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Chemically functionalized glassy carbon spheres: a new covalent bulk modified composite electrode for the simultaneous determination of lead and cadmium

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Abstract A new type of covalent bulk modified glassy carbon composite electrode has been fabricated and utilized in the simultaneous determination of lead and cadmium ions in aqueous medium. The covalent bulk modification was achieved by the chemical reduction of 2-hydroxybenzoic acid diazonium tetrafluroborate in the presence of hypophosphorous acid as a chemical reducing agent. The covalent attachment of the modifier molecule was examined by studying Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and the surface morphology was examined by scanning electron microscopy images. The electrochemistry of modified glassy carbon spheres was studied by its cyclic voltammetry to decipher the complexing ability of the modifier molecules towards Pb^{2+} and Cd^{2+} ions. The developed sensor showed a linear response in the concentration range 1–10 μM with a detection limit of 0.18 and 0.20 μM for lead and cadmium, respectively. The applicability of the proposed sensor has been checked by measuring the lead and cadmium levels quantitatively from sewage water and battery effluent samples.

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Introduction

Lead and cadmium are highly toxic metal ions and are widely distributed in nature [1]. Due to the severe toxicity and longer stability in the environment, exposure of these metal ions to living systems even at trace level may cause irreversible adverse health effects. The adverse effects include anemia, hearing loss, hindered growth, cardiovascular effects, kidney damage, neurological damage, hypertension, and blood pressure [2, 3]. These metal ions are routinely released into the environment from mining, metallurgical, electroplating, dyes and pigments, paper mill and fertilizer industrial operations [3]. The maximum contaminant level in drinking water for lead and cadmium metal ions prescribed by the World Health Organization are 10 and 3 μg/L for lead and cadmium ions, respectively [4, 5]. As a result, the importance of controlling the levels of these pollutants in natural waterways and potable water has generated increasing interest in the development of new sensors for the detection of these metal ions at trace level. Several methods have been developed for the quantification of lead and cadmium ions which include spectroscopic methods like atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy, hydride generation atomic fluorescence spectroscopy, and UV–vis spectroscopy [6–8]. All these methods are highly sensitive but require sophisticated instrumentation, trained personnel to operate, and prolonged sample preparation

procedures. Most of these methods are laboratory based and cannot be used for the field analysis [9]. However, electrochemical methods are simple, cost effective, sensitive, and selective which can be designed into portable devices for field applications [10]. Hence, a significant focus has been made in recent years to develop novel electrochemical sensors to quantify the toxic metal ions at trace level.

Chemically modified electrodes have become a major area of research in electroanalysis due to their tailor-made properties which meet specific requirements like specificity, sensitivity, and selectivity towards a particular analyte as it reduces the overpotential compared to unmodified electrodes [11]. Several chemical modifications have been reported by various research groups, and these were elaborately discussed in the review [12]. Such modifications include surface modification on rigid electrodes through the electrochemical reduction/oxidation of reagents [13] and thin-film modified electrodes [14]. However, the surface modifications on rigid electrodes are prone to surface fouling, difficulty in surface renewal, and poor storage stability [15–18]. Thin-film modified electrodes may require recoating of the modifier molecule which in turn limits the long-term storage stability and also the reproducibility of the analytical signal [19]. The surface renewal coupled with operational stability is required for long-term analytical applications. In this direction, various bulk modified electrodes like carbon paste and carbon ceramic electrodes have been proposed which are beneficial from the point of surface renewability but suffer from the loss of stability due to leaching of modifier molecules into the electrolyte during potential cycling which limits the long-term usage and operational stability [20]. Therefore, it is desirable to design a robust, stable, and surface renewable electrode with a modifier having specific functionalities towards particular analytes covalently attached to the carbon substrate to control the leaching of the modifier molecule. In this regard, our group has developed a simple and scalable method to modify the carbon substrate materials with selective modifier molecules based on the chemical reduction of aromatic diazonium salts in the presence of hypophosphorous acid as chemical reducing agent and subsequently applied in sensing [21], reagentless pH sensors [22].

In the present report, we have proposed a novel, robust, covalent bulk modified surface renewable carbon composite electrode by covalently anchoring the modifier molecule (salicylic acid) onto the surface of glassy carbon spheres through diazonium salt reduction protocol. The composite electrode has been successfully applied to determine trace-level lead and cadmium ions from sewage water and battery effluent samples.

Experimental section

Apparatus

All electrochemical measurements were carried out using an electrochemical analyzer (CH Instruments, TX, USA; model CHI 619B) at room temperature in an electrochemical cell of volume 10 mL with a standard three-electrode configuration. Covalent bulk modified electrode (dia.=5 mm) as the working electrode, A Pt (purity, 99.99%) wire as the counter electrode, and Ag/AgCl (3 M KCl) as a reference electrode (CH Instruments, TX, USA) were used. Before electrochemical measurements, the solutions were degassed using high-purity nitrogen gas for 15 min. Differential pulse anodic stripping voltammetry (DPASV) was carried out in the potential range of −1.0 to 0.0 V with an amplitude of 0.01 V and pulse width of 0.05 s. All pH measurements were carried out using Control Dynamics pH meter (APX 175). Infrared spectrometric measurements were recorded using Fourier transform infrared (FTIR) Shimadzu 8400S in the range 4,000–1,200 cm^{-1} with a resolution of 4 cm^{-1}. XPS spectra were recorded with an ESCA-3 Mark II spectrometer (VG Scientific Ltd., England) using Al Kα radiation (1,486.6 eV). Scanning electron microscopy images were recorded using JEOL (JSM–840 A) scanning electron microscope.

