A robust nitrobenzene electrochemical sensor based on chitin hydrogel entrapped graphite composite

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Abstract

An amperometric nitrobenzene (NB) sensor has been developed based on a glassy carbon electrode (GCE) modified with the composite of chitin hydrogel stabilized graphite (GR-CHI) composite. The physicochemical characterizations confirmed the formation of GR-CHI composite and was formed by the strong interaction between GR and CHI. Furthermore, GR-CHI composite modified GCE was used to study the electrochemical reduction behavior of NB by cyclic voltammetry (CV) and compared with GR and CHI modified GCEs. The CV results confirmed that GR-CHI composite modified electrode has high catalytic ability and lower reduction potential towards NB than other modified electrodes due to the combined unique properties of exfoliated GR and CHI. The GR-CHI composite modified electrode can able to detect the NB in the linear response range from 0.1 to 594.6 μM with the lower detection limit of 37 nM by amperometric *i-t* method. The selectivity of the sensor evaluated in the presence of nitroaromatic, biologically active and dihydroxybenzene compounds. The sensor shows appropriate practicality and good repeatability towards detection of NB in lab water samples.

Keywords: Exfoliated graphite; Chitin hydrogel; Nitrobenzene; Electro-reduction; Amperometry.

1. Introduction

Over the past decades, the detection of toxic nitroaromatic compounds has received significant attention owing to their serious harm and treat to human beings [1]. In particular, nitrobenzene (NB) is highly toxic carcinogenic nitroaromatic compound, has been widely used as a precursor for aniline, pesticides, azo dyes, explosives, and pharmaceuticals [2–4]. Despite of its high toxicity and carcinogenic nature, NB has certified as a Group 2B carcinogen by the United States Environmental Protection Agency (USEPA) [5]. In addition, the USEPA has stated that the high exposure of NB from its threshold limit (5 ppb) can result into the serious damage to the central nervous system, liver and kidney [3, 5]. Different analytical methods have been used so far for detection of NB, yet electrochemical methods have been found simple and sensitive than available chromatographic and spectrophotometric methods [6–8]. To date, many researchers have fabricated different chemically modified electrodes with improved sensitivity, detection limit and selectivity for determination of NB, while the unmodified carbon electrodes are not suitable due to poor selectivity and less sensitivity towards NB [9, 10]. Hence, the selective and sensitive determination of NB with low detection limit is of interest to the sensor development.

Graphite (GR) is an anisotropic abundant carbon material, has contain high number of active edge planes and inert basal planes [11]. Due to the closer arrangement of each GR sheets, it has showed poor electrochemical behavior and sensitivity in electroanalysis when compared to other GR forms such pyrolytic and edge plane GR [12, 13]. Hence, different modifications or pretreatments has been used to improve the electrochemical properties and selectivity of GR [11, 14]. Recently, we have reported that carbohydrate polymers entrapped GR has higher electron transfer ability than pristine GR and its performances have been found similar to graphene

analogous [15–17]. For instance, the β-cyclodextrin, chitosan and chitin (CHI) stabilized GR has showed enhanced electrocatalytic activity and high surface area than GR and its electrochemical behaviors have found similar to graphene-CHI composite [17]. Hence, in the present work we have used GR-CHI composite for sensitive and low level detection of NB. The reasons for choosing the GR-CHI composite for NB detection are; i) the strong interaction of CHI with GR lead to the exfoliation of GR sheets and result to the enhanced surface area than pristine GR, and ii) the CHI in GR-CHI composite could help the adsorption of more number of NB molecules than GR modified electrode. In addition, the GR-CHI composite is inexpensive and shows better analytical performances towards NB than previously reported expensive modified electrodes (please see **Table 1**).

2. Experimental

2.1. Materials and methods

Chitin from crab shells was received from Sigma-Aldrich. Graphite fine powder with an average diameter about > 20 μm and nitrobenzene were obtained from Sigma-Aldrich and used as received. The supporting electrolyte was phosphate buffer pH 7 (PBS) and was prepared using 0.1 M Na_2HPO_4 and NaH_2PO_4. All stock solutions were prepared using doubly distilled water.

