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Electrodeposited Bi-Au nanocomposite modified carbon paste electrode for the simultaneous determination of copper and mercury†

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Composites of bismuth and gold nanoparticles (Bi–AuNPs) were prepared on a carbon paste electrode (CPE) by an electrochemical deposition method. The electrochemical parameters were optimized for the effective deposition of Bi–AuNP composite materials. Microscopic examination revealed that nanoparticle clusters of gold were embedded well within the bismuth films (Bi films) over the surface of the CPE. An analytical anodic stripping voltammetry method has been developed for the simultaneous determination of copper and mercury at ultratrace levels using the Bi–AuNP modified CPE. It was possible to observe well separated stripping peaks of the two metal ions and the modified electrode was successfully applied for simultaneous determination of Cu and Hg. The limits of detection using the optimized analytical procedure were observed as 0.16 μg L^{-1} and 0.28 μg L^{-1} for Cu and Hg respectively. Interference effects of some of the commonly occurring metal ions were investigated and the method was applied for the determination of Cu and Hg in two ground water and two soil samples collected from different places.

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1. Introduction

Due to their interesting properties, Cu and Hg have been extensively used in industry and there are enormous concerns regarding the contamination of the environment with these metal ions through industrial activities. All heavy metal ions, beyond a certain concentration level, are highly toxic to the environment; Cu and Hg are two important toxic elements in the list. In the body, Cu is generally present in the bound form with ceruloplasmin and is non-toxic.[1] Free Cu in the body causes toxicity as it generates reactive oxygen species and damages proteins, lipids and DNA.[1] Stripping voltammetry is one of the most important methods of determination of Cu in wide concentration ranges using a mercury drop electrode.

Presently, due to the toxicity of mercury, mercury drop electrodes are being avoided in stripping voltammetry as out of all the heavy metal ions mercury toxicity is more severe than the others. Mercury exhibits a very complex behavior in the food chain and in the human body.[2,3] Some methods have been used for the determination of mercury such as, gas chromatography-atomic fluorescence spectrometry and atomic absorption spectrometry.[4–9] Other commonly used methods for the determination of total mercury are cold vapor atomic absorption spectrometry (CVAAS) and inductively coupled plasma mass spectrometry (ICP-MS).[10,11] All the methods mentioned are either less sensitive, lack selectivity or require complicated instrumentation and also involve a high operational cost. Voltammetric techniques represent an important method with high sensitivity and low operational cost and have the possibility of portable instrumentation for onsite determination. Bismuth film electrodes are an interesting alternative to mercury drop electrodes for the determination of toxic heavy metal ions. Bismuth, known to be an environmentally friendly material has been used in a wide variety of cosmetics and also in medicines.[12–18] Bi films were deposited over glassy carbon electrodes[19–25] or over CPEs[26–28] and applied in stripping voltammetry. However the easy renewability of CPEs make them a better choice for the present purpose compared to glassy carbon electrodes. It has been observed by previous researchers that a strong stripping peak due to Bi was observed before a Cu peak, which is detrimental to the appearance of the Cu stripping peak on bare Bi film electrodes.[13,29] There was one report based on the decrease in the Bi stripping peak for the determination of Cu using bare Bi film electrodes.[13] We also have reported the determination of Cu from the decrease in the Bi stripping peak on a bare Bi film electrode[29] and a direct determination of Cu using a Bi–graphene composite electrode.[30] In the present investigation we have incorporated gold into the Bi film so that the stripping peak due to Cu could be observed. Gold has a strong affinity towards mercury thus the Bi–AuNP composite material would be the ideal choice for the simultaneous determination of Cu and Hg.

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It has been reported that nanoparticle arrays have increased the effective mass transport and also increased the signal to noise ratio of analytical measurements.[31–36] Merged diffusion layers of nanoparticle modified electrodes have also reduced the requirement of active materials to obtain a similar or enhanced response to the whole electrode. There are a few reports on gold nanoparticle (AuNP) modified electrodes for the determination of mercury either on a carbon electrode or on a screen printed electrode.[37–41] One paper reported a modified electrode using EDTA-like films for the simultaneous determination of Cu and Hg.[42] In a recent publication heavy metal ions were determined using a bismuth nanotube modified glassy carbon electrode.[43] Other than for analytical applications, Au and Bi_2O_3 nanocomposite modified electrodes were also applied in the photocatalytic decomposition of dyes.[44] Thus it is interesting to investigate the applicability of AuNP arrays embedded onto Bi films on a CPE for the simultaneous determination of Cu and Hg. Currently, no such report on the simultaneous determination of Cu and Hg using a Bi–AuNP composite modified CPE exists in the literature. The modified electrode developed in the present investigation was applied for the simultaneous determination of Cu and Hg in water samples.

