

Highly Sensitive Amperometric Sensor for Nitrobenzene Detection Using Functionalized Multiwalled-Carbon Nanotubes Modified Screen Printed Carbon Electrode

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We have developed a cost-effective screen printed carbon electrode (SPCE) modified with functionalized multiwalled carbon electrode (*f*-MWCNT) for the sensitive electrochemical determination of nitrobenzene (NB). First, *f*-MWCNT was prepared through acid treatment and characterized by scanning electron microscopy, Energy-dispersive X-ray spectroscopy and electrochemical impedance spectroscopy. Next, it was dispersed in nafion and the resulting solution was drop casted onto the screen printed carbon electrode (SPCE) in order to prepare modified electrode. The *f*-MWCNT/SPCE showed excellent electrocatalytic ability towards nitrobenzene. The fabricated electrode sensitively detects low concentrations of nitrobenzene and the detection limit is obtained as 45 nM. The linear range of the sensor is 50 nM to 1170 μ M and the sensitivity is 0.6685 μ A μ M cm⁻². Moreover, the electrode delivers satisfactory stability, repeatability and reproducibility. The electrode is successful in the determination of nitrobenzene in spiked human urine sample reveals its potential practical applicability.

Keywords: Nanotechnology, carbon nanomaterials, thin films, one dimensional material, environmental safety, toxic compounds,

1. INTRODUCTION

Nitrobenzene (NB) is one of the noteworthy solvent and also largely used as a raw material in industrial applications [1, 2]. It has widespread applicability in the preparation of several important chemical, such as dyes, aniline, plastics, explosives, pesticides and pharmaceuticals [2]. However, NB is highly toxic, persistent and carcinogenic [3]. Because of its extensive usage, its release to soil and water is a big threat for environmental safety. NB is listed as one of the 129 priority pollutants and its maximum permissible concentration in wastewater is 1 mg/L in order to control water safety [4]. Therefore, several analytical methods and approaches have been developed for the sensitive determination of NB [5, 6]. Although traditional analytical methods such as chromatography and mass spectroscopy are good in accuracy, they are laborious, expensive and require highly trained professionals. On the other hand, electrochemical methods are cheaper, portable, simple, easy-to-use, and consume low power [7–10]. But, the use of unmodified working electrodes led to large overpotential, low sensitivity and poor selectivity. Suitable chemical modifiers on the working electrode surface have the ability to solve the problems associated with unmodified electrodes in order to develop sensitive electrochemical determination platforms [11]. Therefore, numerous specifically designed chemically modified electrodes are reported for the determination of NB which includes, electrochemically activated graphite electrode [12], poly (3, 4-ethylenedioxythiophene)/carbon nanotube nanocomposite modified carbon paste electrode [13], macro-/meso-porous carbon materials [14], Pt nanoparticles/macroporous carbon hybrid nanocomposites [15], Ag nanoparticles/functionalized graphene [16], gold nanoparticles decorated mesoporous silica microspheres [17] and nephrolepis leaf like silver microstructure [18] etc.,

Carbon based nanomaterials such as, multiwalled carbon nanotubes (MWCNTs), graphene, graphene nanoribbons, fullerene, activated carbon are hot materials in nanotechnology due to their excellent physicochemical properties [19–22]. Among them, MWCNTs have excellent electrical conductivity, mechanical stability and electrocatalytic ability and they are proved to be excellent electrode materials for sensing applications [23–29]. However, MWCNTs are hydrophobic and hence they are unable to form aqueous dispersion [30–34]. Acid treatment of MWCNTs led to the formation of functionalized MWCNTs which can easily dispersed in water [35–37]. In this work, we have prepared functionalized MWCNTs (*f*-MWCNTs) and employed it to prepare cheaper working electrode for the determination of NB. The *f*-MWCNTs mixed with nafion was deposited on the screen printed carbon electrode (SPCE) and used for NB sensing. Notably, SPCE is the currently known cheaper and reproducible electrodes for sensor applications and hence we adopted SPCE in our work [38–39]. The advantages of SPCE technology in combination with excellent electrocatalytic ability of *f*-MWCNTs make this electrode suitable for sensitive determination of NB in real samples.

2. EXPERIMENTAL

2.1 Chemicals and Apparatus

Multiwalled carbon nanotubes (MWCNTs) (bundled > 95%), nitrobenzene (NB), Nafion (Nf) and all other reagents including solvents were purchased from Sigma-Aldrich and used as received.

