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# Chitosan Modified Gold Film Microelectrode for the Determination of Iodide

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**Abstract:**
A simple electrochemical method for iodide detection using colloid Au/chitosan modified gold film microelectrode was developed. The modified electrode was prepared by coating colloid Au/chitosan membrane on the surface of a gold film microelectrode, whose working area could be easily adjusted as required. The detection was carried out in 0.1 mol·$L^{-1}$ $KH_2PO_4$ (pH=3) solution, and the obtained Anodic Stripping Voltammetry (ASV) current response increased proportionally with iodide concentration in the range of $3.32\times10^{-7}$ mol·$L^{-1}$~$1.57\times10^{-2}$ mol·$L^{-1}$ with a correlation coefficient of 0.9996. Compared with the commercial iodide selective electrode, it is more sensitive especially at lower concentrations.

**Key words:** iodide, electrochemical detection, gold microelectrode, colloid Au/chitosan, ASV

## Introduction

Iodine is one of the essential elements which are responsible for growth and development in humans. It plays an important part in thyroid hormone synthesis and is normally assimilated in the iodide form which is present in water and in animal. There are many published methods for the determination of iodide such as capillary electrophoresis [1], chemiluminescence [2], ion-selective electrode [3], atomic emission spectrometry [4], while voltametric method provides a convenient, fast, and simple alternative.

In the current work, a modified gold film microelectrode was fabricated by coating a membrane of mixed chitosan with nano-Au colloid. Chitosan, 2-amino-β-1, 4-polylucose, is the N-deacetylated derivative of chitin, which is a naturally abundant mucopolysaccharide. The chemical structure of the chitosan is shown in Fig. 1. With a huge amount of active groups like -OH, $-NH_2$ and many excellent properties such as biocompatibility, biodegradability, non-toxicity, adsorption prosperities, chitosan has a wide application in many fields, including medicine, food, chemistry, and environmental protection. Under acidic conditions, the amino group would change into $-NH_3^+$ which has a strong affinity toward $I^-$, which could be used for $I^-$ detection.

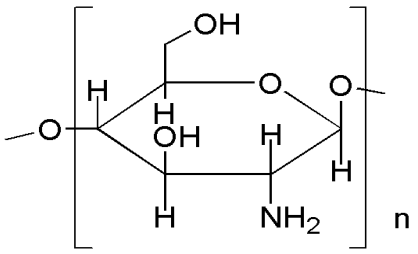


*Fig.1 The chemical structure of chitosan*

## Experimental section

Chitosan solution (1 wt %) and colloidal Au nanoparticles (1:1 / v:v) prepared through the reduction of $HAuCl_4$ with citrate were mixed thoroughly and kept under 4°C overnight.

A gold thin film microelectrode was fabricated by two step chemical deposition of Au nanoparticles over ultraviolet treated polystyrene (PS) [5]. The film electrode was treated by air plasma for about 8 min to clean the surface before the prepared mixture was dropped over for the electrode modification.

Anodic Stripping Voltammetry was performed in 0.1 mol·$L^{-1}$ $KH_2PO_4$ to evaluate the sensing performance of the modified electrode toward iodide detection. The deposition step was 30 s at the potential of 0.3 V vs. a saturated Ag/AgCl reference electrode, and the stripping step was within 0.3 V~1.0 V at a scanning rate of 20 mV·$s^{-1}$.

## Results and Discussion

### CV Performances of the Modified Gold Microelectrode

The cyclic voltammograms of the modified gold microelectrode and bare gold microelectrode in a $5.0\times10^{-3}$ mol·L$^{-1}$ $K_3[Fe(CN)_6]$ solution containing 0.1 mol·L$^{-1}$ KCl were presented in Fig. 2. The redox-label $[Fe(CN)_6]^{4-/3-}$ reveals a reversible CV at the bare gold microelectrode (Fig. 2b). After the pretreated bare gold microelectrode was modified with nano-Au/Chitosan composite, the peak current increased greatly while the reversible behavior was well preserved (Fig. 2a). It indicates that the modified electrode has a much greater surface area, which is favored in electrochemical detection.

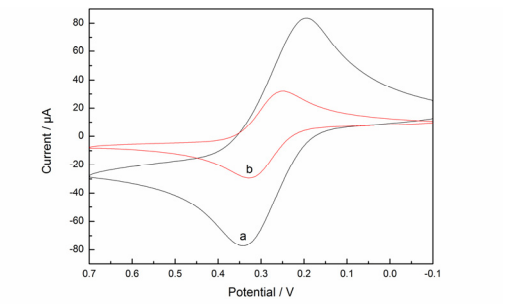


*Fig. 2. Cyclic voltammograms of the modified gold microelectrode (a), the bare gold microelectrode (b). Supporting electrolyte: $5.0\times10^{-3}$ mol·L$^{-1}$ $K_3[Fe(CN)_6]$ solution containing 0.1 mol·L$^{-1}$ KCl; scan rate, 100 mV·s$^{-1}$.*

### Optimization of pH value of the Base Solution

The effect of solution pH on the modified electrode behavior was investigated between 2 and 5, as shown in Fig. 3:

