

An Amperometric Nitrobenzene Electrochemical Sensor Based on Electrochemically Activated Graphite Modified Screen Printed Carbon Electrode

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In the present study involves the fabrication of amperometric sensor for the detection of nitrobenzene (NB) using electrochemically activated graphite (EAG) modified screen printed carbon electrode (SPCE). The EAG modified SPCE was prepared by a simple electrochemical activation of graphite in PBS containing KCl solution at an applied potential of 2.0 V for 300 s. The EAG modified SPCE showed a good electrocatalytic reduction behavior towards NB with a lower overpotential than that of other modified SPCEs. Amperometric results reveals that the reduction peak current of NB was linear over the concentrations from 0.3 to 374.5 μM . The response time of the sensor was calculated as 5 s. The sensitivity was found as $1.445 \mu\text{A}\mu\text{M}^{-1} \text{cm}^{-2}$ with the detection limit of 0.06 μM for NB. In addition, the fabricated electrode showed a good selectivity for NB in the presence of nitroaromatic and phenolic compounds with good operational stability.

Keywords: Screen printed carbon electrode; graphite; electrochemical activation; electrochemically activated graphite; Nitrobenzene; amperometry.

1. INTRODUCTION

Nitrobenzene (NB) is widely considered a highly toxic carcinogenic compound and has been released into the wastewater from the industries and resulting into the high toxicity of water [1–3]. The United States Environmental Protection Agency (USEPA) is listed NB as one of the main toxic compound and it may post a great impact to Human and environment even in very low levels [4]. Furthermore, NB also been widely used as a raw material for the preparation of explosives, herbicide, insecticides, aniline and dyes [5–7]. Therefore, the accurate determination of NB in its low levels is of great importance for the Humans' health. Till date, the chromatographic, spectrophotometry and

electrochemical methods are well known methods for the determination of NB [8–11]. However, electrochemical methods are widely used for the determination of NB due to the low cost and user friendly compared with aforementioned traditional chromatographic methods [11].

Recently, carbon modified electrodes have been widely used for the electrochemical determination of NB owing to their high surface area, large surface defects and excellent electrochemical property [12–15]. For instance, carbon nanotubes, micro and mesoporous carbon, graphene are used for the sensitive detection of NB. On the other hand, electrochemically activated graphite (EAG) has a large number of edge plane surface defects, giving an enhanced surface area and electrochemical properties which is similar to the properties of carbon nanotubes [16]. Our previous studies reveal that EAG has high electron transfer property towards the electrode surface than that of electrochemically activated screen printed carbon electrode (EASPCE), graphite and bare SPCEs [17]. The unique properties of EAG are resulting in a high sensitivity and low detection limit for determination of different analytes [16–20]. In this report, we utilized the special properties of EAG and used for the sensitive determination of NB.

Herein, we report the amperometric determination of NB using EAG modified screen printed carbon electrode (SPCE). The EAG modified SPCE showed enhanced sensitivity and lower overpotential detection for NB compared with other modified SPCEs. The electrochemical behavior of NB, selectivity and operational stability of the fabricated electrode also studied and discussed in detail.

2. EXPERIMENTAL

2.1 Chemicals

Screen printed carbon electrode was purchased from Zensor R&D Co., Ltd., Taipei, Taiwan. The Graphite and Nitrobenzene were purchased from Sigma-Aldrich. The pH solutions were prepared using 0.05 M Na_2HPO_4 and NaH_2PO_4 solutions and pH were adjusted by using either H_2SO_4 or NaOH . All the chemicals used in this work were of analytical grade and all the solutions were prepared using doubly distilled water.

2.2 Apparatus

All the electrochemical experiments, including cyclic voltammetry (CV) was performed using CHI-1205B electrochemical workstation (CH instruments) with a standard three-electrode cell setup. Amperometric (i-t curve) measurements were performed using a CHI-750a potentiostat. In a three electrode system, EAG modified SPCE used as the working electrode (active surface area 0.0798 cm^2), platinum wire (0.5 mm) and an Ag/AgCl electrode (Sat. KCl) used as a counter and reference electrodes, respectively. All electrochemical measurements were carried out at a room temperature in an inert atmosphere (N_2 atmosphere).

2.3. Fabrication of EAG modified SPCE

The graphite (GR) dispersion was prepared by dispersing the GR (10 mg mL^{-1}) in dimethyl sulfoxide (DMSO) with the aid of sonication for 30 mins. The GR modified SPCE was prepared by drop casting of $8 \mu\text{L}$ of GR (optimum) on pre-cleaned SPCE and dried at oven ($50 \text{ }^\circ\text{C}$). The fabricated GR modified SPCE was electrochemically activated in PBS containing KCl at the potential of 2.0 V for 300 s , as reported previously [16–20]. The resulting electrochemically activated GR modified SPCE is denoted as EAG/SPCE and the fabricated electrode was dried at a room temperature. For comparison, EASPCE was also prepared by the same method without GR and the SPCE and GR/SPCE were prepared by using the same method without activation. All electrochemical experiments were performed in N_2 saturated PBS in order to avoid the diffusion of oxygen in the electrolyte solution; the modified electrodes were stored in PBS at room temperature when not in use. The detailed characterization for the fabricated EAG modified SPCE can be found from our previous reports. Our earlier studies revealed that EAG modified SPCE has high surface detects with the enhanced electrochemical surface area than that of EASPCE and GR/SPCE [16–20].

