Modified Ultra Micro-Carbon Electrode for Efficient Ammonia Sensing for Water Quality Assessment

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Abstract—Ammonia is one of the most prominent and hazardous water pollutants; hence its selective and sensitive detection in water is crucial for monitoring water quality and determining its usability. In the present work, a simple, cost-effective electrochemical sensor for the detection of ammonia is presented. Multi-walled carbon nanotubes modified ultra-micro-carbon thread electrode (UME/MWCNT) has been realized. The electro-catalytic activity of ammonia is studied by voltammetry and amperometry techniques and the results are presented. The microscopic characterization of UME/MWCNT for surface morphology analysis was also carried out. Further, the UME/MWCNT based electrochemical sensor was tested for its practical application by exploring various parameters like the effect of scan rate, pH and interference from co-existing bio-chemicals like nitrate, nitrite, phosphate, hydrazine, H_2O_2, uric acid, ascorbic acid and dopamine along with real sample analysis. The developed sensor can efficiently detect ammonia in a linear range of 10 μM to 1 mM which is well within the permissible safe drinking water limit. The limit of detection (LoD) and limit of quantification (LoQ) obtained for the developed sensor were 8.69 μM and 26.33 μM respectively. The negligible interference, good reproducibility, and appreciable recovery values indicated the potential of the developed UME for real-time ammonia detection. As a flexible electrode, UME can be further modified and fabricated as a microfluidic or a miniaturized device for a portable electrochemical sensing platform in future.

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Satish Kumar Dubey is with the MEMS, Microfluidics and Nanoelectronics (MMNE) Laboratory, Hyderabad 500078, India, and also with the Department of Mechanical Engineering, Birla Institute of Technology and Science (BITS) Pilani, Hyderabad 500078, India.

Index Terms—Ammonia, carbon thread, multi-walled carbon nanotube (MWCNT), ultra-microelectrode (UME), electrochemical.

I. INTRODUCTION

ACCORDING to the World Health Organization (WHO), 80% of the prevailing diseases are waterborne and $\sim$3% of the overall fatalities across the globe are due to unhygienic water consumption [1]. Ammonia is one of the most common water pollutants and high levels of ammonia in water may lead to yellow fumes and foul odor in the water bodies. The permissible safe and tolerable level of ammonia in water is 0.5 ppm (approximately 29 μM) [1]. Increased level of ammonia concentration can cause serious illnesses like kidney ailments, liver diseases like hepatitis, Reye syndrome, and may even lead to birth disorders in some cases [2]. Additionally, high levels of ammonia cause growth of algae in water bodies and which leads to eutrophication. The major sources contributing to ammonia are agricultural wastes (fertilizers) and industrial wastes. Hence, it becomes necessary for the detection and quantification of ammonia concentration in water bodies. This also helps in assessing quality of the water body as ammonia is one of the high risk water pollutant.

The conventional approaches to detect ammonia in water samples are either by solid-state methods or optical methods [3]. The solid-state method involves metal oxide-based [4]–[6] conducting polymer [7]–[10], electrochemical-based [11]–[14] and field-effect transistor [15]–[17] type sensors, whereas the optical methods involve tunable laser absorption spectroscopy, non-dispersive infrared, cavity ring-down spectroscopy and photoacoustic spectroscopy [18]–[21]. Since in the majority of applications, remote monitoring of water quality is crucial, solid state-based methods are more convenient than optical methods. In solid state-based metal oxide sensors, metal oxides like TiO_2, SnO_2, ZnO are used for sensing various gases with added advantages like low cost, flexibility [22], miniaturization, etc. Despite such benefits, the key disadvantage is the selectivity in detecting a particular substance from the mixture. This makes electrochemical-based analysis a more popular approach for sensing. In the electrochemical

TABLE I
LITERATURE REPORTS ON AMMONIA SENSING

Electrode	Linear Range (μM)	LoD	Technique	Real sample	Ref
Copper composite @ CNT	3 to 100	3.47 μM	Differential pulse voltammetry	Tap water	[35]
Silver wire@ polyaniline (PANI)	0.1 to100	-	Cyclic Voltammetry	Wastewater	[37]
Electrodeposition of Platinum-Polypyrrole on Ni Foam	0.5 to 400	37 nM	Voltammetry	Artificial water sample	[38]
Carbon nanotubes modified by oxygen plasma treatment	-	10 nM	X-ray photoelectron Spectrometry	Artificial water sample	[39]
Enhanced by PANI/TiO$_2$ Nanocomposites	3 to 500	2.14 μM	-	-	[40]
SnO$_2$-deposited copper electrode	-	-	Voltammetry	Water sample	[41]
Carbon thread coated with MWCNT	10 to 1000	8.69 μM	Voltammetry	Lake water	This work

methods reported [23], [24], various nanoparticles [25], [26], like carbon nanosheets [27], [28], poly-aniline [29], platinum nanosheets, etc., are deposited on the electrode surface for better electrical conductivity [30], improved sensitivity, and selectivity [31]–[33].