2. Instrumentation and procedure

Electrochemical studies were carried out using a cell assembly with a three-electrode configuration consisting of the modified CPE as the working electrode and a saturated calomel electrode (SCE) as the reference electrode. The potentials applied, measured and reported in this study were with respect to the SCE reference electrode at room temperature (298 K). A platinum rod served as the counter electrode. Electrochemical measurements were performed using an Eco Chemie Potentiostat/Galvanostat, Autolab-302N; the data acquisition and analysis were carried out using GPES 4.9 software. Prior to the electrochemical scan, the voltammetric solution was purged with high purity nitrogen for 10 min. Water samples were not required to digest for the determination of Cu and Hg using the Bi–AuNP modified electrode. A field Emission Gun-Scanning Electron Microscope (FEG-SEM) system model JSM-7600F was used for the SEM measurements. Energy dispersive X-ray fluorescence (EDXRF) was carried out using an EX-3600 M spectrometer from Xenemetrix. The electrodeposited samples were dried under vacuum before the SEM images and EDXRF measurements were taken.

2.1 Reagents and solutions

All the chemicals used in the present study were AR grade from Merck India limited or SD Fine-Chem Limited. A stock solution of Au (0.01 M) was prepared by dissolving an accurately weighed amount of high purity Au metal in aqua regia. Appropriate quantities of all the reagents were weighed, dissolved in ultrapure water and made up to the desired volume. High purity nitrogen gas (from Indian Oxygen Ltd.) was used for removing the dissolved oxygen from the voltammetric solution.

3. Results and discussion

3.1 Deposition of Bi–AuNP composite materials on the carbon paste electrode surface

Preparation of the carbon paste has been reported previously;[45] we have adapted a similar method of preparation.[29,30] Bi and Au films were simultaneously deposited over the CPE surface using an electrodeposition technique from a 0.1 M H_2SO_4 solution containing 0.1 mM Bi^{3+} and 0.2 mM Au^{3+}. Electrodeposition was carried out under mild stirring conditions (at 500 rpm) at −0.3 V. The deposited films were washed with ultrapure water and then dried under an air flow. SEM images were recoreded using these films, which are shown in Fig. 1A–C. In Fig. 1A, Au, Bi and the carbon paste substrate are shown in different colours. It was observed that Au and Bi composites were embedded well within the carbon paste matrix. The size of one assembly of the gold nanoparticles was around 100 nm. The individual particle size of these assemblies was in the range of 10–20 nm (*cf.* Fig. S1 of ESI†). Bi and Au components of the composite film were individually mapped and are shown in Fig. 1B and C respectively. Both Bi and Au were well dispersed over the electrode surface. Energy dispersive X-ray fluorescence (EDXRF) measurements were carried out on the CPE/Bi–AuNPs substrate and the results are shown in Fig. 2A and B. The presence of Bi and Au on the CPE/Bi–AuNPs substrate was observed from the measurements at an elemental ratio of 2 : 1 (Au/Bi).

Electrochemical characterization of the CPE/Bi–AuNPs was carried out using electrochemical impedance measurements. Impedance measurements were recorded at a single frequency of 100 Hz with varying potentials as shown in Fig. 3. The impedance performance of the CPE/Bi–AuNP electrode was compared with a CPE modified with gold nanoparticles (CPE/AuNP) and also with a CPE modified with a Bi film (CPE/Bi). It was observed that the capacitance of the Bi film modified CPE was lowest. The capacitance of the CPE/Bi–AuNP composite was also lower, which is useful for the application of the composite electrode in analytical measurements as a modified electrode. The CPE/AuNP composite electrode has shown very high capacitance, much higher than the other two electrodes. The lower capacitance of the CPE/Bi–AuNP composite electrode is beneficial for a lower background in stripping analysis.

3.2 Optimization of the analytical parameters of the measurements

After electrochemical deposition of the Bi–AuNPs over the CPE surface, the electrode was washed with ultrapure water and dipped into the stripping solution containing the analytes. The stripping solution was 0.1 M acetate buffer; the pH of the buffer solution was optimized from the stripping peaks of Cu and Hg and is shown in Fig. 4. At a pH value lower than 4 the stripping peak of Cu was merged with that of the Bi peak (*cf.* plot for pH 3 of Fig. 4). At pH values higher than 4, the Cu stripping peak was well separated from the Bi stripping peak. However at a pH value of more than 6 the stripping response of Cu decreased. Thus a solution pH of 5 was optimized for the analysis for well separated peaks between Bi and Cu and also for a good

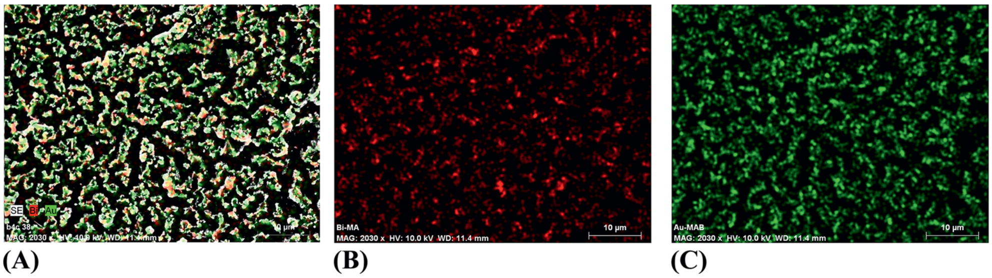


Fig. 1 SEM image of the Bi–AuNP composite films (A) overall image (B) when Bi was mapped (C) when Au was mapped. The composite material was formed by electrochemical deposition at −0.3 V in 0.1 M H_2SO_4 solution containing 0.1 mM Bi^{3+} and 0.2 mM Au^{3+}.

