# Spirally oriented Au microelectrode array sensor for detection of Hg (II)

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## ARTICLE INFO

## ABSTRACT

A simple and reproducible carbon microelectrode array (CMA), designed to eliminate diffusive inter-ference among the microelectrodes, has been fabricated and used as a frame to build a gold (Au) microelectrode array (GMA) sensor. To prepare the CMA initially, rather than use an uncontrollable large number of carbon fibers, only 60 carbon fibers of regular size were used to ensure manageable and reproducible arrangement for array construction. In addition, for efficient spatial arrangement of the microelectrode and easy sensor preparation, carbon fibers were oriented in a spiral fashion by rolling around a Cu wire. The distance between carbon fibers was carefully determined to avoid overlap among individual diffusion layers, one of the important factors governing steady-state current response and sensor-to-sensor reproducibility. After the preparation of a spirally arranged CMA, Au was electrochemi-cally deposited on the surface of individual carbon electrodes to build a final GMA sensor. Then, the GMA sensor was used to measure $Hg^{2+}$ in a low concentration range. Simultaneously, multiple GMA sensors were independently prepared to examine reproducibility in sensor fabrication as well as electrochemical measurement (sensor-to-sensor reproducibility). Overall, highly sensitive detection of $Hg^{2+}$ was possible using the proposed GMA sensor due to efficient arrangement of microelectrodes and the sensor-to-sensor reproducibility was superior owing to simplicity in sensor fabrication.

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## 1. Introduction

A microelectrode is highly efficient for diverse electrochemi-cal measurements since it can enhance mass transport of analytes as well as provide higher current density, which eventually leads to improved signal-to-noise ratio of acquired signals [1–3]. To further realize the advantages of microelectrodes, microelectrode array based sensors have been developed [4–9]. As clearly demon-strated in several publications [1–3], electrochemical response of microelectrode array sensors varies widely and depends on the size of individual microelectrodes, the inter-distance among the microelectrodes as well as the reproducibility of their arrange-ment. Domains of diffusion layers formed on the surface of each microelectrode could be differently formed due to these factors; therefore, careful attention to the above-mentioned factors is essential when microelectrode array sensors are intended for elec-trochemical measurements.

In this publication, we present a simple and reproducible gold (Au) microelectrode array (GMA) sensor by depositing Au on the surface of a carbon microelectrode array (CMA), rather than by constructing a GMA sensor directly using Au fibers. As pointed out in previous publications, there are hurdles for the construction of reproducible GMA sensors [9]. Since Au fiber itself is not physically sturdy enough (rather soft), it is difficult to handle it for the prepa-ration of reproducible array-based sensors. In addition, physical sustainability of a GMA sensor during measurement is a great con-cern. Therefore, to overcome this obstacle, we decided to initially construct a rugged array frame using carbon fibers and directly deposit Au on the carbon microelectrode array (CMA) to build a reliable and reproducible GMA sensor. This proposed method has not been attempted so far. Simultaneously, by this strategy, we efficiently combined the advantages of CMAs, i.e., availability of wide potential range for analysis, low background charging and high current density.

Usually, for the construction of CMAs, large numbers of carbon fibers (up to several thousands in some cases) are incorporated together to improve measurement sensitivity [7]. However, opti-mal and reproducible arrangement of carbon fibers to avoid diffusive interference among them should be a prerequisite to ensure steady-state current response and reproducible measure-ment [10]. Recently lithographically fabricated Au microelectrode arrays have been demonstrated [11–13] and the geographical

control of microelectrodes can be greatly improved using lithography. In this research, we have built a simple and reproducible CMA using only 60 carbon fibers without use of extensive fabrication equipments such as lithography. The use of fewer carbon fibers could be advantageous in terms of reproducible array fabrication. Initially, carbon fibers were arranged as a spiral fashion by simply rolling these around Cu wire for compact orientation as well as easy sensor preparation. The distance among individual carbon fibers was carefully determined and controlled to avoid overlap of individual diffusion layers; thereby, overall electrochemical response is a simple multiple of the number of carbon fibers used. Thus, even without the use of a larger number of carbon fibers, sensitive measurements could be achievable. After the fabrication of CMA, its electrochemical response was checked by observing cyclic voltammograms (CVs) of 0.1 M $Fe(CN)_6^{3-}$ to confirm the absence of abnormal behavior in the electrochemical response.

