



Covalent modification of glassy carbon spheres through ball milling under solvent free conditions: A novel electrochemical interface for mercury(II) quantification

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ABSTRACT

A simple and green chemistry protocol has been proposed based on the covalent anchoring of benzamide molecule on glassy carbon spheres through ball milling under solvent free condition. The modification proceeds through the formation of an amide bond between carboxylic group of glassy carbon spheres and the amino group of modifier molecule. The formation of covalent bond was ascertained using X-ray photoelectron spectroscopy. Scanning electron microscopy was used to study the surface morphology of milled glassy carbon spheres. The aqueous colloidal solution of modified glassy carbon spheres was used in the preparation of thin film electrodes and subsequently used as a novel electrochemical interface in the quantification of mercury at trace level using a differential pulse anodic stripping voltammetric technique. The modified electrode showed good sensitivity and selectivity towards mercury with a detection limit of 1 nM with least interference from most of the ions. The analytical utility of the proposed electrode has been validated by determining the mercury levels in number of sample matrices.

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1. Introduction

Chemical modification of carbon substrates with suitable modifier molecules towards desired application is of great significance in the development of novel class of sensing platforms in the area of electroanalytical chemistry [1]. Chemical modification imports new set of properties to the carbon substrates which were not available in its unmodified counterparts [2]. Several strategies have been reported for their modification, which includes electrochemically assisted covalent modification with aromatic primary amines through an oxidative strategy and with diazonium salts through a reductive strategy [3,4]. This method results in the formation of well organized layers on the carbon substrate which can be used as modified electrodes. Another strategy involves the chemical reduction of aromatic diazonium salts in the presence of hyphosphorous acid as a chemical reducing agent [5]. This approach is well established and proved to be efficient methodology for the covalent bulk derivatization of carbon based substrate materials. The major limitation of this methodology is the use of hyphosphorous acid for reduction purpose as it is highly corrosive and requires large quantities of solvents to remove the

excess of unreacted diazonium salt from the reaction mixture [6]. Further, thermally assisted covalent modification has been widely used for this purpose which in turn proceeds through the formation of carboxylic groups, activation and then coupling with aromatic primary amines [7]. This method is limited due to the corrosive nature of acids, long modification time and requires large quantities of solvent in order to remove the byproducts and also the unreacted reactants [8].

In recent years, solvent free protocols have been used to modify the carbon substrates due to their attribute towards green chemistry perspectives. Microwave assisted covalent modification of the carbon substrate is relatively a new approach and belongs to the category of a solvent free method [9]. A ball milling process is another route which has gained significance in recent years [10]. This route modifies the conditions under which a chemical reaction generally takes place. The reactions under ball milling conditions generally occur either by changing the reactivity of the reagents or by breaking the molecular bonds mechanically [11]. This approach has been used in the alkylation, arylation and introduction of selective functional moieties under specific atmospheres [12–15]. A ball milling approach is used in various types of addition; coupling and transformation reactions have also been carried out which were thoroughly detailed in the review [12]. Although these methodologies can efficiently form covalent bond between carbon and modifier molecules, there is still an increasing need in developing new, novel and some interesting strategies for

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covalent modification of carbon based substrate materials in bulk quantities.

Mercury is considered to be one of the highly toxic elements and its presence in nature is considered to be a major source of environmental pollution. Due to its high toxic profile, exposure even at trace level may cause severe adverse effects to mankind as well as aquatic life [16]. Hence, World Health Organization (WHO) has recommended a maximum threshold limit value as 2 ppb in drinking water [17]. Therefore, its determination at such a low level becomes a major area of research in the area of environmental science and technology.

In the present report, we have proposed a green chemical approach for the covalent bulk modification of glassy carbon spheres in bulk quantities using aromatic primary amine through the formation of amide bond under ball milling condition. The formation of amide bond has been confirmed with the aid XPS techniques. Aqueous colloidal solution of covalently modified glassy carbon spheres was used in the fabrication of a modified electrode using a glassy carbon electrode. The applicability of modified spheres has been shown by determining the mercury selectively at nanomolar levels. The modified interface has been successfully applied in the determination of mercury from various environmental samples.

2. Experimental

2.1. Chemicals and reagents

All reagents used were of Analar grade and used without any further purification. Glassy carbon spheres (2–12 μm dia.), 4-Amino benzamide and IR grade potassium bromide were purchased from Aldrich. Buffer solutions of known pH in the range pH 1–12 were prepared using deionized water from a MilliQ water purifier (Millipore, USA) with a resistivity of not less than 18.2 $\text{M}\Omega\text{ cm}$ at 25 $^{\circ}\text{C}$. The mercury(II) stock solution (1 mM) was prepared by using Analar grade HgCl_2 in Teflon volumetric flasks. The working standards were prepared by diluting the appropriate aliquots of stock solution on the day of use. Double distilled water was used in all reagent preparations.