stripping current of Cu. The stripping peak of Hg has also shown strong pH dependency. The highest peak current of Hg was observed between pH values of 4 and 5. The stripping peak was reduced at pH values higher than 5.5. Considering the stripping response of both Cu and Hg, pH 5 was optimum for their simultaneous determination in a stripping solution of 0.1 M acetate buffer. Furthermore it was observed that the stripping peak of Cu was positively shifted compared to its positions on bare Bi film electrodes.[29] Cu might have formed an intermetallic compound with the AuNPs, which resulted in the positive shifting of the stripping peak. The effect of deposition potential of the analytes on the modified electrodes was investigated by varying the deposition potentials of the measurements from −0.3 V to −1.2 V and the results are shown in Fig. S2 of the ESI.† Initially the peak currents for both Cu and Hg were increased from −0.3 V to −0.5 V, beyond −0.5 V, though the base line of the plots was modified, the stripping peaks of Cu and Hg remained almost unaffected. Therefore a deposition potential of −0.5 V was required for the deposition of Hg and Cu. A more negative deposition potential was avoided as the quality of the deposits would be affected due to the hydrogen evolution process during deposition. In view of this, the deposition potential of −0.5 V was optimized in the present case. In order to optimize the deposition time, it was varied from 50 s to 800 s by keeping the deposition potential fixed at −0.5 V, the results are shown in Fig. 5. The stripping peak

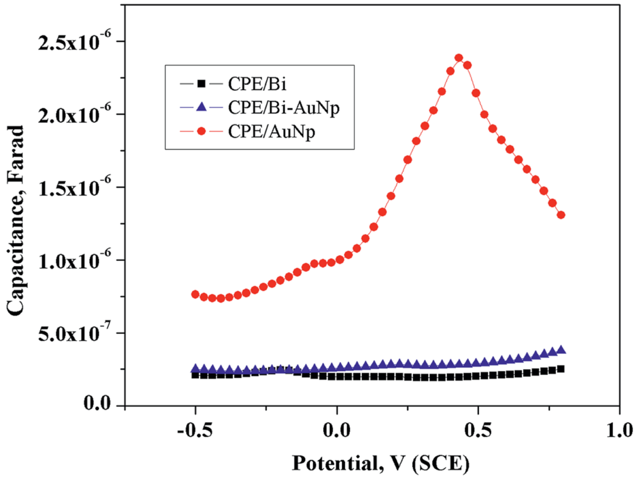
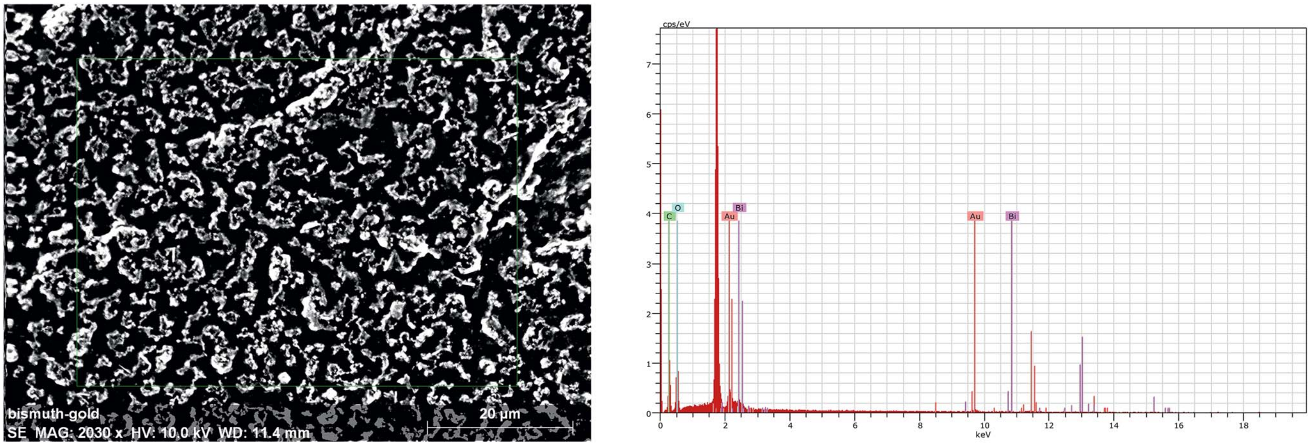


Fig. 3 Impedance plots of different deposits in a 0.1 M acetate buffer solution of pH 4.5.



(A) (B)

Fig. 2 SEM image (A) and EDX plot (B) of the composite electrode.

