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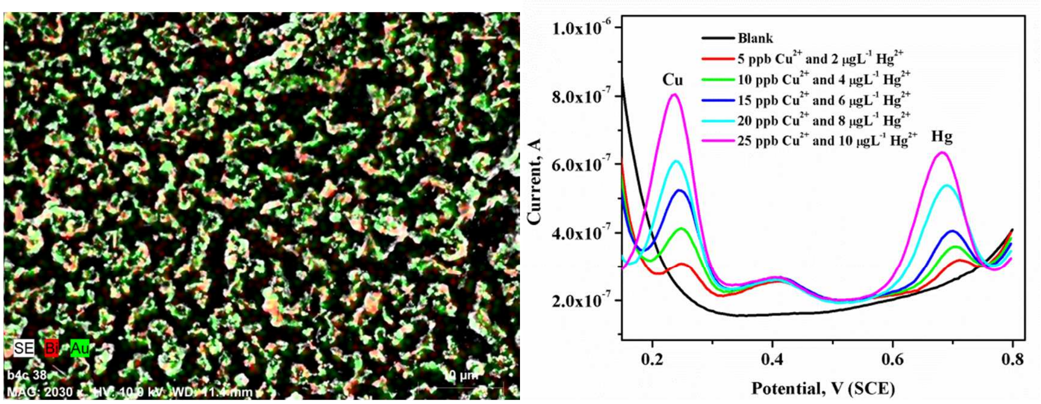

SEM Micrograph of the composite material and the voltammogram of simultaneous determination of Cu^{2+} and Hg^{2+}

Electrodeposited Bi-Au Nano Composites Modified Carbon Paste Electrode for the Simultaneous Determination of Copper and Mercury

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Abstract

Composites of bismuth and gold nano particles (Bi-AuNPs) were prepared on carbon paste electrode (CPE) by electrochemical deposition method. The electrochemical parameters were optimized for the effective deposition of Bi-AuNPs composite materials. Microscopic examination revealed that, nanoparticle clusters of gold were embedded well within the bismuth films (Bi films) over the CPE surface. An analytical method has been developed for the simultaneous determination of copper and mercury at ultra trace levels using the Bi-AuNPs modified CPE by anodic stripping voltammetry. 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. 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.

Keywords: Bi-AuNPs composite; carbon paste electrode (CPE); stripping voltammetry; determination of Cu and Hg.

1. Introduction

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

Present days, due to the toxicity of mercury, mercury drop electrodes are being avoided in the stripping as among 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 system [2, 3]. There have been some methods of 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), inductively coupled plasma mass spectrometry (ICP-MS) [10, 11]. All the methods mentioned are either less sensitive, lack in selectivity or require complicated instrumentations and also involve high operational cost. Voltammetric techniques represent important method with high sensitivity and low operational cost and have the possibility of portable instrumentations for onsite determination. Bismuth film electrode is an interesting alternative to mercury drop electrode for the determination of toxic heavy metal ions. Bismuth, known to be an environment friendly material has been used in wide variety of cosmetics and also in medicines [12-18]. Bi film electrodes were deposited over glassy carbon electrode [19-25] or over CPE [26-28] and applied in stripping voltammetry. However the easy renewability of CPE is a better choice for the present purpose compared to glassy carbon electrode. It has been observed by previous researchers that a strong stripping peak due to Bi was observed before Cu peak, which is detrimental to the appearance of 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 bare Bi film electrode [29] and a direct determination of Cu using 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 the strong affinity towards mercury thus the Bi-AuNPs composite material would be the ideal choice for the simultaneous determination of Cu and Hg.

It has been reported that the 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 also reduced the requirement of active materials to obtain similar or enhanced response to the whole electrode. There are a few reports on the gold nanoparticles (AuNPs) modified electrode for the determination of mercury either on the carbon electrode or on screen printed electrode [37-41]. One paper reported the 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 bismuth nano tube modified glassy carbon electrode [43]. Other than analytical application Au and Bi_2O_3 nano composite modified electrode was also applied for photocatalytic decomposition of dyes [44]. Thus it is interesting to investigate the applicability of AuNPs arrays embedded onto the Bi film on CPE for the simultaneous determination of Cu and Hg. There is no such reports exists in the literature on the simultaneous determination of Cu and Hg using Bi-AuNPs composite modified CPE. The modified electrode developed under 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 the cell assembly with a three-electrode configuration consisting of the modified CPE as the working electrode and 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 by GPES 4.9 software. Prior to electrochemical scan, 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 Bi-AuNPs modified electrode. Field Emission Gun-Scanning Electron

Microscopes (FEG-SEM) system model JSM-7600F was used for the SEM measurements. Energy dispersive X-ray fluorescence (EDXRF) was carried out using EX-3600 M spectrometer from Xenemetrix. Electrodeposited samples were dried under vacuum before the measurements with SEM and EDXRF.

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 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-AuNPs composite materials on carbon paste electrode surface

Preparation of carbon paste has been reported previously [45]; we have adapted the similar method of preparation [29. 30]. Bi and Au films were simultaneously deposited over the CPE surface using electrodeposition techniques from 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 condition (at 500 RPM) at -0.3 V. Deposited films were washed with ultrapure water and then dried under air flow. SEM images were recorded using these films, which are shown in Figure 1A, 1B and 1C. In Figure 1 A, Au, Bi and the carbon paste substrate are shown in different colours. It was observed that Au and Bi composite were embedded well within the carbon paste matrix. The sizes of one assembly of the gold nanoparticles were around 100 nm. Individual particle size of these assemblies was in the range of 10-20 nm. (*cf*. Figure S1 of supporting information). Bi and Au component of the composite film were individually mapped and show in Figure 1B and 1C respectively. Both Bi and Au were dispersed well over the electrode surface. Energy dispersive X-ray fluorescence (EDXRF) measurements were carried out on CPE/Bi-AuNPs substrate and the results are shown in Figure 2(A) and 2B. Presence of Bi and Au on the CPE/Bi-AuNPs substrate was observed from the measurements at the elemental ratio of Au/Bi as 2:1.

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 Figure 3. Impedance performance of CPE/Bi-AuNPs electrode was compared with CPE modified with gold nanoparticles (CPE/AuNP) and also with the CPE modified with Bi film (CPE/Bi). It was observed that the capacitance of the Bi film modified CPE was lowest. Capacitance of the CPE/Bi-AuNPs composite was also less, which is useful for the application of the composite electrode in analytical measurements as 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-AuNPs composite electrode is beneficial to have lower background in stripping analysis.

