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## Anthraquinone functionalized carbon composite electrode: Application to ammonia sensing

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## ABSTRACT

A simple strategy has been used to covalently modify the glassy carbon spheres with anthraquinone moieties through the diazonium salt reduction. The derivatized glassy carbon spheres were used to modify the basal plane pyrolytic graphite electrode by immobilizing them on its surface and examining its electrochemical behaviour. The composite electrode has been used to detect trace level ammonia in the concentration range  $5 \times 10^{-8}$  to  $3 \times 10^{-5}$  M and it was successfully applied to detect low levels of ammonia present in natural samples like urine and soil.

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## 1. Introduction

Ammonia is very important to plant, animal and human life. It is found in water, soil, air and is a source of much needed nitrogen for plants and animals. Due to its toxicity, the determination of ammonia is more essential in a number of applications including industrial hygiene, environmental protection, clinical diagnosis and the monitoring of leakage from refrigeration systems etc. [1–3]. Ammonia may be released to the atmosphere by volatilization from the following sources: decaying organic matter, livestock excreta, fertilizers applied to soils, venting of gas, leaks or spills during commercial synthesis, production, transportation, or refrigeration equipment failure, sewage or waste water effluent; burning of coal, wood and other natural products and volcanic eruptions. Ammonia based fertilizers are extensively used in agriculture sector to improve the crop yield and hence its quantification in soil samples provides very valuable information in deciding the soil fertility. Several ammonia sensors have been reported, majority of them are based on gas diffusion cell approach. In these systems ammonia gas diffuses through a gas permeable hydrophobic membrane (mainly PTFE—polytetrafluoro ethylene) into a recipient solution where ammonia can be detected by means of a simple and inexpensive detection technique like colorimetric, pH indicator [4,5], a

$\text{NH}_4^+$  ion selective electrode [6] or a pH sensor [7,8]. The oxidation of ammonia in alkaline solution by an electrochemical method has been the subject of continuous investigations [9–17].

Prasad and coworkers have reported the synthesis of water soluble polyelectrolyte templated polyaniline film modified electrode for ammonia sensing [18]. It exhibits stable, reproducible and reversible resistance changes in presence of ammonia. Somnath et al. have used barium strontium titanate (BST) thin films deposited by sol–gel spin coating technique for sensing ammonia at trace level [19]. Compton and coworkers have recently reported a method for ammonia sensing based on lead oxide modified carbon powder. A composite lead oxide modified carbon epoxy electrode was examined with respect to oxidation of ammonia in aqueous solution [20]. The electrochemical response of hydroquinone in presence of ammonia in the propylene carbonate and its analytical utility for ammonia sensing was explored by the same group at lower concentration level by measuring the peak current as a function of ammonia concentration by Ji et al. [17]. Polycarbazole LB thin films have been studied for ammonia sensing in the lower concentration range [21]. Deshpande et al. have used tin oxide–intercalated polyaniline nanocomposites thin films which remain inert on  $\text{NH}_3$  gas exposure at room temperature. The presence of  $\text{SnO}_2$  crystallites in the nanocomposite thin film changes the electronic property of polyaniline matrix abnormally with high sensitivity [22].

The chemically modified glassy carbon electrodes act as catalysts which promote oxygen reduction with high efficiency [23].

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The immobilization of catalytic material onto the electrode surface is useful because they reduce the large overpotentials that are required at most of the electrode substrates [24]. It has been shown that modification of the electrode surface by quinones via chemisorption or covalent attachment enhances the rate of oxygen reduction [25]. Covalent modification can be easily achieved by the electrochemical reduction of corresponding diazonium salts under suitable conditions [26]. However in alkaline medium quinonyl moieties can desorb easily from the electrode surface during long time electrochemical study, hence it is more beneficial to attach the quinone moiety covalently on the substrate surface [25,27]. Recently the covalent functionalization has been achieved by the chemical reduction of the aryl diazonium salts in presence of hypophosphorous acid as a reducing agent. It provides a simple, cost effective and promising functionalization methodology for covalent attachment of the modifier molecule on the carbon substrate surface [28].

In this report we are presenting a simple strategy for the detection of ammonia quantitatively, based on its oxidation in presence of anthraquinone modified glassy carbon composite electrode (AQGC) in aqueous medium at trace level. This is the first report of its kind explored for ammonia quantification based on the modification of glassy carbon spheres with anthraquinonyl moieties.