Chemicals and reagents

All reagents used were analar grade and used without further purification. Glassy carbon spheres (2–12 μm dia.) and potassium bromide for IR spectroscopy (FTIR grade) were purchased from Sigma–Aldrich (purity, >99.95%) and used directly. 2-Hyroxybenzoic acid diazonium tetrafluroborate was synesized from 4-amino salicylic acid according to the procedure [23]. Buffer solutions of known pH in the range pH 1–12 were prepared using deionized water from MilliQ water purifier (Millipore, USA) with a resistivity of not less than 18.2 MΩ cm at 25 °C. Lead nitrate and cadmium nitrate stock solutions were prepared using analar-grade reagents. The working standards were prepared from the stock solutions.

Covalent modification of glassy carbon spheres

The modification of glassy carbon spheres with 2-hyroxybenzoic acid diazonium tetrafluroborate (Scheme 1) was carried out using the following protocol: 1 g of glassy carbon spheres were mixed with 10 mL of a solution containing 10 mM diazonium salt to which 30 mL of hypophosphorous acid (H_3PO_2, 50%; Aldrich) was added. The reaction mixture was then left to stand at 5 °C for
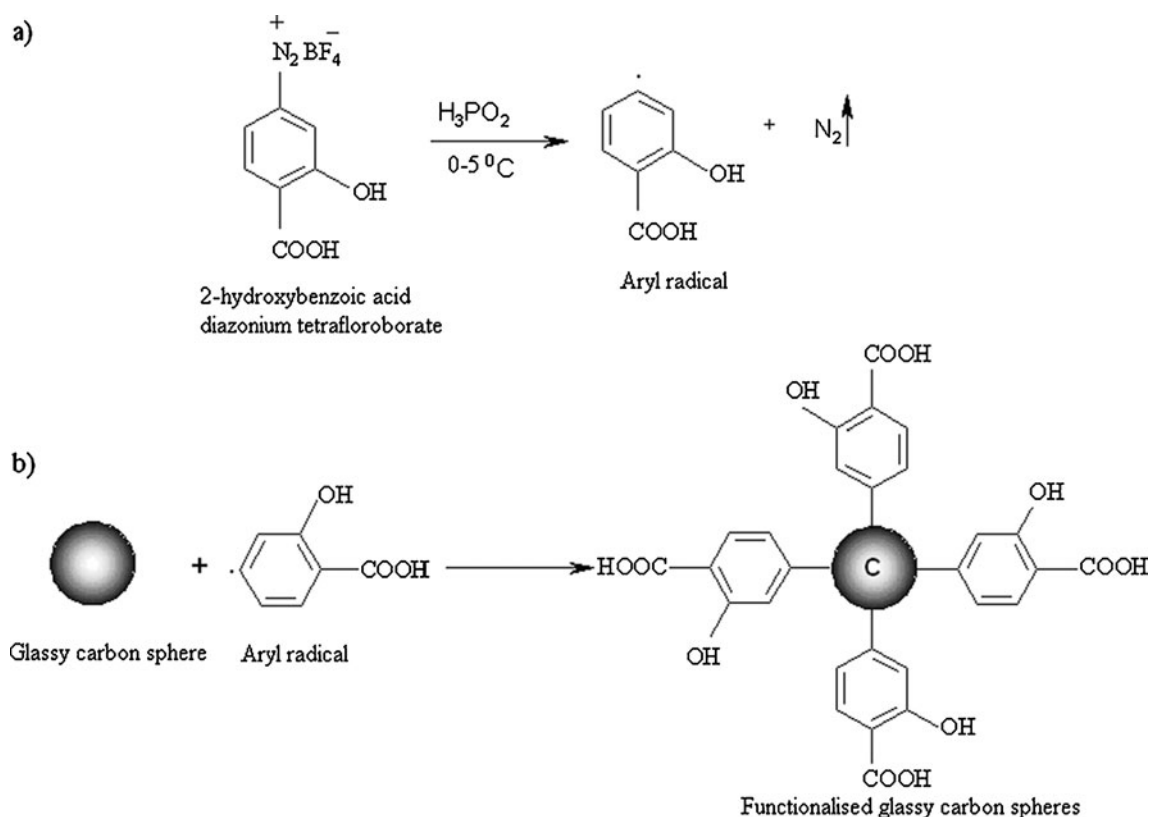
Scheme 1 Schematic representation of the covalent bulk modification process. **a** Generation of aryl radical, **b** covalent attachment of aryl radical on the carbon surface