2.2. Materials and methods

All electrochemical measurements were carried out by using an electrochemical analyzer [CH Instruments, Texas, USA, model CHI 619B] at room temperature in an electrochemical cell of 10 mL volume with a standard three electrode configuration. The glassy carbon electrode modified with a thin film of modified glassy carbon spheres acted as the working electrode, a Pt (purity 99.99%) wire as the counterelectrode and Ag/AgCl (3 M KCl) as a reference electrode (CH Instruments, Texas, USA). Before electrochemical

measurements all the solutions were degassed using ultra-pure nitrogen gas for 10 min. Differential pulse anodic stripping voltammetry (DPASV) was carried out in the potential range -0.3 to 0.3 V with an amplitude of 0.01 V and a pulse width of 0.05 s. All pH measurements were carried out using a Control Dynamics pH meter (Model APX 175). The surface morphology of ball milled spheres was characterized using a field emission scanning electron microscope (Ultra plus, Carl Zeiss, NTS GmbH). The samples for FESEM analysis were prepared by the drop casting of dilute ethanolic solution of modified glassy carbon spheres on ITO slides. Ball milling of glassy carbon spheres was carried out using Fritsch Pulverisette-7, Germany.

2.3. Electrode fabrication

The glassy carbon electrode of 3 mm diameter was used as an electrode substrate and prior to its modification, the electrode surface was polished with 1, 0.3 and 0.05 μm alumina particles to get a mirror like surface. Then the electrode was washed

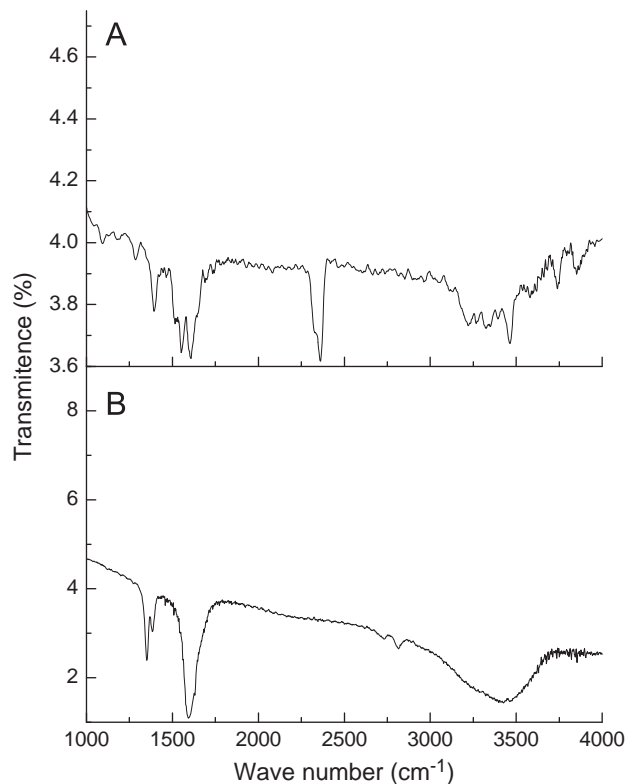
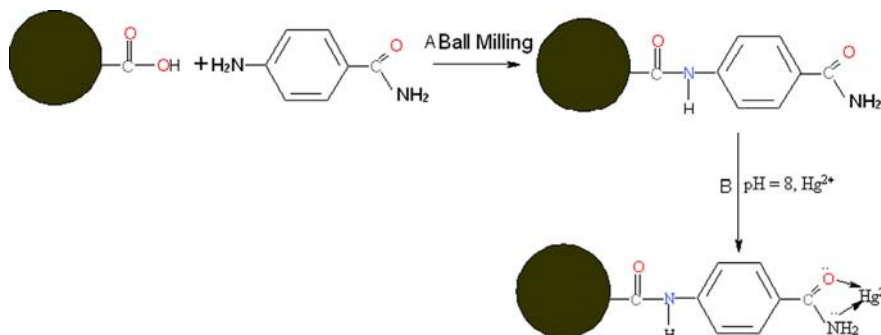


Fig. 1. IR spectra of modified (A) and unmodified (B) glassy carbon spheres.



Scheme 1. (A) Schematic representation of covalent modification of glassy carbon spheres with 4-amino benzamide modifier molecule. (B) Mode of interaction of modified interface with mercury ion.

thoroughly with doubly distilled water using ultrasonic bath and finally dried at room temperature.