After the fabrication of spirally arranged CMA, a GMA sensor was prepared by electrodeposition of Au on individual carbon microelectrodes and was used for the measurement of $Hg^{2+}$ in an ultra-low concentration range. As is generally known, Au surfaces are highly sensitive for the detection of $Hg^{2+}$. Three separate GMA sensors were prepared and the resulting performances such as sensitivity and sensor-to-sensor reproducibility were evaluated.

## 2. Experimental

### 2.1. Fabrication of spirally oriented Au microelectrode array sensor

Carbon fibers were kindly supplied from the chemistry department at The Royal Institute of Technology, Sweden. SEM images of carbons fibers used in this study are shown in Fig. 1(a). The
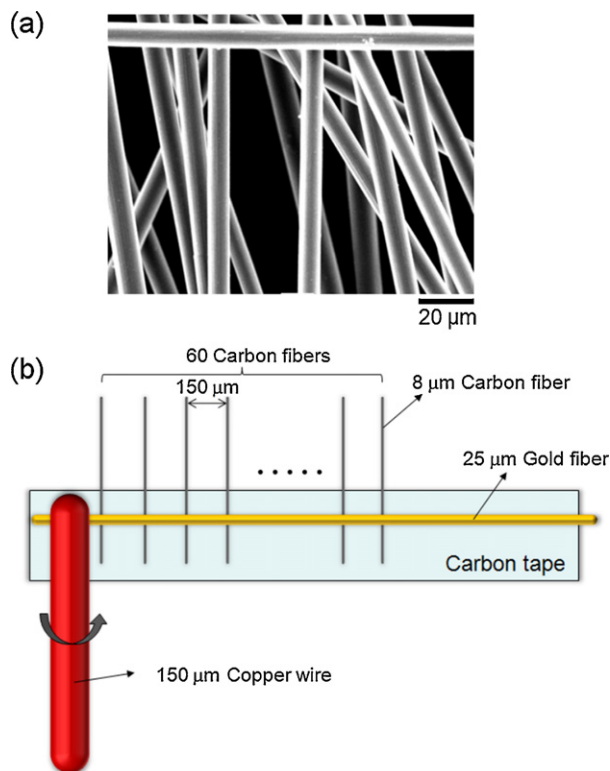


**Fig. 1.** SEM image of carbon fibers (a) and graphical description showing the preparation of carbon microelectrode array (b). Carbon fibers were arranged with an interval of 150 μm on a carbon tape and then Cu wire was rolled to construct the array.
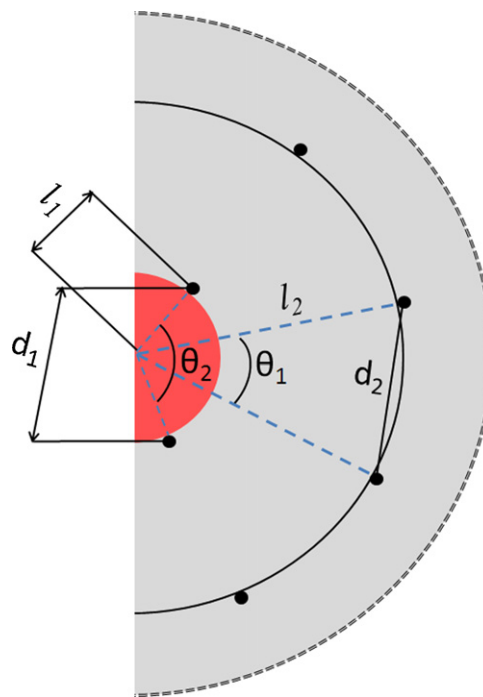


**Fig. 2.** Schematic top view of the array surface. Only first two layers are shown (half view) for simpler graphical presentation. (For interpretation of the references to color in text, the reader is referred to the web version of the article.)

sizes of carbon fibers were highly consistent with a diameter of $8.0 \pm 0.2$ μm (measurement from 20 individual fibers). The preparation of CMA is graphically shown in Fig. 1(b). Initially, 60 carbon fibers (length: 0.5 cm) were rinsed with a pure ethanol solution and regularly arranged with an interval of 150 μm on a carbon tape (1.0 cm × 0.3 cm, thickness: 150 μm) with an imprinted gold microfiber (diameter: 25 μm) for electrical contact with each carbon fiber. Each fiber was covered by a thin layer of epoxy to prevent mechanical fracture during array preparation.