30 min with occasional stirring at regular time intervals (every 5 min). Then the solution was filtered by water suction in order to remove the bulk of the reactants from the carbon surface. Excess acid was removed by washing thoroughly with deionized water and finally with acetonitrile to remove unreacted diazonium salt from the reaction mixture. The functionalized glassy carbon spheres were then air-dried by placing them inside a fume hood for a period of 12 h and finally stored in an air-tight container [24]. The degree of functionalization has been measured according to Boehm's method [25] which has been found to be 8.3 mM/g (9.3%).
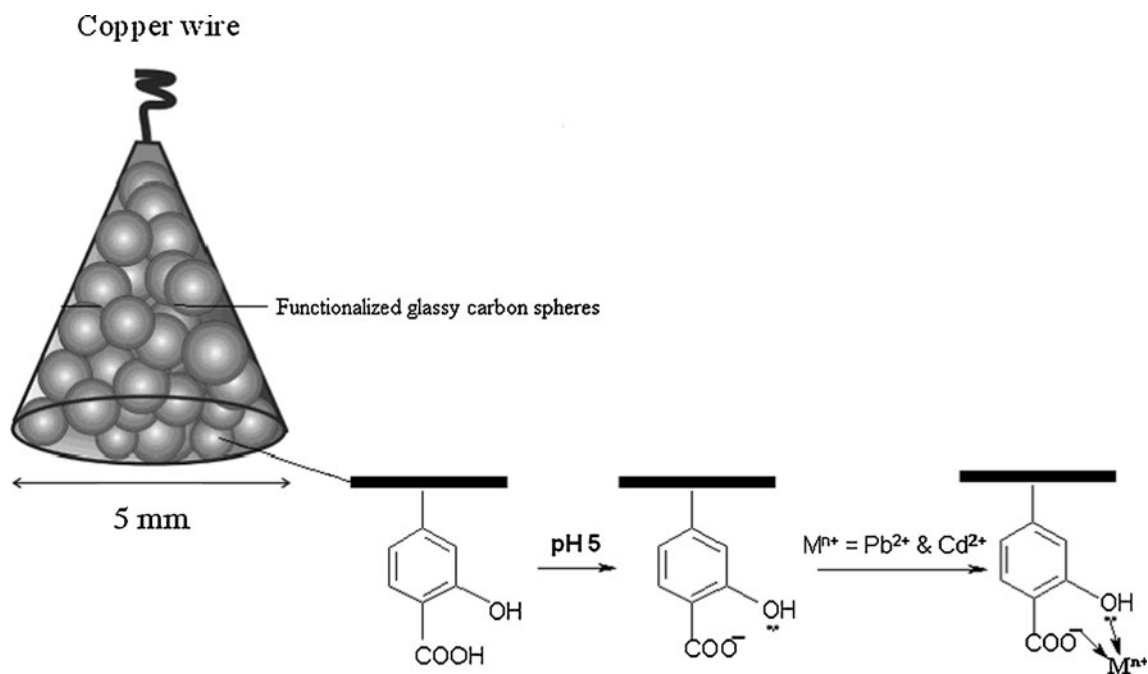
Fabrication of composite electrode

The surface renewable covalent bulk modified electrode was fabricated by hand mixing the epoxy resin (Mecaprex MA 2 epoxy resin, PRESI, Grenoble, France) with modified glassy carbon spheres in 30:70% (w/w) ratio using a pestle and mortar, and the resulting paste was moulded into Teflon tips of micropipette of 5 mm diameter. Electrodes were then allowed to dry for 24 h at ambient temperature to form a hard and durable electrode. The electric contact was taken from the back of the capillaries using a copper wire during drying

period. The surface of the electrode substrate was polished with 400 and 600-grit polishing papers and washed thoroughly with deionized water before its use. The resistance of the fabricated electrode was measured across the two ends which were found to be $10–12\,\Omega$. For reproducible results, the surface of the electrode substrate is mechanically polished using 600-grit emery sheets unidirectionally. The schematic presentation of the fabricated electrode and the proposed scheme of metal ion complexation with the modifier molecules are shown in Scheme 2.

Results and discussion

Chemically modified glassy carbon spheres were characterized by using spectroscopic techniques like FTIR spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) in order to examine the nature of the bond formed between the carbon substrate and the modifier molecule during the derivatization process. The electrochemical behavior of the composite electrode towards the metal ions has been examined by studying its cyclic voltammetry and DPASV.

Scheme 2 Schematic view of bulk modified composite electrode and the possible mode of metal ion complexation with the functional moieties present on the modifier molecules

Characterization of functionalized glassy carbon spheres

FTIR study

The modified glassy carbon spheres were characterized by studying their IR spectral characteristics in order to know whether the modifier molecule is covalently attached or not during the functionalization process. The modified carbon spheres were mixed with KBr in 1:100 ratio to make a pellet and was exposed to infrared radiation in the range of 1,200–4,000 cm^{-1} (Fig. 1). The transmission spectrum of the derivatized carbon spheres has revealed the presence of peaks due to –OH and C=O groups of –COOH at 3,450 and 1,670 cm^{-1}, respectively. The peak at 1,250 cm^{-1} might be due to the stretching of the –OH group of phenol, and the peaks at 1,460 and 2,800 cm^{-1} are due to symmetric and asymmetric stretching of aromatic protons which are in good agreement with the reported literature [26]. However, the IR spectrum of the native glassy carbon spheres did not show any significant peaks in the region studied (Fig. 3). All these observations reveal that the covalent attachment of modifier molecules has occurred during the functionalization process through diazonium salt reduction.

Fig. 1 FTIR spectra of **a** native and **b** modified glassy carbon spheres
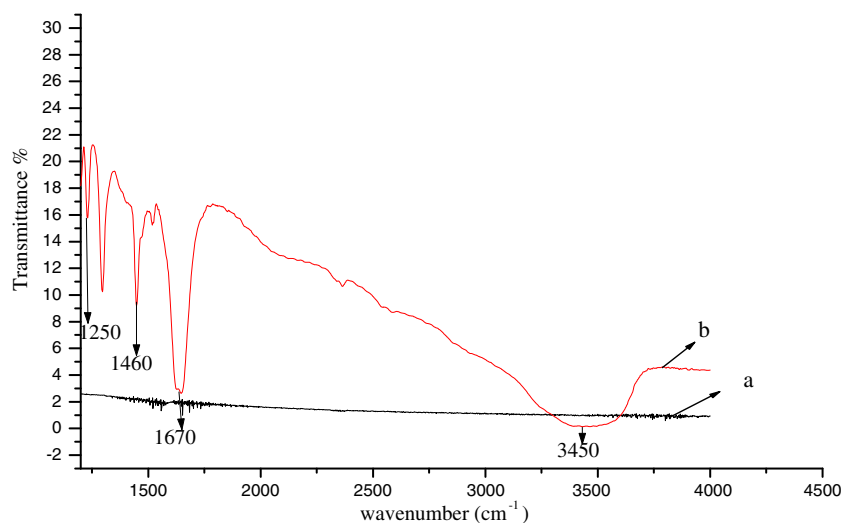
Surface morphology of modified glassy carbon spheres

The surface morphology of the modified and native glassy carbon spheres was examined using SEM. The images were recorded by dispersing the carbon spheres on a small conducting strip. The SEM images of the modified and native glassy carbon spheres are shown in Fig. 2 which revealed that the modified glassy carbon spheres have similar surface morphology when compared to their unmodified counterparts.