Cyclic voltammetry (CV) and amperometry measurements were performed using a computerized CHI 750A electrochemical analyzer from CH instruments, U.S.A. model. Fourier transform infrared spectroscopy (FTIR) measurements were performed using a Thermo SCIENTIFIC Nicolet iS10 instrument. Scanning electron microscopy (SEM) images were acquired using Hitachi S-3000 H electron microscope. X-ray diffraction (XRD) studies were performed in a XPERT-PRO (PANalytical B.V., The Netherlands) diffractometer. Glassy carbon

electrode (GCE) with an apparent surface area of 0.08 cm^2 was used as a working electrode. Sat. Ag/AgCl and platinum wire were used as a reference and counter electrodes, respectively.

2.2. Preparation of GR-CHI composite and electrode modifications

The GR-CHI composite was prepared by our previously reported method [**17**]. Briefly, the stable CHI solution was first prepared by adding CHI (5 mg mL^{-1}) into the 5% acetic acid with the aid of sonication. The as-prepared CHI solution was used for the preparation of GR-CHI composite. To prepare GR-CHI composite, the pristine GR (5 mg mL^{-1}) was added into the CHI solution and bath sonicated for 30 min and leads to the successful formation of GR-CHI composite. To prepare GR-CHI composite modified electrode, about 8 µL (optimum) of as prepared GR-CHI composite solution was coated on GCE and dried in an air oven. The as-prepared GR-CHI composite modified electrode was used for electrochemical sensing of NB. For comparison, GR and CHI modified electrodes were independently prepared without CHI and GR. The GR dispersion was prepared by dispersing GR (5 mg mL^{-1}) in dimethylformamide. The electrochemical measurements were performed in an inert atmosphere under ambient conditions unless otherwise stated.

3. Results and Discussion

3.1. Characterizations

The surface changes of the materials were analyzed by SEM and corresponding SEM images of GR and GR-CHI composite is shown in **Fig. 1**. The SEM image of GR clearly reveals the flake morphology where bundle of micro graphitic sheets arranged in an irregular order (**Fig. 1A**). On the other hand, the SEM image of GR-CHI composite (**Fig. 1B**) shows that a dense CHI was uniformly covered on the GR microsheets, which is resulting from the strong interaction between CHI and GR microsheets.
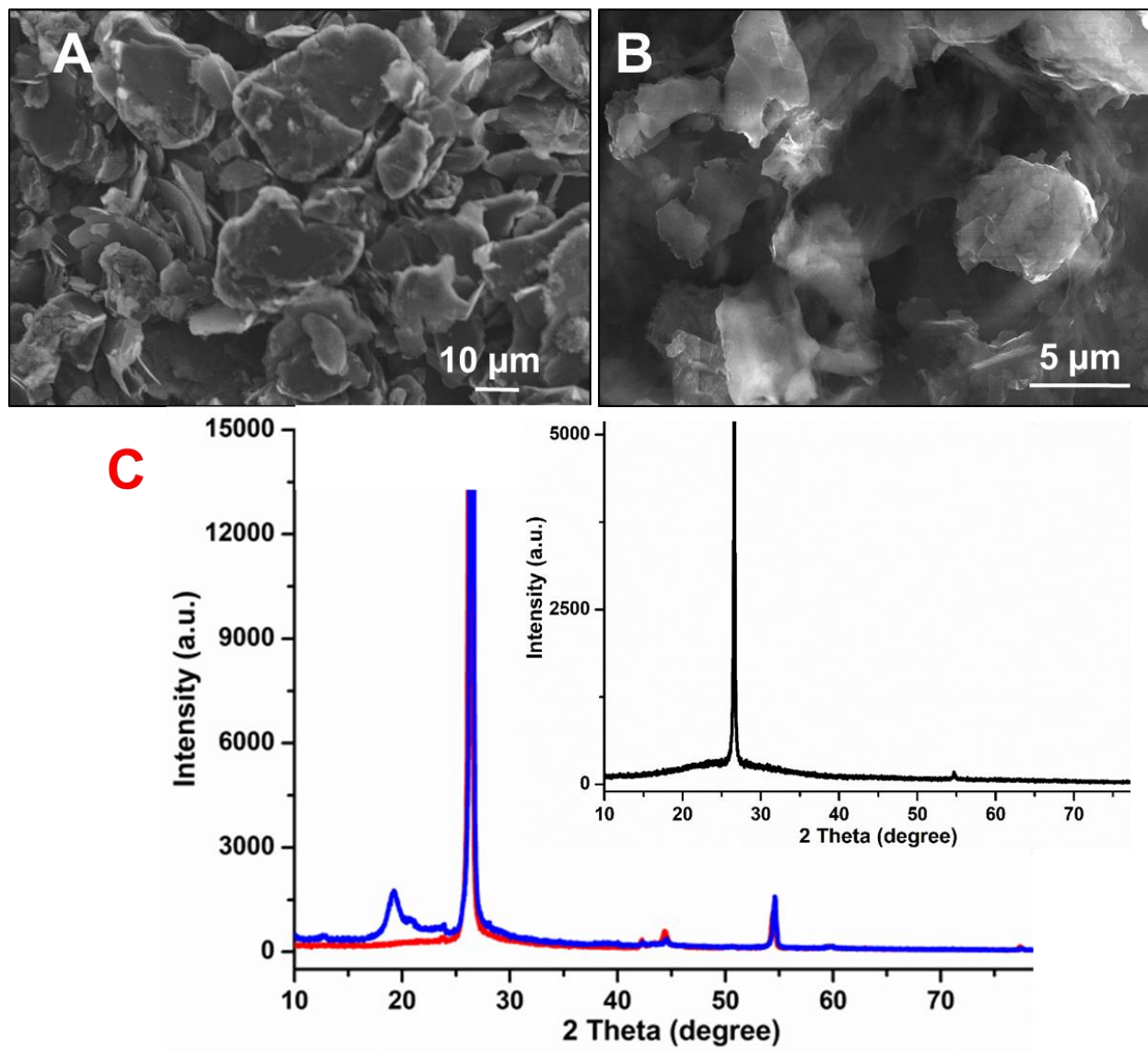
Fig. 1 SEM images of GR (A) and GR-CHI composite (B). C) XRD pattern of GR-CHI composite (blue profile) and GR (red profile). Inset of C shows the XRD pattern of pristine GR.