In a recent study, nanosheets (Ni(OH$_2$)) were deposited on carbon cloth by solvothermal method to form (Ni(OH$_2$)) – CC, and then platinum sheets were deposited by amperometric technique to form Pt-(Ni(OH$_2$))–CC [34]. Further, researchers have used carbon nanotube (CNT)/copper composite paste electrodes to demonstrate the detection of ammonia [35]. A thin film of an ionic liquid was used as an electrolyte and a flattened micro-sized electrode was fabricated to form a sensor platform in [25]. This electrochemical sensor effectively detected ammonia of 1 ppm concentration at 25°C, neutral pH, and 1 atm conditions [36]. A summary of the few remarkable approaches reported in the literature for electro-chemical detection of ammonia in water samples is presented in Table I.

In this work, a three-electrode system is proposed for the detection of ammonia, in which an ultra-micro carbon thread modified with multiwalled carbon nanotube (MWCNT) designated as UME/MWCNT is used as a working elec-trode. The presented UME electrode is tested for its stabil-ity and repeatability. A real sample analysis is performed using the lake water to validate the efficacy of the proposed sensor.

II. EXPERIMENTAL PROCEDURE

A. Materials and Reagents

Anhydrous monobasic Sodium Phosphate (NaH$_2$PO$_4$), Dibasic Sodium Phosphate dihydrate (Na$_2$HPO$_4$.2H$_2$O), and Ammonium chloride (NH$_4$Cl) were acquired from AVRA chemicals. The DI water, used throughout the experiment, was from Milli-Q (18.2) MΩ.cm. Scanning Electron Micro-scope (SEM) characterization was performed using the Apreo scanning electron microscope from Thermo Fisher Scientific, Massachusetts, USA. MWCNTs, with a purity of approxi-mately 95%, were procured from NanoLab Inc. (Brighton, MA). The carbon thread was acquired commercially from Fuel

Cell store, Texas, USA. All the other common chemicals and reagents of analytical grade were used.

B. Ultra-Micro–Electrode (UME) Preparation

The UME was prepared by taking 2 mg of MWCNT in 500 μL of 99.9 % pure ethanol. The proper dispersion of MWCNT was achieved by probe sonicating the mixture for 15 minutes with a start and stop of 30 seconds each. After that, the evenly dispersed MWCNT mixture was drop cast on carbon thread homogeneously, and later oven-dried at a temperature of 60°C for 10 minutes. Fig. 1 (a) demonstrates the procedure for the preparation of UME with MWCNT and Fig. 1 (b) shows the electrochemical sensing setup of ammonia and the possible reaction mechanism of ammonia with modified UME surface.

C. Electrolytic Solution Preparation

0.1 M of phosphate buffer solution (PBS) of pH 7 was prepared. For the preparation of ammonia solution, weighed amount of NH$_4$Cl salt was homogeneously dissolved in pH 7 PBS. 5 mM K$_3$[Fe(CN)$_6$] in 1 mM KCl was prepared.

III. RESULTS AND DISCUSSION

A. Morphological and Electrical Characterization

SEM characterization was performed to understand the distribution of MWCNT on the surface of carbon thread. The images were captured at the same level of magnification of 500 nm for further comparison. Fig. 2 (a) and Fig. 2 (b) show the morphological behavior of UME before and after the surface modification using MWCNT. The even distribution of MWCNT on carbon thread surface is also clearly evident from Fig. 2 (b).