XPS study

X-ray photoelectron spectroscopy is a non-destructive technique in which the electron-binding energies of the atoms have been used to analyze the elemental composition, chemical states, and also the type of bonding of the modifier molecule on the substrate surface [27]. The XPS spectra of the native and modified glassy carbon spheres are shown in Fig. 3, and the peaks observed at 284.61 and 532.42 eV correspond to the C1s and O1s regions, respectively. The C1s region revealed the presence of

Fig. 2 SEM images of native (**a**) and modified (**b**) glassy carbon spheres

carbon, and the O1s region revealed the presence of oxygen-containing functionalities which are in good agreement with the literature [28]. The high peak intensity of the C1s and O1s regions of the modified one (Fig. 3b) compared to the native one (Fig. 3a) clearly indicates the increased content of carbon and oxygen functionalities of the modifier on the surface of glassy carbon spheres. These results clearly indicate the covalent attachment of salicylic acid molecules on the surface of glassy carbon spheres.

Electrochemical characterization

Voltammetric behavior of Pb^{2+} and Cd^{2+} ions at native and modified electrode

The electrochemical behavior of functionalized glassy carbon spheres composite electrode was initially carried out by studying the cyclic voltammetry of lead and cadmium ions in various buffers like acetate, phosphate, and Robinson buffer of different pH values containing different electrolytes like NaCl, KCl, $HClO_4$, and KNO_3 as supporting electrolyte. The highest peak current, sharp signals with good reproducibility, were obtained with an acetate buffer of pH 5 in the presence of 1 M KNO_3 as supporting electrolyte. Therefore, cyclic voltammograms of 1 mM of each Pb^{2+} and Cd^{2+} ions were recorded at native and salicylic acid-modified electrode in a buffer solution of pH 5 containing 1 M KNO_3 as supporting electrolyte (Fig. 4). The voltammograms at both native and modified GCs showed well-defined peaks for the reduction and oxidation of both lead and cadmium ions, respectively, with a considerable peak-to-peak separation. The voltammograms clearly revealed the increase of peak currents at the salicylic acid-modified electrode compared to native electrode towards lead and cadmium redox processes. The oxidation (stripping) potential remains the same at −0.50 and −0.76 V for both Pb^{2+} and Cd^{2+} ions at both native and modified electrodes. The reduction and oxidation potential of Pb^{2+} is similar to that of the reported values in the literature [26, 29]. The peaks at −0.87 and −0.76 V may be due to the reduction and oxidation of Cd^{2+} ions, respectively. The increased peak currents with respect to the modified electrode for both the analytes may be due to the complexing ability of the functional groups present on the surface as compared to the native electrode. Since the functionalities can also detect other metal ions like zinc, copper…etc., even if we consider the HSAB concept, it is not possible to explain the selectivity. Hence, it needs further work to understand the selectivity of these functional groups towards lead and cadmium ions. The oxidation (stripping) peaks for both Pb^{2+} and Cd^{2+} ions predominate over the reduction peaks at both native and modified glassy carbon spheres; hence, the anodic peaks were systematically studied by DPASV
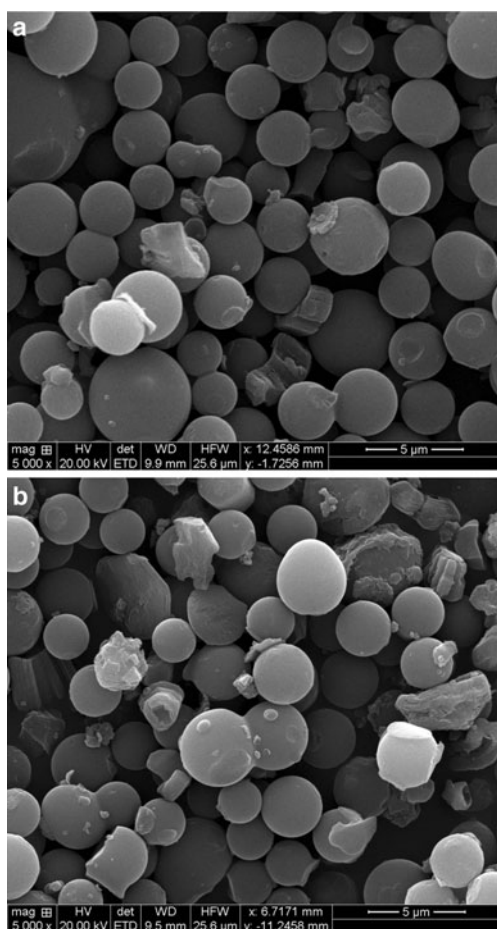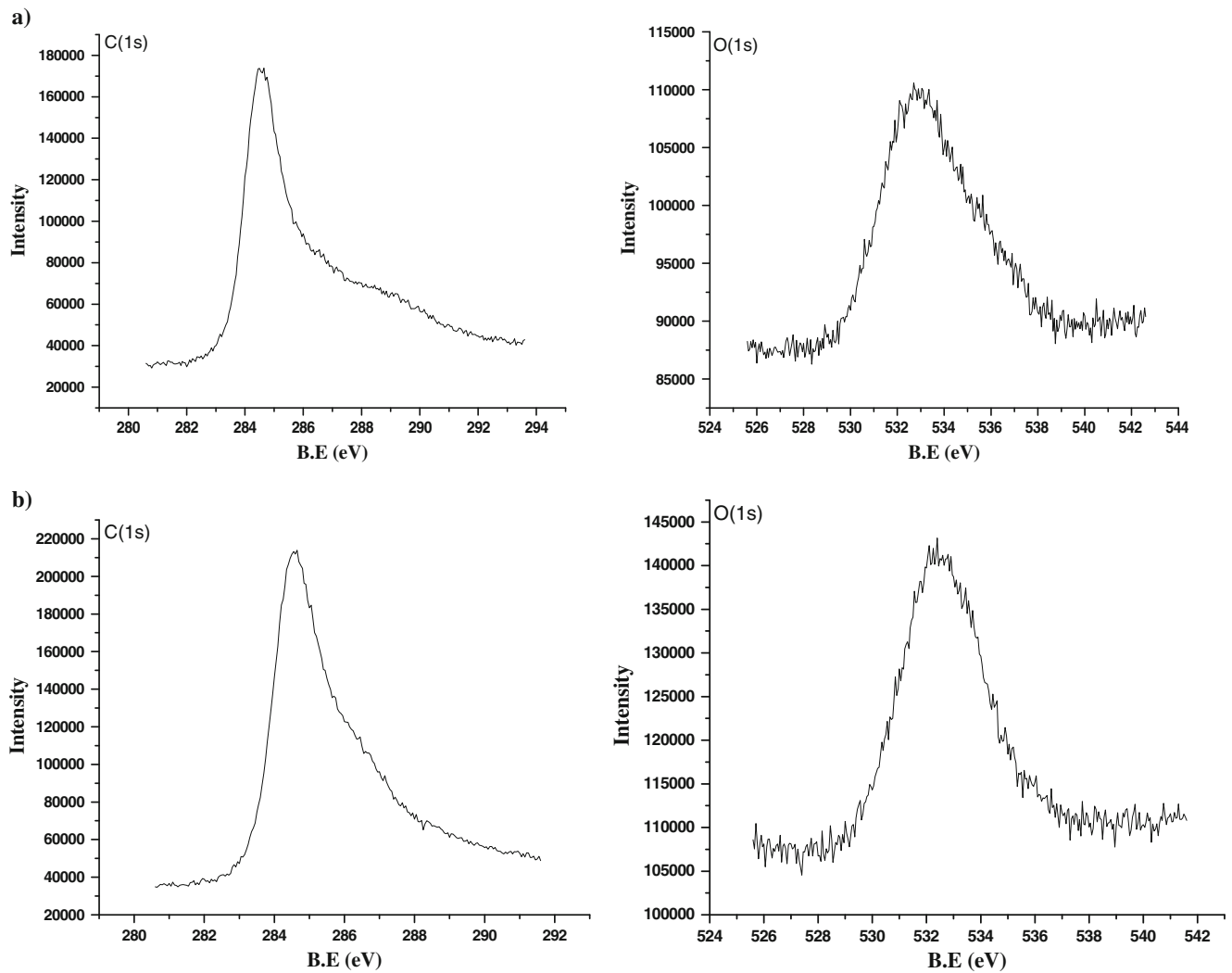
a)