In addition, XRD was used to study the degree of transformation of graphite by CHI. Fig. 1C shows the XRD pattern of GR (red profile), GR-CHI (blue profile) and graphene (inset). The broad diffraction peaks were observed at 19.6 and 26.4° for GR-CHI composite, which are characteristic peak of crystalline CHI and graphite [35]. Whereas, pure graphene and graphite

shows the diffraction peaks at 26.44 and 26.38°. The result clearly demonstrates that the CHI was firmed attached on CR surface and the edges were grafted like graphene [**17**].

3.2. Electrochemistry of NB at different modified electrodes

The electrochemical behavior of pristine GR (a), GR-CHI (b) and graphene-CHI modified electrodes by CV. **Fig. 2A** shows the CV response of GR (a), GR-CHI (b) and graphene-CHI modified electrodes in PBS containing 5 mM $[Fe(CN)_6]^{3-/4-}$ at a scan rate of 50 mV/s. As shown in **Fig. 2A**, GR modified electrode shows a quasi-reversible behavior with a peak-to-peak separation of 248 mV. However, the GR-CHI and graphene-CHI modified electrodes show the peak to peak separation about 136 and 121 mV, respectively. The GR-CHI modified electrode shows the peak to peak separation about 112 mV lower than GR modified electrode, which indicates the fast electron transfer towards electrode surface. It also noted that the CV behavior of GR-CHI is quite similar to the graphene-CHI modified electrode and confirms that GR-CHI composite has similar electrochemical properties to graphene.
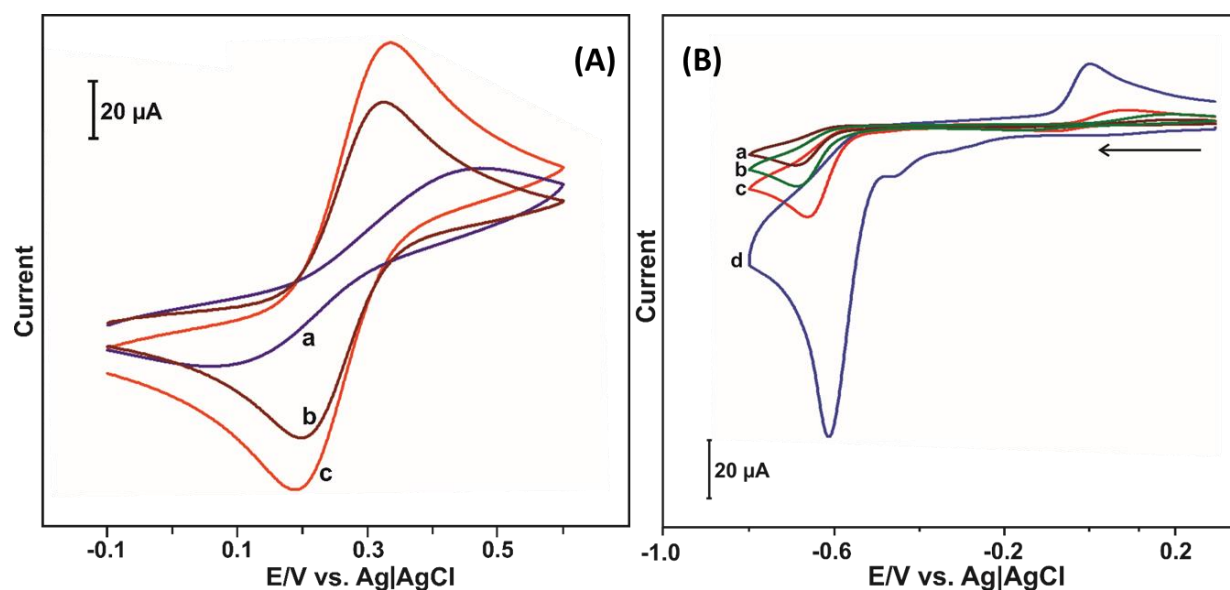

Fig. 2 A) Cyclic voltammetry response of GR (a), GR-CHI (b) and graphene-CHI modified electrodes in PBS containing 5 mM $[Fe(CN)_6]^{3-/4-}$ at a scan rate of 50 mV/s. B) Cyclic

voltammetric response obtained for bare (a), CHI (b), GR (c) and GR-CHI composite (d) modified electrodes in 100 μM NB containing PBS at a scan rate of 50 mV/s.

The electrochemical behavior of NB was investigated using different modified electrodes by CV. **Fig. 2B** displays the CV response of bare (a), CHI (b), GR (c) and GR-CHI composite (d) modified electrodes in 100 μM NB containing PBS at a scan rate of 50 mV/s. The NB undergoes two electron-proton irreversible reduction to phenyl hydroxylamine at modified electrodes [**18, 19**]. In addition, the reduction of NB is more significance from the electrochemical point of view than oxidation of reduced product of NB [**18**]. The bare, CHI and GR modified electrodes show a well-defined reduction peak for the presence of NB. The bare electrode shows the reduction peak of NB at -0.692 V, which is about 4 and 32 mV higher than those appeared at CHI and GR modified electrodes. In addition, the GR modified electrode shows an enhanced reduction peak current to NB than bare and CHI modified electrodes. The result clears that GR modified electrode shows a less reduction potential and higher sensitivity to NB than bare and CHI modified electrodes. On the other hand, GR-CHI composite modified electrode shows 6 folds enhanced current response to NB than GR modified electrode, which suggests that GR-CHI composite is favorable for adsorption of more number of NB than GR. In addition, the reduction peak of NB is appeared at -0.606 V, which is about 54 mV lower than GR modified electrode. The enhanced electro-reduction ability and lower reduction potential of GR-CHI composite towards NB is due to the large electroactive surface area (see Sec. 3.3) and strong interaction of the GR-CHI composite with NB. The plausible reason for more adsorption of NB in the composite is mainly due to the electrostatic attractions between the protonated amine group of CHI and the negative dipole of the nitro group of NB [**20**]. The above result confirmed that GR-

CHI composite modified electrode can be used for sensitive and lower potential detection of NB than other modified electrodes.

