Gold Microelectrode Arrays Based Electrode for Determination of Trace Copper in Seawater

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We report a novel and facile gold microelectrode array (Au MEA) for the determination of trace Cu^{2+} by differential pulse anodic stripping voltammetry (DPASV). The gold microelectrode array was fabricated by a multi-step micro-fabrication approach combining sputtering for the deposition of metals and the dielectric material (SiO_2) on the surface of a silicon wafer and photolithography for the definition of the geometry of the electrode. Due to the rapid mass transporting and low background current of gold microelectrode array, low detection limit (1.3 pM) and wide linear range (10-150 pM) can be obtained for the determination of Cu^{2+}. The practical application of the proposed electrode has been carried out for the determination of trace level of Cu^{2+} in real seawater sample.

Keywords: Microelectrode, Array, Determination, Copper, Seawater.

INTRODUCTION

The determination of toxic heavy metals in the environment is of great importance from the toxicological point of view[1,2]. As a typical heavy metal, copper plays an important role in human beings since it is an essential component of several enzymes and it can help the Fe transportation[3-5]. However, excessive absorption of Cu^{2+} can create health risks such as the blood and kidneys problems and also make large influence on the growth of plants, such as the shortened root length, fewer leaves and decline in the plants biomass[6]. Therefore, it is very important to efficiently detect Cu^{2+} in environmental water samples. Many techniques have been developed for sensitive analyses of various heavy metal ions, including inductively coupled plasma mass spectrometry[7], X-ray fluorescence spectrophotometry[8] and atomic absorption spectrophotometry[9]. However, these methods generally require expensive instruments and time-consuming pretreatments[10].

Anodic stripping voltammetry (ASV) has been recognized as one of the most sensitive methods for trace analysis of heavy metals. Anodic stripping voltammetry measurement has great potential for on-site environmental monitoring due to its favorable portability, suitability for automation, short analysis time, low power consumption and inexpensive equipment [11,12]. Anodic

stripping voltammetry measurement also allows monitoring low concentration of metals by electrochemical accumulation of the metal on the electrode surface[13-15]. The proper choice of the working electrode is crucial for the successful application of the stripping operation. For many years, mercury electrode has been the best choice of electrode material in heavy metal detection, considering that not only does it have a high hydrogen overvoltage and a highly reproducible and readily renewable surface, but also can form diluted amalgams which prevent the formation of intermetallic compounds[16,17]. However, its use has been completely banned in many countries due to its hypertoxicity[18]. To avoid the use of toxic mercury in the detection of Cu^{2+}, researchers have focused on silver electrode[19], glassy carbon disk[20], silver-coated[21], bismuth-coated[22], graphite electrode[23] and iridium electrode[24] for their possible ability to substitute mercury electrode. But none of these electrodes are found to be acceptable for their relatively low hydrogen overvoltage (usually below -0.8V[17]), large background current, or poor precision and resolution[25]. It is necessary therefore, to develop new electrode materials to meet the need for a nontoxic electrode material in voltammetry.

In recent years, the development of microelectrodes has received considerable attention and the domain of their electrochemical applications has been widened. Microelectrodes

are devices with a critical dimension smaller than the thickness of the Nernst diffusion layer. Due to their small size, they offer a series of advantages compared with the conventional electrodes such as rapid mass transporting, enhancement of signal-noise ratio and low background current[26]. As a result of these characteristics improved response time, greater sensitivity and improved response are achieved[27]. However, a drawback in the use of microelectrodes is the extremely low currents that are obtained[26,28]. A solution to this is the use of arrays of microelectrodes, whereby multiple microelectrodes are operated in parallel. When microelectrode arrays (MEAs) have sufficient interelectrode distances, they would lead to an increase of the electrochemical signal in proportion to the number of electrodes in the array. This results in a substantial improvement in the current magnitude and also to an improved signal-to-noise ratio[29].