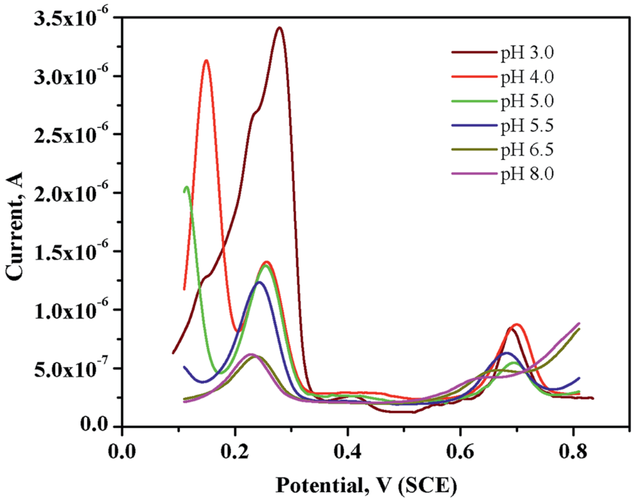


Fig. 4 Effect of pH on the stripping peak of 40 µg L^{-1} Cu^{2+} and 10 µg L^{-1} Hg^{2+} in 0.1 M acetate supporting electrolyte medium.

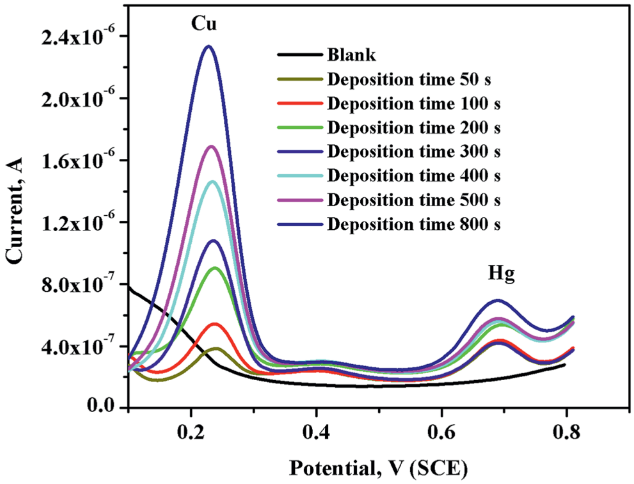


Fig. 5 Effect of deposition time on the stripping peak of 20 µg L^{-1} Cu^{2+} and 8 µg L^{-1} Hg^{2+} in 0.1 M acetate supporting electrolyte medium.

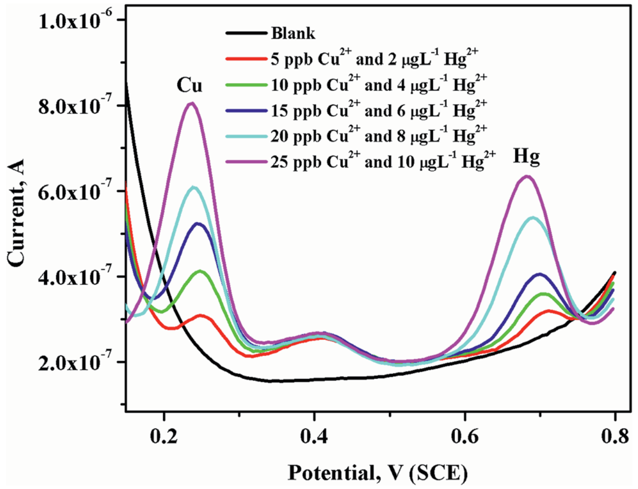


Fig. 6 Voltammetric plot of Cu^{2+} and Hg^{2+} in 0.1 M acetate buffer solution at pH 5 with a deposition potential of −0.5 V for 200 s.

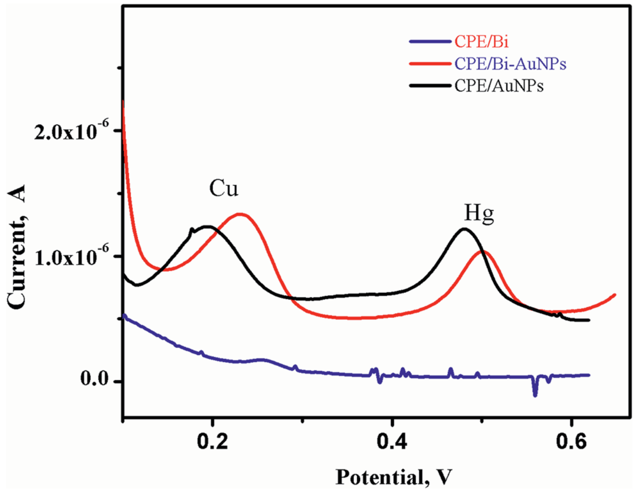


Fig. 7 Stripping response of Cu^{2+} and Hg^{2+} on different modified carbon paste electrodes.

current due to Cu^{2+} increased with an increase in the deposition time up to 800 s. Unlike the Cu stripping peak, the stripping peak of Hg did not increase as sharply with the deposition time of the measurements. Considering the time taken for analysis a deposition time of 200 s was chosen in the present case.

