



L-Aspartic acid/L-cysteine/gold nanoparticle modified microelectrode for simultaneous detection of copper and lead

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ABSTRACT

This paper presents an electrochemical microsensor for simultaneous detection of copper (II) and lead (II) using an L-aspartic acid/L-cysteine/gold nanoparticle modified microelectrode. The microelectrode was fabricated by Micro Electro-Mechanical System technique. The complex of gold nanoparticles (AuNPs) and amino acid with carboxyl group was used as the selective ligand for metal ions. The microelectrode was firstly modified with AuNPs to increase the sensitive area of the working electrode. Subsequently, the AuNPs/gold electrode was modified with L-cysteine and then covalently linked with a monolayer of L-aspartic acid using glutaraldehyde. Electrochemical analysis of metal ions was achieved by using square wave voltammetry without stirring. The microsensor exhibited an excellent linear range from $5 \mu\text{g L}^{-1}$ to $2000 \mu\text{g L}^{-1}$ with the limit of detection of $1 \mu\text{g L}^{-1}$. This metal ion detection method based on L-aspartic acid/L-cysteine/gold nanoparticle modified microelectrode is simple, sensitive and it could be used for electrochemical analysis of copper (II) and lead (II).

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1. Introduction

The heavy metal pollution in the natural waters is increasingly becoming a serious environmental problem throughout the world because of the increased use of heavy metals in industrial processes and products. Heavy metal poisoning may cause many disorders in plant and animal kingdoms, and their accumulation leads to various systemic diseases of nervous and other systems [1]. Copper is an essential trace element required for the human body to maintain normal, however, excess consumption of copper may lead to toxic effect. Excess soluble copper levels in drinking water may pose a health risk to humans and animals [2]. Lead is a common and persistent environmental contaminant with high toxicity, and it has physical and neurotoxic effects on human, particularly on children with low-level exposure [3]. Owing to the potential danger to the environment and human, there is a growing need for monitoring of copper (II) and lead (II) in water environment. Many methods have been investigated for the detection of copper (II) and lead (II), such as atomic absorption spectroscopy [4,5], X-ray fluorescence [6,7], mass spectrometry [8,9] and electrochemical voltammetry [10,11]. Electrochemical voltammetry has been proved to be a particularly suitable method for on-site determination of copper (II) and lead (II), due to its properties such as small in size, simple, portable, reliable and low-cost.

The traditional electrodes for heavy metal detection are hanging-drop mercury electrode and mercury film electrode. However, due to

mercury's toxic character and its tedious handling, these two types of electrodes limit their application in electrochemical detection of heavy metals. Recently, the alternative materials which are less toxic and more environmentally friendly than mercury were investigated. One strategy is to modify the electrodes with selective ligands, which provide a sensitive interface and an ability to pre-concentrate the given metal ion before voltammetric measurement. As the sensitive interface for the detection of copper (II) and lead (II), some selective ligands have been reported. These selective ligands included polyaspartate [12], gly-glyhis [13], 3-mercaptopropionic acid [14], cysteamine [15], 4-amino-6-hydroxy-2-mercaptopyrimidine [16] and carbidopa [17]. In this paper, L-cysteine (L-cys) cooperated with L-aspartic acid (L-asp) are used as the sensitive interface to detect copper (II) and lead (II). L-cysteine, containing sulfhydryl group and carboxyl group, is often used to modify gold interface. Because of the strong interactions of sulfur-gold, the L-cys monolayer can be assembled to the gold electrode in a short time and it is reasonably stable in aqueous solutions [18]. L-aspartic acid (isoelectric point is 2.77), as one of the naturally occurring amino acids, possesses two carboxyl group and one amine group that can share three pairs of electrons with a single metal ion [19]. It can be easily introduced to modify electrode as selective ligands. Many references have indicated that heavy metal ions coordinate via the oxygen atoms from the carboxyl groups [12,20].

Nanotechnology was induced into electrochemical sensors for detection of heavy metals in the past several decades [21–23]. Nanomaterials often exhibit unique chemical, physical, and electronic properties that can be suitable for construction of electrochemical sensors. Gold nanoparticles (AuNPs), which can enlarge active surface

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area of the electrode and have strong adsorptive capability to organic molecules, have been proven to be a promising material to improve the performance of the chemical sensors [24–26]. There are also some literatures about AuNPs modified electrode for voltammetric sensing [27–30].

The aim of this paper is to combine the unique properties of nanomaterials with the specific complexing ability of amino acid to fabricate an electrochemical sensing platform toward copper (II) and lead (II). Gold nanoparticles were induced to enlarge the surface area of microelectrode and to increase the loading amount of L-cys. Then the L-asp molecules were crosslinked with L-cys to increase the complexing sites. Due to the combination of gold nanoparticles and the two kinds of amino acid, the sensitivity of the microsensor was largely improved. In addition, the materials used for electrodes modification are “green”, and the detection method is easy to control. The further research is to incorporate the microsensor into microfluidic system for on-site heavy metal analysis. The fabrication process and the regeneration of the microsensor may restrict the performance of the microfluidic analysis. More improvement is required to make this method more suitable for the microfluidic analysis.