The modified electrode was prepared by the drop casting of 10 μL of aqueous colloidal solution of benzamide modified glassy carbon spheres (1 mg mL⁻¹) on the surface of the precleaned glassy carbon electrode. Then the modified electrode was air dried for an extent of 45 min and subsequently at 70 °C for 5 min.

2.4. Analytical procedure

The mercury(II) measurement was carried out using a differential pulse anodic stripping voltammetry (DPASV) technique. The voltammetry has been performed in the potential window -0.3 to 0.3 V with amplitude of 0.01 V and a pulse width of 0.05 s. Known aliquots of mercury(II) were taken in an electrochemical cell of 10 mL volume containing buffer solution of pH 8 which is fitted with a tab controlled magnetic stirrer. The fabricated modified electrode was immersed into the pH solution containing mercury and continuously stirred for 3 min to preconcentrate the metal ions at the interface by applying a reduction potential of -0.4 V in order to reduce all the preconcentrated mercury ions into its atomic state and subsequently stripped off from the electrode surface into the bulk of the electrolytic solution by scanning the potential in the positive direction after 15 s of equilibration time.

2.5. Sample preparation

The samples from lead-acid battery effluents, chrome plating industry and from textile industry were collected from their sources and stored in polyethylene containers. The samples were filtered through a Whatman filter paper to remove any suspended

colloidal matter present. The pH of the resulting filtrate solutions was adjusted to pH 8 and used for further analysis using the procedure described under analytical procedure part.

2.6. Covalent modification of glassy carbon spheres with 4-amino benzamide

Covalent bulk modification has been carried out using the following protocol (Scheme 1). 1 g of glassy carbon spheres was mixed with 0.5 g of 4-amino benzamide in an agate jar and milled for different time intervals i.e. 1, 4, and 8 h. The contents in the jar were washed thoroughly with water and filtered. The unreacted benzamide was removed by treating with acetonitrile followed by water. Finally, the resulting modified glassy carbon spheres were vacuum dried and stored in an air tight container.

3. Results and discussions

Covalently modified glassy carbon spheres (GCs) were spectroscopically characterized by using IR, XPS and FESEM techniques. The covalent modification of glassy carbon spheres with 4-amino benzamide modifier molecule has been deciphered using Fourier transform infrared and X-ray photoelectron spectroscopy techniques. Cyclic voltammetry has been used to decipher the interacting ability of the modified interface towards mercury and differential pulse anodic stripping voltammetry (DPASV) was used for its quantification.

The FTIR spectra of both as received and functionalized glassy carbon spheres were recorded and compared to confirm the covalent modification. The spectra were recorded by using pellets