In order to provide more information about the simultaneous stripping response and to obtain a calibration plot of Cu^{2+} and Hg^{2+}, voltammograms were recorded using the CPE/Bi–AuNP electrode with successive additions of Cu and Hg standard concentrations in the test solution. The corresponding voltammetric plots are shown in Fig. 6. The peak positions of Cu and Hg were well separated and useful for their simultaneous determination. Stripping peak currents were increased with an increase in Cu^{2+} and Hg^{2+} concentration in the stripping solution. The peak positions of both the elements remained unaltered on successive addition of the standards. The calibration plot of Cu^{2+} followed the regression equation $i_p = 2.03 \times 10^{-8}C + 8.61 \times 10^{-10}$ with a correlation coefficient of 0.998 and a standard deviation of 1.06×10^{-9} where C is in µg L^{-1}. The calibration plot of Hg^{2+} followed the linear regression equation as $i_p = 4.28 \times 10^{-8}C + 1.52 \times 10^{-11}$ with a correlation coefficient 0.996 and a standard deviation of 4.02×10^{-9} where C is in µg L^{-1}. Three sigma detection limits of Cu and Hg were obtained as 0.16 µg L^{-1} and 0.28 µg L^{-1} respectively. The corresponding linear calibration plots are shown in the ESI as Fig. S3 and S4.† The linear ranges for Cu and Hg were 5 to 25 µg L^{-1} and 2 to 10 µg L^{-1} respectively under the optimized experimental conditions.

Bi produces a strong stripping signal during the anodic scanning process and it is difficult to separate the Cu stripping peak from that of Bi, therefore the determination of Cu is difficult on a Bi film electrode. A proportional decrease of the Bi-stripping peak with the addition of Cu was successfully

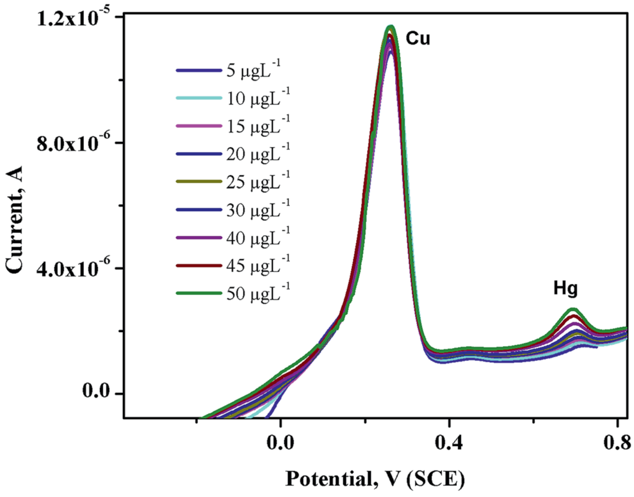


Fig. 8 Voltammetric plots of Hg^{2+} with its successive addition as shown inside the figure and at a constant concentration of Cu^{2+} of 200 μg L^{-1}.

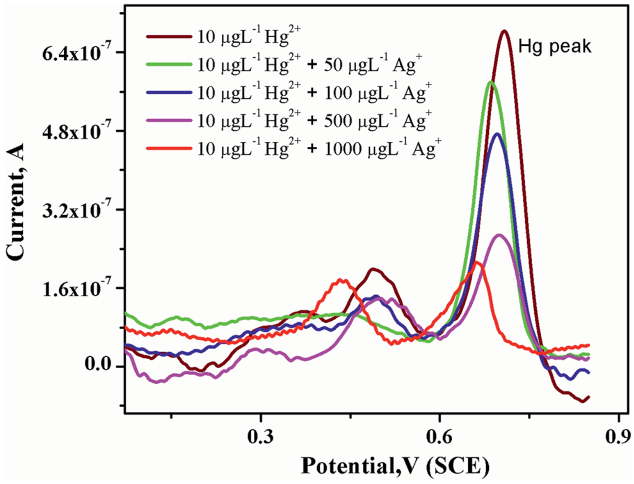


Fig. 9 Interference effect of Ag(I) on the Hg stripping peak.

Table 2 Analysis results of Cu^+ and Hg in two ground water samples and two soil samples collected from different important regions of India, using the CPE/Bi–AuNP electrode

Sample	Cu	Hg
Punjab	7.9 (9.5)[a] (μg L^{-1})	3.6 (4.2)[a] (μg L^{-1})
OSCOM	65 (63)[a] (μg L^{-1})	4.9 (4.6)[a] (μg L^{-1})
Jadugoda-2	16 (15)[a] (μg kg^{-1})	9.1 (9.5)[a] (μg kg^{-1})
Vizac-2	2.5 (2.3)[a] (μg kg^{-1})	19.5 (18.5)[a] (μg kg^{-1})

[a] Values in the brackets were determined using an inductively coupled plasma atomic emission spectrometry (ICPAES) technique for Cu^{2+} and using a total mercury analyzer based on atomic absorption technique for Hg^{2+}. The percent standard deviation for Cu^{2+} was 3.6% and for Hg 4.5% for 6 repetitive measurements.