In similar lines, to understand the electron transfer behavior, electrochemical characterization was performed. Herein, 5 mM K$_3$[Fe (CN)$_6$] with 1 mM KCl as a supporting electrolyte was taken and cyclic voltammetry (CV) was performed at 50 mV/s, for 10 cycles in a potential window of −1 V to +1 V. As it can be seen in Fig. 3 (a), the UME alone
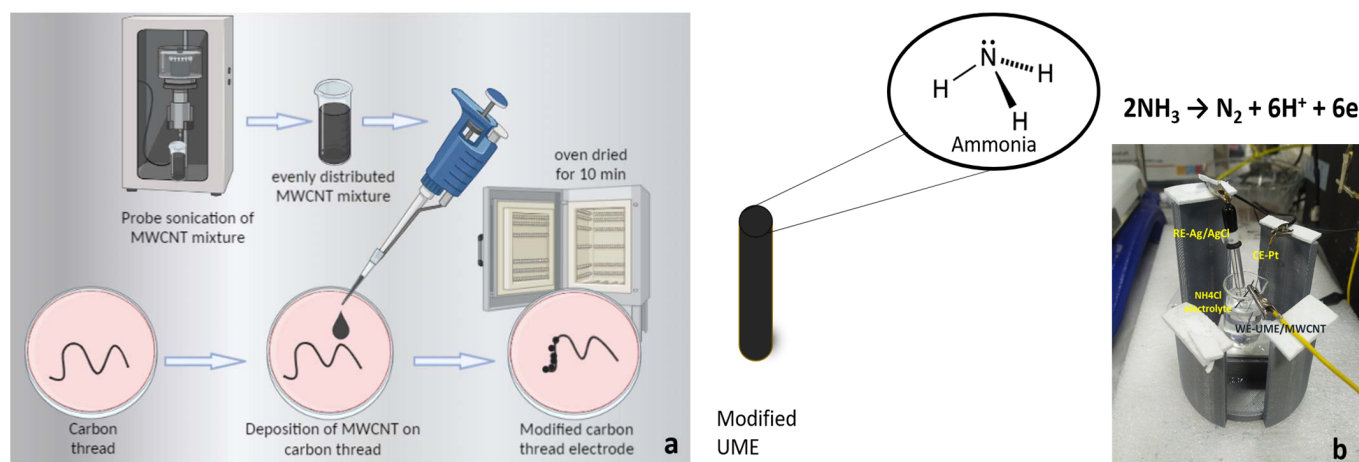
Fig. 1. (a) Schematic representation of UME/MWCNT fabrication. (b) Electrochemical sensing setup of ammonia and the reaction mechanism of ammonia with modified UME surface.
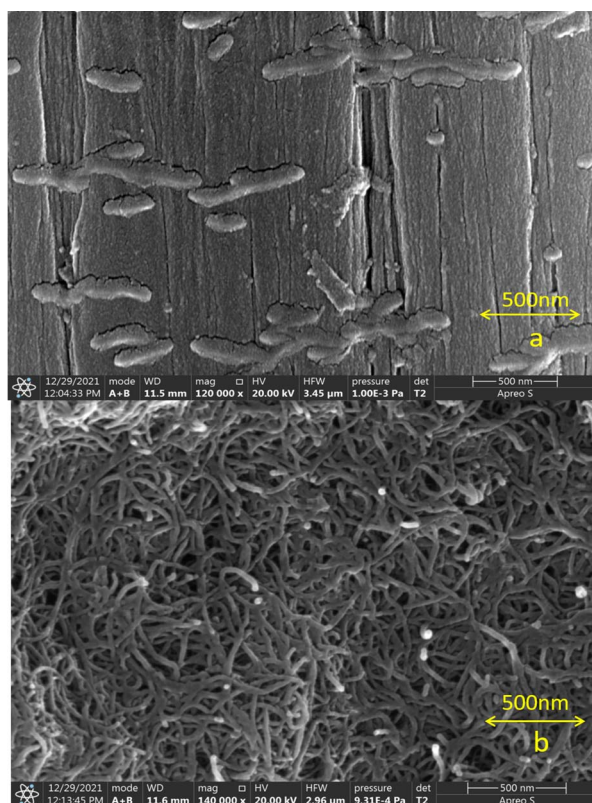

Fig. 2. (a) SEM characterization of carbon thread (b) Carbon thread with MWCNT modification.

Fig. 3. (a) Comparative CV response of carbon thread and modified UME electrode in $K_3[Fe(CN)_6]$ solution at 25°C and 1atm (b) EIS curve of carbon thread and modified UME electrode along with Randel's circuit.