3.2 Optimization of the analytical parameters of the measurements.

After electrochemical deposition of Bi-AuNPs over 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; pH of the buffer solution was optimized from the stripping peak of Cu and Hg and is shown in Figure. 4. At pH lower than 4 the stripping peak of Cu was merged with that of the Bi peak (*cf.* Plot for pH 3 of Figure.4). At pH values higher than 4, the Cu stripping peak was well separated from the Bi stripping peak. However at pH more than 6 the stripping response of Cu was decreased. Thus a solution pH of 5 was optimized for the analysis for well separated peaks between Bi and Cu and also for good stripping current of Cu. Stripping peak of Hg has also shown strong pH dependency. The highest peak current of Hg was observed in between pH 4 and 5. Stripping peak was reduced at a higher pH values 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 their positions on bare Bi film electrodes [29]. Cu might have formed the inter-metallic compound with AuNPs, which made the positive shifting of the stripping peak. 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 Figure S2 of the supporting information. 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 were modified the stripping peak 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 deposits will 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 800s by keeping the deposition potential fixed at -0.5 V, the results were shown in Figure 5. Stripping peak current due to Cu^{2+} was increased with increase in the deposition time up to 800s. Unlike Cu stripping peak, the stripping peak of Hg was not increased so sharply with the deposition time of the measurements. Considering the time taken for an 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 the calibration plot of Cu^{2+} and Hg^{2+}, voltammograms were recorded using CPE/Bi-AuNPs electrode with successive additions of Cu and Hg standard concentrations in the test solution. Corresponding voltammetric plots are shown in Figure 6. Peak positions of Cu and Hg were well separated and useful for their simultaneous determination. Stripping peak currents were increased with increase in the 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. Calibration plot of Cu^{2+} followed the regression equation $i_p=2.03 \times 10^{-8}$ C + $8.61\text{x}10^{-10}$ with the correlation coefficient of 0.998 and standard deviation of 1.06×10^{-9} where C in μg L^{-1} unit. The calibration plot of Hg^{2+} followed the linear regression equation as $i_p = 4.28 \times 10^{-8}$ C + 1.52×10^{-11} with the correlation coefficient 0.996 and standard deviation of 4.02×10^{-9} where C in μg L^{-1} unit. Three sigma detection limits of Cu and Hg were obtained as 0.16 μg L^{-1} and 0.28 μg L^{-1} respectively. Corresponding linear calibration plots are shown in the supporting information as Figure S3 and S4. Linear ranges for Cu and Hg are 5 to 25 μg L^{-1} and 2 to 10 μg L^{-1} respectively under the optimized experimental conditions.

Bi produces strong stripping signal during anodic scanning process and it is difficult to separate the Cu stripping peak from that of Bi, due to which determination of Cu is difficult on Bi film electrode. Proportional decrease of Bi-stripping peak with the addition of Cu was successfully attempted as an alternate way to determine Cu [13]. It would always be 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 positive potential and it was clearly observed. Cu has the stronger affinity to form inter-metallic with Au which has shifted its stripping peak towards more positive directions. Due to that, its stripping peak was well separated from the Bi-stripping peak. 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 Figure 7. The surface area from the cyclic voltammetry measurements were obtained as It was observed that on CPE/Bi electrode, no stripping response due to Cu and Hg was observed. Though the stripping peak heights in the case of CPE/Bi-AuNPs modified electrode was only marginally higher than that of CPE/AuNPs, the base line was improved in the case of CPE/Bi-AuNPs composite modified electrode. Modified electrodes by AuNPs alone are 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 on AuNPs modified electrode. However its stripping response was not proportional, as Cu never stripped back proportionally from the composite film. Corresponding plot of the stripping response of Cu on AuNPs modified CPE is shown Figure S5 of the supporting information. In the presence of Bi along with the AuNPs have increased 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 proportional stripping response and enhanced the linear range. In the present experiments all the three modifications were carried out over the same CPE as the substrate electrode with 2 mm diameter. The surface area of the CPE/Bi, CPE/AuNPs and CPE/Bi-AuNPs electrodes were determined from the 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/AuNPs and CPE/Bi-AuNPs electrodes were obtained as 0.05 cm^2, 0.08 cm^2 and 0.09 cm^2 respectively.

In real water samples Cu remains at much higher concentration compared to Hg. To evaluate if the modified electrode could work in presence of Cu, voltammetric experiments were carried out using dummy sample containing 200 μg L^{-1} Cu^{2+}, and Hg^{2+} was added successively in the solution. Corresponding plots are shown in Figure 8. It was observed that the Hg stripping peak was increased proportionately and unaffected due to the presence of Cu^{2+}. 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 other at high concentration. Reproducibility of the stripping responses was evaluated by recording voltammetric scans repeatedly and the results are shown in Figure S6 of supporting information. 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 due to some of the commonly occurring metal ions Fe(III), Cr(VI), As(III), Ag(I), Pb(II), Cd(II), Zn(II), U(VI) were investigated on the stripping peak of 20 µg L^{-1} Cu and 8 µg L^{-1} Hg. Except due to Ag(I) and As(III) no interference was observed from all the other metal ions up to 500 time higher concentration than Cu(II) and Hg (II). Ag(I) interfered with both the Cu and Hg peaks. Effect of interference due to Ag(I) on the Hg stripping peak was shown in Figure 9. It was observed that Hg stripping peak was reduced with the addition of Ag(I) in the test solution from 50 µg L^{-1} Ag(I) concentration. Observable Hg stripping peak was observed with the addition of Ag(I) up to 1000 µg L^{-1}. 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 higher compared to the Ag(I) concentration is recommended to minimize the interference due to Ag(I) on the Hg stripping peak. Tolerance of Ag(I) on the stripping peak has increased due to the incorporation of Bi along with the AuNPs. As only AuNPs modified electrodes were heavily interfered by Ag(I) for Hg^{2+} determination. As(III) has interference with the Cu stripping peak beyond 200 times higher concentration than Cu by broadening the Cu stripping peak.