The effect of scan rate and pH on the electrochemical behavior of NB was studied using GR-CHI composite modified electrode by CV. **Fig. 3A** displays the CV response obtained for GR-CHI composite modified electrode in 100 µM NB containing PBS at different scan rates. The scan rates were used in the range from 20 to 200 mV/s. The GR-CHI composite shows a well-defined reduction peak for NB at 20 mV/s scan rate. In addition, a pair of well-defined redox couple is appeared in the same CV, which is due to the redox electrochemical behavior of nitrosobenzene from the phenyl hydroxylamine. It is interesting to note that the reduction peak current of NB increases with further increasing the scan rates from 20 to 200 mV/s. Furthermore, the reduction peak potential of NB had a slight shift towards negative direction upon increasing the scan rates. As shown in **Fig. 3A inset**, the reduction peak current response of NB had a linear dependence against the scan rates from 20 to 200 mV/s with a correlation coefficient of 0.9976. The above result clearly suggests that the electro-reduction of NB at GR-CHI composite modified electrode is adsorption controlled electrochemical process [**19**]. The result also implies that the more NB molecules can be easily adsorb on the composite surface via the interaction of CHI and nitro group of NB.
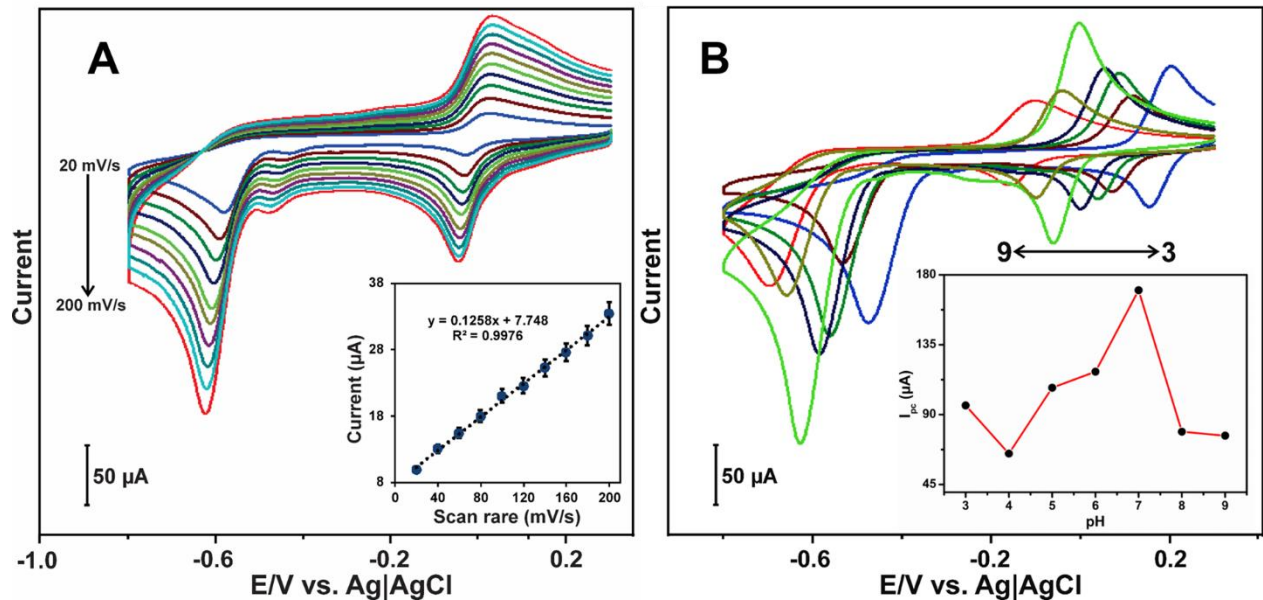
Fig. 3 A) Cyclic voltammetric response obtained for GR-CHI composite modified electrode in 100 μM NB containing PBS at different scan rates from 20 to 200 mV/s. Inset: linear plot for cathodic peak current response vs. scan rate. B) Cyclic voltammetric response obtained for GR-CHI composite modified electrode in 100 μM NB containing different pH (pH 3, 4, 5, 6, 7, 8 and 9) at a scan rate of 50 mV/s. Inset is the plot of pH vs. cathodic peak current response of NB at -0.606 V.