attempted as an alternate way to determine Cu.[13] It would always be a good idea to observe the direct electrochemical stripping response of Cu with its proportional increment with concentration. Interestingly in the present case, on simultaneous deposition of AuNPs and the Bi-films, the stripping response of Cu was shifted to a positive potential and it was clearly observed. Cu has the stronger affinity to form intermetallic compounds with Au, which has shifted its stripping peak towards a more positive potential. Due to that, its stripping peak was separated well from the Bi stripping peak. The stripping response of Cu and Hg was compared using three different electrodes; CPE/Bi, CPE/AuNPs and CPE/Bi–AuNPs, the results are shown in Fig. 7. The surface area from the cyclic voltammetry measurements were obtained as it was observed that on the CPE/Bi electrode, no stripping response due to Cu and Hg was observed. Although the stripping peak heights in the case of the CPE/Bi–AuNP modified electrode was only marginally higher than that of the CPE/AuNPs, the base line improved in the case of the CPE/Bi–AuNP composite modified electrode. Modified electrodes by AuNPs alone have been applied for the determination of Hg.[37–41] However, as seen in the present case the stripping response of Hg has improved due to the incorporation of Bi in the composite. Similarly, the stripping response of Cu could also be observed using an AuNP modified electrode. However its stripping response was not proportional, as Cu never stripped back proportionally from the composite film. The corresponding plot of the stripping response of Cu using an AuNP modified CPE is shown Fig. S5 of the ESI.† The presence of Bi along with the AuNPs increases the conductivity of the individual particles and also the inter-particle conductivity. Incorporation of Bi has also improved the holding capacity of the material, which has produced a proportional stripping response and enhanced the linear range. In the present experiments all three modifications were carried out over the same CPE as the substrate electrode with a 2 mm diameter. The surface areas of the CPE/Bi, CPE/AuNP and CPE/Bi–AuNP electrodes were determined from cyclic voltammetry measurements by monitoring the reduction current of methyl viologen at different scan rates. The surface area values from the cyclic voltammetry measurements of CPE/Bi, CPE/AuNP and CPE/Bi–AuNP electrodes were obtained as 0.05 cm^2, 0.08 cm^2 and 0.09 cm^2 respectively.

Table 1 Recovery test results of Cu^{2+} and Hg^{2+} using the CPE/Bi–AuNP electrode

Element	Spiked concentration (μg L^{-1})	Recovery concentration (μg L^{-1})	% of recovery
Hg	5	5.02	100.4%
Cu	5	4.71	94%

Table 3 Comparison of the present method and the methods already reported in the literature

Technique details	Detection limit Cu, $\mu g\ L^{-1}$	Detection limit Hg, $\mu g\ L^{-1}$	Reference
RGO/Au nanocomposite carbon paste electrode	0.16	0.28	This work
Bismuth film coated glassy carbon electrode	5	—	13
Poly EDTA-like film modified electrode	0.1	0.1	42
GO–chitosan–AuNPs/MTU modified Indium Tin Oxide (ITO)	—	0.78	46
CuO nanoshuttles/poly(thionine) modified glassy carbon electrode	—	8.5	47
Hg^{2+}-induced DNA hybridization modified electrode	—	0.6	48
Gold film modified screen-printed electrodes and metal ion preconcentration with thiol-modified magnetic particles	—	7.5	49

In real water samples Cu remains at a much higher concentration compared to Hg. To evaluate if the modified electrode could work in the presence of Cu, voltammetric experiments were carried out using a dummy sample containing 200 $\mu g\ L^{-1}$ Cu^{2+}, and Hg^{2+} was added successively to the solution. The corresponding plots are shown in Fig. 8. It was observed that the Hg stripping peak increased proportionately and was unaffected in the presence of Cu^{2+}. The Cu stripping peak was also unaffected with the addition of Hg^{2+}. This observation concluded that both Cu and Hg stripping responses remained unaffected due to the presence of the other at high concentrations. Reproducibility of the stripping responses was evaluated by recording the voltammetric scans repeatedly and the results are shown in Fig. S6 of the ESI.† The percent standard deviation for Cu^{2+} was obtained as 3.6% and for Hg 4.5% for 6 repetitive measurements.

3.3 Interference effect

Interference effects on the stripping peak of 20 $\mu g\ L^{-1}$ Cu and 8 $\mu g\ L^{-1}$ Hg due to some of the commonly occurring metal ions Fe(III), Cr(VI), As(III), Ag(I), Pb(II), Cd(II), Zn(II) and U(VI) were investigated. Except those due to Ag(I) and As(III) no interference from all the other metal ions was observed up to a concentration 500 times higher than Cu(II) and Hg(II). Ag(I) interfered with both the Cu and Hg peaks. The effect of interference due to Ag(I) on the Hg stripping peak is shown in Fig. 9. It was observed that the Hg stripping peak was reduced with the addition of Ag(I) in the test solution from a concentration of 50 $\mu g\ L^{-1}$ Ag(I). An observable Hg stripping peak was observed with the addition of Ag(I) up to 1000 $\mu g\ L^{-1}$. The Hg stripping peak was recoverable with the increase in the gold content in the modified electrode. During preparation of the modified electrode a gold concentration of 100 times the Ag(I) concentration is recommended to minimize the interference due to Ag(I) on the Hg stripping peak. The tolerance of Ag(I) on the stripping peak increased due to the incorporation of Bi along with the AuNPs. Ag(I) only heavily interfered with AuNP modified electrodes for Hg^{2+} determination. As(III) interfered with the Cu stripping peak beyond a concentration 200 times higher than that of Cu by broadening the Cu stripping peak.