3.4 Recover test and analysis of water and soil sample

Recovery test was carried out in tap water samples by spiking both 5 µg L^{-1} of Cu^{2+} and Hg^{2+} standards. Test results are shown in Table 1. Both the elements were recovered within 10% deviation from the added concentration. Two ground water samples were collected from two different regions of India, and analysed using the modified electrode, results are shown in Table 2. OSCOM (Odissa sands company) sample was collected from the industrial region, important for the mining activities. Other sample was collected from bore well from the Pujab state of

India. Lowering of ground water is a concern in Punjab due to the excessive use of ground water for irrigation purposes. Both the samples were analyzed at undigested conditions using the presently developed CPE/Bi-AuNPs electrode. Two soil samples were collected; one from Jadugoda, a mining region of and the other from Vizac a coastal region. Digestion of the soil samples was carried out using 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 the volume of 50 mL. Aliquot of this sample solution was taken in to the voltammetric cell for electrochemical measurements. The analysis results are shown in Table 2. Values were verified using the results from inductively coupled plasma optical emission spectrometry (ICPOES) technique for Cu and mercury analyser based on thermal decomposition atomic absorption technique for Hg. Results were comparable thus, with CPE/Bi-AuNPs electrode digestion was not required to analyse Cu and Hg in ground water samples. The Cu content in OSCOM ground water sample was higher due to the mining activity in the region other values were within the prescribed limit by 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 inside water. 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 from the table, present method stands well in terms of sensitivity and easy of application compared to the reported literature.

4. Conclusion

Bismuth gold composite material was electrodeposited on CPE surface. Microscopic examination revealed that gold nanoparticle clusters were well spread over the Bi-films. Conductivity of the modified surface was improved due to the Bi-films. Well spread gold nanoparticles on Bi film have enhanced the sensitivity of mercury determination. Three sigma detection limits of Cu and Hg were 0.16 µg L^{-1} and 0.28 µg 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 positive shifted the Cu stripping peak; useful for the direct determination of Cu using Bi containing film electrode.

5. References

[1]. G. J. Brewer, *Clinical Neurophysiology*, 2010, **121,** 459.

[2]. J. R. Miller, J. Rowland, P. J. Lechler, M. Desilets and L. C. Hsu, *Water, Air, Soil Pollution* 1996, **86**, 373.

[3]. R. E. Clement, G. A. Eiceman and 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. and 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 in Anal. Chem.*, 2005, **24,**334.

[17]. A. Krolicka and A. Bobrowski, *Electrochem. Commun.*, 2004, **6 ,**99.

[18]. I. Svancara and K. Vytras, *Chemicke Listy*, 2006, **100 ,**90.

[19]. G.J. Lee, C.K.Kim, M.K. Lee, C. K. Rhee and *J. Nanosci. Nanotechnol*., 2012, **12**,5673

[20]. J. Wang, U. A. Kirgoz and J. M. Lu, *Electrochem. Commu,*,. 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, Biosen. *Bioelectr.,* 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. and Actu*. 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. Stevenson Ranch: American Scientific Publishers*: 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.and Actu***,** B*,* 2011, **158**, 383.

[49] A. Mandil, L. Idrissi and A. Amine, *Microchim. Acta*, 2010, **170**, 299.

Figure captions

Figure 1. SEM image of the Bi-AuNP composite films (A) low resolution (B) high resolution, formed by electrodeposition at -0.3 V in 0.1 M H_2SO_4 solution containing 0.1 mM Bi^{3+} and 0.2 mM Au^{3+}. (C) EDXRF results of the modified electrode.

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

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

Figure 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.

Figure 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.

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

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

Figure 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}.

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

Table 1 Recovery test result of Cu^{2+} and Hg^{2+} using CPE/Bi-AuNPs 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 2 Analysis results of Cu^{+} and Hg in two ground water samples and two soil samples collected from different important regions of India, using CPE/Bi-AuNPs electrode.

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

*Values under the bracket are determined using inductively coupled plasma atomic emission spectrometry (ICPAES) technique for Cu^{2+} and using total mercury analyzer based on atomic absorption technique for Hg^{2+}. Percent standard deviation for Cu^{2+} was 3.6 % and for Hg 4.5% for 6 repetitive measurements.

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

Technique in details	Detection limit Cu, µg L^{-1}	Detection limit Hg, µg 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 films modified screen-printed electrodes and metal ion preconcentration with thiol-modified magnetic particles.	-	7.5	[49]

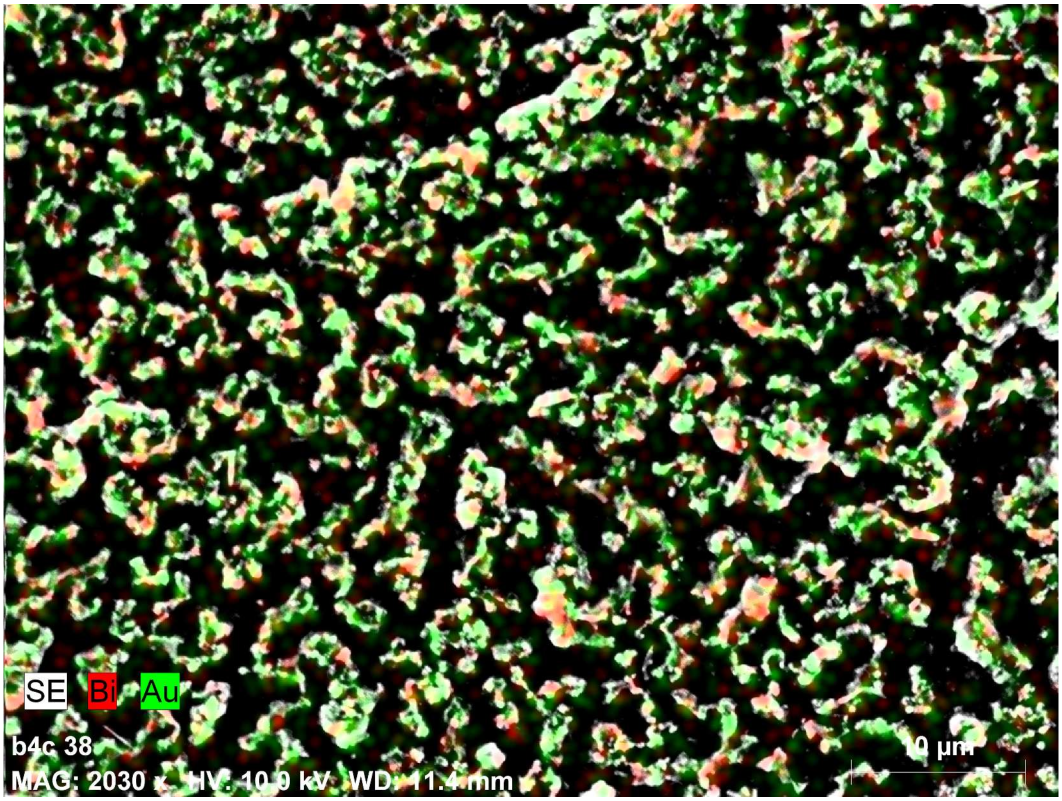


Figure 1 A.