We have also studied the effect of pH on the electro-reduction behavior of NB at GR-CHI composite modified electrode, since the electrochemical behavior of NB can easily be affected by the pH. **Fig. 3B** shows the CV response of GR-CHI composite modified electrode in 100 μM NB containing different pH (pH 3 to 9) at a scan rate of 50 mV/s. One can easily see that GR-CHI composite modified electrode shows a well-defined reduction peak and redox couple for NB in each pH. However, a maximum reduction peak current response (inset) and enhanced redox couple of NB was observed in pH 7.0 than that of other pH. In addition, reduction peak current response and redox couple of NB decreased below or above pH 7.0 (inset).

This is due to the high stability of phenyl hydroxylamine in pH 7 than other pH [**19**]. Hence, pH 7 was selected as an optimum pH for further electrochemical studies.

3.3. Amperometric determination of NB

The NB was quantified using GR-CHI composite modified electrode by amperometric *i-t* method. **Fig. 4A** displays amperometric *i–t* response of GR-CHI composite modified electrode for successive additions of different concentration of NB (0.1–676.6 µM) into constantly stirred (1200 rpm) PBS with an applied potential of -0.6 V. A well-defined and sensitive amperometric response was observed at GR-CHI composite modified electrode for different concentration addition of NB (0.1, 0.3, 0.5, 1.0, 3.0, 5.0, 10.0, 25.0 and 50.0 µM) into the PBS. The NB response at GR-CHI composite modified electrode reaches its 95% of steady state current within 4 s, which indicates the fast electrocatalytic reduction of NB. As shown in **Fig. 4A inset**, the amperometric response of NB was linear over the concentrations from 0.1 µM to 594.6 µM with the correlation coefficient of 0.9921. The LOD was calculated as 0.037 µM based on IUPAC recommendations (S/N=3). The sensitivity was estimated to be 1.98 $\mu A \mu M^{-1} cm^{-2}$ based on the slope of the calibration plot/electrochemically active surface area (EASA) of the GR-CHI composite modified electrode. The ESCA of the bare, GR and GR-CHI composite modified electrode was calculated using Randles–Sevcik equation and was 0.79, 0.91 and (0.19 cm^2, respectively [**21**]. To verify the analytical advantages and novelty of the sensor, the LOD, sensitivity and linear response range was compared with the previously reported NB sensors. For fair comparison with graphene, graphene-CHI composite was prepared and its analytical results (sensitivity, LOD, and linear range) towards sensing of NB (amperometric data not shown) are also compared with GR-CHI composite. The graphene-CHI composite was prepared by sonication of graphene in CHI solution. The comparative results are shown in **Table 1**. The

