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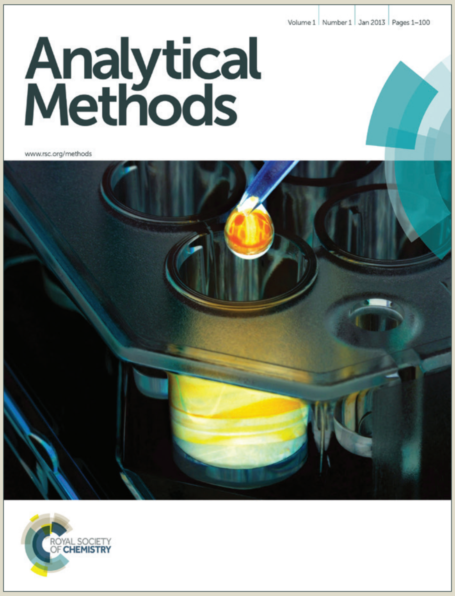

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Highly sensitive and selective electrochemical determination of Hg(II) based on electrochemically activated graphite modified screen printed carbon electrode

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In the present study, a highly sensitive and selective Hg(II) sensor was developed based on electrochemically activated graphite (EAG) modified screen printed carbon electrode (SPCE) for the first time. The fabricated EAG modified SPCE showed an enhanced current (I_{pa}) response towards Hg(II) than that of graphite/SPCE, activated SPCE and bare SPCE. Under optimum conditions, the EAG modified SPCE exhibited a wider linear range to Hg(II) in concentrations from 0.05 to 14.77 ppm. The limit of detection (LOD) was calculated as 4.6 ppb with a sensitivity of 81.5 μAppm^{-1} cm^{-2}. The World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) recommended the maximum contaminant level of Hg(II) in drinking water as 30 and 10 ppb, respectively. Thus, the observed LOD (4.6 ppb) is much below the guideline value of Hg(II) in drinking water as set by the WHO and USEPA. In addition, the EAG modified SPCE exhibits high selectivity for the electrochemical detection of Hg(II) in the presence of other heavy metal ions.

1. Introduction

The mercury ion, Hg(II), is considered as a priority toxic heavy metal ion which accumulates easily in the liver, brain, and bone tissue of organisms.[1] Moreover, Hg(II) can possibly cause poisoning in the environment as result in serious health problems. Therefore, the trace level detection of Hg(II) is much important and is of great significance for health security, safety and environmental protection.[2] Electrochemical methods are widely used for the trace level detection of Hg(II) owing to its high sensitivity and simplicity along with portability compared with the other traditional methods like Atomic absorption spectrometry and atomic fluorescence spectrometry.[3, 4] Over the past decades, the carbon modified electrodes such as glassy carbon electrode (GCE), carbon paste electrode and screen printed carbon electrodes (SPCEs) have been widely used for the determination of heavy metal ions including Hg(II).[5-7] Among different electrode materials, SPCEs have special advantages in electrochemical analysis such as better signal to noise ratio and low ohmic drop.[8-12]

Currently, chemically modified electrodes have also been extensively employed for the electrochemical determination of Hg(II) including carbon nanomaterials, metal nanoparticles and conducting polymers and so on.[13-15] The unique electronic, chemical and mechanical properties of the chemically modified electrodes are more reliable on the electrochemical determination of Hg(II) with a high sensitivity and lower detection limit.[16] The carbon nanoparticles, carbon nanotubes (CNTs), graphene and activated carbon modified electrodes have predominantly used in the modified electrodes to achieve the ultra high sensitivity for the determination of Hg(II).[17-23] The high sensitvity of the carbon nanomaterials owing to their large surface area along with excellent electrochemical properties compared with other modified electrodes. However, the selective determination of Hg(II) at chemically modified electrodes are quite challenging, due to the interferences of other metal ions.[24] According to our previous report, the electrochemically activated graphite (EAG) has more edge plane surface defects with enhanced surface area and the electrochemical properties of EAG are found similar as like the properties of CNTs.[25, 26] Herein we utilize the special properties of EAG modified SPCE to the sensitive and selective determination of Hg(II). To the best of our knowledge, electrochemically activated graphite modified SPCE never been used for the selective determination of heavy metal ions.