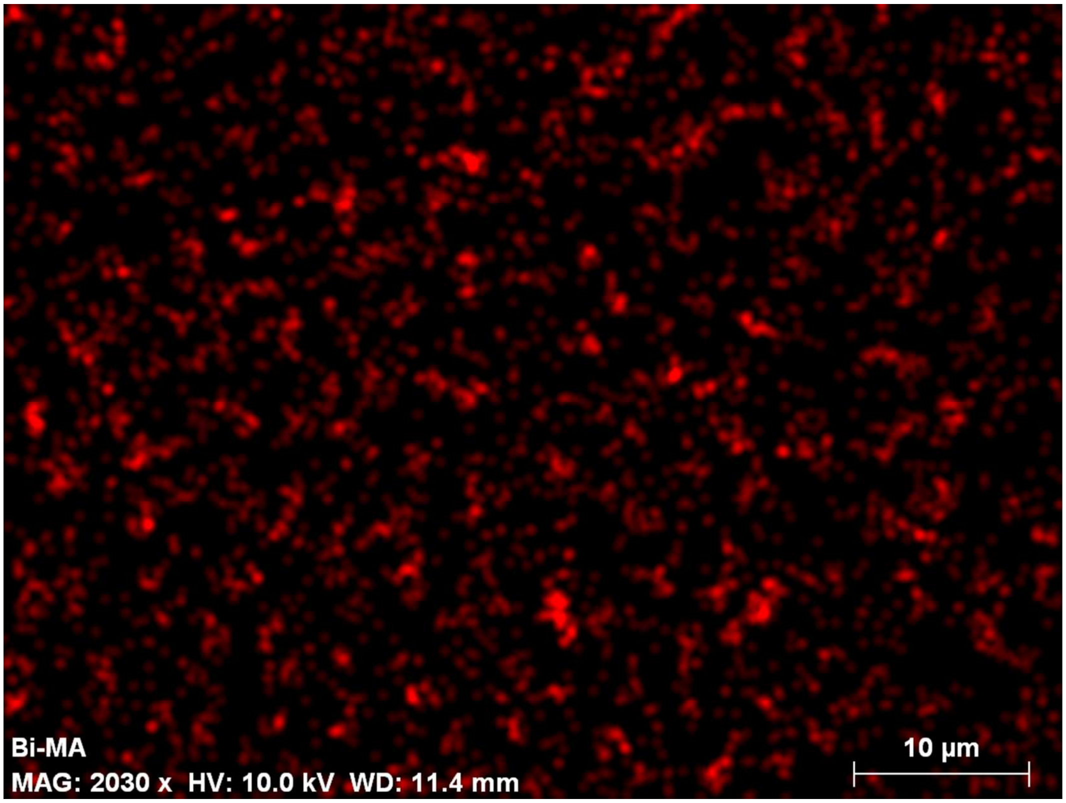


Figure 1 B.

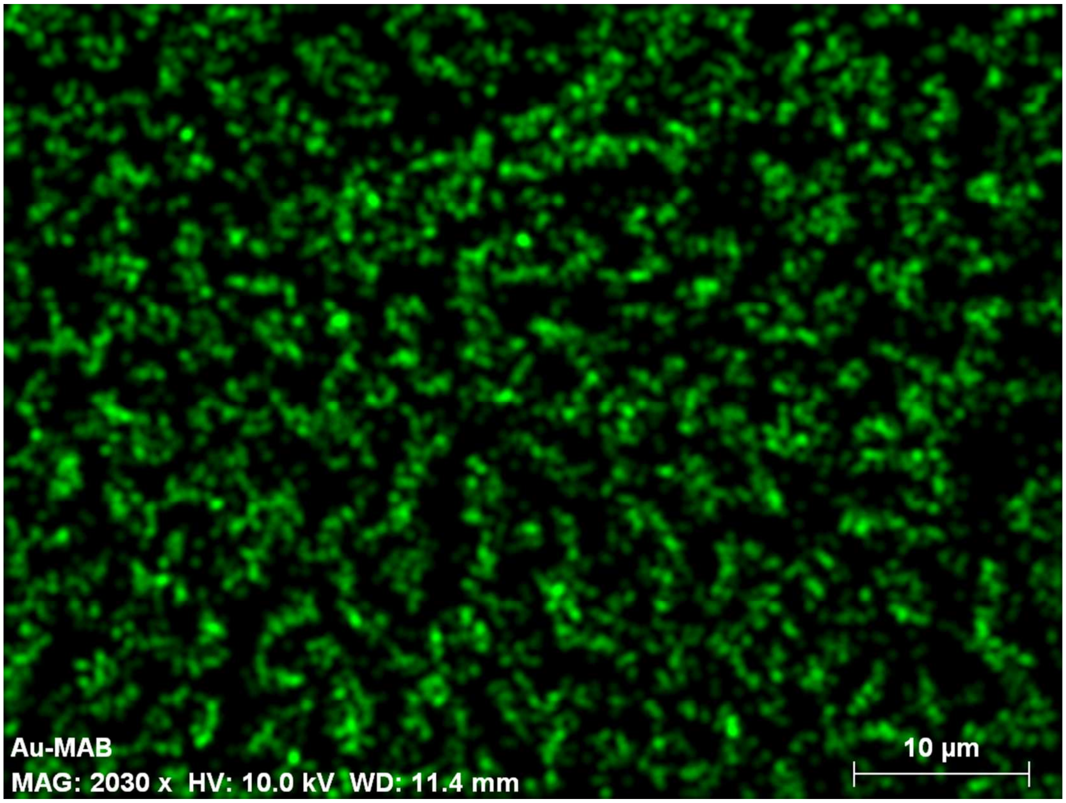
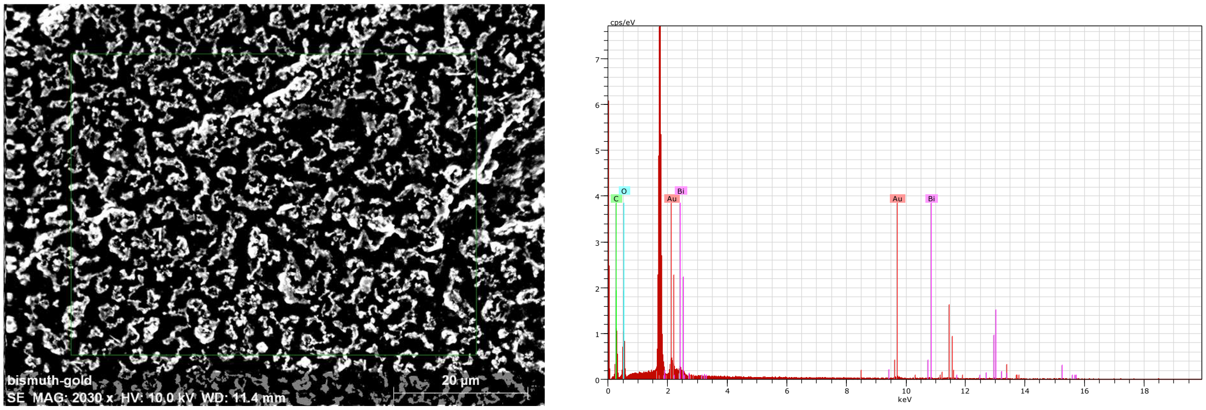