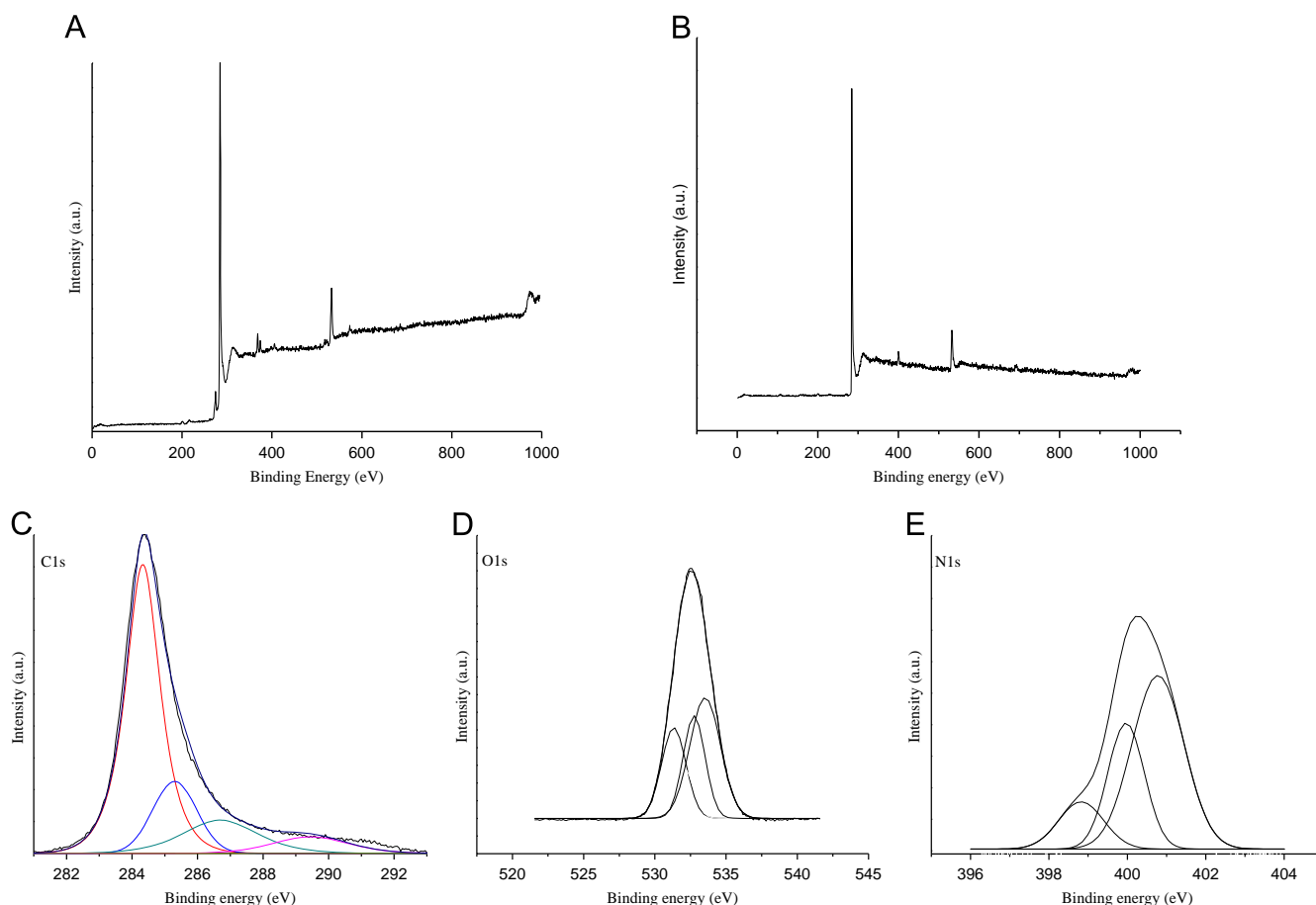


Fig. 2. XPS spectra of modified glassy carbon spheres: (A) survey spectra of unmodified GCs, (B) survey spectra of modified GCs, (C) C 1s, (D) O 1s and (E) N 1s regions.

prepared by the hand mixing of glassy carbon spheres with KBr in 1:100 ratio and then these were subsequently exposed to infrared radiation in the range of 1000–4000 cm^{-1} (Fig. 1). The unmodified glassy carbon spheres have revealed the presence of peaks due to –OH and C=O groups of –COOH at 3435 and 1600 cm^{-1} , respectively. The peak at 1351 cm^{-1} might be due to the stretching of –OH group of phenol, and the peak at 2800 cm^{-1} is due to the stretching of aromatic protons which are in good agreement with the reported literature [18]. However, the IR spectrum of the modified glassy carbon spheres showed peaks at 1618 and 3336.4 cm^{-1} , revealing the presence of C=O and –NH groups of amide bond. In addition to this, it also showed a peak at 3319 cm^{-1} due to the stretching of –NH₂ groups [19,20]. The disappearance of –COOH groups and appearance of amide group in the modified glassy carbon spheres have confirmed that the formation of amide bond takes place during the ball milling process in the chemical modification of glassy carbon spheres.

The XPS survey spectrum of both unmodified and modified glassy carbon spheres has been recorded in the range 0–1000 eV. Both the spectra revealed the presence of emission peaks at ca. 283.7 and 532.7 eV which corresponds to the C 1s and O 1s containing functional groups (Fig. 2A and B) except the N 1s emission in case of modified glassy carbon spheres (Fig. 2B) [21]. The multiple scans were studied over C 1s region from 281 to

293 eV which showed peaks at 284.03, 285.2, 286.4 and 289 eV. It has revealed the presence of different types of carbon atoms present on the modified glassy carbon spheres and were assigned to C=C, C–N, C–O and N–C=O types of functional groups (Fig. 2C). The successive scans over O 1s region from 522 to 542 eV showed the presence of three superimposed peaks at 531.9, 532.80 and 533.6 eV (Fig. 2D) and these peaks might be due to the presence of N–C=O, C–O and HO–C=O functional groups of the modifier molecule. Then, the scan was extended to N 1s region from 396 to 404 eV. It showed the presence of three peaks corresponding to N–C, N–C=O (amide) and NH₂ (amine) functionalities which were located at 398.7, 399.93 and 400.7 eV (Fig. 2E) and these binding energy values are in good agreement with the literature [22]. All these observations confirmed the formation of covalent bond (amide bond) during the ball milling process and also the presence of functional groups of the modifier molecule.