In the present study, a sensitive and selective Hg(II) sensor was developed by using electrochemically prepared EAG modified screen printed carbon electrode (SPCE). The performance of the EAG modified SPCE towards Hg(II) has been compared with activated SPCE, bare and graphite/SPCE. The result indicates that EAG/SPCE has high activity towards Hg(II) than that of other modified electrodes employed in this study.

2. Experimental

Materials and methods

Raw graphite with an average diameter of about >20 μm was obtained from Sigma–Aldrich. Screen printed carbon electrode with geometric area of 0.07 cm^{-2} was purchased from Zensor R&D Co., Ltd., Taipei, Taiwan. The supporting electrolyte pH 5 (acetate buffer) solution was prepared by using 0.05 M CH_3COOH and CH_3COONa solutions in doubly distilled water. All the chemicals used in this work were of analytical grade and all the solutions were prepared using doubly distilled water without any further purification.

A computerized electrochemical workstation CHI 750a was used for the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements. Scanning electron microscopy (SEM) was performed using Hitachi S-3000 H electron microscope. Conventional three-electrode system was used for the electrochemical experiments, the modified screen printed carbon electrode (active surface area = 0.0798 cm^2) was used as a working electrode. An external saturated Ag/AgCl was used as a reference electrode and a platinum wire as the auxiliary electrode. All measurements were carried out at room temperature in an inert atmosphere.

Fabrication of EAG modified SPCE

The EAG modified SPCE and activated SPCE (ASPCE) was fabricated according to our previous reported method.[25] briefly, first the graphite dispersion was prepared by dispersing graphite flakes (10 mg mL^{-1}) in 10 mL of DMF and followed by sonication at room temperature. About 8 μL (optimized concentration) of prepared graphite solution was drop coated on the SPCE and dried in room temperature. The EAG modified SPCE was fabricated by immersing the graphite modified SPCE into electrochemical cell containing 0.1 M PBS and KCl solution and applying a constant potential of 2.0 V for 300 s. For comparison, the ASPCE was also prepared by the similar procedure of immersing the SPCE into electrochemical cell containing 0.1 M PBS and KCl solution and applying a constant potential of 2.0 V for 300 s. Fig. 1A and 1B show the SEM image of pristine graphite and EAG modified SPCEs. It can be seen it clearly that the graphite sheet edges were greatly affected by electrochemical pre-treatment and leads to successful transformation of graphite microsheets. The amount of graphite microsheets was not optimized and the detailed study is in underway. Whereas the observed morphology of pristine graphite modified SPCE relatively smooth when compared with EAG modified SPCE. The SEM of EAG modified SPCE also further confirms that the electrochemical pre-treatment greatly affected the edge plane of the graphite sheets rather than basal planes. The more characterization studies (Surface and electrochemical analysis) about EAG and ASPCE can be found from our recent reports.[25-28] The fabricated EAG modified SPCE was used for the further electrochemical experiments. All experiments were performed in N_2 saturated pH 5 solution and the EAG modified SPCE was stored in pH 5 solution at room temperature when not in use.

