammetry	1×10^{-6} ~ 2×10^{-5}	5×10^{-7}	[12]
silver nanowires modified platinum electrode	cyclic voltammetry	5.0×10^{-5} ~ 2.02×10^{-3}	10×10^{-6}	[14]
poly(3-aminophenylboronic acid) (PAPBA) film electrode	potentiometry	10^{-6} ~ 10^{-1}	8×10^{-7}	[16]
$VO(OC_3H_7)_3$–PPC film-modified glassy carbon electrode	cyclic voltammetry	5×10^{-7} ~ 1×10^{-3}	1×10^{-7}	[18]
chitosan/colloid Au modified gold film microelectrode	voltammetry	3.32×10^{-7} ~ 1.57×10^{-2}	1.20×10^{-7}	This work

3.4.3 Selectivity

To evaluate interference from other halides that are expected to coexist with iodide, certain amount of chloride or bromide was added into the test solution and the sensing performance was examined for the mixture modified electrode. With the chloride concentration increased from 18 to 4165 times that of the iodide in the solution, the current response is still within the error range (6%) (data not shown). Similar results were obtained for bromide with its concentration changed from 0 to 1416 times that of the iodide (data not shown). It demonstrates that the modified electrode has good selectivity against Cl^- and Br^-. Other ions like ClO_4^-, BrO_3^-, IO_3^-, Ac^-, Na^+, K^+ were also investigated, and the mixture modified electrode also exhibited good selectivity. While SCN^- and NO_2^- had effect on the detection process, the sensing performance of the electrode toward NO_2^- is currently under investigation.

3.4.4 Reproducibility

The reproducibility for the mixture modified electrode was checked by successive determination of 6.73×10^{-5} mol·L^{-1} iodide solution. The relative standard deviation (RSD) for the current with a same electrode was found as 3.3% (n=7) within a one week experimental period. Between measurements, the electrodes were stored in a desiccator without special care.

3.4.5 Real sample analysis

Iodide content of potassium iodide dietary supplement was evaluated by the chitosan/colloid Au composite modified gold film microelectrode and ultraviolet spectrophotometry [29] as a control. The results are summarized in Table 2.

Table 2. Iodide determination results for a potassium iodide dietary supplement

	Labeled concentration*	UV spectrophotometry	Current method
1	7.2×10^{-4}	7.39×10^{-4}	7.268×10^{-4}
2	7.2×10^{-4}	7.08×10^{-4}	6.928×10^{-4}

* The concentration was calculated from labeled level of 30 mg KI per tablet (by dissolving one tablet weight of 30 mg into high-purity water then diluted to 250.00 mL).

RSD for the UV spectrophotometric method was 2~3% and that for the current method was 4~5% respectively. It is obvious that the developed microelectrode proves to be suitable for voltammetric determination of iodide content in real sample.

4. CONCLUSIONS

In this work, a simple and stable chitosan/colloid Au modified gold film microelectrode was developed for the determination of iodide. Under optimized experimental conditions, the results show that the modified film is an appropriate sensing material for sensitive and selective determination of iodide with a wide linear range. Chitosan layer was to absorb iodide target under acidic conditions for voltammetric detection, while colloid Au can improve the current response. It is the combination of the two materials that makes the modified electrode more sensitive toward iodide. And real sample analysis was also carried out with the electrode and satisfactory results were obtained. Besides, it is easy to change the electrode shape with the microfabrication technique and its small size makes it possible to integrate into microfluidic system to facilitate fast and on-line determination of iodide.

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