In this paper, a novel and effective gold microelectrode array (Au MEA) consisting of 400 microdiscs with 20 µm in diameter and interelectrode distances of 200 µm was fabricated for determination of Cu^{2+} by anodic stripping voltammetric without any deoxygenating and electro-plating pretreatment. The characteristics of the gold microelectrode array were investigated by the scanning electron microscopy and electrochemistry. Under the optimized conditions, low detection limit, wide linear range and high sensitivity to the determination of Cu^{2+} can be obtained at gold microelectrode array.

EXPERIMENTAL

A 0.01 M stock standard of Cu^{2+} solution was prepared by dissolving copper nitrate trihydrate (Sinopharm Chemical Reagent Beijing Co., Ltd, China) into deionized water and then diluted to various concentrations of working solutions. 0.01 M HNO_3 (pH 2) was used as the supporting electrolyte for Cu^{2+} determination. All other chemicals were analytical reagents and used without further purification. Deionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout.

All electrochemical experiments were carried out in a conventional three-electrode cell controlled by a CHI 660D Electrochemical Work Station (CH Instruments, Inc). Au MEA (array of 400 microdiscs with 20 µm in diameter and distance 200 µm between microdiscs) was used as working electrode. A platinum foil was applied as the counter electrode and an Ag/AgCl (saturated KCl) electrode served as the reference electrode. The pH measurements were performed at an E-201-C Model pH meter (Shanghai Leici Instrument Factory). The morphology of Au MEA was characterized by the scanning electron microscopy (SEM, Hitachi S-4800). All the electrochemical experiments were carried out at room temperature.

Facile gold microelectrode array are fabricated by the successive deposition and patterning of dielectric and conductive materials on top of a flat substrate by the following way. Silicon wafers (100 in diameter, 500 µm in thickness) were covered with a layer of SiO_2 1 µm thick by means of wet and dry thermal oxidation. A layer of Au (250 nm in thickness) was sputtered onto the wafer after an intermediary titanium adhesion layer (100 nm in thickness). This was followed by plasma enhanced chemical vapour deposition (PECVD) of a silicon dioxide insulating layer (500 nm). Then, the wafer was spin-coated at 3000 rpm for 20 s with a layer of photoresist (LC100a cp) 1 µm thick followed by heating at 110 °C for 90 s. The mask (which was transparent except for the electrode areas and the grip pads which were patterned as black areas) was attached firmly on the wafer and the wafer was immersed in MF320 developer for 45 s followed by being exposed for 2 s. Finally, the wafer was immersed in etching solution and ACT930 organic solution, respectively, to removed bared SiO_2 film and photoresist. The finished wafer was cleaned and diced into 9.5×4.5 mm² chips, Au MEA was obtained.

The Au MEA was washed with alcohol and deionized water, respectively. After that, a copper wire was used as the conductor to contact the Au MEA and then insulating glue was used to seal it. Finally, the sealed wires were then put into the oven to dry at 60 °C for 1 h for the following experiments.

Before each measurement, the Au MEA was activated in 0.1 M H_2SO_4 by cyclic voltammetric sweeping from -0.15 V to 1.5 V at a scan rate of 0.1 V/s. The analysis of Cu^{2+} was performed in 25 mL beaker containing 20 mL HNO_3 solution (pH 2) without removal of oxygen. It had two main steps including accumulation and stripping out. First, Cu^{2+} ions were reduced to Cu under -0.3 V for 40 s onto the Au MEA under stirring conditions. Then, the reduced Cu was oxidized at around 0.32 V during the potential sweeping from 0 to 0.6 V. The stripping peak current was measured for Cu^{2+} quantification. Prior to the next measurements, the Au MEA was activated at 0.6 V for 30s in the supporting electrolyte to remove the previous deposit completely.

The parameters applied for the differential pulse anodic stripping voltammetry (DPASV) were as follows: accumulation potential, -0.3 V; accumulation time, 40 s; equilibration time, 10 s; increment potential of each step, 4 mV; pulse amplitude, 50 mV.