## 2. Experimental

### 2.1. Chemicals and instrumentation

All reagents used were AnalaR grade and used without further purification. The glassy carbon spheres (2–12  $\mu\text{m}$  dia) were purchased from Aldrich (purity >99.95%) and used directly. Hypophosphorous acid (50%) and Fast red AL salt AR Grade (Purity 90%) were purchased from Merck grade. Solutions of known pH in the range pH 1–12 were prepared using deionised water from milliQ water purifier (Millipore, USA) with a resistivity of not less than  $18.2 \text{ M}\Omega \text{ cm}$  ( $25^\circ\text{C}$ ), pH 1 (0.1 M HCl). The cell contained  $4 \text{ cm}^3$  of buffer and  $4 \text{ cm}^3$  of 0.1 M KCl as supporting electrolyte.

Voltammetric measurements were performed using a CH Instruments (Texas, USA) Model 619B series computer controlled Potentiostat. All electrochemical measurements were carried out at room temperature ( $26 \pm 2^\circ\text{C}$ ) after degassing the solutions using ultra pure nitrogen gas for 15 min in an electrochemical cell of volume  $10 \text{ cm}^3$  with a standard three-electrode configuration. A basal plane pyrolytic graphite (bppyg, 3 mm, Le Carbone Ltd., Sussex, UK) electrode acted as the working electrode. A Pt (99.99%) wire was used as a counter electrode and Ag/AgCl (3 M KCl) CH Instruments (Texas, USA) as a reference electrode. All pH measurements were carried out using Control Dynamics pH meter (model APX 175).

### 2.2. Homogeneous derivatization of glassy carbon spheres

The derivatization of glassy carbon spheres forming anthraquinone modified glassy carbon spheres (AQGC) were achieved using the following protocol.

One gram of glassy carbon spheres were mixed with a  $15 \text{ cm}^3$  of acetonitrile containing 10 mM Fast red AL salt to which  $50 \text{ cm}^3$  of hypophosphorous acid was added slowly. The reaction mixture was then left to stand at  $5^\circ\text{C}$  for 30 min with occasional stirring at regular intervals and the resulting modified carbon spheres were then filtered under suction and the residue was washed with ample quantities of acetonitrile followed by acetone and water to remove any unreacted and reduced diazonium salt. This washing facilitates the removal of any physisorbed diazonium salt present on the surface of glassy carbon spheres. The AQGC were then dried by placing inside a fume hood for a period of 12 h and finally stored in an airtight container [27].

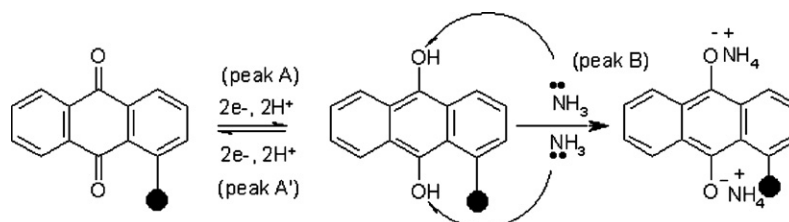
### 2.3. Electrode modification by grafting method

The AQGC were immobilized onto the electrode surface by grafting method. The basal plane pyrolytic graphite electrode was initially polished on glass polishing paper (H00/240) after which it was again polished on silicon carbide paper (P1000C) for smoothness. The AQGC were dispersed in toluene and sonicated for 30 min. Then the dispersed glassy carbon spheres were dispensed drop wisely onto the bppyg electrode surface using micropipette and the electrode was allowed for drying for the desolvation of the solvent at room temperature. This procedure has been repeated several times until substantial quantity of modified glassy carbon spheres accumulates and gets deposited as a thin film on the electrode surface [22].