(without MWCNT) provided lesser current density than the modified UME/MWCNT. A stable redox peak at E'= 0.061 V was observed with $\Delta E_p = 0.187$ V. The modification with MWCNT gave enhanced redox peak current and lesser peak-to-peak separation ($\Delta E_p = 0.187$ V) thereby improving the electron transfer mechanism.

The Electron Impedance Spectroscopy (EIS) study was also performed with and without MWCNT modified UME in 5 mM $K_3[Fe(CN)_6]$ with 1 mM KCl as a supporting electrolyte. Fig. 3 (b) clearly depicts that the modified and unmodified
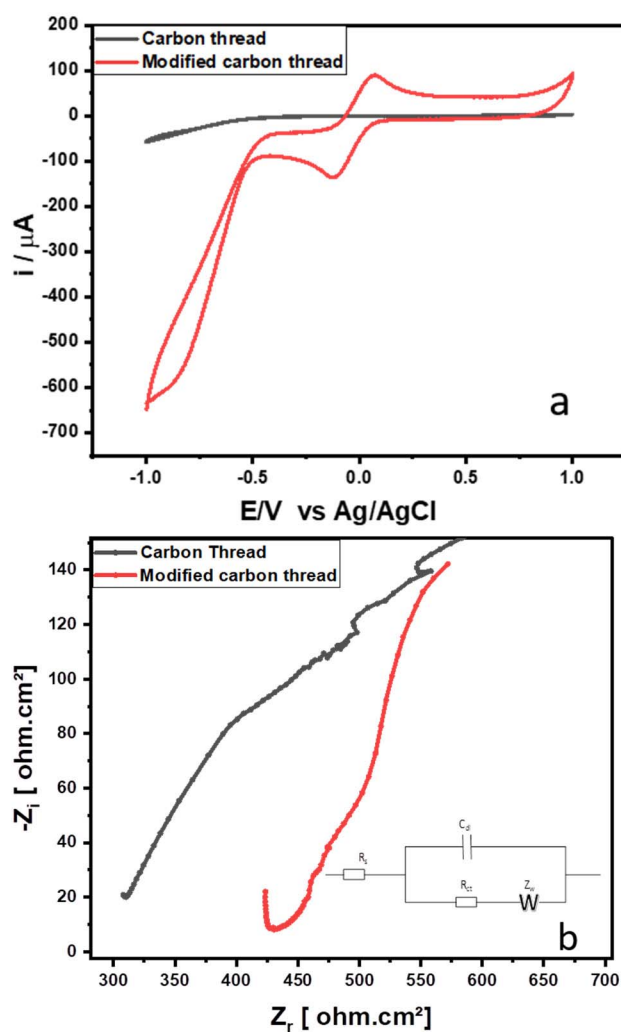
UME showed semicircle behavior with varied R_{ct} (charge transfer resistance) values. The R_{ct} for UME alone was 3.89 Ω

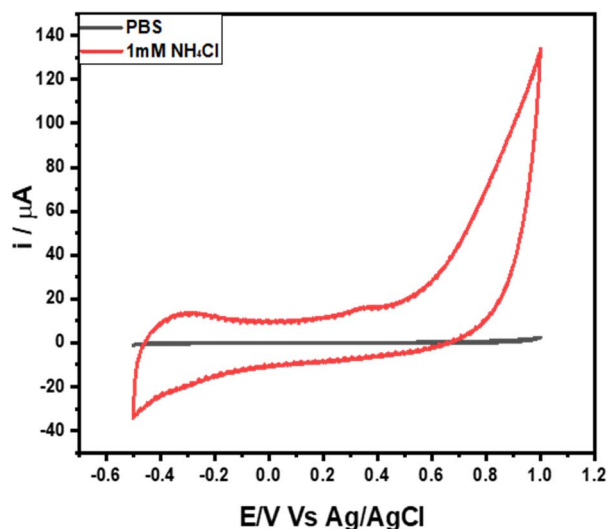Fig. 4. Comparative CV responses of UME/MWCNT in PBS and 0.5 mM ammonia in pH 7 PBS at 10 mV/s.
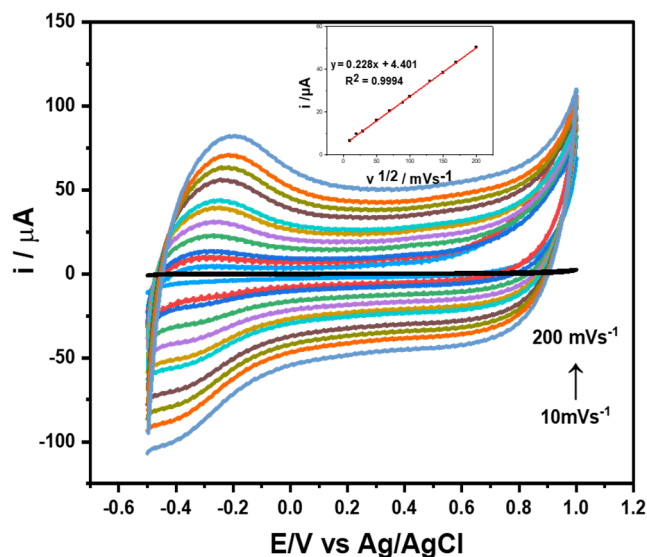