Figure 1 C.



(A) (B)

Figure 2 A and 2 B

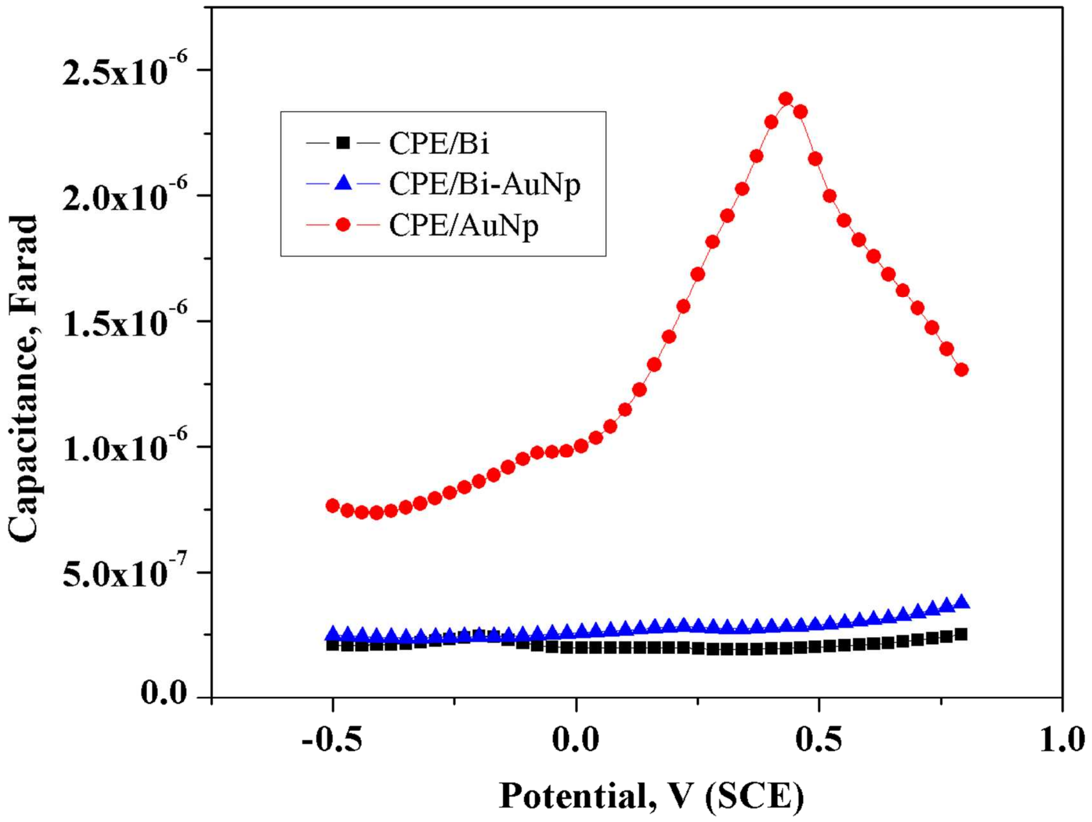

2.5x10^{-6}
2.0x10^{-6}
1.5x10^{-6}
1.0x10^{-6}
5.0x10^{-7}
0.0
Capacitance, Farad
-0.5
0.0
0.5
1.0
Potential, V (SCE)
CPE/Bi
CPE/Bi-AuNp
CPE/AuNp