## 3. Results and discussion

### 3.1. Voltammetry of AQ glass carbon spheres

The electrochemistry of anthraquinone modified glassy carbon spheres (AQGC) were studied by immobilizing them onto the bppyg electrode by the grafting technique and studying its cyclic voltammetry. Initially three scans were performed between the potential window 0.2 to  $-0.5 \text{ V}$  in a buffer solution of pH 1 containing 0.1 M HCl (0.1 M KCl was used as a supporting electrolyte) to understand the redox behaviour of modified glassy carbon spheres (Fig. 1). Upon first scanning in a reductive direction from 0.2 V, a reductive wave was observed at ca.  $-0.191 \text{ V}$ , but on reversing the scan direction at  $-0.5 \text{ V}$  the corresponding oxidative wave was observed at  $-0.143 \text{ V}$ . In the subsequent scans we could observe only two peaks in the potential range 0.0 to  $-0.3 \text{ V}$  corresponding to oxidative and reductive peaks of quinonyl groups of modifier molecule present on the carbon surface. This behaviour ensures that the system is electrochemically reversible process. A reduction peak and its corresponding oxidative peak were observed at  $-0.191$  and  $-0.143 \text{ V}$ , respectively (Fig. 1) in a two electron, two proton reversible redox process. The exact peak potentials of this wave were found to depend on the pH. This voltammetric behaviour is consistent with previous studies of glassy carbon spheres covalently modified with anthraquinonyl groups and can be attributed to the two electron, two proton reduction/oxidation of the anthraquinonyl moiety to the corresponding hydroquinone species [27]. A small shoulder



**Scheme 1.** Proposed redox pathway of anthraquinone modified glassy carbon spheres in presence of ammonia.

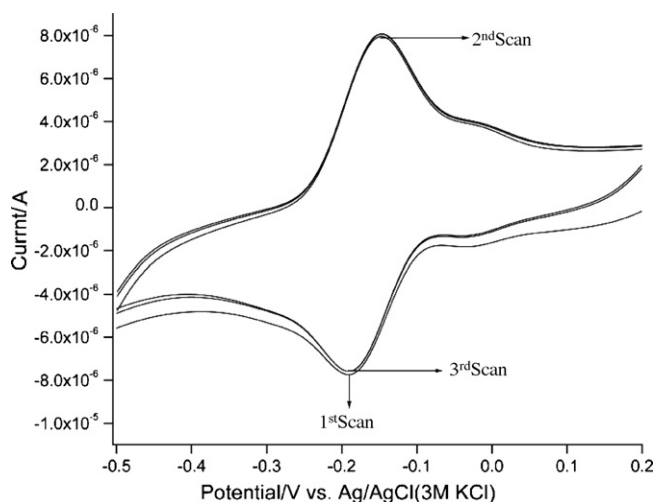


Fig. 1. Cyclic voltammogram of anthraquinone modified glassy carbon spheres (4 mL 0.1 M HCl + 4 mL 0.1 M KCl, pH 1), scan rate 25 mV s<sup>-1</sup>.

has been observed in the potential range 0 to -0.1 V which might be due to intermediate reduction/oxidation of the quinone/semi-quinone species. It may be due to kinetic control appearing within the overall two-electron, two-proton redox process [29,30].

### 3.2. Electrochemical behaviour of anthraquinone modified glassy carbon spheres in presence of ammonia

The electrochemical behaviour of AQGC in presence of ammonia was examined by studying its cyclic voltammetry in 0.1 M KCl solution. Initial scan was performed between the potential window -1.2 to +1.5 V for AQGC in presence of ammonia. The first scan in an oxidative direction from -1.2 to +1.5 V has resulted a small oxidative peak at -0.364 V followed by a large oxidative peak at 1.21 V (designated as A and B in Fig. 2). Reverse of the scan at 1.5 V has not showed any corresponding reductive wave of large oxidative peak (peak B) indicating that it is an electrochemically irreversible process. But the new reductive peak was observed at ca. -0.272 V (designated as peak C in Fig. 2) followed by one more reductive peak at -0.467 V (designated as peak A<sup>1</sup> in Fig. 2), which is corresponding to the reduction of oxidized species at ca. -0.364 V (designated as peak A in Fig. 2). The peaks correspond-