b)

Fig. 3 XPS spectra of **a** native **b** and modified glassy carbon spheres

which gives better sensitivity and selectivity than cyclic voltammetry [30]. Therefore, DPASV is used in further analysis. In DPASV, the analytes are preconcentrated by

keeping the electrode at constant potential for a given period of time and subsequently stripped off. A typical stripping voltammogram has been shown in Fig. 5 which

Fig. 4 Cyclic voltammograms of 1 mM solution of each Pb^{2+} and Cd^{2+} ions at native **A** and modified **B** electrodes in an acetate buffer solution of pH 5 containing 1 M KNO_3 as supporting electrolyte. Scan rate, 100 mV/s
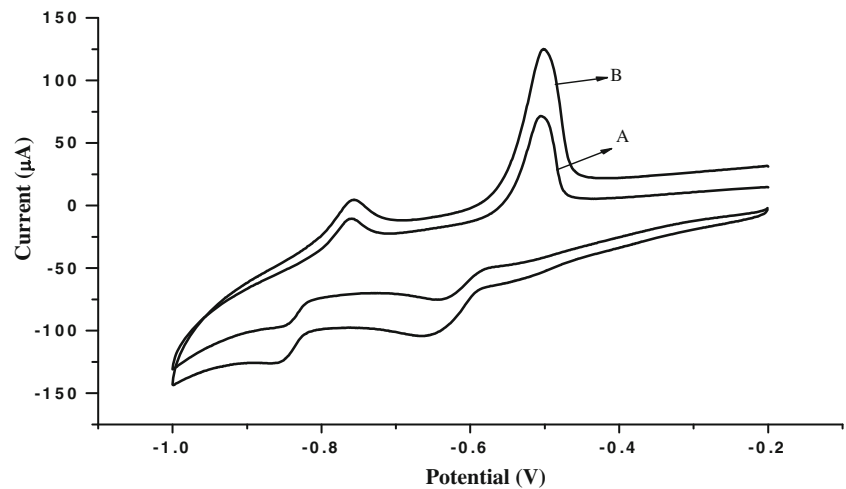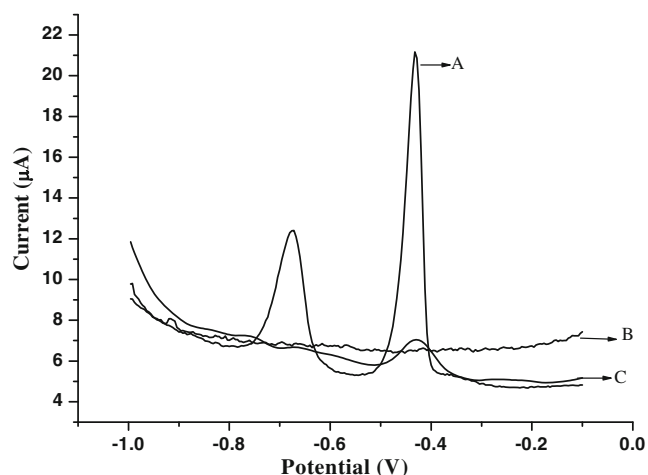
Fig. 5 Differential pulse voltammograms of 1 μM of each Pb^{2+} and Cd^{2+} ions in a buffer solution of pH 5 containing 1 M KNO_3 as supporting electrolyte. *A* and *C* modified and native electrodes in the presence of metal ions, *B* modified electrode in the absence of metal ions