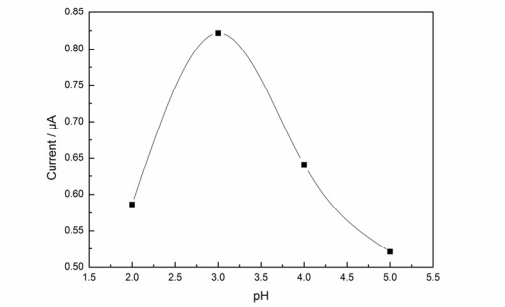


*Fig. 3. Influence of pH of the base solution on the ASV current response of the modified electrode toward with $6.73\times10^{-5}$ mol·L$^{-1}$ $I^-$ in 0.1 mol·L$^{-1}$ $KH_2PO_4$ solution.*

The pH value of the base solution has a significant effect on the performance of the modified gold microelectrode. From Fig. 3, the current response had a maximum at pH 3.0, hence pH 3.0 was chosen through the whole of the study. The pH of the solution affects number of $-NH_3^+$ on the surface of the modified gold microelectrode greatly, which is critical to the absorption of $I^-$. With the increase of the pH value, the current response decreases.

### Optimization of Deposition Time

With pH value of the base solution 3.0, different deposition time from 0 to 90 s were investigated, the ASV current response results were shown in Fig. 3:

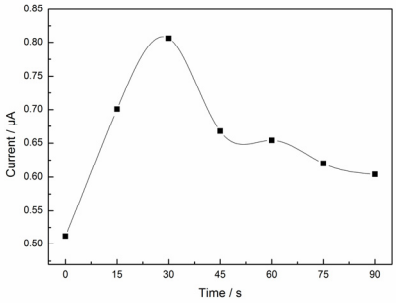


*Fig. 4. The effect of deposition time on the ASV current response of the modified electrode toward with $6.73\times10^{-5}$ mol·L$^{-1}$ $I^-$ in 0.1 mol·L$^{-1}$ $KH_2PO_4$ solution (pH 3.0).*

With the appropriate pH value of the base solution, the maximum current response was at 30 s. The amperometirc response of the modified electrode varied little after 45 s with increasing deposition time, indicating the saturated formation of $I^-$ in the modified matrix.

### Sensitivity of the Modified Gold Microelectrode toward Iodide Detection

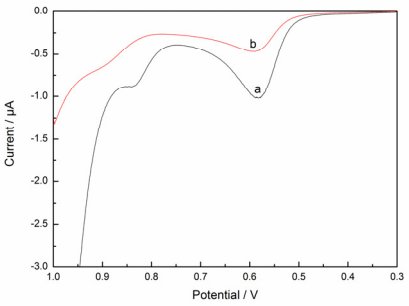


*Fig. 5. Comparison of ASV current response results of the modified gold microelectrode (Fig. 5a) and the bare gold microelectrode (Fig. 5b) for iodide detection. The test was taken in $6.73\times10^{-5}$ mol·L$^{-1}$ $I^-$ in 0.1 mol·L$^{-1}$ $KH_2PO_4$ (pH 3.0) solution with deposition step of 30 s.*

With the optimized experimental parameters, the performance of the modified gold

microelectrode toward $6.73\times10^{-5}$ mol·L$^{-1}$ iodide was evaluated and compared with the bare gold microelectrode in Fig.5. A greater signal at the potential of 0.582 V for the modified gold microelectrode was observed compared with the bare gold microelectrode at the potential of 0.593 V.

The ASV current response obtained increased proportionally with iodide concentration in the range of $3.32\times10^{-7}$ mol·L$^{-1}$~$1.57\times10^{-2}$ mol·L$^{-1}$ with a correlation coefficient of 0.9996.

### Selectivity of the Modified Gold Microelectrode for Iodide Detection

Interferences arising from other halides expected to coexist in solution with iodide are used to evaluate the selectivity of the modified gold film microelectrode, and ASV current response results were shown in Fig. 6 with chloride as a demonstration.

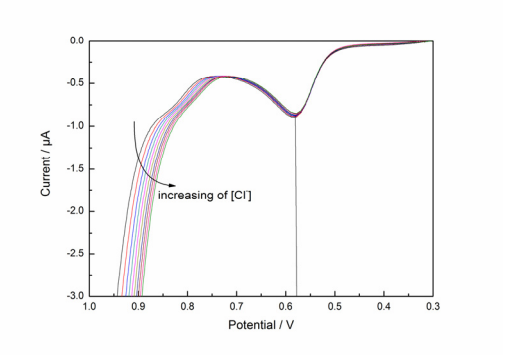


*Fig.6. Interference evaluation of the chitosan modified gold film microelectrode toward I⁻. The experiment was taken in 0.1 mol·L$^{-1}$ $KH_2PO_4$ solution (pH 3.0) containing $6.73\times10^{-5}$ mol·L$^{-1}$ I⁻.*

With the chloride concentration increased from 18 to 4165 times of the iodide concentration, the current response is still within the error range (6%) (Fig. 6). And the stripping voltammetry changed little from 0.588 V to 0.578 V. Similar results were obtained for bromide (data not shown). It demonstrates that the modified electrode has good selectivity toward $I^-$.

### Conclusions

Colloid Au/chitosan modified gold microelectrode is described for the determination of iodine. Under the optimized experimental conditions, the results show that the modified film is an appropriate sensing material for sensitive and selective determination of iodide. Besides, it is easy to change the electrode shape with the microfabrication techniques and its small size makes it possible to integrate into microfludic system to facilitate fast and on-line determination of iodide.

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