3.1. Surface morphology of modified glassy carbon spheres

The covalent modification of glassy carbon spheres with benzamide modifier molecule has been carried out under the ball milling approach. During milling, the surface morphology of the spheres is expected to be changed. Therefore, the morphological

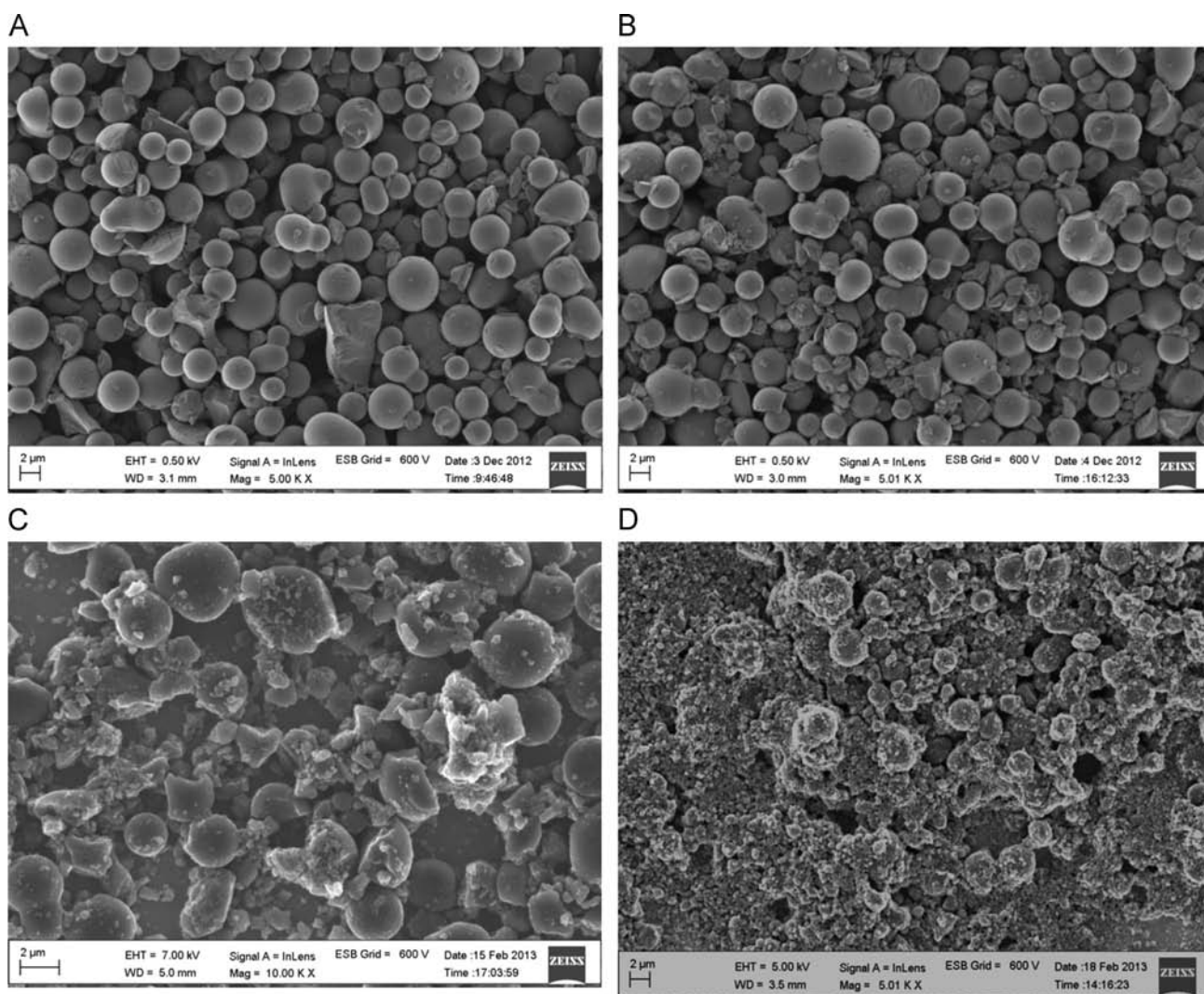


Fig. 3. Field emission scanning electron microscopy images of (A) native glassy carbon spheres before milling, (B) functionalized GCs after 1 h milling, (C) 4 h milling and (D) 8 h milling.

changes of the glassy carbon spheres have been studied with the help of field emission scanning electron microscopy (FESEM) (Fig. 3A–D). The images were taken at the same magnification for better comparison. From these figures it has been found that the unmilled spheres are spherical in shape (Fig. 3A) and the spheres milled for 1 h has not revealed any considerable change in its surface morphology (Fig. 3B), whereas the spheres milled for about 4 h has showed the destruction of spherical shape and also reduction in size of the spheres (Fig. 3C). The FESEM image of the extended milled spheres for 8 h has no spherical shape and the smooth surface has been changed to rough surface (Fig. 3D). This signifies that the ball milling process facilitates the modification on the surface of glassy carbon spheres.