Electrochemical studies were performed in a conventional three electrode cell using modified screen printing carbon electrode (SPCE) (Bioanalytical Systems, Inc., USA) as a working electrode (area 0.071 cm^2), saturated Ag|AgCl (saturated KCl) as a reference electrode and Pt wire as a counter electrode. Prior to each electrochemical experiment, the electrolyte solutions were deoxygenated with pre-purified nitrogen for 15 min unless otherwise specified. The supporting electrolyte used for the electrochemical studies was 0.1 M phosphate buffer (pH 7.0) prepared using sodium dihydrogen phosphate and disodium hydrogen phosphate.

All the electrochemical measurements were carried out using CHI 1205A electrochemical work station (CH Instruments, Inc., U.S.A). Surface morphological studies were carried out using Hitachi S-3000 H scanning electron microscope (SEM). Energy-dispersive X-ray (EDX) spectra were performed using Horiba Emax x-act (Sensor + 24 V=16 W, resolution at 5.9 keV). EIM6ex Zahner (Kronach, Germany) was used for electrochemical impedance spectroscopy (EIS) studies.

2.2 Preparation of *f*-MWCNTs and *f*-MWCNTs/Nf

About 20 mg of MWCNTs were added to the solution consisting mixture of 30 mL H_2SO_4 and 10 mL HNO_3 and subsequently ultrasonicated for 3 h. Then, the solution was transferred to a round-bottom flask and refluxed at 80°C for 3 h. Finally, the solution was cooled, filtered, washed and dried. The *f*-MWCNTs powder was redispersed in water (1 mg mL^{-1}). 50 μL of 0.5% Nafion and 70 μL of *f*-MWCNTs aqueous solution were mixed and ultrasonicated for 20 min to form *f*-MWCNTs/Nf composite.

2.3 Preparation of modified SPCE

First, the surface of SPCE was pre-cleaned by voltammetric cycling between -1.0 V and 1.2 V , in 0.1 M phosphate buffer (pH 7.0). Then, 5 μL dispersion of *f*-MWCNTs/Nf composite is drop casted on the pre-cleaned SPCE surface and dried at ambient conditions.

3. RESULTS AND DISCUSSION

3.1 Characterizations

Figure 1 shows the SEM images of MWCNTs (1A) and *f*-MWCNTs (1B). The images clearly revealed the presence of typical tubular morphology of carbon nanotubes and this type of morphology is consistent with previously reported works on *f*-MWCNTs [40, 41]. The EDX profile of the *f*-MWCNTs displays elements for carbon and oxygen (Figure 1C) which confirmed the presence of oxygen functionalities formed at the MWCNTs during functionalization. EIS is an efficient tool to examine the electrical and interfacial properties of the modified films on the electrode surface [42]. Figure 1D displays the EIS curves obtained for unmodified SPCE (a), *f*-MWCNTs/SPCE (c) and *f*-MWCNT/Nf/SPCE (b) using $\text{Fe}(\text{CN})_6^{3-/4-}$ as redox mediator. The charge transfer coefficient (R_{ct})

values obtained for the unmodified SPCE, *f*-MWCNTs/SPCE and *f*-MWCNT/Nf/SPCE are 600.14, 100.65 Ω and 326.51, respectively. The R_{ct} value obtained for *f*-MWCNT/SPCE is about six times lower than the unmodified SPCE which indicating that the charge transfer resistance at *f*-MWCNT/SPCE is lowered compared with unmodified SPCE. After coating of Nf, the electrical conductivity of the *f*-MWCNT/Nf/SPCE electrode decreases because of insulating property of Nf. However, Nf is an efficient polymer to enhance the electrocatalysis of NB and coating of Nf provide good anti-interference ability to the electrode [43].