comparative table clearly reveals that GR-CHI composite modified electrode has lower LOD, high sensitivity and wider linear response range towards NB than previously reported modified electrodes [**8, 9, 19, 22–30**]. The comparative results also reveal that the reported electrode material has comparable analytical characteristics with graphene-CHI composite. Hence, GR-CHI composite can be used for the advanced electrode material for sensitive and low-level detection of NB. In addition, the fabricated electrode material is cost-effective, highly stable and can prepare in short period when compared to previously reported electrode materials for NB sensing that shown in **Table 1**.
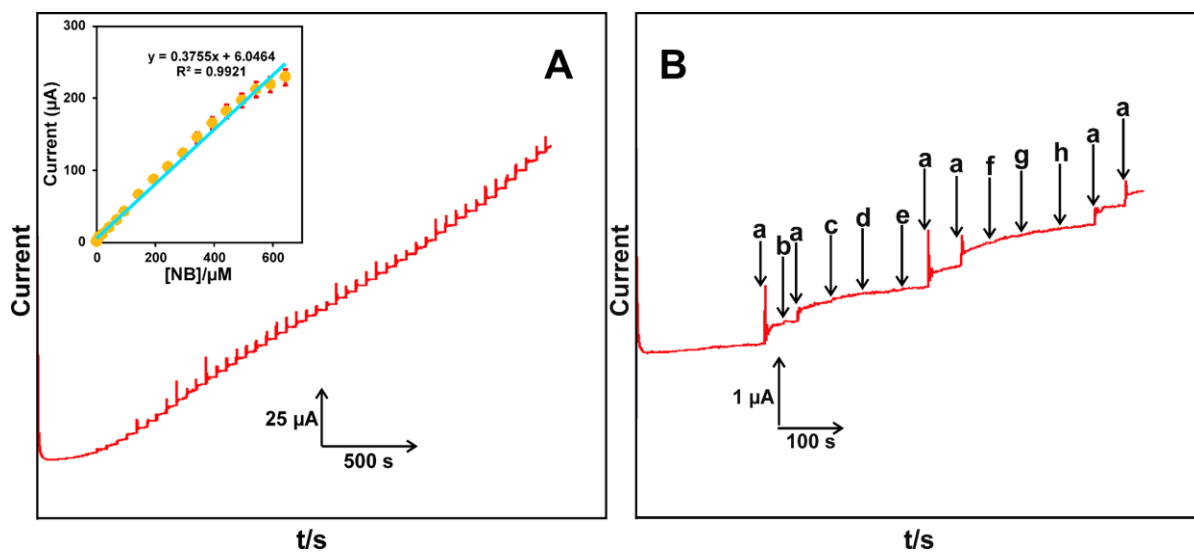

Fig. 4 A) Amperometric i–t response of GR-CHI composite modified electrode for successive additions of different concentration of NB into PBS with an applied potential of -0.6 V. Inset is the linear plot for I_{pc} vs. [NB]. B) At similar conditions, amperometric i–t response of GR-CHI composite modified electrode for addition of 1 µM NB (a) and 50 µM additions of p-Nitromethane (b), o-Nitrophenol (c), m-Nitrophenol (d), uric acid (e), ascorbic acid (f), dopamine (g) and catechol (h) into continuously stirred PBS. Applied potential = -0.6 V.

Table 1 Comparison of electroanalytical characteristics of as-prepared GR-CHI composite modified electrode with previously modified electrodes for determination of NB.

Modified electrode	LOD (μM)	Linear range (mM)	Sensitivity (μAμM^{-1} cm^{-2})	Ref.
[1]EAG/SPCE	0.06	up to 374.5 μM	1.445	[8]
[2]RGO-AgNPs/GCE	0.26	up to 900.0	0.836	[9]
[3]γ-Al$_2$O$_3$/GCE	0.15	up to 145.5	1.27	[19]
[4]Au-NPs/GCE	0.016	up to 600.0	1.01	[22]
[5]C60/CPE	0.3	up to 600.0	–	[23]
[6]MMPCMs/GCE	0.008	up to 40.0	2.36	[24]
[7]Co-MOF–MPC/GCE	0.21	up to 15.0	–	[25]
[8]NPC-2/GCE	0.47	up to 300.0	0.126	[26]
[9]Au-MOF-5/GCE	15.3	up to 500.0	0.43	[27]
[10]NiCu0.04 electrode	40.0	up to 2000.0	0.298	[28]
[11]PNMPC/Nafion/GC	0.05	up to 200.0	6.93	[29]
[12]TPDT-Ag NPs/GCE	1.0	up to 7.0	0.1684	[30]
Graphene-CHI/GCE	0.06	up to 300.0	2.4	This work
GR-CHI/GCE	0.037	up to 594.6	1.98	This work

[1]EAG/SPCE – Electrochemically activated graphite modified screen-printed carbon electrode

[2]RGO-AgNPs/GCE – Silver nanoparticles decorated reduced graphene oxide modified glassy carbon electrode

[3]γ-Al$_2$O$_3$/GCE – γ-Al$_2$O$_3$ polished glassy carbon electrode

[4]Au-NPs/GCE – Gold nanoparticles modified glassy carbon electrode

[5]C60/CPE – Fullerene C60 modified carbon paste electrode

[6]MMPCMs/GCE – Macro-/meso-porous carbon materials modified glassy carbon electrode