The schematic top view of the array surface is shown in Fig. 2. Actually carbon fibers were spirally arranged along with the carbon tape, however, for simplicity, the diagram describes it as a serial circular layer. Although the array has 9 layers, only the first two layers are schematically shown (half view) for clarity. A red half circle and black circle dots are Cu wire and carbon fibers, respectively. The thickness of each layer was 150 μm, corresponding to the thickness of carbon tape. $\theta$ and $l$ are angle between two adjacent carbon fibers with respect to the center of the Cu wire and the distance between the center of the Cu wire and each carbon fiber, respectively. Direct distance between two adjacent carbon fibers is symbolized by $d$. The subscripts in each symbol indicate the $i$th layer.

Design of reliable microelectrode array sensors essentially requires the determination of $d$ to avoid diffusive interference (overlap of individual diffusion layers) among microelectrodes. For this purpose, the calculation suggested by Fletcher et al. was employed [7], which enables estimation of the diffusion layer domain at each microelectrode by simultaneously considering the size of microelectrodes and the distance between them. Based on the calculation, $d/r \geq 20$ is required to eliminate diffusive interference among carbon fibers, in which $r$ is the radius (4 μm in this scheme) of each carbon fiber, so $d$ should be greater than 80 μm.

To sufficiently ensure diffusive interference-free measurement and compensate for possible error in the array preparation, $d$ was chosen to be 120 μm. To meet the requirements of $d$ (120 μm), determination of the interval ($L$) among vertically aligned carbon

fibers on carbon tape before the rolling was necessary. Since each carbon fiber is circularly arranged at different layers, $d$ should vary depending on where the carbon fibers are in the array. As shown in the figure, $\theta$ is larger for carbon fibers in the inner layer ($\theta_1 > \theta_2$) while $d$ is shorter ($d_1 < d_2$). Conversely, $\theta$ is smaller for carbon fibers in the outer layer while $d$ is longer. By simple trigonometric calculation, $L$ was determined to be 150 μm, resulting in $d_1$, $d_2$ and $d_3$ values of 126.2, 147.3 and 149.0 μm, respectively. There was no significant variation from $d_4$ to $d_9$ due to their large curvature. Consequently, $d$ in the spirally arranged array varied from 126.2 to nearly 150 μm.

In addition, based on the guidelines of design for microdisk electrode arrays shown by Lindner's group [10], the minimum inter-electrode distance ($d$) necessary for steady-state current response should be larger than $23r$, where $r$ is the radius of an individual electrode. Since the radius of a carbon fiber is 4 μm in this study, the required $d$ in this case must be larger than 92 μm. The arrangement of carbon fibers in the array fully complies with these guidelines.

Under a microscope, each carbon fiber was carefully arranged on the carbon tape, as shown in Fig. 1. After the preparation of CMA, the top part was carefully cut to make a flat surface. Then, the surface was treated using abrasive paper (3000) before reactivation in a 0.1 M HNO$_3$ solution by using cyclic voltammetry. Cyclic voltammetric scans continued until the resulting voltammograms became steady.

## 2.2. Chemicals and data acquisition

A standard solution of 1000 ppm Hg$^{2+}$ was purchased from Merck, Germany. Different concentrations (2–20 ppb) of Hg$^{2+}$ solutions were prepared by properly diluting a standard solution. Carbon tape was purchased from NEM TAPE, Nisshin EM Co, Tokyo, Japan.