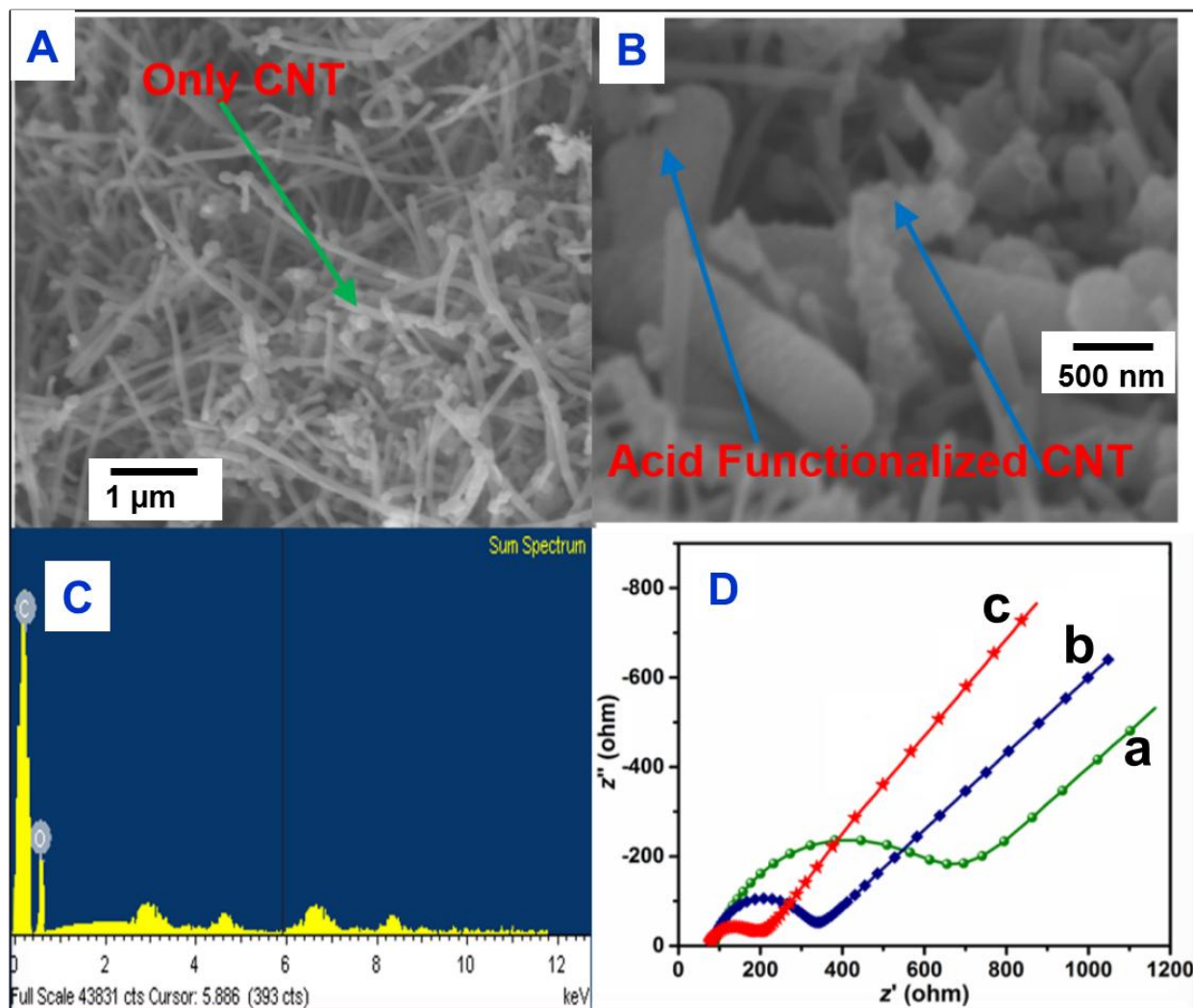
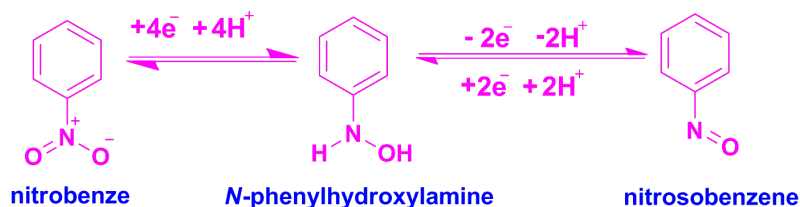


Figure 1. SEM images of MWCNTs (A) and *f*-MWCNTs (B). (C) EDX profile of *f*-MWCNTs. EIS curves of unmodified SPCE (a), *f*-MWCNTs/SPCE (b) and *f*-MWCNT/Nf/SPCE (c)