RESULTS AND DISCUSSION

A SEM image of Au MEA (Fig. 1a) shows a regular disc electrode with a well defined area. The Au MEA is square and consisted of 400 microdiscs. Fig. 1b shows a SEM image of Au MEA (150 × magnification). It can be seen that each microdisc is circular and 20 µm in diameter with a center-to-center spacing of 200 µm. This is in good agreement with the literature data which recommends interelectrode distances 10 times the diameter of the microelectrodes[30]. This distance between the microdiscs is thus found to be sufficient to avoid the shielding effects due to the overlapping of the diffusion layers of adjacent electrodes.

The electrochemical behaviour of the Au MEA was characterized by cyclic voltammetry. Fig. 2 shows the cyclic voltammograms recorded at the Au MEA from -0.2 to 0.6 V in 0.1 M KNO_3 solution containing 1 mM potassium ferricyanide. The voltammogram of the gold microelectrode exhibits the typical sigmoid shape, indicating the predominance of radial diffusion to electrode surface[31]. Due to the micro-size effect, an enhanced mass transport can be obtained at the Au MEA rather than traditional electrode, which results in the improved signal-to-noise ratio and low analytical detection limit[32,33]. Accordingly, the Au MEA has great potential for determination of trace heavy metals.
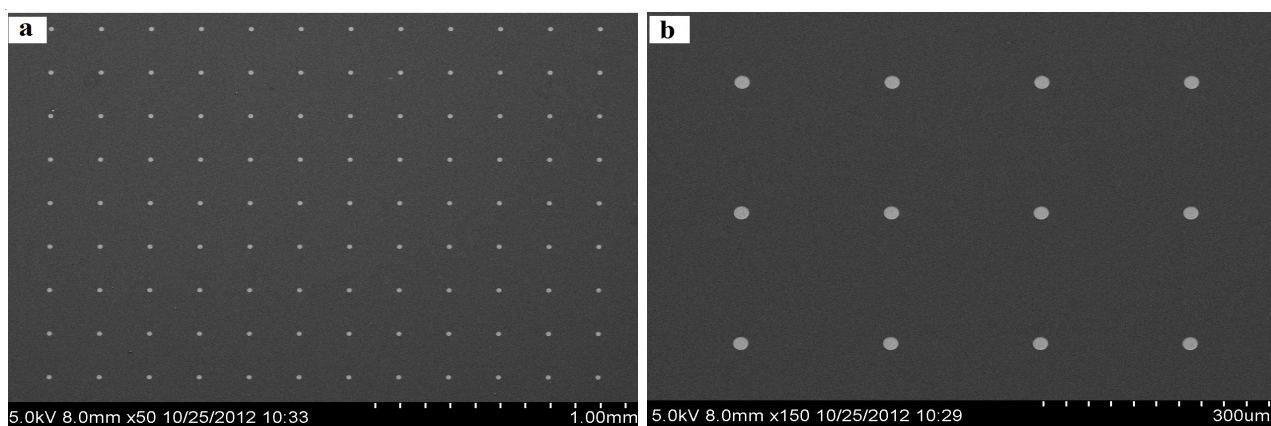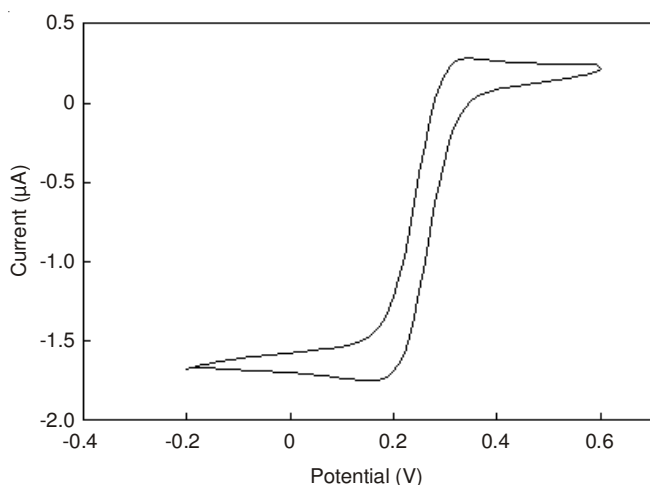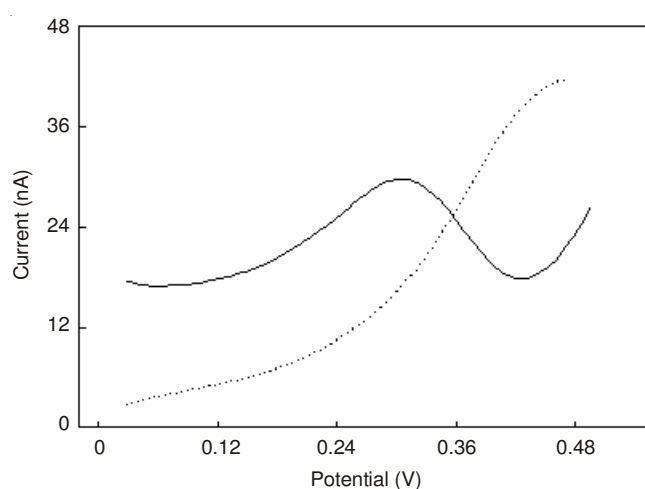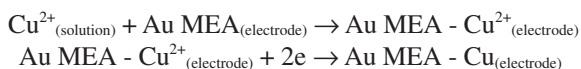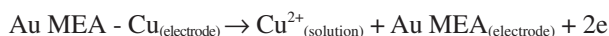
Fig. 1. SEM images of Au MEA