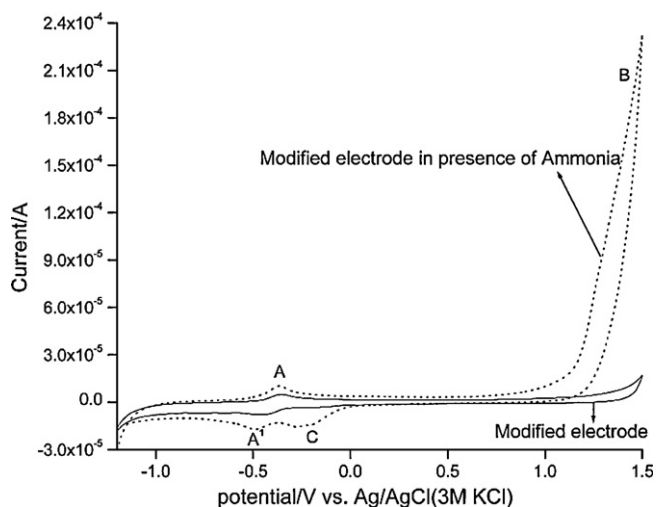
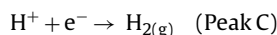
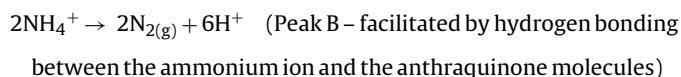


Fig. 2. Cyclic voltammetric response of anthraquinone modified electrode: (---) in presence of ammonia, (—) in absence of ammonia (4 mL 0.1 M KCl), scan rate 25 mV s<sup>-1</sup>.

ing to AA<sup>1</sup> are due to the electrochemically reversible process of quinonyl/hydroquinonyl species [17].

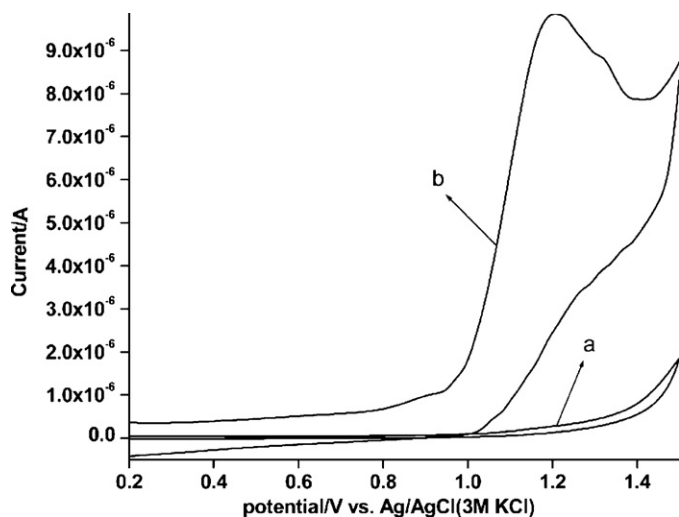
After the oxidation of ammonia, the formed products undergo a chemical reaction followed by further electron transfer. The products of this chemical reaction can then be electrochemically reduced at the electrode surface consistent with the new reduction wave observed on the reductive scan (peak C). Initially ammonia undergoes oxidation to produce ammonium ions and nitrogen in a three electron process. In the second step the ammonium ion undergoes pre-equilibrium step with a loss of proton and regenerates ammonia. In the next step the proton may undergo electrochemical reduction to produce hydrogen (peak C). Based on these observations the following mechanism has been proposed for the peaks that have been observed in the experimental study [31].



The peak B corresponds to chemically and electrochemically irreversible oxidation of the ammonia to form ammonium ion with the liberation of nitrogen gas (peak B). Then it undergoes an electrochemically reversible two electron, two proton reduction (peaks AA<sup>1</sup>) to form the quinonyl/hydroquinonyl species. Therefore it is a chemically and electrochemically reversible process which leads to electrochemically irreversible mechanism. The analytical approach shown as above facilitates the use of 0.1 M KCl solution as the working electrolyte in sensing ammonia. In the context of direct amperometric ammonia sensing, the ammonia will be irreversibly converted into the electro inactive NH<sub>4</sub><sup>+</sup> ion. The observed voltammetric behaviour and their wave shapes are consistent with the reported literature on ammonia sensing in aqueous media at modified glassy carbon electrode. The proposed redox pathway of anthraquinone modified glassy carbon spheres in presence of ammonia is shown in Scheme 1.