reveals that the analyte can be clearly detected in the differential pulse mode. The mechanism of preconcentration and subsequent stripping is given as follows [31].
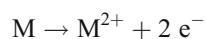
Step I.   Complexation and preconcentration (M=Pb^{2+} and Cd^{2+})

$$M^{2+} + 2HL \rightarrow ML_2 + 2H^+$$
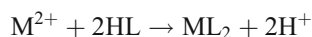
where HL represents the functionalities of the modifier molecules on the surface of the glassy carbon spheres.

$$ML_2 + 2\,H^+ + 2\,e^- \rightarrow M + 2HL$$

Step II.   Stripping

$$M \rightarrow M^{2+} + 2\,e^-$$
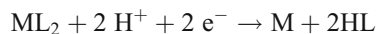
Optimization study

In order to achieve the maximum efficiency of the composite electrode in the electrochemical determination of Pb^{2+} and Cd^{2+} ions in aqueous solution, the parameters like pH of the buffer solution, preconcentration time, and preconcentration potential which influence the response of analytical signal have been optimized.

Effect of pH

The determination of lead and cadmium ions depends on the interaction with the surface functionalities of the modifier molecule which in turn is related to the pKa values of the surface functionalities. The pKa values for salicylic acid were experimentally determined according to

Boehm's method [25] and were found to be 4.01 and 11.23 for the –COOH and –OH groups of salicylic acid, respectively. Since the metal ion complexation depends on the nature of existence of functional groups, the effect of the pH of the preconcentration solution on the accumulation (complexation) of Pb^{2+} and Cd^{2+} ions at the modified electrode was studied in the range from 4 to 6 and is shown in Fig. 6. The peak current increased from pH 4 to 5, since the working pH is 5, the –COOH groups are in deprotonated form, and the –OH groups are undissociated; hence, the increase of the peak current is attributed to the interaction of the carboxylate group and the lone pair of electrons present on the oxygen atom of the –OH group of salicylic acid according to Scheme 2. Above pH 5, the peak current decreases due to the formation of lead and cadmium hydroxide complexes respectively at higher pH values which prevents the further complexation of Pb^{2+} and Cd^{2+} during the preconcentration (accumulation) step [32]. The maximum response was observed at pH 5; hence, an acetate buffer of pH 5 was used in all further studies.

Preconcentration potential

It is the potential at which the preconcentration can be done by holding the electrode at a particular potential to reduce the metal ions to their metallic form; hence, a higher reduction potential can be expected to give the maximum current due to the reduction of more and more complexed metal ions. Therefore, the dependence of peak current with respect to preconcentration potential was studied from −0.6 to −1.4 V (Fig. 7). The peak current increases with increase of potential from −0.6 to −1.0 V and decreases above −0.1 V. Hence, a preconcentration potential of −1.0 V has been fixed as an optimum potential in all further studies.
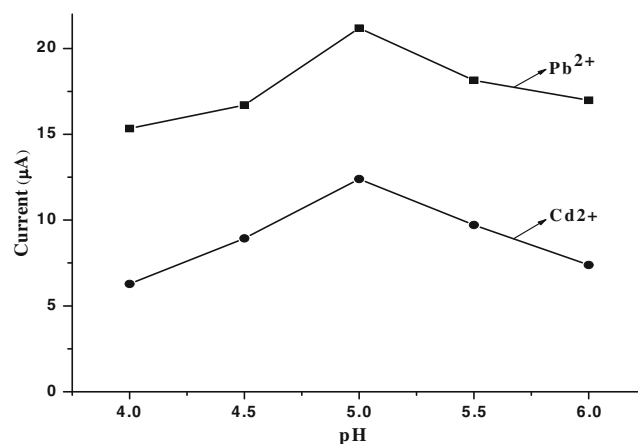

Fig. 6 Effect of pH on the anodic peak current observed for 1 μM concentration of each of Pb^{2+} and Cd^{2+} ions. Preconcentration time, 5 min; preconcentration potential, −1.0 V; supporting electrolyte, 1 M KNO_3
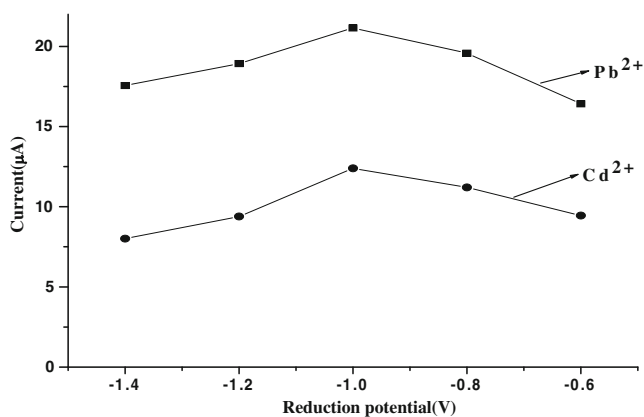
Fig. 7 Effect of preconcentration potential on the anodic peak current observed for 1 μM concentration of each of Pb^{2+} and Cd^{2+} ions in acetate buffer of pH 5 containing 1 M KNO_3 as supporting electrolyte. Preconcentration time, 5 min