3. Results and Discussion

Electrochemical Behavior of Hg(II) at EAG modified SPCE

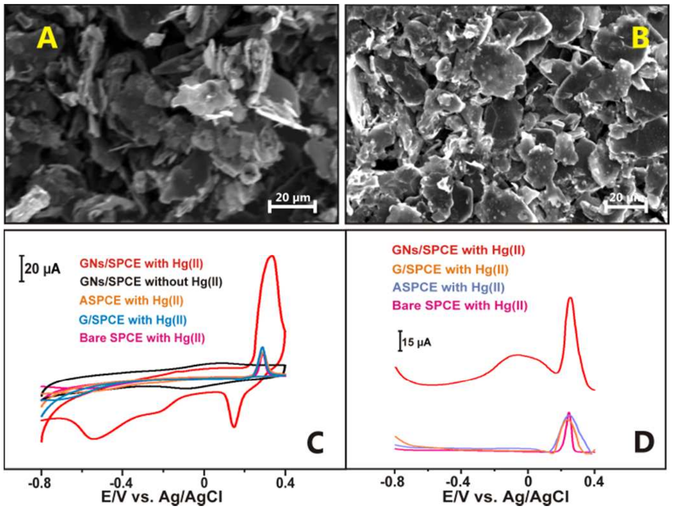

Fig. 1 (A) SEM image of pristine graphite SPCE and EAG (B) modified SPCE. C) The cyclic voltammetric response of bare, electrochemically activated, graphite and EAG modified SPCEs in pH 5 solution containing 100 ppm Hg(II) at a scan rate of 50 mV s^{-1}. D) DPVs of bare, electrochemically activated, graphite and EAG modified SPCEs in the presence of 5 ppm Hg(II) containing pH 5 solution.

The electrochemical response of the different modified SPCEs toward Hg(II) were examined by using CV. Fig. 1C displays the CVs of bare, graphite, activated and EAG modified SPCEs in the presence of 100 ppm Hg(II) containing pH 5 solution at the scan rate of 50 mV s^{-1}. The CVs were performed on the potential scanning from -0.8 to 0.5 V. It can be seen that EAG does not show any peak response in the absence of Hg(II), suggesting that EAG modified SPCE electrochemically inactive in this potential window at pH 5. Whereas, a sharp anodic peak was observed at 0.3 V in the presence of 100 ppm Hg(II), owing to the transformation of Hg(0) to Hg(II).[29] A cathodic peak at 0.185 V due to the reduction of generated Hg(II) to Hg(0).[29] The bare, activated and graphite SPCEs showed a less intense response for Hg(II). Moreover, a diminished cathodic peak of Hg(0) observed only at activated SPCE and other modified SPCEs (bare and graphite) does not show any cathodic response for Hg(0). However, the observed anodic peak current intensity was ~3.8 folds higher than that of bare, activated and graphite modified SPCEs. In order to confirm the electrochemical performance of the EAG modified SPCE toward Hg(II), the DPV was performed for bare, activated, graphite and EAG modified SPCEs in the presence of 5 ppm Hg (II) containing pH 5 solution. As shown in Fig. 1D, a sharp and well-defined oxidation peak of Hg(0) was observed at 0.3 V. However, the other modified SPCEs showed a less intense peak current response compared with EAG modified SPCE. The large edge plane defects and higher surface area of EAG is the possible reason for the enhanced sensitivity toward Hg(II) compared with other modified electrodes. The result further confirms that the EAG modified SPCE is more suitable for the detection of Hg(II) than that of other modified SPCEs.

In order to evaluate the electrochemical properties of untreated graphite and pre-treated graphite modified SPCEs, cyclic voltammograms were performed in 1 mM ferricyanide containing 0.1 M KCl at the scan rate of 100 mV s^{-1}. As shown in Fig. 2, the untreated graphite modified SPCE exhibited a quasi reversible behavior with the peak to peak separation (ΔE_p) of 250 mV. On the other hand, EAG modified shows well defined redox peak with the ΔE_p of 145 mV, which is 105 mV lower than pristine graphite modified SPCE. The heterogeneous electron transfer constant (K_0) was calculated for bare and EAG modified SPCE by Equ. 1 as reported by C. E. Banks et al.[30]

$$K^0 = \varphi\left[D_0 \pi \vartheta \left(\frac{nf}{RT}\right)^{\frac{1}{2}}\right]\left(\frac{D_r}{D_0}\right)^{\alpha/2} \qquad (1)$$

Where, φ is a kinetic parameter, the scan rate used 0.01 V $S^{-1.}$ All other terms are usual meanings. The K_0 of bare and EAG modified SPCE was calculated as 4.18×10^{-3} s^{-1} and 2.62×10^{-3} s^{-1}, respectively. The K_o was greatly deduced after the electrochemical pretreatment of graphite modified SPCE. The result indicates that EAG modified SPCE has more electron transfer than graphite modified SPCE. The fast electron transfer of EAG modified SPCE is due to the presence of more edge plane defects on the EAG surface.[31, 32]

It is well known that the basal plane defects offer an electrochemically less active zone on the graphite surface.[32, 33] Whereas edge plane defects on the graphite surface provides more electrochemically active zones compared with inner basal plane zones. Thus the presence of more edge plane defects of EAG leads to the lower ΔE_p of ferricyanide along with high conductivity.[34] The result confirms that the EAG modified SPCE contains more edge plane defects than that of pristine graphite modified SPCE.