Fig. 2.   Cyclic voltammograms recorded at the Au MEA in 0.1M KNO_3 containing 1 mM $K_3[Fe(CN)_6]$. Scan rate, 0.1 V/s

Fig. 3.   DPASV obtained in HNO_3 (pH 2) solution without (dash line) and with (solid line) 130 pM Cu^{2+} at the Au MEA in the potential range of 0 to 0.6 V. Accumulation potential, -0.3 V; accumulation time, 40 s; equilibration time, 10 s; increment, 0.004 V; pulse amplitude, 0.05 V

Differential pulse anodic stripping voltammetry was used for the determination of trace Cu^{2+}. The corresponding results were shown in Fig. 3. Compared to the voltammetric curve of the Au MEA in electrolyte without Cu^{2+} (dotted line in Fig. 3), a large anodic peak at around 0.32 V can be observed at the same electrode in electrolyte containing 130 pM Cu^{2+} (solid line in Fig. 3). Since no electro-deposition was applied during the ASV, the rapid chemical redox of Cu^{2+} at the Au MEA is the logical explanation of this result. These results indicate the Au MEA can be used to sensitively detect Cu^{2+}. The whole mechanism of the electrochemical behaviour of Cu^{2+} by ASV at the Au MEA can be described as the following steps:

(1) Accumulation:

$Cu^{2+}_{(solution)}$ + Au MEA$_{(electrode)}$ $\rightarrow$ Au MEA - $Cu^{2+}_{(electrode)}$
Au MEA - $Cu^{2+}_{(electrode)}$ + 2e $\rightarrow$ Au MEA - $Cu_{(electrode)}$

(2) Stripping:

Au MEA - $Cu_{(electrode)}$ $\rightarrow$ $Cu^{2+}_{(solution)}$ + Au MEA$_{(electrode)}$ + 2e

In the accumulation step of the ASV, the accumulated Cu^{2+} was reduced at -0.3 V and electrochemically deposited at the electrode surface. Then the deposited Cu was oxidized, *i.e.*, electrochemically stripped off. The stripping peak current was measured for Cu^{2+} quantification. Additionally, the proposed microelectrode arrays allow sensitive detection of copper without any interference from dissolved oxygen. This may be the

reason that the reduction of copper occurs at almost -0.6 V and does not interfere the reduction of Cu^{2+}.