All electrochemical measurements in this study were performed at room temperature using a three-electrode system, in which Ag/AgCl and Pt wire were used as a reference and counter electrode, respectively. The potential measurement was performed relative to a Ag/AgCl reference electrode. The three electrode system was connected to a custom-made multi-function potentiogalvanostat manufactured at Vietnam Academy of Science and Technology, Hanoi, Vietnam. It was equipped with 12 byte analog–digital converter (ADC) and the signal was amplified by two operational amplifiers with an active filter. Noise was reduced by an active filter and a custom-written noise reduction algorithm. Overall, it provided current resolution down to 0.008 nA, valuable for sensitive measurements. The data acquisition was performed using custom-written software.

## 3. Results and discussion

As shown in previous publications [3,16], the scan rate influences on the formation of diffusion layer at each microelectrode and needs to consider for diffusive interference-free measurement. Using Einstein equation [3], the distance among microelectrodes to avoid diffusive interference was calculated with the consideration of scan rates at 5, 10, 25, 50 and 100 mV/s. For the calculation, a sample of Fe(CN)$_6^{3-}$ was used, in which the diffusion coefficient ($D$) of Fe(CN)$_6^{3-}$ and potential difference ($\Delta E$) determined by linear sweep voltammetry (LSV) were $6.5 \times 10^{-6}$ cm$^2$/s and 0.15 V, respectively. The calculated distances at the scan rates of 5, 10, 25, 50 and 100 mV/s were 390, 280, 175, 125 and 88 μm, respectively. Since the distances among microelectrodes in the CMA vary from 126.2 to nearly 150 μm, the diffusive interference does not occur as long as the scan rate is higher than 50 mV/s.



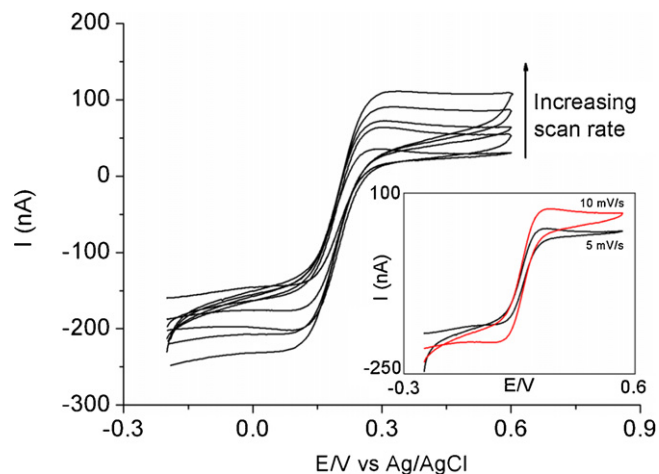**Fig. 3.** Cyclic voltammograms (CVs) of 0.1 M Fe(CN)$_6^{3-}$ collected using CMA in the range from −200 to 600 mV with five different scan rates (5, 10, 25, 50 and 100 mV/s). The direction of the arrow corresponds to increasing scan rate. CVs (scan rate: 50 mV/s) of a 0.1 M Fe(CN)$_6^{3-}$ solution acquired with GMA sensors prepared by varying the deposition time from 150 to 400 s (a) and SEM image on the surface of GMA sensor prepared with 200 s electrodeposition (b).

For the confirmation, cyclic voltammograms (CVs) of 0.1 M Fe(CN)$_6^{3-}$ were collected using CMA in the range from −200 to 600 mV with five different scan rates (5, 10, 25, 50 and 100 mV/s). The acquired CVs are shown in Fig. 3. The shapes of CVs with different scan rates clearly show sigmoidal steady state current without indication of an unusual electrochemical response. However, the CVs at 5 and 10 mV/s are not symmetric as shown in the inset due to the diffusive interference as calculated above. While, the CVs acquired over scan rate of 50 mV/s are symmetric.