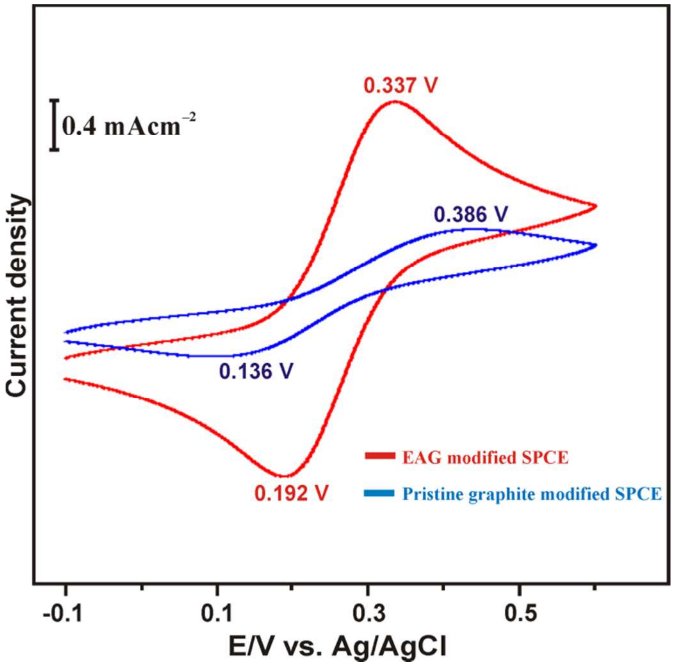

Fig. 2 The cyclic voltammetry response of 1 mM $K_3Fe(CN)_6$ in 0.1 M KCl at the untreated graphite and EAG modified SPCEs at the scan rate of 100 mV s^{-1}.

Fig. 3 shows the cyclic voltammetry response of EAG modified SPCE in 100 ppm Hg(II) containing pH 5 at different scan rates (50 to 500 mV s^{-1}). The anodic (I_{pa}) and cathodic (I_{pc}) peak currents were increased with the increasing scan rates from 50 to 500 mV s^{-1}. The anodic and cathodic peaks were shifted towards the positive and negative direction upon increasing the scan rates and also it has a linear dependence with the scan rates from 50 to 500 mV s^{-1} (not shown). In addition, the logratherm of anodic peak current of Hg(II) has a linear dependence with the logratherm of scan rates (R^2= 0.9978) from 50 to 500 mV s^{-1} (Fig. 3 inset). The result indicates that the electrochemical behaviour of Hg(II) at the modified electrode was controlled by a mixed diffusion-adsorption process.[35]