3.2. Electrochemical behavior of modified glassy carbon spheres towards mercury(II)

Cyclic voltammetry has been used to explore the potential affinity of modified interface towards mercury. A typical cyclic voltammetric experiment has been performed using unmodified and modified electrodes in the presence of 50 μM of mercury(II) in the potential window -0.9 to 0.4 V with a scan rate of 50 mV/s (Fig. 4A). From the voltammetric profile, it has been found that the unmodified electrode did not show any voltammetric signature for the presence of mercury (Fig. 4Aa). Whereas the modified electrode showed a peak at -0.4 V in the reductive scan which can be attributed to the reduction of Hg(II) to Hg(0), another sharp peak was observed at -0.15 V in the oxidative scan which corresponds to the reoxidation of Hg(0) to Hg(II) (Fig. 4Ab). Therefore, it is evident that the presence of modifier molecule is responsible for the observed electrochemical signal for mercury which is

attributed to the interacting ability of the modifier functionalities with mercury. The interaction of modifier molecule with mercury is expected to be through amine and carbonyl functionalities of amide group according to Scheme 1B. In these groups, the carbonyl oxygen and amine nitrogen act as donor atoms and these donor atoms are known to show potential affinity towards mercury ion according to the hard and soft acid base theory (HSAB) concept [23,24].

It was observed that the oxidation peak is more significant than the reduction peak. Hence, the quantification of mercury was systematically carried out by using DPASV. A typical voltammogram of the modified electrode in the presence and in the absence of 100 nM of mercury is shown in Fig. 4B. In the absence of mercury the modified electrode did not show any signal for the presence of mercury (Fig. 4Ba). However, in the presence of mercury the modified electrode showed a peak at -0.04 V due to the stripping of mercury (Fig. 4Bb). These studies have revealed that the modified electrode showed potential affinity towards mercury even at trace concentration level. Hence the use of DPASV for mercury determination is expected to result very low detection limit in its measurement.

3.3. Optimization study

In order to achieve the maximum efficiency of the developed sensor towards the electrochemical determination of mercury it is required to optimize the parameters like pH of the working solution, deposition time and potential which influence the analytical response of the analyte.

The choice of a suitable buffer pH of the electrolytic solution governs the magnitude of the stripping currents in all types of

