In-Situ Growth of Gold Nanoparticle Conductive Layer on Plastic Films as an Integrated Electrochemical Sensor Strip of Trace Lead

Xuan Zhang * **, Chengguo Hu * **, Shengshui Hu * **

*Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, PR China, sshu@whu.edu.cn
**State Key Laboratory of Transducer Technology, Chinese Academy of Sciences, Beijing 100084, PR China, sshu@whu.edu.cn

ABSTRACT

In this work, an in-situ chemical growth method was reported for grafting patterned gold nanoparticle (GNP) conductive layers on polyethylene terephthalate (PET) substrates. The resulting gold three-electrode assemble can be used as an easy-fabricated thin-film platform for developing disposable electrochemical sensors with excellent performance, in comparison with conventional carbon-based sensor strips using commercially available carbon inks as conductive materials. As an example of practical applications, the integrated gold film electrodes exhibit a sensitive response for the determination of lead by differential pulse anodic stripping voltammetry when using bismuth as a modifier, which can act as an inexpensive electrochemical sensor strip of trace lead for clinic analysis.

Keywords: in-situ growth, gold strip, lead

1 INTRODUCTION

Lead is one of the most harmful heavy metal ions to human health, especially for children. Though mercury-based electrodes have been regarded as the most sensitive electrochemical sensors for lead by anodic stripping voltammetry (ASV), the high toxicity and the volatility of mercury seriously hinder their wide practical applications. To overcome these deficiencies, more and more works begin to employ bismuth as an environment-friendly modifier for the sensitive determination of lead, on the basis of the formation of alloys for lead with bismuth, just as amalgam does [1]. This, coupled with screen print techniques, leads to the production of various low-cost and high sensitive applicable electrochemical sensors of lead [2, 3]. Unfortunately, the screen print methods usually require special print equipments and are often restricted to planar substrates. In contrast, in-situ chemical growth method can form dense and uniform conductive layers on various substrates (e.g., glass, metal and polymer materials), regardless of the shape or size of substrates. This, together with template-based screen techniques, is able to form patterned conductive layers on substrates to produce functional electrochemical sensor with special designs.

Recently, we developed a simple method for the in-situ chemical growth of gold nanoparticle (GNP) conductive layer on human hair to prepare a novel gold hair microelectrode. The resulting flexible microelectrode exhibited excellent electrochemical responses toward a variety of biomolecules [4]. In this work, a modified in-situ chemical growth method was reported for grafting patterned GNP conductive layers on polyethylene terephthalate (PET) substrates. The method generally comprise of four steps (Fig. 1): (1) a cationic surfactant monolayer was formed on the patterned PET substrates by a simple solution adsorption procedure; (2) high-density GNP seeds were immobilized on the positively charged PET film via electrostatic attractions; (3) the discrete GNP seeds grew into continuous GNP conductive layers through the catalytic reduction of HAuCl₄ to GNP on the GNP seeds by NH₂OH; (4) the removal of templates produced patterned GNP conductive layers on PET. The following electrodeposition of Ag/AgCl composite on one of the three electrode strips produced an integrated three-electrode electrochemical sensor strip [5].

2 EXPERIMENTAL

2.1 Regents and apparatus

All chemicals were of analytical grade and used as received. The bismuth (III) standard stock solution was prepared with 0.01 mol/L HNO₃, and other solutions were prepared with double-distilled water. All electrochemical measurements were carried out with a CHI 660A electrochemical analyzer (Shanghai Chenhua Co., China).

2.2 Preparation of gold strips

The 2.6-nm colloidal Au was made according to a previous report [6] and used as the GNP seeds. One milliliter of 1.0 wt% HAuCl₄ was added to 90 mL of H₂O at room temperature. After 1 min of stirring, 2.0 mL of 38.8 mmol/L sodium citrate was added. One minute later, 1.0 mL of fresh 0.075 wt% NaBH₄ in 38.8 mmol/L sodium citrate was added. The colloidal solution was stirred for additional 5 min and stored in darkness at 4 ℃.

placed in 6.0 mmol/L NaCl solution and polarized at +0.4 V for 150 s to produce the Ag/AgCl reference electrode.

### 2.4 Anodic stripping determination of lead at the strip sensor by differential pulse voltammetry

![Fig. 2 Test models: (1) the stir mode in bulk solution, (2) the drop-on-strip mode.](image)

The determination of trace lead at the strip sensor by differential pulse stripping voltammetry (DPSV) can be performed in two test modes, i.e., the stirring mode in bulk solutions and the drop-on-strip mode. The stirring test mode was carried out by immersing the sensor strip in 5.0 mL 0.1 mol/L acetate buffer solution (pH 4.5) containing 100 µg/L Bi^{3+} and a certain amount of Pb^{2+}. As for the drop-on-chip test mode, the working solution of 50 µL 0.01 mol/L HNO₃ containing 5 mg/L Bi^{3+} and a certain amount of Pb^{2+}.