3.4 Recovery test and analysis of water and soil samples

Recovery tests were carried out in tap water samples by spiking both 5 $\mu g\ L^{-1}$ of Cu^{2+} and Hg^{2+} standards. The test results are shown in Table 1. Both elements were recovered within a 10% deviation from the added concentration. Two ground water samples were collected from two different regions of India, and analysed using the modified electrode; the results are shown in Table 2. An OSCOM (Odissa sands company) sample was collected from an industrial region, which is important for monitoring mining activities. Another sample was collected from a bore well in the Punjab state of India. Lowering of the quality of ground water is a concern in Punjab due to the excessive use of ground water for irrigation purposes. Both samples were analyzed under undigested conditions using the presently developed CPE/Bi–AuNP electrode. Two soil samples were collected; one from Jadugoda, a mining region and the other from Vizac, a coastal region. Digestion of the soil samples was carried out using an Anton Paar Microwave Digester, Multiwave-3000. An aliquot of 0.5 g of the solid was taken with 5 mL of concentrated nitric acid and digested at 150 °C for 20 min. After complete digestion, the solutions were diluted with ultrapure water and made up to a volume of 50 mL. An aliquot of this sample solution was used in the voltammetric cell for the electrochemical measurements. The analysis results are shown in Table 2. The values were verified using the results from the inductively coupled plasma optical emission spectrometry (ICPOES) technique for Cu and a mercury analyser based on the thermal decomposition atomic absorption technique for Hg. The results were comparable thus, with the CPE/Bi–AuNP electrode digestion was not required to analyse Cu and Hg in ground water samples. The Cu content in the OSCOM ground water sample was higher due to the mining activity in the region. The other values were within the prescribed limit by the World Health Organization (WHO) in potable water. Once fabricated, this sensor can be used for 15 scans. We have tested the stability of the sensor; it remains stable up to 7 days when stored in water. The analytical performance of the presently developed electrode was compared with the methods reported previously in the literature for Cu and Hg and the results are reported in Table 3. As reflected in the table, the present method stands well in terms of sensitivity and ease of application compared to the reported literature.

4. Conclusion

A bismuth–gold composite material was electrodeposited on the surface of a CPE. Microscopic examination revealed that the gold nanoparticle clusters were spread well over the Bi-films. The conductivity of the modified surface was improved due to the Bi films. Well spread gold nanoparticles on the Bi film have enhanced the sensitivity for mercury determination. The three sigma detection limits of Cu and Hg were 0.16 $\mu g\ L^{-1}$ and 0.28 $\mu g\ L^{-1}$ respectively. Direct determination of Cu and Hg was reported in ground water samples collected from two different regions. High affinity of Cu towards Au has positively shifted the Cu stripping peak; this is useful for the direct determination of Cu using a Bi containing film electrode.