3.2 Electrocatalysis of NB at *f*-MWCNTs/Nf/SPCE

Electrocatalytic ability of the *f*-MWCNTs/Nf/SPCE towards NB reduction has been investigated in phosphate buffer (pH 7) and the results were compared with control electrodes (Figure 2). The mechanistic pathway of NB electrocatalytic is given in scheme 1. As shown in the scheme,

first NB undergoes irreversible reduction to *N*-phenylhydroxylamine. In the next step, *N*-phenylhydroxylamine oxidizes to nitrosobenzene and this reaction is reversible and hence it can undergo reduction back to *N*-phenylhydroxylamine [44]. Therefore, three voltammetric peaks are expected and the voltammogram of *f*-MWCNTs/Nf/SPCE exhibits with these voltammetric peaks (curve c, Figure 2)



Scheme 1. Mechanistic pathway of nitrobenzene reduction

However, the cathodic peak current responsible for the reduction of NB to *N*-phenylhydroxylamine is more sensitive and hence we have adopted this reaction for developing sensitive sensor for NB. At *f*-MWCNTs/Nf/SPCE, NB has produced a sharp reduction peak at -0.58 V. The overpotential for NB reduction at *f*-MWCNTs/Nf/SPCE is 100 mV lower than the unmodified SPCE which revealed accelerated NB reduction at the modified electrode. Besides, the reduction peak current obtained at *f*-MWCNTs/Nf/SPCE is about 8 and 11 times higher than the *f*-MWCNTs/SPCE and unmodified SPCE, respectively. The electrocatalytic activity of the modified electrode is mainly due to the absorption of NB through π stacking interaction between benzene ring of NB and aromatic moieties of *f*-MWCNTs [3, 45]. Also, the oxygen functionalities created on the MWCNTs also significantly accelerates the electrocatalysis. Figure 2B displays the voltammograms obtained at *f*-MWCNTs/Nf/SPCE towards different concentrations of NB. The reduction peak current linearly increases with respect to NB concentration and the plot between reduction peak current and concentration of NB is exhibited linear curve (Figure 2C) which indicating the occurrence of reduction without fouling on the electrode surface.

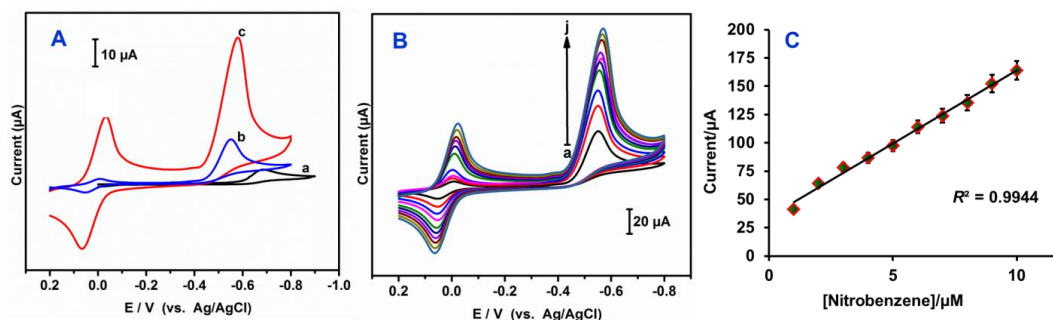


Figure 2. (A) Cyclic voltammograms obtained at bare SPCE (a), *f*-MWCNTs (b) and *f*-MWCNTs/Nf/SPCE in 0.1 M phosphate buffer solution (pH 7.0) containing 2 μM NB. Scan rate = 50 mV s^{-1} . (B) Cyclic voltammograms obtained at *f*-MWCNTs/Nf/SPCE towards different concentrations of NB (a = 1, b = 2, c = 3, d = 4, e = 5, f = 6, g = 7, h = 8, i = 9 and j = 10 μM). (C) Calibration plot: Current (μA) vs. [Nitrobenzene] (μM)

Next, the effect of scan rate on the reduction of NB was studied by applying different scan rates from 20 to 200 mVs^{-1} (Fig. 3A). The reduction peak current is linearly increases as the scan rate increases. The plot between reduction peak current and scan rate exhibits linear relationship which is a characteristic behaviour of surface-confined diffusion controlled electrocatalytic process (Fig. 3B) [42,46].