Figure 3

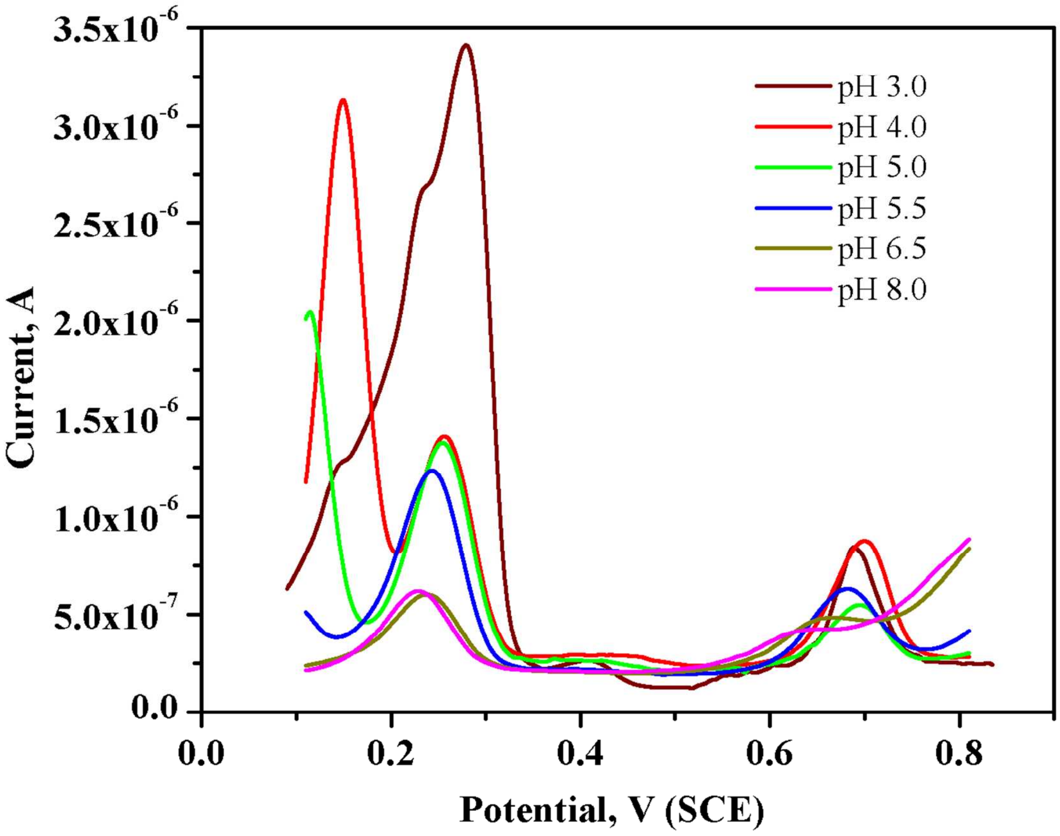

3.5x10^{-6}
3.0x10^{-6}
2.5x10^{-6}
2.0x10^{-6}
1.5x10^{-6}
1.0x10^{-6}
5.0x10^{-7}
0.0
0.0
0.2
0.4
0.6
0.8
Current, A
Potential, V (SCE)
pH 3.0
pH 4.0
pH 5.0
pH 5.5
pH 6.5
pH 8.0

Figure 4

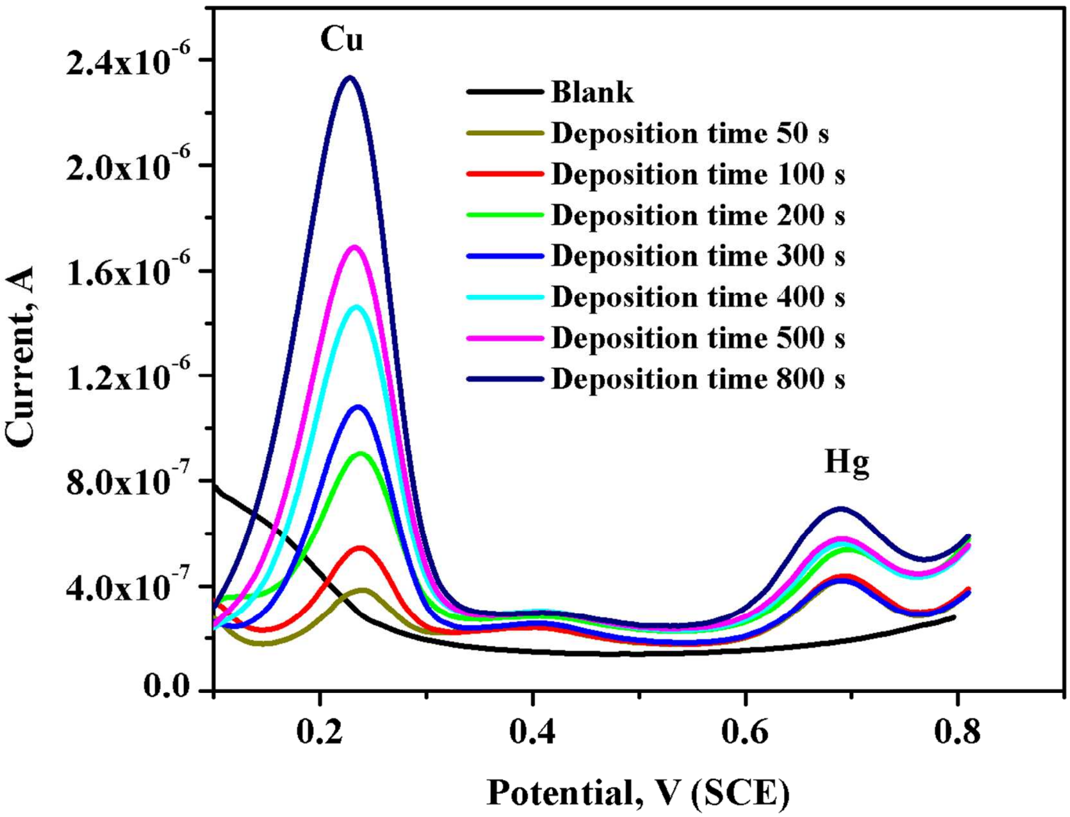

Cu
Hg
Blank
Deposition time 50 s
Deposition time 100 s
Deposition time 200 s
Deposition time 300 s
Deposition time 400 s
Deposition time 500 s
Deposition time 800 s
Current, A
2.4x10^{-6}
2.0x10^{-6}
1.6x10^{-6}
1.2x10^{-6}
8.0x10^{-7}
4.0x10^{-7}
0.0
0.2
0.4
0.6
0.8
Potential, V (SCE)