[7]Co-MOF–MPC/GCE – Electrocatalytically active cobalt-based metal-organic framework with incorporated macroporous carbon composite modified glassy carbon electrode

[8]NPC-2/GCE – Nitrogen-doped porous carbon modified glassy carbon electrode

[9]Au-MOF-5/GCE – Gold nanoparticles incorporated zinc based metal-organic framework modified glassy carbon electrode

[10]NiCu0.04 electrode – NiCu alloy electrode

[11]PNMPC/Nafion/GC – Pt nanoparticles/macroporous carbon hybrid modified glassy carbon

[12]TPDT-AgNPs/GCE – Silicate sol-gel stabilized silver nanoparticles modified glassy carbon electrode

The selectivity of the GR-CHI composite modified electrode towards NB is more important in the presence of other nitro and potentially interfering compounds. Hence, the selectivity of the GR-CHI composite modified electrode was evaluated in the presence of 50-fold additions of nitro compounds and other potentially active compounds by amperometric *i-t* method. **Fig. 4B** shows the amperometric response of GR-CHI composite modified electrode towards NB for the addition of 1 µM NB (a) and 50 µM additions of p-Nitromethane (b), o-Nitrophenol (c), m-Nitrophenol (d), uric acid (e), ascorbic acid (f), dopamine (g) and catechol (h) into the PBS. The working potential was -0.6 V. One can clearly see that the modified electrode shows a well-defined amperometric response was observed for the addition of NB, while other potentially active compounds such as o-Nitrophenol, m-Nitrophenol, uric acid, ascorbic acid, dopamine and catechol did not show any obvious response on the modified electrode. However, a slight response was observed for the addition of p-Nitromethane, and the observed response is negligible when compared to the response of NB. The result clearly confirmed that GR-CHI composite modified electrode could be used for selective detection of NB in presence of nitro compounds, biologically active molecules and dihydroxybenzene isomers.

Table 2. Determination of NB in lab water samples using GR-CHI composite modified electrode. (Relative standard deviation (RSD) is relative 3 measurements)

Sample	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
Lab water	1.0	0.96	98.0	2.6
(NB free)	3.0	2.86	97.8	2.9

The practical ability of the GR-CHI composite modified electrode towards detection of NB containing lab water samples was evaluated using amperometry. The standard addition method was used for the calculation of recovery of NB. The lab water samples were tested and shows that they are NB free, and then the known concertation NB containing lab water sample was spiked into the water samples (pH 7.3) and the recoveries calculated. The obtained recoveries of NB in lab water samples are summarized in **Table 2**. **Table 2** clearly reveals that the GR-CHI composite modified electrode has appropriate recovery towards NB in lab water samples, and the average recovery was 97.6% with good repeatability (relative standard deviation = 2.8%). Therefore, GR-CHI composite modified electrode can be used for accurate detection of NB in investigated water samples. The stability of the sensor was studied periodically (every week) by cyclic voltammetry and the experimental conditions are similar to Fig. 2B. The sensor retains 76.2% of its initial sensitivity to NB after 5 weeks (not shown), which indicates the good storage stability of the sensor. However, graphene-CHI composite modified sensor shows high stability (83.6%) towards NB than GR-CHI modified electrode.

4. Conclusions

In conclusion, a simple and sensitive NB sensor has been constructed using GR-CHI composite modified electrode for the first time. The GR-CHI composite modified electrode showed excellent analytical features (low LOD (37 nM), high sensitivity (1.98 $\mu A \mu M^{-1}\ cm^{-2}$)

and wider linear response range (up to 594.6 µM) towards detection of NB than other available NB sensors. In addition, GR-CHI composite can be prepared in short period of time and less expansive when compared to available modified electrodes for detection of NB. The appropriate practicality of the NB sensor confirmed its potential ability for real time monitoring of NB in water samples. The high selectivity of the GR-CHI composite towards NB further authenticated that it can be used for selective detection of NB. However, the selectivity of the sensor in the presence of high concentration of nitromethane (>50 µM) would be a problematic, yet GR-CHI composite showed good selectivity towards NB in the presence of lower concentration of nitromethane (50 µM).

Acknowledgments

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