### 3.3. Electrochemical oxidation of ammonia at AQGC

The oxidation behaviour of ammonia was examined initially by adding 10 μL of 5 mM ammonia in 0.1 M KCl solution at native basal plane pyrolytic graphite (BPPG) electrode very weak oxidative peak at 1.21 was observed (Fig. 3). However the addition of same ammonia concentration in fresh 0.1 M KCl solution in presence of modified electrode (BPPG was grafted with anthraquinone modified glassy carbon spheres) gave much enlarged oxidative peak at 1.21 V. Compared to the response of ammonia at native BPPG, the response of ammonia at modified electrode with AQGC was significant and confirms that quinones show highly effective enhancement to ammonia, which makes for easier adsorption of ammonia and provides enough effective reaction sites. No peaks were observed in the cathodic segment, indicating that the ammonia oxidation is an irreversible process. The oxidative peak may be attributed to the irreversible oxidation of the ammonia molecule, which is in accordance with the proposed redox mechanism for oxidation of ammonia in presence of quinone molecule. A well-defined oxidative peak was observed at 1.21 V at the first anodic sweep in the scan range 0.2–1.5 V. On reversing the scan, no corresponding reductive peak was observed. However during following successive cyclic sweeps, the oxidation peak current decreases slightly which might be due to the diffusion of immobilized species from the electrode interface. This result confirmed the irreversibility of the ammonia oxidation process and it might be resulted from the



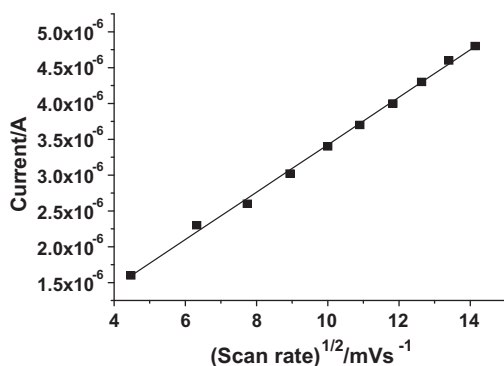
**Fig. 3.** Cyclic voltammetric response of (a) bare electrode in presence of ammonia and (b) anthraquinone modified electrode in presence of ammonia (4 mL 0.1 M KCl), scan rate  $25 \text{ mV s}^{-1}$ .

fact that the electrode surface was blocked by the adsorption of the oxidation products which reduces the effective reaction sites at the modified electrode surface.

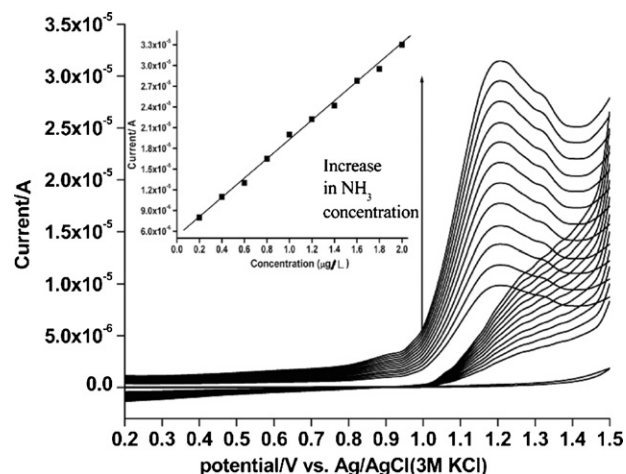
The influence of the scan rate on electrochemical behaviour of 5 mM ammonia at AQGC/BPPG in presence of 0.1 M KCl solution was also investigated (Fig. 4). The oxidation peak currents are proportional to square root of scan rate in the range from 20 to  $200 \text{ mV s}^{-1}$ . These studies revealed that the electrochemical behaviour of ammonia at AQGC/BPPG was controlled by an adsorption step. The oxidation of ammonia is irreversible and it occurs at 29.5 mV potential. The potential of the ammonia oxidation varies with scan rate and it shifts from 25 to 29.5 mV when the scan rate increases from 100 to  $200 \text{ mV s}^{-1}$ . All these studies clearly indicate the irreversibility of the oxidation process.