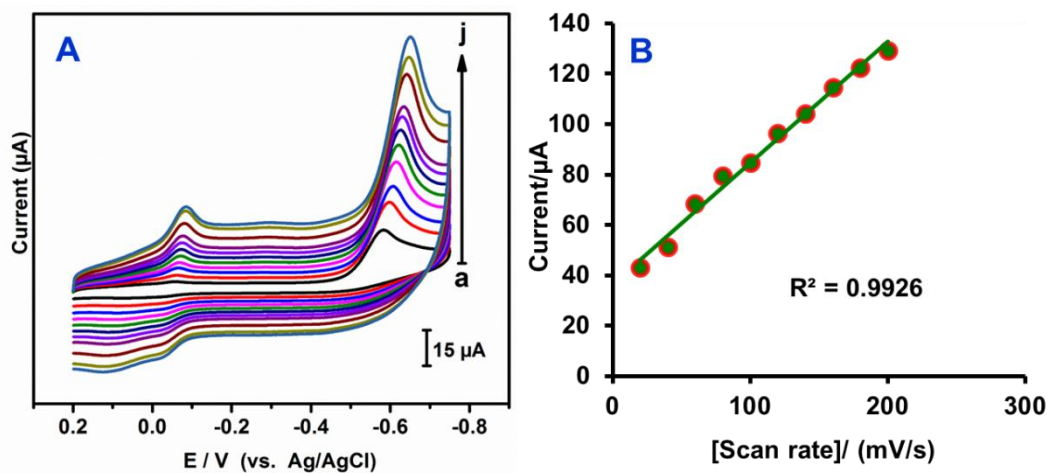


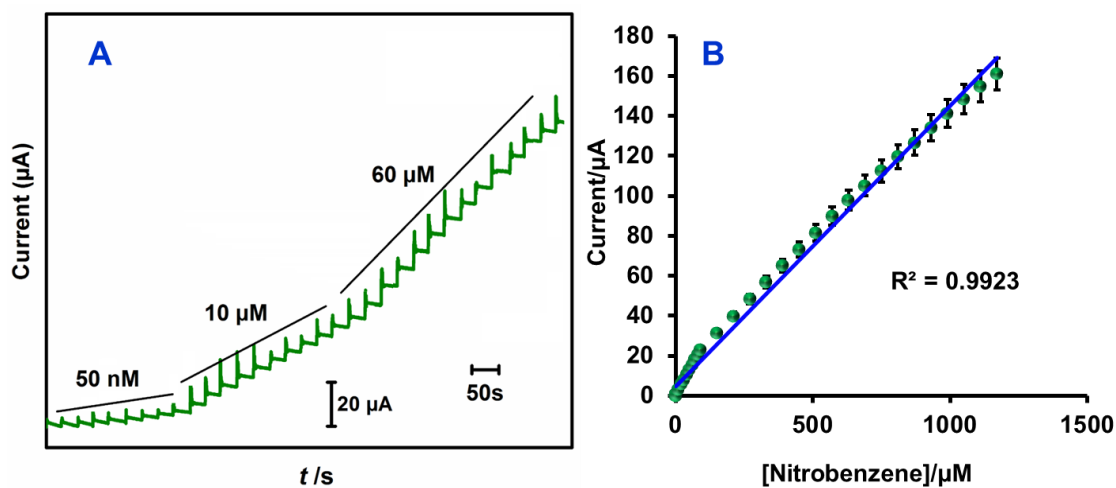
Figure 3. Effect of the scan rate on the NB reduction: Cyclic voltammograms obtained at f -MWCNTs/Nf/SPCE at different scan rates from 20 to 200 mV s^{-1} . (B) Scan rate (mV/s) vs. current (μA)

3.3 Determination of NB

Figure 4A represents the amperometric curves obtained at f -MWCNTs/Nf/SPCE for sequential additions of NB into phosphate buffer (pH 7). The applied potential was -0.58 V and the rotation speed of electrode was 1500 RPM. A sharp increase in the amperometric current is observed for each addition and the response current reached 95% steady-state current within 5 s of NB injection. Thus, the fabricated electrode delivered prompt responses and allowed fast sensing of NB. The concentration dependent linear plot displayed good linearity (Fig. 4B). The working concentration range was linear from 50 nM to 1170 μM with sensitivity of $0.6685 \mu\text{A}\mu\text{M}^{-1} \text{cm}^{-2}$. The detection limit is 45 nM. The limit of detection (LOD) was calculated as 0.015 μM . The LOD was calculated using the formula, $\text{LOD} = 3 s_b/S$ where, s_b is the standard deviation of ten blank measurements and S is the sensitivity [47, 48]. The excellent analytical parameters such as wide linear range, high sensitivity and low detection limit achieved at the f -MWCNTs/Nf/SPCE are revealing its great potential in the determination of NB. The sensor performance of the f -MWCNTs/Nf/SPCE in terms of linear range, sensitivity and detection limit is compared with previously reported NB sensors [2, 3, 13, 15, 17, 18, 49-51] (**Table 1**). As shown in the table, our sensor performance is either superior or comparable to the previous reports which authenticated the good performance of newly developed modified electrode. Besides, we use cheaper and highly reproducible SPCE technology which adds additional advantage to NB sensor.