Figure 5

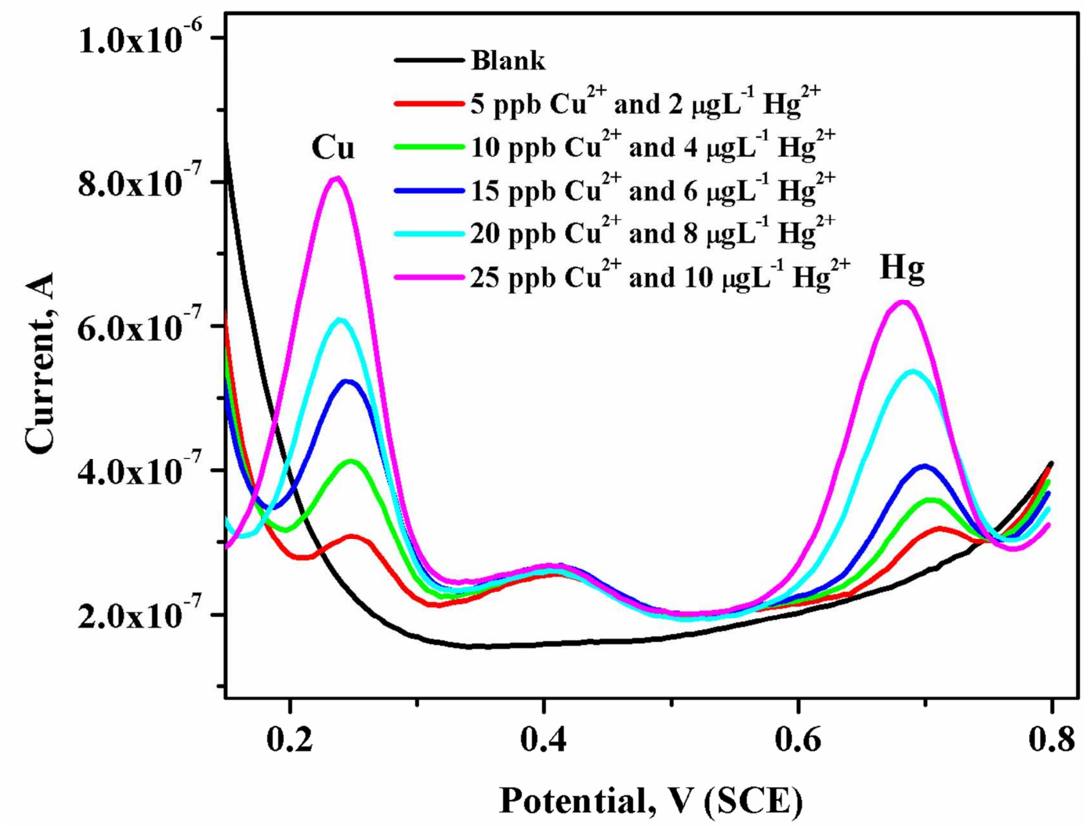

Blank
5 ppb Cu^{2+} and 2 μgL^{-1} Hg^{2+}
10 ppb Cu^{2+} and 4 μgL^{-1} Hg^{2+}
15 ppb Cu^{2+} and 6 μgL^{-1} Hg^{2+}
20 ppb Cu^{2+} and 8 μgL^{-1} Hg^{2+}
25 ppb Cu^{2+} and 10 μgL^{-1} Hg^{2+}
Cu
Hg
Current, A
$1.0x10^{-6}$
$8.0x10^{-7}$
$6.0x10^{-7}$
$4.0x10^{-7}$
$2.0x10^{-7}$
0.2
0.4
0.6
0.8
Potential, V (SCE)

Figure 6

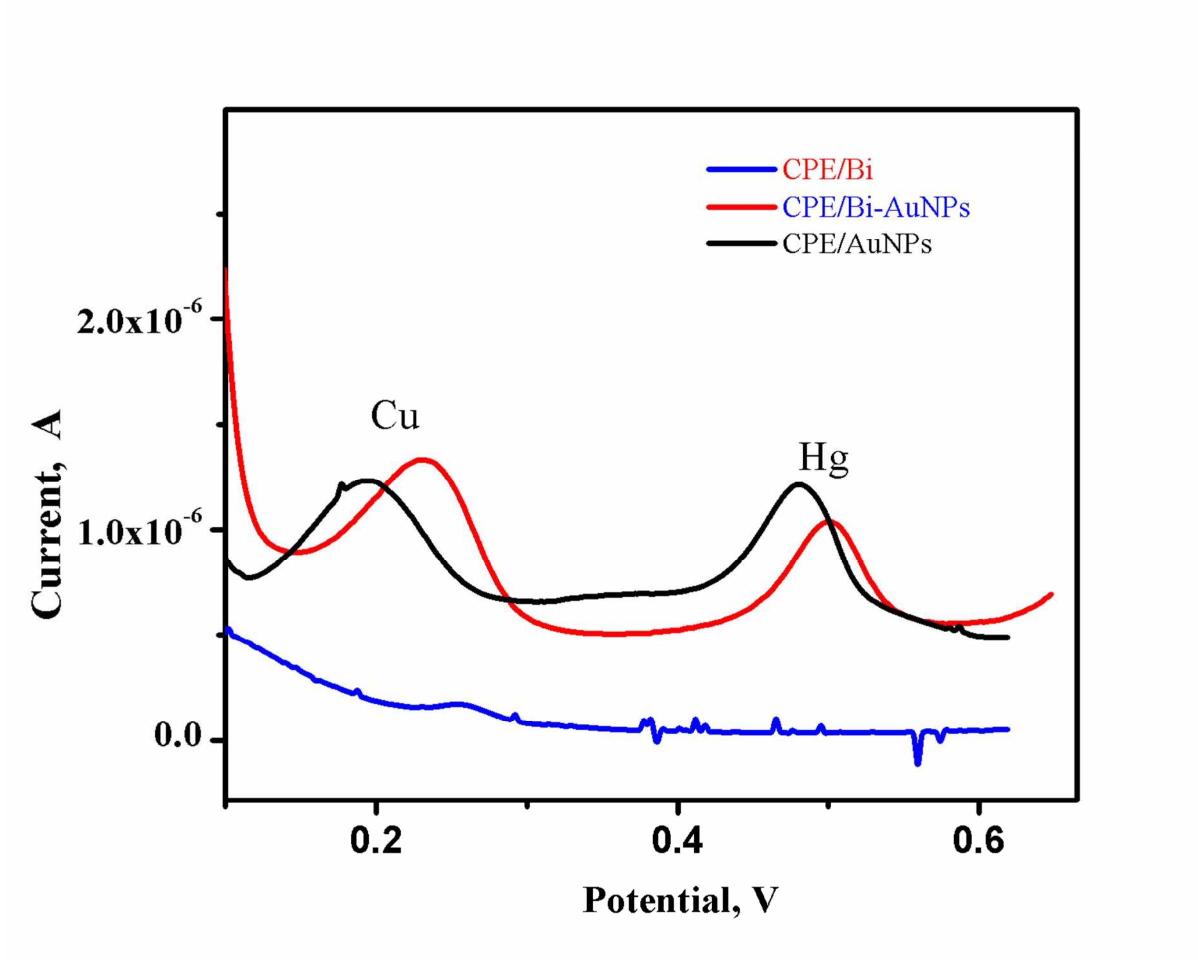

CPE/Bi
CPE/Bi-AuNPs
CPE/AuNPs
Cu
Hg
$2.0\mathrm{x}10^{-6}$
$1.0\mathrm{x}10^{-6}$
0.0
Current, A
0.2
0.4
0.6
Potential, V