2. Experimental details

2.1. Reagents and apparatus

All chemicals were of analytical reagent grade. L-cysteine, L-aspartic acid, glutaraldehyde and HAuCl_4 were purchased from Beijing Chemical Reagent Company (China). The copper (II) and lead (II) solution with different concentrations were diluted from 500 mg L^{-1} copper (II) and lead (II) standard solution (atomic absorption standard solutions), which were obtained from Sino-Japan Friendship Centre for Environmental Protection (China). Acetate buffer solutions (0.1 mol L^{-1}) with different pH were prepared by mixing acetic acid solution and sodium acetate solution, and the pH values were accurately adjusted using a pH meter. Acetic acid solution (0.1 mol L^{-1}) for regeneration was diluted from high concentration of acetic acid.

Experiments were carried out in a conventional electrochemical cell with a three-electrode-system, including a saturated calomel electrode (SCE) as the reference electrode and a microelectrode chip on which a working electrode and a counter electrode were prepared using microfabrication techniques. Electrochemical characterization of the microsensor was carried out with a Gamry Reference 600 electrochemical measurement system (Gamry Instruments Co., Ltd., USA). All experiments were carried out at room temperature. The surface morphology analysis was carried out using the S-4800 field emission scanning electron microscope (SEM) produced by Hitachi (Japan), and the operating voltage was 5 kV.

2.2. Microelectrode fabrication

The microelectrode chip including gold microelectrode and platinum microelectrode was fabricated by Micro Electro-Mechanical System technique. Firstly, 30 nm Cr and 200 nm Au were deposited and patterned on a glass to form the working electrode by photolithography and lift-off process. After cleaning and drying process, the counter electrode was prepared by depositing 30 nm Cr and 200 nm Pt on the same glass wafer through lift-off process. Then a SU-8 layer was patterned around the gold electrodes to form a micropool to control the active area of working electrode. The glass wafer was then diced into individual microelectrode chips, which were subsequently attached, wire-bonded and encapsulated on suitable print circuit board strips. The structure of the microelectrode chip is shown in Scheme 1. The sensitive area of the working electrode is 1 mm^2 .

2.3. Preparation of modified microelectrode

The microelectrode chip was sonicated in acetone, ethanol and deionized water for 3 min respectively, and electrochemically cleaned by cycling the electrode potential between -0.2 and $+1.2$ V versus SCE in 0.5 M H_2SO_4 until a reproducible voltammogram was obtained. Then the microelectrode was modified with gold nanoparticles by electrodeposition of 2 mM gold chloride (HAuCl_4) in the solution of 0.5 M H_2SO_4 at the potential of -0.3 V for 300 s [31]. In order to prepare the L-cys/AuNPs/gold electrode, L-cys layer was assembled on the gold nanoparticle surface by immersing the microelectrode in 2 mL aqueous solution of 20 mM L-cys in darkness for 5 h. To remove non-adsorbed L-cys, the microelectrode was washed by pouring deionized water (flow rate of 0.5 mL s^{-1} , 2 s one time) on the electrode surface for three times. Then the microelectrode was immersed in 2 mL 5% glutaraldehyde for 2 h. Finally the microelectrode was immersed in 2 mL 20 mM L-asp for 2 h to attach the L-asp onto the L-cys/AuNPs/gold electrode. Glutaraldehyde was used for covalent binding of the $-\text{NH}_2$ of the L-cys and the $-\text{NH}_2$ of the L-asp. The schematic illustration of modified process on the microelectrode is shown in Scheme 1. The microsensors (L-cys/gold electrode and L-cys/AuNPs/gold electrode) for comparison were fabricated by the same process.

2.4. Analytical procedure

Accumulation of copper (II) and lead (II) on L-asp/L-cys/AuNPs/gold electrode at open-circuit potential was performed by immersing the microsensors into voltammetric cell containing 3 mL copper (II) and lead (II) standard solution with various concentrations (0.1 M acetate buffer of pH 4.5) for 5 min. Then the electrochemical characteristics of the microsensors were investigated by square wave voltammetry (SWV) using a frequency of 50 Hz, a pulse size of 50 mV, a step size of 2 mV and the scan potentials from -0.6 to $+0.6$ V. The peak currents of SWV were proportional to the amount of copper (II) and lead (II) accumulated on the L-asp/L-cys/AuNPs/gold electrode surface. After each SWV measurement, the microsensors were washed with acetate buffer solution for three times, and placed in an acetic acid solution (0.1 mol L^{-1} , 2 mL) without stirring for 10 min under room temperature for regeneration. The acetic acid solution can make the carboxylate protonate, and then dissociated the heavy metals from the surface complex.

3. Results and discussion

3.1. The electrocharacteristic of modified microsensor

The characteristics of the modified microsensors were tested by cyclic voltammetry in the presence of 2.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$ ($\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$). As shown in Fig. 1A, it can be seen that the voltammograms of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ showed a typical reversible redox peak at the bare gold electrode surface (curve a). When the electrode was modified with gold nanoparticles (curve b), the redox current increased owing to good conductive effect of gold nanoparticles and the increasing effective area of the working electrode. Another reason for the increasing current was that the dominating planar diffusion incorporated with some radial diffusion after the surface of the microelectrode became porous [32]. The redox peak current decreased after the modification of electrode surface with L-cys layer (curve c). This blocking effect was based on the insulating properties of L-cys, which indicated that the L-cys layer was successfully assembled on the AuNPs/gold electrode surface. After the covalent binding of L-asp to the L-cys/AuNPs/gold electrode (curve d), the redox peak current decreased because of the insulation of glutaraldehyde and L-asp, which blocked the electron transfer.

Fig. 1B shows the proportional relationship between the anodic peak current and the square root of the scan rates, indicating a

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