Preconcentration time

It is the time required to accumulate the analyte from the bulk solution onto the surface of the electrode through the specific interaction of metal ions with the surface functionalities of the modifier molecule either at open circuit or under applied potential. In the present study, preconcentration was carried out under an applied potential of −1.0 V in a buffer solution of pH 5 containing 1 M KNO_3 as supporting electrolyte. The dependence of peak current with respect to the preconcentration time is shown in Fig. 8. The peak current for both Pb^{2+} and Cd^{2+} was studied from 1 to 7 min. It is found that the peak current for both Pb^{2+} and Cd^{2+} increases with an increase of preconcentration time from 1 to 5 min. This is due to the fact that the longer the preconcentration time, the more and more analytes get accumulated with the surface functionalities at the electrode/solution interface, hence the maximum current. After 5 min, the peak current becomes almost constant due to either surface saturation or the attainment of
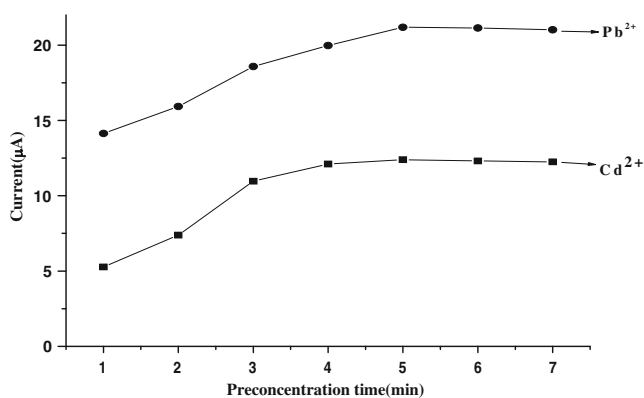

Fig. 8 Effect of preconcentration time on the anodic peak current observed for 1 μM concentration of each of Pb^{2+} and Cd^{2+} ions in an acetate buffer of pH 5 containing 1 M KNO_3 as supporting electrolyte. Preconcentration potential, −1.0 V
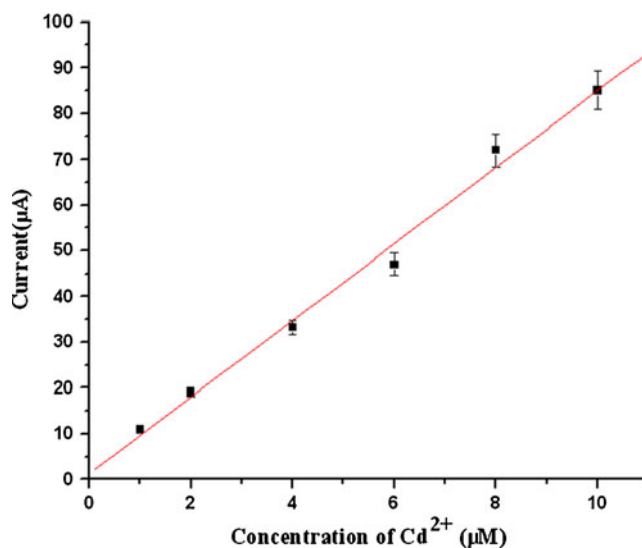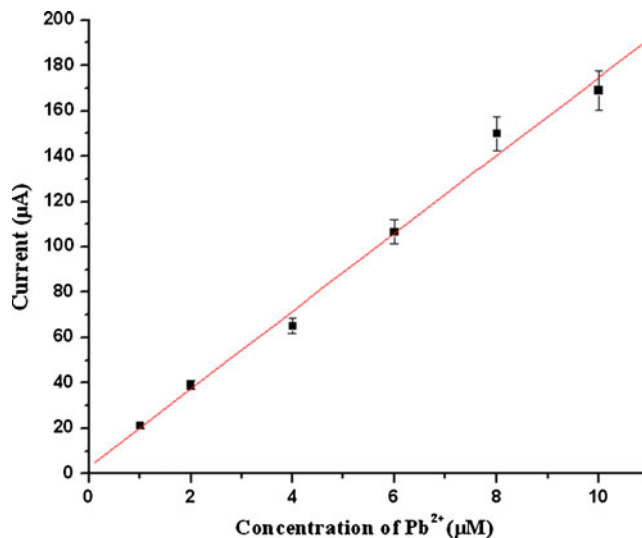

Fig. 9 Calibration plots for lead and cadmium metal ions under optimized conditions

equilibrium between the complexed metal ions and the free ions in solution. Therefore, a preconcentration time of 5 min has been used in all further studies. Thus, the experimental parameters like preconcentration potential of −0.1 V, preconcentration time of 5 min, and acetate buffer of pH 5 were optimized for the simultaneous detection of Pb^{2+} and Cd^{2+} ions.