The electrodeposition of Au on the surface of electrodes was carried out by immersing the CMA in a solution of 1 mM AuCl$_4^-$ in 0.5 M H$_2$SO$_4$ with an applied potential of 0.5 V. The deposition time could influence on the inter-electrode distances because the size of Au on each carbon fiber varies depending on the deposition time. Therefore, the deposition time was varied from 150 to 400 s with an increment of 50 s and then CVs of a 0.1 M Fe(CN)$_6^{3-}$ solution were acquired using these electrodes as shown in Fig. 4(a). The sigmoidal shape of CV is generally apparent for all the cases; however, from the deposition of 250 s, the shape start to change gradually with the appearance of red-ox signals. This is from the formation of larger Au film on the surface of carbon fiber due to the longer electrodeposition, thereby inducing diffusive interference among microelectrodes. Consequently, the electrodeposition of Au on the surface of CMA was performed over 200 s in this study.

For the confirmation of Au deposition, SEM image on the surface of GMA sensor prepared with the deposition time of 200 s was obtained as shown Fig. 4(b). In the SEM image, three Au microelectrodes arranged as a curved fashion are clearly observed and the diameter of individual microelectrodes is 9.6 μm approximately, slightly larger than that of carbon fiber (8.0 μm). The size of each microelectrode is now larger, so the inter-electrode distance ($d$) necessary for steady-state current response needs to evaluate again as described in the experimental section. Based on the calculation, the $d$ must be larger than 110.4 μm, suitable for electrochemical measurement without diffusive interference as confirmed by the corresponding CV in Fig. 4.

To examine the reproducibility in fabrication of sensors as well as their electrochemical response, CVs acquired from three separately prepared GMA sensors were examined as shown in Fig. 5. Three different colors indicate CVs obtained from each GMA sensor. In the CVs, the reduction peaks of Au are clearly observed and similar in terms of peak position and shape, indicating consistent
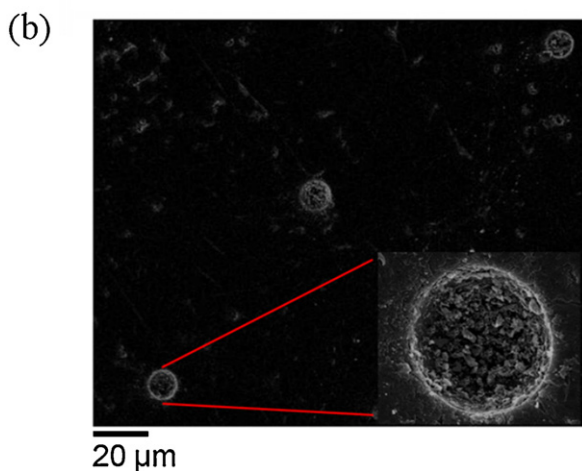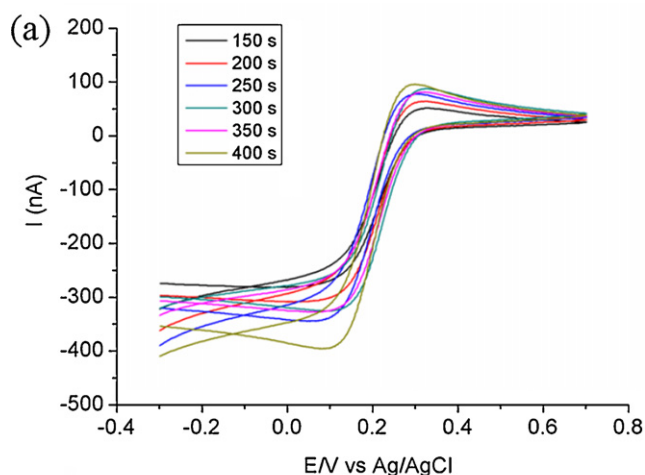
(a)



(b)

**Fig. 4.** CVs (scan rate: 50 mV/s) of a 0.1 M Fe(CN)$_6^{3-}$ solution acquired with GMA sensors prepared by varying the deposition time from 150 to 400 s (a) and SEM image on the surface of GMA sensor prepared with 200 s electrodeposition (b).

sensor fabrication and reproducible electrochemical response of three GMA sensors.