Fig. 5. CV responses of UME/MWCNT at various scan rates from 10 mVs^{-1} to 200 mVs^{-1} in 0.5 mM ammonia in pH 7 PBS. Inset is the linear plot of current v/s v$^{1/2}$.

whereas, for UME/MWCNT was 435 Ω, further proving the enhanced electron transfer behavior [42].

B. Electro-Catalytic Behavior

To examine the electro-catalytic behavior of UME/MWCNT when exposed to ammonia, the prepared electrode was subjected to CV analysis at 10 mV/s scan rate, number of electrons (n = 2), in a potential window of -0.5 V to $+1$ V in 0.5 mM ammonia solution taken in pH 7 PBS at room temperature. As it can be observed from Fig. 4, UME/MWCNT gave no significant response in PBS alone, whereas a sharp oxidation current of 16.32 μA at the $E^0 = 0.37$V was observed in the presence of ammonia indicating the electro-catalytic oxidation of ammonia. Similarly, a control experiment was performed wherein bare UME was exposed to ammonia gave negligible response, henceforth, proving the role of MWCNT in detection of ammonia.

C. Scan Rate Effect

The consequence of potential scan rate on UME/MWCNT with ammonia in pH 7 PBS was investigated by varying the scan rate from 10 mV/s to 200 mV/s to understand the optimum electron transfer mechanism. The obtained CV responses are presented in Fig. 5. The subsequent increase of cathodic peak current as the scan rate increases can be clearly noted from Fig. 5. The corresponding linear fit plot of the maximum current v/s the scan rate shows that the modified electrode has a surface-confined electron transfer behaviour as per Randel's Sevcik equation given in (1) [43].

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} v^{1/2} C \qquad (1)$$

where n = 2, A is the surface area of the electrode (410 mm^2), D is the coefficient of diffusion, v is the scan rate (0.01 V/s) and C is the concentration of the NH$_4$Cl (1 mM). Using (1), the diffusion co-efficient, D is calculated as 8.5×10^{-6} cm^{2}s^{-1}.
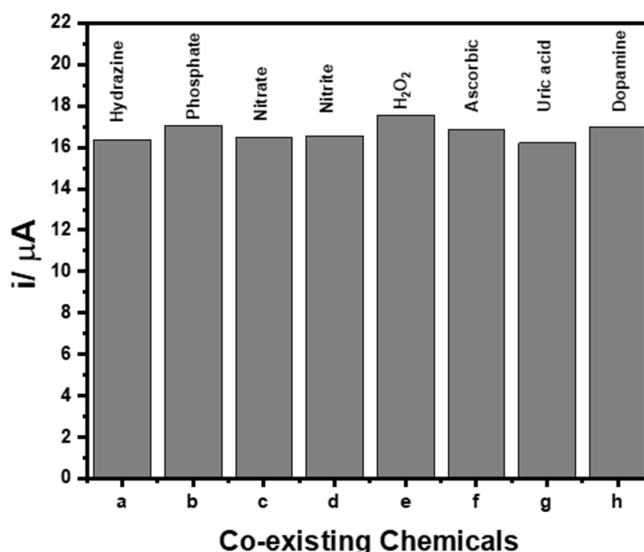

Fig. 6. Interference effect from co-existing chemicals like Hydrazine, Phosphate, Nitrate, Nitrite, H$_2$O$_2$, ascorbic acid, uric acid and dopamine with UME/MWCNT electrode.