Figure 7

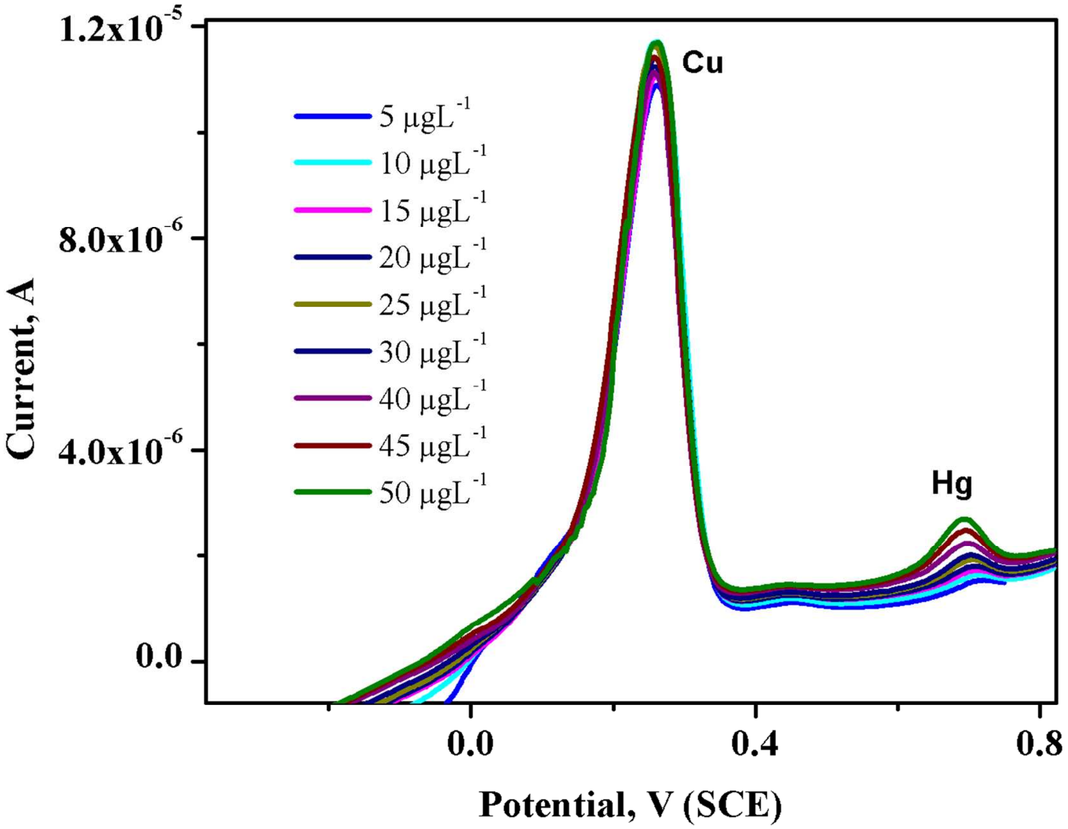

1.2x10-5
8.0x10-6
4.0x10-6
0.0
Current, A
0.0
0.4
0.8
Potential, V (SCE)
Cu
Hg
5 μgL-1
10 μgL-1
15 μgL-1
20 μgL-1
25 μgL-1
30 μgL-1
40 μgL-1
45 μgL-1
50 μgL-1

Figure 8

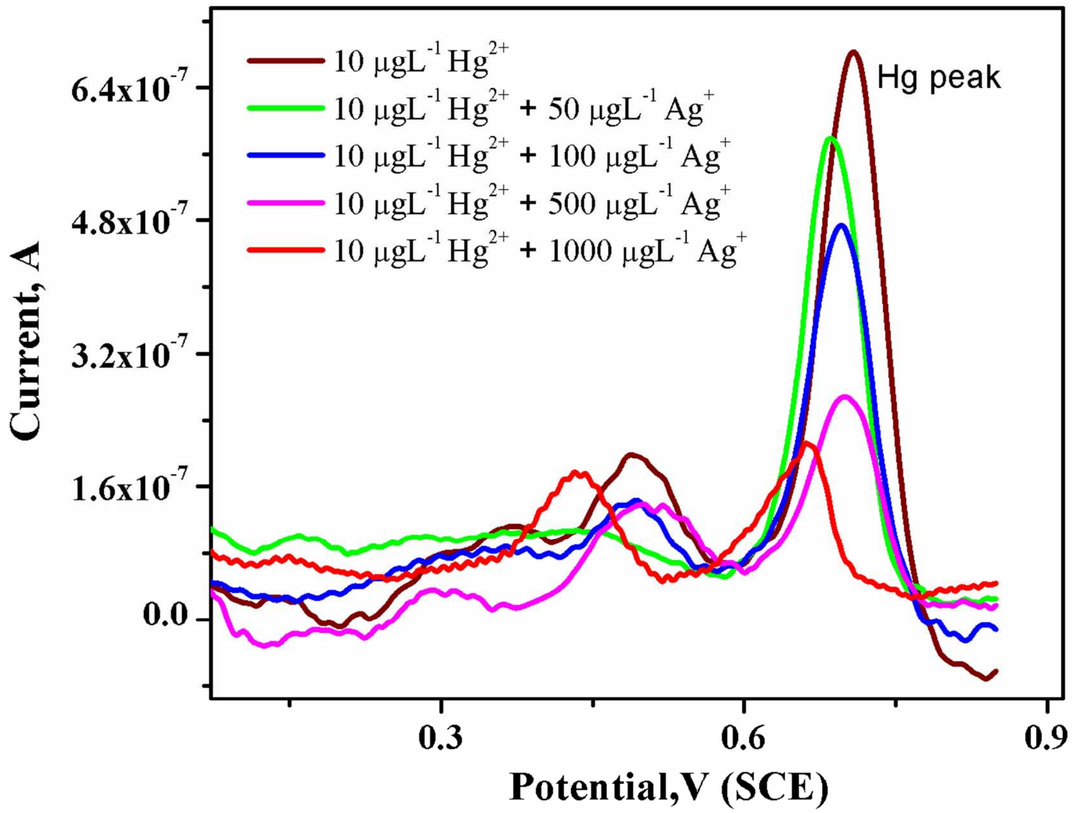

10 µgL^{-1} Hg^{2+}
10 µgL^{-1} Hg^{2+} + 50 µgL^{-1} Ag^{+}
10 µgL^{-1} Hg^{2+} + 100 µgL^{-1} Ag^{+}
10 µgL^{-1} Hg^{2+} + 500 µgL^{-1} Ag^{+}
10 µgL^{-1} Hg^{2+} + 1000 µgL^{-1} Ag^{+}
Hg peak
6.4x10^{-7}
4.8x10^{-7}
3.2x10^{-7}
1.6x10^{-7}
0.0
Current, A
0.3
0.6
0.9
Potential,V (SCE)

Figure 9