With the use of these sensors, the determination of Hg$^{2+}$ concentration was accomplished using differential pulse anodic stripping voltammetry (DPASV). A stripping potential of $-0.2$ V was applied over 300 s for electrodeposition of Hg. DPV was scanned from 0.4 to 0.9 V with a scan rate of 100 mV/s. Fig. 6 shows the acquired
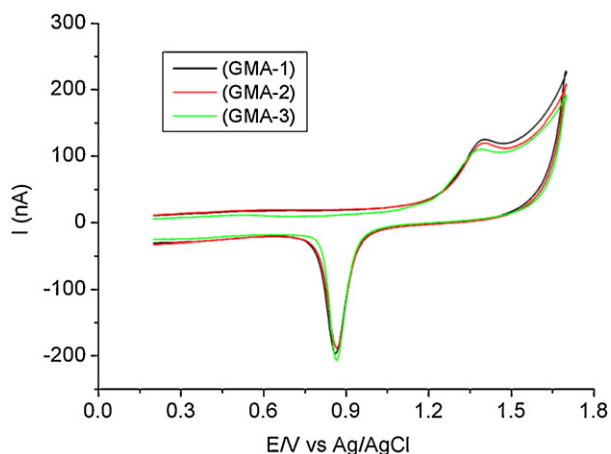


**Fig. 5.** CVs collected from three separately prepared GMA sensors in 0.5 M H$_2$SO$_4$ (scan rate: 100 mV/s). Three different colors indicate CVs from each sensor.
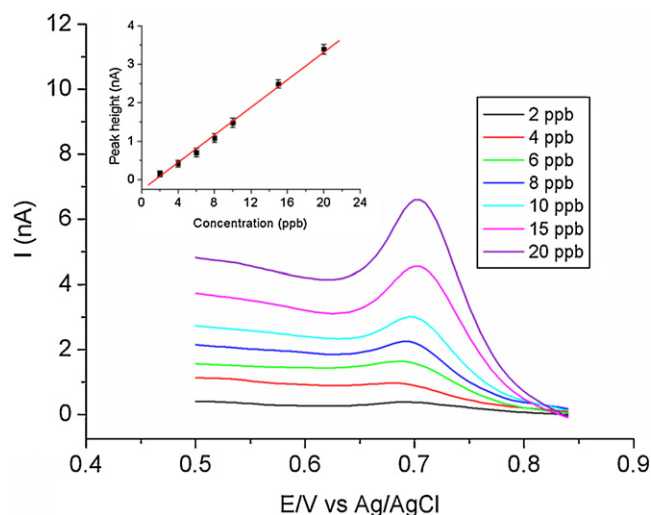


**Fig. 6.** Voltammograms corresponding to different concentrations of Hg$^{2+}$ (2, 4, 6, 8, 10, 15 and 20 ppb) in a 0.1 M HNO$_3$ solution. The response curve (concentration vs. peak height) generated from the measurements using three separate GMA sensors is also shown inside the figure. DPVs were recorded under the conditions below; amplitude: 25 mV, scan rate: 100 mV/s (scan followed cathode direction) and frequency: 20 Hz.

voltammograms corresponding to different concentrations of Hg$^{2+}$ (2, 4, 6, 8, 10, 15 and 20 ppb) in a 0.01 M HNO$_3$ solution. Voltammograms obtained from only one GMA sensor are shown in Fig. 6. The reduction peak of Hg$^{2+}$ around 0.7 V is apparent as observed in previous studies [9,14] and clearly increases with the concentration of Hg$^{2+}$. The response curve (concentration vs. peak height) generated from measurements from three separate GMA sensors is also shown inside the figure. The error bars indicate standard deviation of peak heights acquired from these three measurements. As shown, the sensor response is linear ($R^2$: 0.997) and three separate measurements are highly reproducible as indicted by the error bars. The limit of detection (LOD) was 0.8 ppb based on the calculation from the response curve. Highly sensitive and reproducible measurements of Hg$^{2+}$ were possible with the use of the GMA.

The uptake of mercury on Au could lead to mechanical instability through contraction/expansion cycles, especially in the case of macroelectrodes as demonstrated in previous publication [17,18]. Therefore, it is worthwhile to evaluate the repeatability of GMA sensor. For this purpose, a solution of 5 ppb Hg$^{2+}$ were continuously measured eighteen times and then relative standard deviation (RSD) of peak heights was calculated. The resulting RSD was 3.8%, indicating good repeatability without mechanical degradation of Au. This issue would be less problematic in the case of a micro-electrode due to the very small size of Au surface.