### 3 RESULTS AND DISCUSSION

The cyclic voltammograms (CVs, Fig. 3A) and the electrochemical impedance spectra (EIS, Fig. 3B) of a bare gold strip sensor with a drop of K₃[Fe(CN)₆] solution covering the working area were examined to evaluate the electrochemical quality of the sensor. Clearly, K₃[Fe(CN)₆] exhibited a pair of well-defined and peak-shaped waves on the integrated sensor strip. Moreover, the redox potential

---

Fig. 1 Procedures for fabricating integrated gold strip electrodes.

A piece of PET film was cleaned in turn in water, ethanol and water with sonication, each for 10 min, on which a three-electrode strip pattern was formed by covering unwanted area with insulating adhesive tapes. The patterned PET film was then placed in a cuvette containing 0.01 mol/L cetyltrimethyl ammonium bromide (CTAB) solution at 50 °C for 1 hour, thoroughly rinsed with water and immersed in the gold nanoparticle solution for 2 hours. The resulting GNP decorated PET film was placed in a cuvette containing 3.0 mL of double-distilled water, 30 µL of 0.2 mol/L hydroxylamine hydrochloride solution and 60 µL of 1.0 wt% HAuCl₄, and allowed to grow for 30 min with occasional shaking, producing a golden film on the PET film. At last, the tape masks were removed, and the center of the exposed film gold electrodes was sealed with epoxy resin glue to separate the conductive parts from the working areas.

### 2.3 Preparation of reference electrode

The reference electrode of the sensor strip was prepared by an electrodeposition method. Briefly, one of the gold strips, together with a saturated calomel reference electrode (saturated potassium nitrate salt bridge) and a Pt wire counter electrode, was placed in 5.0 mmol/L AgNO₃ solution, on which a deposition potential of -0.4 V was applied for 200 s to form a silver layer. This silver coated gold strip was then
hardly changed with increasing scan rate from 50 ~ 250 mV/s. These results suggested that the gold strip sensor possessed excellent electrochemical performance, on which the electron transfer rate was fast, foreseeing its promising applications in electroanalytical chemistry. This conclusion is also supported by the EIS data, i.e., a semicircle with a small diameter at high frequencies and a declined line at low frequencies occurred on the Nyquist plot.

Fig. 3A CVs of a bare gold strip sensor in 5 mmol/L K₃[Fe(CN)₆] containing 0.1 mol/L KNO₃ with different scan rates.

Fig. 3B Nyquist plots (-Z” vs. Z’) of the EIS measurement in the presence of 5 mmol/L K₃[Fe(CN)₆] containing 0.1 mol/L KNO₃ at a bare gold strip sensor. Frequency range: 0.1 ~ 100 KHz, amplitude: 0.005 V.

Fig. 4 DPSV responses of a gold strip sensor in 5 mL 0.1 mol/L ABS (pH 4.5) containing 100 µg/L Bi³⁺ and different concentrations of Pb²⁺. Deposition potential: -1.0 V; deposition time: 180 s; quiet time: 5 s; stripping potential: 0.1 V.

Fig. 5 DPSV responses of a gold strip sensor, 50 µL of 0.01 mol/L HNO₃ containing 5 mg/L Bi³⁺ and different concentrations of Pb²⁺. Deposition potential: -1.2 V; deposition time: 180 s; quiet time: 10 s; stripping potential: 0.1 V.

Fig. 4 shows the DPSV signal of the sensor for the determination of lead with the stirring test mode. It is clear that the sensor exhibited a sensitive response for trace lead with a detection limit lower than 10 µg/L and a good linear relationship at low concentrations. To further improve the
applicability of this sensor, the drop-on-strip test mode was also carried out for the determination of lead (Fig. 5). The results indicated that the sensor also exhibited a sensitive response for lead in this mode except that the detection limit is a little poorer than the stirring mode.

It was demonstrated that the bismuth modified gold strip sensor offered reliable quantity of trace lead in connection to differential pulse anodic stripping voltammetry. Coupling this favorable performance with the negligible toxicity of bismuth and the excellence of the in-situ growth method, makes the integrated gold strip sensor extremely attractive for simple, portable and disposable determination of lead in various fields, such as clinical, environmental and industrial. Research in our laboratories is in progress for further assessing the strip sensor application for mass-produced disposable test strip for lead.

4 ACKNOWLEDGEMENTS

This research is supported by the National Nature Science Foundation of China (Nos. 30770549, 20805035 and 90817103).

REFERENCES