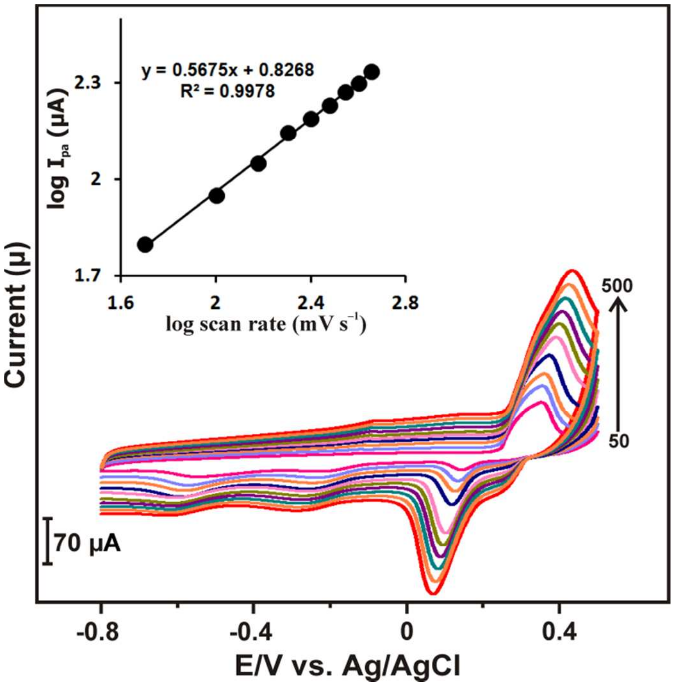

Fig. 3 The cyclic voltammetry response obtained at EAG modified SPCE in the presence of 100 ppm Hg(II) containing N_2 saturated pH 5 solution at different scan rates (50 – 500 mV s^{-1}), inset shows the calibration plot for the log scan rate vs. log I_{pa}.

Optimization of EAG modified SPCE

In order to optimize the essential parameters (accumulation potential and time), DPVs were performed using EAG modified SPCE in the presence of 10 ppm containing pH 5 solution. The deposition potential is very important parameter to achieve the best sensitivity for Hg(II) detection. Hence, the effect of the deposition potential on the peak current response was studied using DPV in the potential range from 0 to – 1.0 V in pH 5. As shown in Fig. 4A, the best current response was obtained when the deposition potential at -0.8 V. When the deposition potential sweep at more negative and positive potential than -0.8 V, a decrease in the response current of Hg(II) was observed. Therefore, we choose -0.8 V as the optimal deposition potential for the further experiment. We also investigated the deposition time on the peak current response by using the DPV. The utmost sensitivity was observed when the deposition time was 60 s; the current response was stable when the deposition time was more than 60 s (Fig. 4B) and the sensitivity was decreased when the deposition time was less than 60 s.

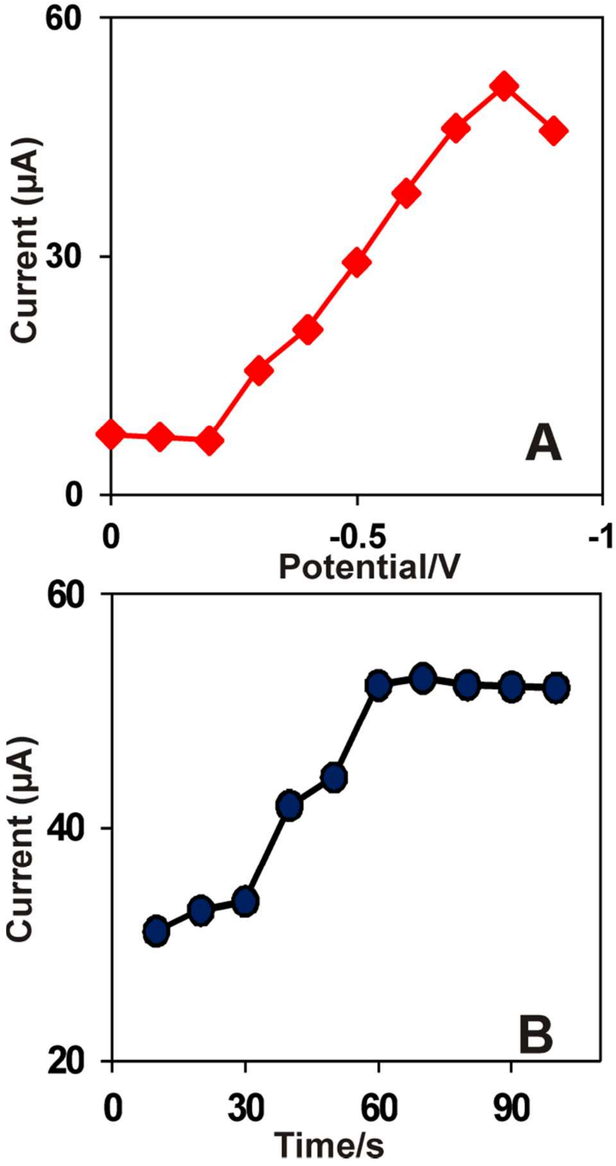

Fig. 4 (A) Calibration plot for cyclic voltammetric response of the EAG modified SPCE in pH 5 solution containing 100 ppm Hg(II) at 50 mV s^{-1} scan rate upon different accumulation potential. B) At the same conditions, calibration plot for cyclic voltammetric response of the EAG modified SPCE upon different accumulation time.