#### 3.4. Calibration plot

Under the optimized experimental conditions, the calibration curve for ammonia in presence of 0.1 M KCl solution at AQGC/BPPGE was characterized by studying its cyclic voltammetry. The linear range was comprised from  $5 \times 10^{-8}$  to  $3 \times 10^{-5}$  M in terms of the relationship between the concentration of ammonia and the oxidative peak current (Fig. 5) with a detection limit of  $9 \times 10^{-9}$  M. After each measurement the modified electrode was cleaned by polishing on glass polishing paper (H00/240) followed by silicon carbide paper (P1000C) for smoothness. After which functionalized glassy



**Fig. 4.** Effect of scan rate: peak current vs. square root of scan rate (range 20– $200 \text{ mV s}^{-1}$ ).



**Fig. 5.** Cyclic voltammetric behaviour of anthraquinone modified electrode to increasing concentrations of ammonia. Inset: current vs. concentration (4 mL 0.1 M KCl), scan rate  $25 \text{ mV s}^{-1}$ .

carbon spheres were grafted onto the bppg electrode by gently rubbing the electrode surface on a fine qualitative filter paper containing the derivatized glassy carbon spheres. The relative standard deviation (RSD) was found to be 3.8% for 5 determinations at  $10 \mu\text{L}$  of 5 mM ammonia concentration. These results revealed that the anthraquinone composite electrode provides good reproducibility and repeatability in the measurement of ammonia at trace level.

#### 3.5. Application study

##### 3.5.1. Ammonia in urine samples

The anthraquinone modified electrode was used to determine the ammonia content in human urine samples. One mL of urine sample was diluted 10 times using 0.1 M KCl solution and 1 mL of the aliquot has been subjected to cyclic voltammetric studies. An oxidation peak at 1.21 V which is assigned to ammonia oxidation has been observed. In order to ascertain that the observed peak is due to the oxidation of ammonia, the sample has been spiked with known quantities of ammonia. The observed increase in the peak current after the addition of ammonia to the urine sample clearly indicates that the observed peak at 1.21 V for the human urine sample corresponds to the oxidation of ammonia. These results facilitated us to propose the determination of ammonia in the real sample using anthraquinone modified glassy carbon spheres. The increase in the oxidation current was proportional with each addition of the sample concentration. The calibration curve method was adopted to determine the original concentrations of ammonia in urine sample and the results obtained for two human urine samples are given in Table 1. These results indicate that the oxidation of ammonia at the interface of modified electrode provides a simple strategy to detect submicromolar ammonia concentrations from real samples.

##### 3.5.2. Ammonia in soil extract samples

1 g of ground and sieved soil sample was taken in a beaker and soaked by adding 5 mL of 2 M KCl solution. It was stirred for 30 min, centrifuged and the clear supernatant was transferred into 25 mL volumetric flask. This process has been repeated with 5 mL portions of 2 M KCl solution several times and the clear centrifugates were collected in 25 mL volumetric flask and diluted to the mark. 1 mL aliquot of diluted sample was used for the analysis. The interference study has been carried out in order to apply the composite electrode to measure nitrite levels in soil extract samples. In this study, the effect of various anions and cations has been examined by the addi-

**Table 1**  
Determination of ammonia in urine samples.

Urine sample <sup>a</sup>	Ammonia found ( $\mu\text{M}$ )	Ammonia added ( $\mu\text{M}$ )	Total ammonia ( $\mu\text{M}/\text{mL}$ )	Recovery of added ammonia (%)
1	20	5	25.0	100
2	25	10	35.5	103

<sup>a</sup> Urine samples were collected from different individuals.

**Table 2**  
Determination of ammonia in soil extract samples.

Soil sample	Ammonia found ( $\mu\text{M}/\text{g}$ )	Ammonia added ( $\mu\text{M}/\text{g}$ )	Total ammonia ( $\mu\text{M}/\text{g}$ )	Recovery of added ammonia (%)
1	30	5	36	105
2	16.25	10	26	99.04
3	40	10	50	100

tion of corresponding species in the form of respective salts. Nitrite has interfered seriously in this method due to its oxidative peak potential i.e. +1.25 V at bppg electrode. The nitrite interference has been overcome by the addition of small quantity of sulphamic acid to the soil extract before the quantification of ammonia using AQ composite electrode (Table 2).

#### 4. Conclusions

A simple strategy has been followed to develop a modified electrode using glassy carbon spheres functionalized with anthraquinone moieties by the reduction of corresponding diazonium salts in presence of hypophosphorous acid as a reducing agent. The direct oxidation of ammonia at anthraquinone modified electrode provides a simple and sensitive protocol for the measurement of ammonia at lower concentration from aqueous environment. The modified electrode has been applied to determine trace levels of ammonia present in the natural samples like human urine and soil extract samples. This protocol can be used as an alternative to the existing methods in ammonia quantification from a variety of matrices.

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