D. Interference Effect

In general, in real water sample, many other chemicals, like nitrate, nitrite H$_2$O$_2$, hydrazine, phosphate, uric acid, dopamine and ascorbic acid are also present and therefore may cause interference during ammonia detection. Hence, the selectivity of the UME/MWCNT towards ammonia has been evaluated. 0.5 mM of each of the interfering agents were tested by exposing it to the fabricated electrode and CV was performed in the potential window of -0.5 V to 1 V, at a scan rate of 10 mV/s. Fig. 6 shows that there is no significant peak is observed with other analytes whereas, a characteristic peak of ammonia was seen at $E^0 = 0.37$V.
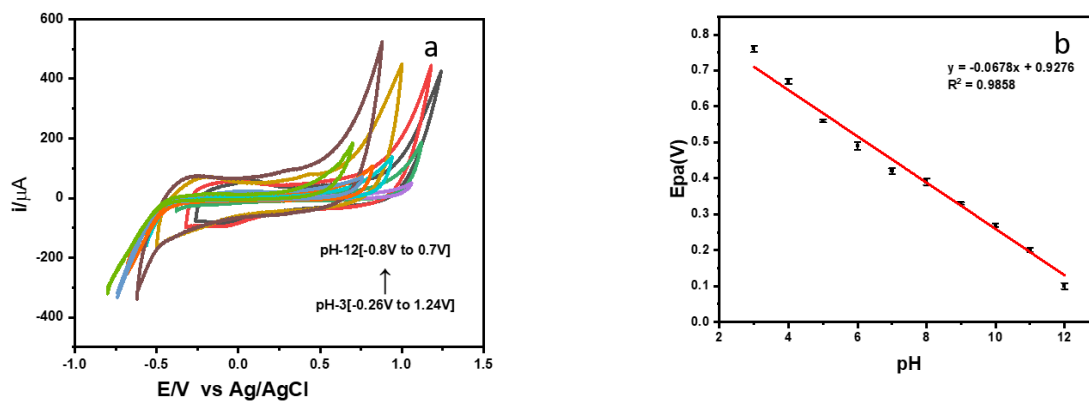
Fig. 7. (a) CV response of UME/MWCNT electrode for pH values ranging from 3 to 12. (b) Calibration plot showing E_{pa} v/s pH with error bars.

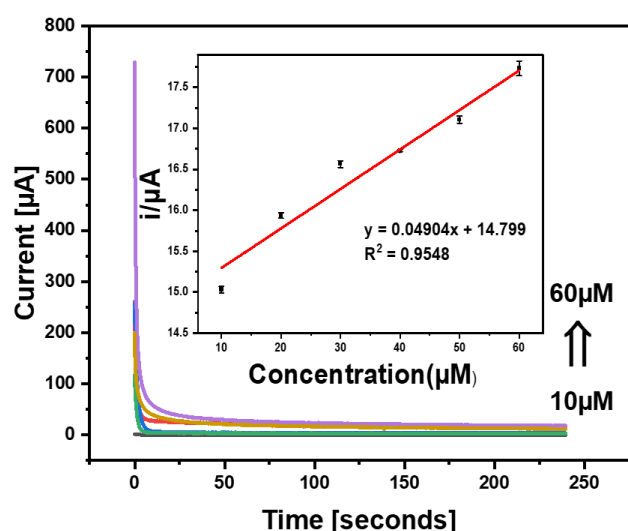Fig. 8. Chrono-amperometry response for of various concentrations for LoD study. Corresponding calibration plot for oxidation peak currents ipa vs v1/2.

Fig. 9. Repeatability study of the developed sensor using various electrodes with a concentration of 0.5 mM of ammonia.

E. Influence of Solution pH

The influence of solution pH on the UME electrode was studied by preparing various pH solutions ranging from pH values of 3 to 12 of 0.5 mM ammonia in PBS and the results are plotted and shown in Fig. 7 (a). The calibration plot for the same is plotted between pH and peak potential and is shown in Fig. 7 (b). The variation in the pH from acidic to basic did not change the value of the peak current which confirms that the UME electrode is pH independent [44].