Determination of Hg(II) at EAG modified SPCE.

Under optimum conditions, the EAG modified SPCE was used for the determination of Hg(II) by DPV. Figure 5 shows the

DPV response of the EAG modified electrode toward the successive addition of different concentrations Hg(II) in pH 5 solution. A sharp anodic peak current response was observed with the addition of 0.05 ppm Hg(II). The anodic peak current was increased further increasing the concentration of Hg(II). The EAG modified SPCE shows a linear range for Hg(II) up to 14.77 ppm with a correlation coefficient of 0.9882 (inset). The sensitivity was calculated as 81.5 μAppm^{-1} cm^{-2}. The LOD was estimated as 4.6 ppb based on a signal-to-noise ratio equal to 3. The observed sensitivity and LOD are more comparable than that of recently reported carbon nanomaterials modified electrodes.[36-40] Moreover, the obtained results demonstrate that the fabricated EAG modified SPCE is more reliable for the determination of Hg(II) and also the observed LOD is well below the guideline value of Hg(II) in drinking water as set by the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA).[16]

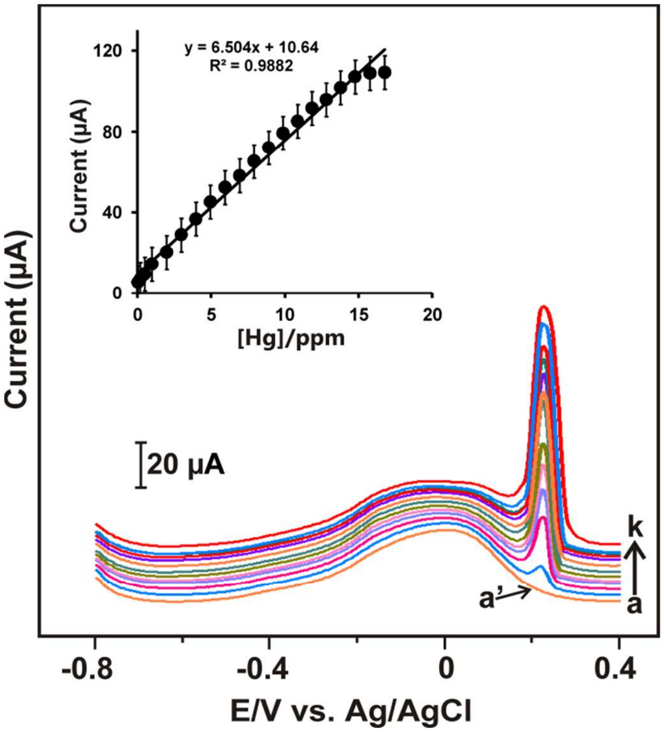

Fig. 5 DPV response obtained at EAG modified SPCE upon the addition of different concentration (0.05 to 14.77 ppm) of Hg(II) into pH 5 solution. Inset shows the corresponding calibration plot for the current response vs [Hg(II)]. Error bar shows the relative standard deviation for 3 measurements.