Table 1 Interference study

Interfering ions	Tolerence limits (μM)
NH_4^+, Ba^{2+}, Mg^{2+}, Ca^{2+}, Cl^-, F^-, P^-, Mn^{2+}, Li^+, Ag^+ SO_4^{2-}, SO_3^{2-}, NO_2^-, NO_3^-, I^-, PO_4^{3-}, Zn^{2+}	>1,000
Co^{2+}, $C_2O_4^{2-}$, CO_3^{2-}	>40
Hg^{2+}, Bi^{2+}, Sn^{2+}, Fe^{3+}	>20
Ni^{2+}, Cu^{2+}	>10

Table 2 Determination of lead and cadmium from sewage water samples

Sample	Originally found (μM)		Added (μM)		Found (μM)				Recovery (%)			
	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Proposed method		AAS method		Proposed method		AAS method	
					Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
A[a]	7.00	3.69	2	2	8.99	5.70	8.93	5.63	99.88	100.17	99.22	98.94
B[a]	6.49	3.34	2	2	8.47	8.47	8.43	5.28	99.76	99.81	99.27	98.87

[a] Samples were collected from different sewer lines

Calibration

With the above optimized conditions, the salicylic acid-modified GCs composite electrode showed a linearity in the concentration range 1–10 μM for both Pb^{2+} and Cd^{2+} ions with a detection limit of 0.18 μM for Pb^{2+} and 0.20 μM for Cd^{2+}, respectively. The experiments were repeated five times, and the calibration plot constructed is shown in Fig. 9. The error bar in the figures denotes the average as the data point and the vertical line denote the maximum and minimum currents observed for these analyte species.

Interference study

In order to apply the proposed method for the industrial applications, the fabricated composite electrode has been examined in the presence of common cations and anions which coexist in most of the industrial and effluent liquid samples. The interference study has been carried out by the standard addition of commonly existing cations and anions into an electrochemical cell containing 1 μM of each of lead and cadmium ions. Above the tolerance limit (given in Table 1), the added ions interfere and alter the peak currents produced by the oxidation of lead and cadmium ions. The developed sensor has showed least interference from most of the common ions due to specific and selective interaction of the modifier functionalities with lead and cadmium ions. Table 1 gives the effect of interfering ions on the anodic peak current in the presence of 1 μM each of lead and cadmium metal ions.

Surface renewability and reproducibility

Surface renewability of the electrode and reproducibility of the analytical signal are essential for continuous and reliable monitoring of analyte concentration in the field of sensor technology. Since the developed sensor is a covalent bulk modified composite electrode, the surface can be easily renewed simply by the mechanical polishing of the exposed layer using different grades of emery sheets. The reproducibility of the sensor was evaluated by exposing the ten renewed fresh surfaces into a solution containing 4 μM each of lead and cadmium ions. The magnitude of stripping current varies with a standard deviation of ±5%. This confirms that the covalent bulk modification is uniform throughout the modified carbon substrate material which has been used for electrode fabrication. Hence, this kind of bulk modification provides the material with selective functionality on its surface, and the electrodes fabricated can be used repeatedly for analytical measurements.

Long-term storage stability

In industrial applications, the fabricated electrode should meet some requirements like long-term storage and operational stability as essential features. The long-term storage stability of the sensor was tested by using the same electrode stored under ambient conditions over a period of 6 months. The measurements were made under identical

Table 3 Determination of lead and cadmium from battery effluent samples

Sample	Originally found (μM)		Added (μM)		Found (μM)				Recovery (%)			
	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Proposed method		AAS method		Proposed method		AAS method	
					Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
A[a]	3.61	ND	2	2	5.54	1.99	5.49	1.90	98.75	99.50	97.86	95.0
B[a]	6.50	ND	2	2	8.46	1.95	8.41	1.89	99.76	99.81	98.94	94.5

ND not detected

[a] Samples were collected from different sources

conditions with successive intervals of 2 months. The peak currents for the oxidation of both lead and cadmium ions decrease by an amount of 6% in the first 2 months, 7% in the 4th month, and 13% in the 6th month, which is indicative of long-term stability of the fabricated sensor electrode. Such a good stability over a long period is accepted for most of the practical applications for repeated measurements. This confirms that the electrode is stable over a long period without any loss in its activity.

Application study

In order to evaluate the performance of salicylic acid-modified glassy carbon composite electrode, lead and cadmium metal ion concentrations from sewage and battery effluent samples from different sources were carried out. Sewage water samples were collected from different sewer lines and filtered to remove any suspended particulate matter. Then the sample pH was adjusted to 7 using very dilute sodium hydroxide. Then a 5-mL aliquot of the sample was diluted to 25 mL, and 1 mL of the diluted solution was added into the electrochemical cell containing the modified glassy carbon electrode. The current due to the oxidation of the analyte was measured by DPASV. Similarly, battery effluent samples were collected from different sources and analyzed by the proposed method similar to sewage water samples. The concentrations of these metal ions obtained by the proposed composite electrode in aqueous medium have been compared by analyzing with the AAS technique. The results obtained by the proposed method are in good agreement with the AAS (Tables 2 and 3). The present electrode measurement shows a linear range of 1–10 μM for each of the lead and cadmium ions. This is well within the limits of lead and cadmium ions in the real sample matrices whose compositions are given in Tables 2 and 3. Hence, the composite electrode prepared by using salicylic acid-modified glassy carbon spheres can be used to quantify these toxic metal ions from a variety of industrial effluents as well as water samples.

Conclusion

A new composite electrode was prepared using bulk derivatized glassy carbon spheres. The covalent modification of the glassy carbon spheres was carried out by the reduction of the corresponding aryl diazonium salt in the presence of a chemical reducing agent. The fabricated composite electrode has been successfully applied in the simultaneous determination of Pb^{2+} and Cd^{2+} ions from sewage and battery effluent samples at trace level by differential pulse anodic stripping voltammetry. The methodology of the present approach is towards green, and the modified electrode has the advantages of being non-toxic, ease of preparation in bulk quantities, long-term storage, and operational stability over a period of several months without leaching of the modifier compared to other carbon paste and surface-modified electrodes. The electrode surface can be renewed easily by simple mechanical polishing, and the same electrode can be used for multiple determinations. Therefore, the developed composite electrode offers an alternative route to monitor the heavy metal ion concentrations at trace level, and it has been successfully applied to determine lead and cadmium ions from environmental and industrial effluent samples.

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