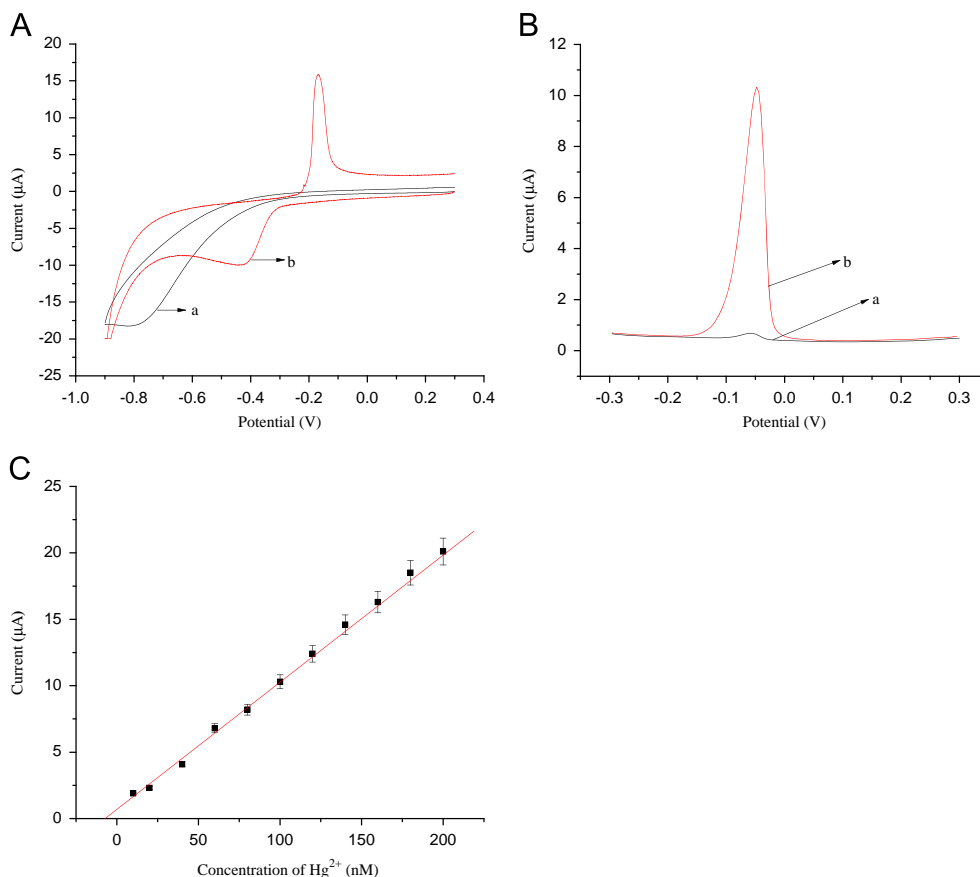


Fig. 4. (A) Cyclic voltammogram of Hg²⁺ (50 μM) in a phosphate buffer solution of pH 8: (a) at native electrode and (b) at modified electrode. (B) DPASV of Hg²⁺ (100 nM) in a phosphate buffer solution of pH 8: (a) in the absence of Hg²⁺ and (b) in the presence of Hg²⁺. Reduction time—3 min, reduction potential— -0.4 V. (C) Calibration plot.

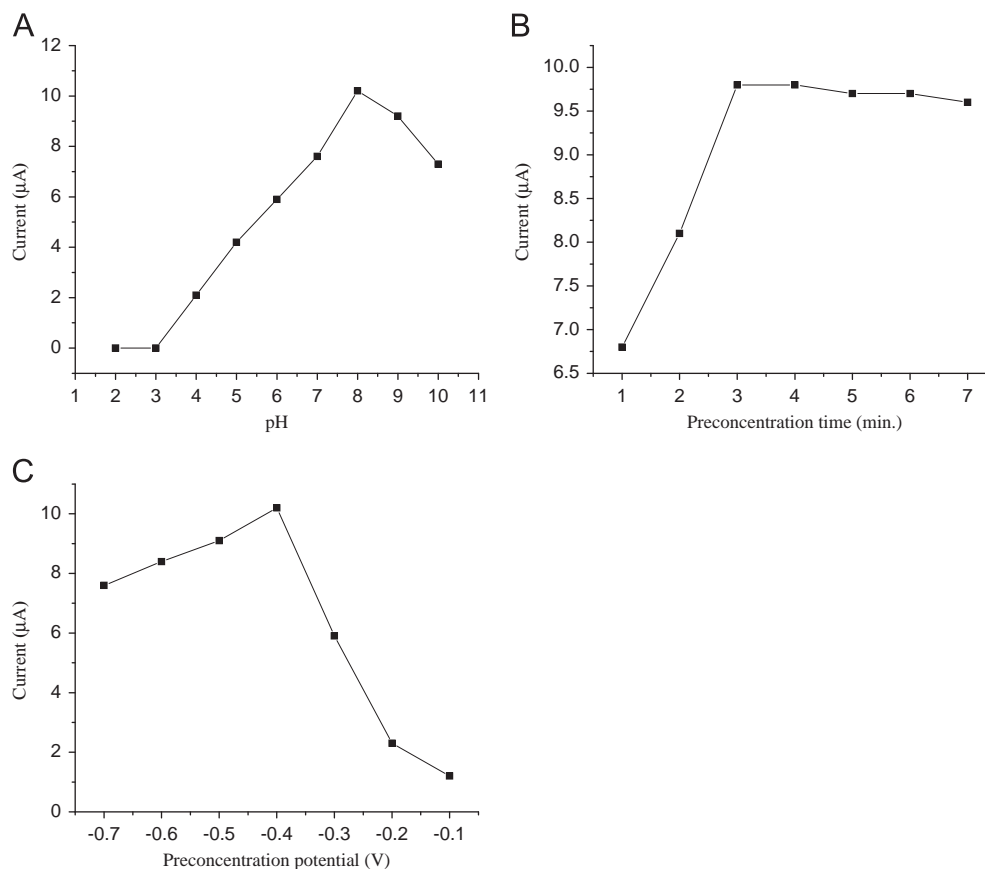


Fig. 5. Optimization study. Effect of (A) pH, (B) preconcentration time and (C) preconcentration potential.

electrochemical measurements. Hence different buffer solutions like ammonia–ammonical, phosphate, Robinson and borate buffers have been examined in the present investigation. Among these, phosphate buffer has shown well resolved and sharp peaks with enhanced peak currents. Hence, phosphate buffer has been used as an optimum medium for the accumulation of mercury at the modified electrode. The interaction of functional groups of the modifier molecule with mercury ion mainly depends on the availability of lone pair of electrons present on nitrogen and oxygen donor atoms of the amide functional group of the modifier molecule which in turn depends on the medium pH. The lone pair of electrons present on the amide nitrogen and carbonyl oxygen atoms is attributed to be protonated in an acidic medium and deprotonated in a basic medium. Therefore, the pH of the working solution plays a very important role in the complexation of mercury with these functional groups. The effect of pH of buffer solution was studied in the pH range 4–9 (Fig. 5A). The peak currents increase from 4 to 8 and thereafter they decrease. The increased current might be due to the increase in the deprotonation behavior of oxygen and nitrogen atoms of the amide functionality and also the availability of lone pair of electrons towards mercury complexation.