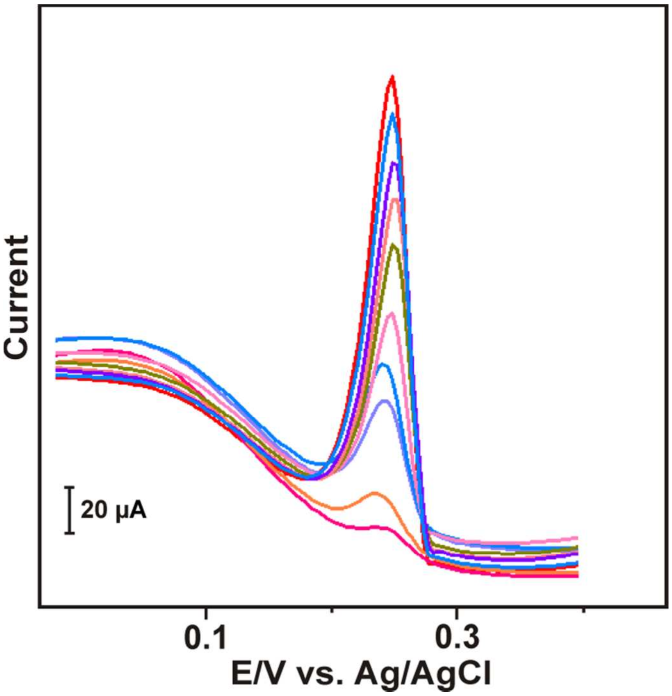

Fig. 6 DPV response obtained at EAG modified SPCE upon the addition of different concentration (0.05 to 14.77 ppm) of Hg(II) into the river water.

As shown in Fig. 6, the EAG modified electrode was successfully applied for the determination of Hg (II) in river water using the DPV. The recovery results of Fig. 6 are summarized in Table. 1. The Table. 1 is evident that the recoveries of Hg(II) are found in the range of 96.0 – 99.6 %. The good recovery of the EAG modified SPCE toward Hg(II) authenticates that the proposed method is more suitable for the determination of Hg(II) in water samples with high accuracy.

The selectivity of Hg(II) at the modified electrode is likely to be a challenging task, thus we investigated the selectivity of the EAG modified SPCE in the presence of other metal ions which are commonly present in the drinking water. The experimental conditions are similar as like Fig. 5 and the selectivity results are summarized in Table. 2.

Table. 1 Determination of Hg(II) in river water samples at EAG modified SPCE.

Sample labeled	Added (ppm)	Found[a] (ppm)	Recovery (%)	RSD[b]
A	-	-	-	-
B	0.5	0.48	96.0	2.9
C	2.0	1.96	98.0	3.4
D	5.0	4.96	99.2	2.3
E	9.0	8.97	99.6	2.8

[a] Standard addition method.

[b] Relative standard deviation of 3 measurements.

A to E = Spiked diluted samples of Hg(II) in river water.

Table. 2 Effects of various metal ions (20-fold excess concentrations) on the electrochemical signals of 1 ppm Hg(II) at EAG modified SPCE

Interference	[a]Relative error (%)
Pb(II)	1.15
Cu(II)	3.75
Zn(II)	0.32
Fe(II)	0.27
Cd(III)	0.90
Ni(II)	1.25

[a] I_{pa} of Hg(II) is 100%

The Table 2 is evidence that the EAG modified electrode exhibits excellent selectivity for the response to 1 ppm Hg(II) in the presence of 20 fold additions of Pb(II), Cd(III), Fe(II), Zn(II), and Ni(II). Although the Cu(II) a showed a little effect (3.75 %) on the current response to the detection of Hg(II). The reason may be due to the detection potential of Cu(II) close to the detection potential of Hg(II). However, Cu(II) appears at much positive potential than Hg(II) at EAG modified electrode, and thus the modified electrode can be used for the selective detection of Hg(II) in the presence of other metal ions. The result clearly demonstrates the high selectivity of the EAG modified electrode toward the determination of Hg(II).

The relative standard deviation (RSD) for 5 successive determinations was 2.3 % and 3 independent electrodes were 3.3 % for 1 ppm Hg(II) determination, indicating good repeatability and reproducibility of the EAG modified electrode.

4. Conclusions

In conclusion, a highly sensitive and selective Hg(II) sensor has been fabricated by using EAG modified SPCE for the first time. The EAG modified SPCE showed higher sensitivity (81.5 $\mu Appm^{-1}$ cm^{-2}) with lower LOD (4.6 ppb) for the determination of Hg (II). The observed LOD is much below the guideline value of Hg(II) in drinking water (30 ppb) as set by the World Health Organization. In addition, the EAG modified SPCE electrode displayed a good selectivity along with good practicality for the determination of Hg(II) in river water samples. We believe that the proposed EAG modified SPCE could be an attractive electrode material for the determination of Hg(II) in water samples.

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Notes and references

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