Table 1. Comparison of sensor performance of *f*-MWCNTs/Nf film with previously reported chemical modifiers

Electrode modifiers	Linear range / μM	Detection limit / μM	Sensitivity / $\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$	Ref.
Ag NPs/reduced graphene oxide	0.5–900	0.261	0.836	[2]
AgNPs/poly-melamine/multi-walled carbon nanotube	20–1000; 1000–6000	0.55	–	[3]
poly(3,4-ethylenedioxythiophene)/CNTs	0.25–43	0.083	–	[13]
Pt NPs/macroporous carbon hybrid	1–200	0.050	6.93	[15]
Au decorated mesoporous silica microspheres	0.1–2500	0.015	0.348	[17]
Ag Microstructure	0.05–38.8	0.01	0.665	[18]
N-doped porous carbon	2–100	0.62	0.646	[49]
Green synthesized Au nanoparticles	0.1–600	0.016	1.01	[50]
Graphene oxide	0.1–120	0.02	–	[51]
<i>f</i> -MWCNTs/Nf	0.05–1170	0.045	0.6685	This work

**Figure 4.** Amperometric response of *f*-MWCNTs/Nf/SPCE towards each addition of NB into continuously stirred phosphate buffer (pH 7) at the rotation speed of 1500 RPM. $E_{\text{app}} = -0.58$ V.

3.4 Real sample analysis

Table 2. Determination of NB at *f*-MWCNTs/Nf/SPCE in water samples

Sample	Added (nM)	Found (nM)	Recovery (%)	* RSD (%)
Tap water	100	99.17	99.17	3.02
	200	197.73	98.86	3.40
River water	100	97.30	97.30	3.95
	200	198.49	99.24	4.25

* Relative Standard Deviation of three individual measurements.

Practical feasibility of the *f*-MWCNTs/Nf/SPCE is demonstrated in water samples. The water samples are collected from tap water and river water. Next, known amount of NB were spiked. The standard addition method was adopted to calculate found and recovery values and the results were summarized in Table 2. As given in the table, the fabricated *f*-MWCNTs/Nf/SPCE has shown recoveries in the range of 97.30–99.24%. The obtained ranges are satisfactory and hence the developed electrode has good potential to be used in real-time analysis of NB [52].

3.5 Stability, repeatability and reproducibility studies

In order to determine storage stability of the *f*-MWCNTs/Nf/SPCE, its electrocatalytic response to 100 nM NB was monitored every day. The electrode kept stored at 4°C when not in use. The electrode has delivered quick and sensitive amperometric responses to NB during two weeks of storage period. About 94.03% of initial response current was retained after one week of its use which indicates its high level of stability. Next, repeatability and reproducibility of the electrode are verified. The electrode exhibits appreciable repeatability with RSD of 4.11% for five repetitive measurements performed using single modified electrode. Similarly, the electrode exhibits good reproducibility with RSD of 3.95% for five independent measurements performed in five independent modified electrodes. Thus, the electrode has shown acceptable range of stability, repeatability and reproducibility which are consistent with previous reports [12, 18]

4. CONCLUSIONS

In summary, a cheaper and easily reproducible modified electrode, *f*-MWCNTs/Nf/SPCE nanocomposite is developed for the determination of NB. The composite is successfully characterized by SEM, EDX, EIS and CV methods. The modified electrode has shown comparatively better electrocatalytic performance to NB over control electrodes. Furthermore, the electrode delivered excellent amperometric sensing performance to NB and exhibited wide linear range (50 nM to 1170 µM) and low detection limit (45 nM). The other advantages of the electrode are repeatability, reproducibility and storage stability. Most importantly, the developed electrode has good practical applicability which has great potential in water safety management for NB screening.

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