References

1 G. J. Brewer, *Clin. Neurophysiol.*, 2010, **121**, 459.
2 J. R. Miller, J. Rowland, P. J. Lechler, M. Desilets and L. C. Hsu, *Water, Air, Soil Pollut.*, 1996, **86**, 373.
3 R. E. Clement, G. A. Eiceman and C. J. Koester, *Anal. Chem.*, 1995, **67**, 221R.
4 A. D'Ulivo, V. Loreti, M. Onor, E. Pitzalis and R. Zamboni, *Anal. Chem.*, 2003, **75**, 2591.
5 X. P. Yan, X. B. Yin, D. Q. Jiang and X. W. He, *Anal. Chem.*, 2003, **75**, 1726.
6 S. J. Christopher, S. E. Long, M. S. Rearick and J. D. Fassett, *Anal. Chem.*, 2001, **73**, 2190.
7 Y. A. Vil'pan, I. L. Grinshtein, A. A. Akatove and S. Gucer, *J. Anal. Chem.*, 2005, **60**, 45.
8 E. Kopysc, K. Pyrzynska, S. Garbos and E. Bulska, *Anal. Sci.*, 2000, **16**, 1309.
9 H. Xu, L. P. Zing, S. J. Xing, G. Y. Shi, J. S. Chen, Y. Z. Xian and L. T. Jin, *Electrochem. Commun.*, 2008, **10**, 1893.
10 S. Rio-Segade and J. F. Tyson, *Talanta*, 2007, **71**, 1696.
11 F. Ubillus, A. Algeria, R. Barbera, R. Farre and M. J. Lagarda, *Food Chem.*, 2000, **71**, 529.
12 J. Wang, J. Lu, S. B. Hocevar, P. A. M. Farias and B. Ogorevc, *Anal. Chem.*, 2000, **72**, 3218.
13 J. Wang, J. M. Lu, U. A. Kirgoz, S. B. Hocevar and B. Ogorevc, *Anal. Chim. Acta*, 2001, **434**(1), 29.
14 J. Wang, *Electroanalysis*, 2005, **17**, 1341.
15 J. Wang, R. P. Deo, S. Thongngamade and B. Ogorevc, *Electroanalysis*, 2001, **13**(14), 1153.
16 A. Economou, *Trends Anal. Chem.*, 2005, **24**, 334.
17 A. Krolicka and A. Bobrowski, *Electrochem. Commun.*, 2004, **6**, 99.
18 I. Svancara and K. Vytras, *Chem. Listy*, 2006, **100**, 90.
19 G. J. Lee, C. K. Kim, M. K. Lee and C. K. Rhee, *J. Nanosci. Nanotechnol.*, 2012, **12**, 5673.
20 J. Wang, U. A. Kirgoz and J. M. Lu, *Electrochem. Commun.*, 2001, **3**, 703.
21 S. B. Hocevar, J. Wang, R. P. Deo and B. Ogorevec, *Electroanalysis*, 2002, **14**, 112.
22 S. B. Hocevar, B. Ogorevc, J. Wang and B. Pihlar, *Electroanalysis*, 2002, **14**, 1707.
23 J. Wang and J. M. Lu, *Electrochem. Commun.*, 2000, **2**, 390.
24 G. Kefala, A. Economou, A. Voulgaropoulos and M. Sofoniou, *Talanta*, 2003, **63**, 603.
25 A. Alberich, N. Serrano, C. Arino, J. M. Diaz-Cruz and M. Esteban, *Talanta*, 2009, **78**, 1017.
26 A. Krolicka, R. Pauliukaite, I. Svancara, R. Metelka, A. Bobrowski, E. Norkus, K. Kalcher and K. Vytras, *Electrochem. Commun.*, 2002, **4**, 193.
27 G. U. Flechsig, M. Kienbaum and P. Grundler, *Electrochem. Commun.*, 2005, **7**, 1091.
28 K. Vytras, I. Svancara and R. Metelka, *Electroanalysis*, 2002, **14**, 1359.
29 M. K. Dey, A. K. Satpati, S. Sahoo, R. Kameswaran, A. V. R. Reddy and T. Mukherjee, *Anal. Methods*, 2011, **3**, 2540.
30 P. K. Sahoo, B. Panigrahy, S. Sahoo, A. K. Satpati, D. Li and D. Bahadur, *Biosens. Bioelectron.*, 2013, **43**, 293.
31 X. Dai, G. G. Wildgoose, C. Salter, A. Crossley and R. G. Compton, *Anal. Chem.*, 2006, **78**, 6102.
32 T. J. Davies and R. G. Compton, *J. Electroanal. Chem.*, 2005, **585**, 63.
33 T. J. Davies, C. E. Banks and R. G. Compton, *J. Solid State Electrochem.*, 2005, **9**, 797.
34 A. O. Simm, C. E. Banks, S. Ward-Jones, T. J. Davies, N. S. Lawrence, T. G. J. Jones, L. Jiang and R. G. Compton, *Analyst*, 2005, **130**, 1303.
35 A. O. Simm, S. Ward-Jones, C. E. Banks and R. G. Compton, *Anal. Sci.*, 2005, **21**, 667.
36 W. Cheng, S. Dong and E. Wang, *Langmuir*, 2002, **18**, 9947.
37 T. Hezard, K. Fajerwerg, D. Evrard, V. Collière, P. Behra and P. Gros, *J. Electroanal. Chem.*, 2012, **664**, 46.
38 O. Abollino, A. Giacomino, M. Malandrino, G. Piscionieri and E. Mentasti, *Electroanalysis*, 2008, **20**, 75.
39 O. Abollino, A. Giacomino, M. Malandrino, S. Marro and E. Mentasti, *J. Appl. Electrochem.*, 2009, **39**, 2209.
40 E. Bernalte, C. Marín Sánchez and E. P. Gil, *Sens. Actuators, B*, 2012, **161**, 669.
41 E. Bernalte, C. Marın Sanchez and E. P. Gil, *Talanta*, 2012, **97**, 187.
42 G. O. Buica, C. Bucher, J. C. Moutet, G. Royal, E. S. Aman and E. M. Ungureanu, *Electroanalysis*, 2009, **21**, 77.
43 Y. Li, G. Sun, Y. Zhang, C. Ge, N. Bao and Y. Wang, *Microchim. Acta*, 2014, **181**, 751.
44 C. Lee, S. Jeong, N. Myung and K. Rajeshwar, *J. Electrochem. Soc.*, 2014, **161**(10), D499.
45 K. Kalcher, I. Svancara, R. Metelka, K. Vytras and A. Walcarius, Heterogeneous Electrochemical Carbon Sensors, in *The Encyclopedia of Sensors*, American Scientific Publishers, Stevenson Ranch, 2006, vol. 4.
46 N. Zhou, H. Chen, J. Li and L. Chen, *Microchim. Acta*, 2013, **180**, 493.
47 Z. Yin, J. Wu and Z. Yang, *Microchim. Acta*, 2010, **170**, 307.
48 X. Niu, Y. Ding, C. Chen, H. Zhao and M. Lan, *Sens. Actuators, B*, 2011, **158**, 383.
49 A. Mandil, L. Idrissi and A. Amine, *Microchim. Acta*, 2010, **170**, 299.