Then the time required for the preconcentration of mercury ion (preconcentration time) was studied from 1 to 7 min (Fig. 5B). The peak current for the stripping of mercury ions increases from 1 to 3 min and thereafter it decreases. The increase of peak current is due to the fact that the longer the preconcentration time more and more the analytes at the electrode/solution interface. After 3 min, the peak decrease of peak current may be attributed to either surface saturation or the attainment of equilibrium between the metal ions at the interface and the ions in the bulk of the solution. Hence a preconcentration time of 3 min has been used as an optimized time in all future studies.

The effect of reduction potential on the anodic peak current of mercury was varied in the range -0.1 to 0.7 V (Fig. 5C); the peak current increased up to -0.4 V and thereafter it decreased. The increase of peak current is due to increase in extent of reduction of more and more mercury ions and the decrease in peak current may be due to the interference from an extraneous process. Therefore a reduction potential of -0.4 V was used as an optimum potential in all subsequent study.

3.4. Calibration plot and detection limit

A calibration plot was constructed under optimized conditions by measuring the peak currents for the successive additions of known concentrations of mercury. Each experiment was repeated five times and the error bar in the calibration plot denotes the average peak current as the data point and the vertical line denote the maximum and minimum currents observed. The peak current for the stripping of mercury increased linearly with increase of mercury(II) up to 200 nM (Fig. 4C). The detection limit (3σ) was found to be 1 nM which is well below the prescribed threshold limit value (TLV) of 2 ppb for drinking water as per World Health Organization standard [17].

3.5. Interference study

To check the selectivity of the proposed sensor towards the electrochemical determination of mercury, the interference effect of commonly existing cations and anions was studied in the presence of 100 nM mercury. The interference study was carried out by preconcentrating 100 nM of mercury on the electrode interface in the presence of different cations and anions in the electrolyte solution. The tolerance limits for different cations and

Table 1
Interference study.

Interfering ions	Tolerance limit (μM)
Cd^{2+} , Fe^{2+} , Ni^{2+} , Co^{2+} , Cu^{2+} , Mn^{2+} , Zn^{2+}	400
Na^+ , K^+ , Ag^+ , Cs^+	700
Ca^{2+} , Mg^{2+} , Ba^{2+} , Be^{2+} , Cr^{3+} , Fe^{3+} , As^{3+} , Pb^{2+}	370
Co^{2+} , $\text{C}_2\text{O}_4^{2-}$, CO_3^{2-} , Cl^- , F^- , Li^+ , SO_4^{2-} , PO_4^{3-} , SO_3^{2-} , NO_2^- , NO_3^-	460

Table 2
Application study.

Sample	Hg(II) originally present (nM)	Hg(II) spiked (nM)	Total Hg(II) found (nM)	Recovery (%)
Battery sample 1	20	20	40.7	101.75
Battery sample 2	32	20	52.0	100.00
Battery sample 3	43	20	62.4	99.04
Battery sample 4	59	20	79.0	100.25
Chrome plating	90	20	110.1	100.09
Industry effluent				
Textile industrial effluent	83	20	102.8	99.80

Battery samples 1 and 2: Exide batteries of 6 years old used in UPS.

Battery samples 3 and 4: Exide batteries of 8 years old used in UPS.

anions are presented in Table 1. Above the tolerance limits, the interfering species interferes and affected the preconcentration of Hg(II) by competing with the modifier functionalities and subsequently alter the peak currents produced by the stripping of mercury from the electrode interface. It is clear from the results (Table 1) that the developed sensor showed least interference from most of the common ions. This specificity has been attributed to the selective interaction of the modifier functionalities of the benzamide molecule with mercury(II) ion. The developed sensor has been successfully applied in the determination of mercury from a wide variety of environmental sample matrices.

3.6. Application study

The analytical utility of the proposed sensor has been validated by measuring mercury levels present in various sample matrices like lead acid batteries, chrome plating and textile industrial effluent samples. The recovery study was carried out for all these samples by spiking with known concentrations of mercury along with the originally present mercury in these samples (Table 2).

4. Conclusions

A simple and solvent free chemical protocol has been developed for the covalent modification of glassy carbon spheres in bulk quantities. This modified carbon has been successfully utilized in the development of sensitive and selective interface towards the electrochemical determination of mercury at nanomolar level. It showed a detection limit of 1 nM with least interference from commonly encountered foreign ions normally present in environmental samples. The analytical utility of the sensor has been demonstrated by measuring trace level mercury from various natural samples. The proposed sensor could be used as an alternative method to the existing ones in mercury quantification.

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