F. Concentration Effect

The consequence of increase in concentration was studied by chronoamperometry from 10 μM to 1 mM at 0.37 V. Fig. 8 clearly shows that there is a substantial rise in the amount of current from lower to higher concentration. The respective calibration plots gave LoD and LoQ as 8.69 μM and 26.33 μM respectively.
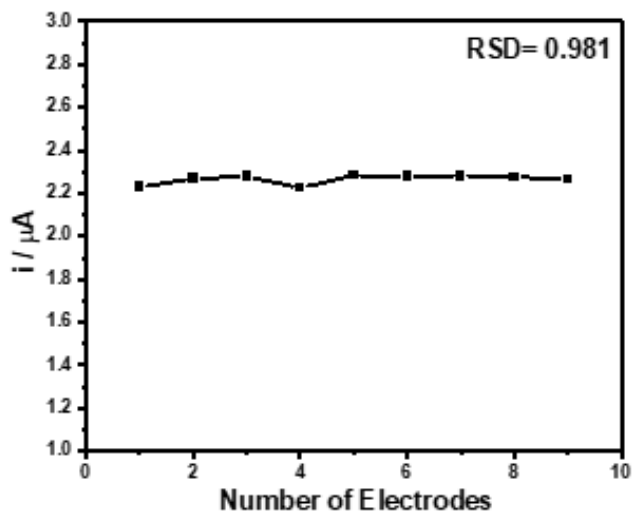
TABLE II
REAL SAMPLE ANALYSIS

Sample	Ammonia added (μM)	Ammonia Recovered (μM)	Recovery (%)
Pond water	100	102.4	102.4
	200	214.1	107
	300	293	97.6

G. Sensor Reproducibility and Stability

The reproducibility of the proposed UME electrode is tested with nine different fabricated electrodes in 0.5 mM ammonia solution and the relative standard deviation (RSD) is found to be 0.981 as shown in Fig. 9. The stability study was also performed for a period of 7 days and the graph is shown in Fig. 10. From the results it is observed that the proposed sensor has a good reproducibility and stability towards ammonia sensing.
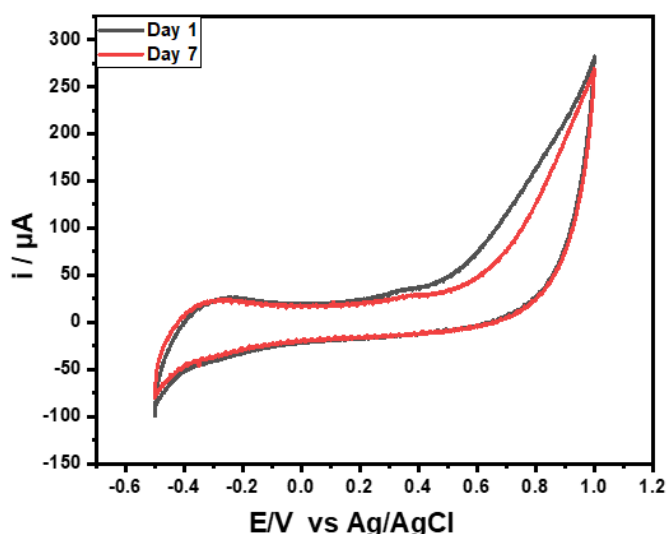
Fig. 10. Stability study of the proposed system for a period of 7 days with a concentration of 0.5 mM ammonia.

H. Real Sample Analysis

In order to understand the practicality of the proposed sensor in ammonia detection, a real sample testing was performed using pond water from BITS Pilani Hyderabad Campus. The standard addition method was used, where 10 ml of pond water was taken and 100 μM of ammonium chloride was added by the method of spiking for three subsequent times. The concentrations were chosen from the linear range of the fabricated UME, wherein 100 μM of NH$_4$Cl was spiked in real water sample solution. The results are summarized in Table II, manifesting appreciable recovery values.

IV. CONCLUSION

This work presents the utilization of modified carbon thread as working electrode for sensing ammonia while employing Pt and Ag/AgCl as a counter and reference electrodes respectively. A significant increase in peak current has been observed for various concentrations utilizing CV. The effect of pH, scan rate and concentration were also studied and the results have been presented. Further, reproducibility and stability analysis are also performed. The linear range is found to be from 10 μM to 1 mM and the LoD obtained is 8.69 μM. The electrode was subjected to interference test with co-existing water pollutants and it was found that the device is not interfering with any other electrolyte. Further, real sample analysis was conducted using pond water and the proposed sensor showed good recovery. Hence, the proposed sensor can be effectively utilized for real-time detection of ammonia in water. In future, the proposed sensor can be fabricated as a device for point-of-care applications.

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