The LOD acquired in this study is comparable to those of other Au-based sensors for the detection of Hg$^{2+}$ using stripping voltammetry. Hatle et al. demonstrated Au film coated glassy carbon electrode and the resulting LOD was 0.3 ppb [15]. However, it was a bulk sensor rather than a microelectrode array sensor. Ordeig et al. fabricated a GMA sensor by directly incorporating 256 Au fibers (diameter: 5 μm) and demonstrated the ability to measure Hg$^{2+}$ concentration down to 3.2 ppb [9]. Recently, Bernalte et al. used commercially available screen printed Au strip electrodes for the same measurement and demonstrated an LOD of 0.8 ppb [15]. Although the GMA sensor in this study incorporated only 60 individual electrodes, highly sensitive detection of Hg$^{2+}$ was possible due to optimal arrangement of microelectrodes to maximize current density

without diffusive interference. In addition, the sensor-to-sensor reproducibility was superior due to the simplicity of fabrication.

The selectivity of the GMA sensor needs to be addressed since some heavy metal ions, such as $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$ and $Zn^{2+}$, would also undergo electrochemical reactions at the potential applied for measurement of $Hg^+$. In addition, $SO_4^{2-}$ and $Cl^-$ could also indirectly interfere with the measurement. To evaluate the selectivity, variations in the reduction peak (such as peak intensity and/or shape changes) were investigated by measuring 20 ppb $Hg^{2+}$ solutions with different concentrations of the above-mentioned ions individually at a stripping potential of $-0.2$ V. The concentrations of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ were varied from 5 to 200 ppb with an increment of 25 ppb, while the concentration of $Cu^{2+}$ was increased from 5 to 50 ppb with an increment of 5 ppb. For the case of anions, both concentrations increased from 0.5 to 15.0 mM with an increment of 0.5 mM.

In the presence of cations, only $Cu^{2+}$ interfered with the measurement since its reduction potential range ($-0.2$ to $-0.3$ V) overlapped with the applied potential while those of other cations were farther away. When the concentration of $Cu^{2+}$ was below 40 ppb, the variation in peak height was minimal and within the range of repeatability. However, the peak height decreased beyond the range of repeatability when the concentration of $Cu^{2+}$ was over 40 ppb, showing a simultaneous reduction of $Cu^{2+}$ at the surface.

In the presence of an anion, $Cl^-$ interfered with the measurement when its concentration was over 10 mM. That is, along with the $Hg^{2+}$ reduction peak at 0.7 V, a peak corresponding to the reduction of $Hg^+$ at 0.4 V occurred additionally when the concentration $Cl^-$ exceeded 10 mM. When $Cl^-$ is present with $Hg^{2+}$ in a sample, the formation of $Hg_2Cl_2$ (calomel) is possible [9]. Then, this calomel could also dissociate to generate $Hg^+$, even though it should be in trace quantities. Therefore, the reduction of $Hg^+$ as well as $Hg^{2+}$ simultaneously occurred, resulting in the two reduction peaks mentioned above. The peak heights at 0.7 V and 0.4 V synchronously decreased and increased, respectively, in the presence of $Cl^-$ over 10 mM.

## 4. Conclusion

A sensitive and reproducible GMA sensor for the measurement of $Hg^{2+}$ has been demonstrated. The sensor-to-sensor reproducibility was superior due to the utilization of minimal controllable number of carbon fibers for reproducible arrangement and optimal orientation of each microelectrode to eliminate diffusive interference. In addition, the demonstrated CMA frame with proper metal deposition on a carbon fiber can be further applicable for detection of diverse analytes, or it can be directly utilized as a sensor. With the use of CMA directly for electrochemical measurement, simultaneous detection of $Pb^{2+}$ and $Cu^{2+}$ were possible with LODs of 1.0 and 4.0 ppb, respectively, although detail results were not presented in this publication.

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