At the optimization condition, the calibration curve for determination of Cu^{2+} at the Au MEA was established in Fig. 4 by using DPASV. In Fig. 4, for 40 s accumulation, a proportional relationship between the stripping peak current and the concentration of Cu^{2+} was obtained in the range of 10 to 150 pM by fitting the following regression equation:

$$y = 0.47 + 0.085x, r = 0.996$$

where y is the stripping peak current in nA, x is the concentration of Cu^{2+} in pM. The sensitivity of the Au MEA to Cu^{2+} is 0.085 nA/pM. The detection limit was given by the equation, where is the standard deviation of the blank measurements and is the sensitivity of the calibration graph. The detection limit of Cu^{2+} was calculated to be 1.3 pM, which was lower than those obtained at carbon paste electrode[34], carbon nanotube tower electrode[35], 4-carboxyphenyl-grafted screen printed electrode[36] and poly(2-aminothiazole)/multi-walled carbon nanotubes composite film modified electrodes[37], *etc*. It can be proved that the Au MEA has a wider linear dynamic range, lower detection limit and larger sensitivity than most of other methods for voltammetric stripping determination of Cu^{2+}.
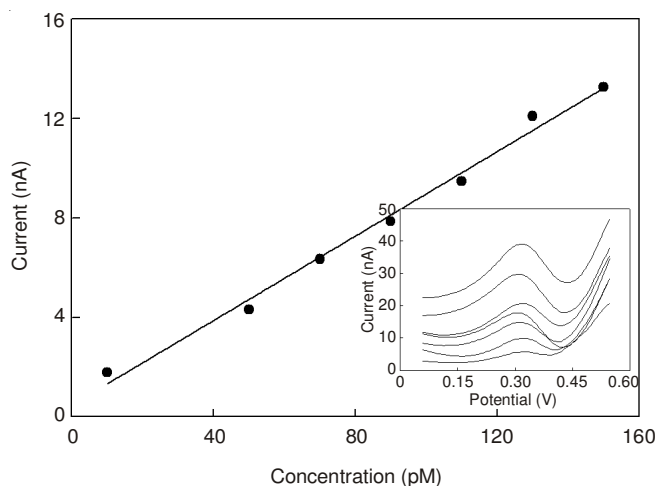
Fig. 4. Calibration curve of Cu^{2+} at the Au MEA. The concentrations of Cu^{2+} for the inset curves are 10, 50, 70, 90, 110, 130, and 150 pM from bottom to top, which are in the linear range. Other conditions are the same as in Fig. 3

On the other hand, the reproducibility of three Au MEAs and one Au MEA with eight measurements for 50 pM of Cu^{2+} were estimated. The results reveal that the Au MEA has satisfactory reproducibility and repeatability with relative standard deviation of 6 and 2.3 %, respectively. Low detection limit, wide linear dynamic range and excellent reproducibility and repeatability may attribute to the excellent and unique properties of the Au MEA. Additionally, in order to illustrate its accuracy in practical analysis, the comparison between the proposed Au MEA electrode and ICP-MS for determination of Cu^{2+} in real coastal seawater sample was carried out. The result detected from Au MEA electrode (1.41 mM) is almost same with that from ICP-MS determination (1.47 mM). The recoveries of the Au MEA electrode varied between 102 % and 111 %. These results indicate that the Au MEA electrode has a great potential for real sample analysis with a high accuracy and good reliability.

Conclusion

Gold microelectrode array as a novel, facile and effective electrode had been fabricated for sensitive determination of Cu^{2+}. The use of microelectrode implies a series of advantages with respect to conventional bulk electrodes, which can be resulted in the improvement of the electroanalytical responses of the corresponding analytes, especially concerning the signal-to-noise ratio and the precision of the measurements. Under optimized experimental conditions, excellent linear dynamic range (10-150 pM) with a correlation coefficient of 0.996 and a detection limit of 1.3 pM with 40 s accumulation was obtained. Further work will be carried out by our laboratory to establish a disposable sensor based on the promising electrode to determine Cu^{2+} and other heavy metals for on site marine environmental monitoring applications.

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