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of NB at different modified SPCEs

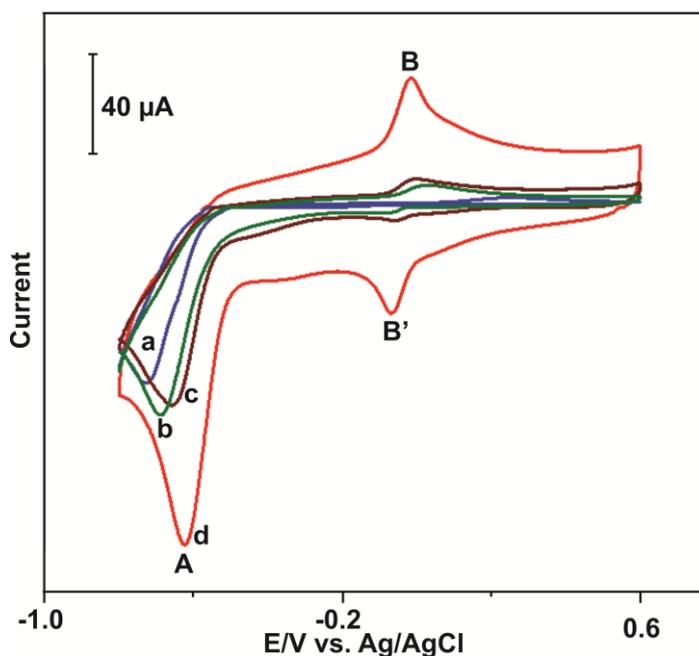


Figure 1. Cyclic voltammetric behavior of SPCE (a), GR/SPCE (b), EASPCE (c) and EAG/SPCE (d) in $500 \mu\text{M}$ NB containing PBS at a scan rate of 50 mVs^{-1} .

The electrochemical behavior of NB was studied at different modified SPCEs by using CV. Fig. 1 shows the cyclic voltammetric behavior of SPCE (a), GR/SPCE (b), EASPCE (c) and

EAG/SPCE in 500 μM NB containing PBS at a scan rate of 50 mVs^{-1} . In the presence of NB, three distinct peaks were observed in all modified SPCEs; the observed peak is denoted as A, B and B'. At bare SPCE, the redox couple is not observed and the reduction peak is appeared in high negative potential (-0.728 V). On the other hand, the reduction peak of NB appeared at -0.658 and -689 V at the GR/SPCE and EASPCE, respectively. The EASPCE showed a well-defined reduction peak with a lower overpotential (-0.624 V) for NB compared with other SPCEs. The peak at -0.624 V (A) is related to the direct reduction of NB to phenyl hydroxylamine (Fig. 2, step 1).

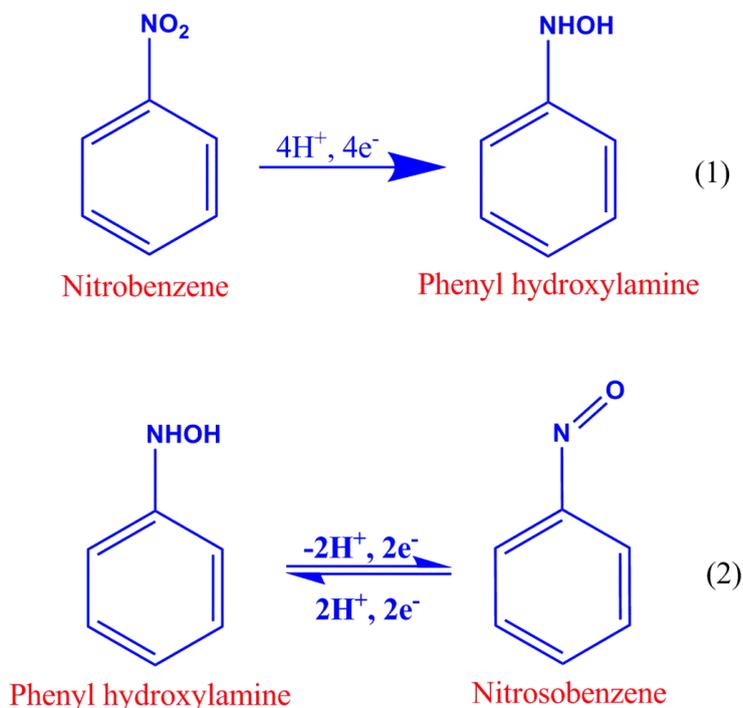


Figure 2. Scheme of electron transfer processes involved in NB electrochemistry at EAG/SPCE.

The redox peak at $-0.069/-0.015 \text{ V}$ (B/B') is corresponding to the redox electrochemical behavior of phenyl hydroxylamine to nitrosobenzene. The reduction peak current intensity of B' is quite low than A, which indicates that the NB reduction is more favored at -0.624 V rather than -0.069 V (Fig. 2, step 2). The scheme of electron transfer processes involved in NB electrochemistry at EAG/SPCE is shown Fig. 2. Moreover, the reduction peak current of phenyl hydroxylamine on EAG/SPCE is ~ 2 folds higher than that of other modified SPCEs. The result clearly reveals that the enhanced current response and lower overpotential of EAG/SPCE toward NB is due to presence of more surface defects of EAG which allows fast diffusion of NB on the electrode surface.

3.2. Effect of scan rate and pH

The effect of scan rate on the electrocatalytic behavior of EAG/SPCE towards NB was also investigated by using CV and the results are shown in Fig. 3.

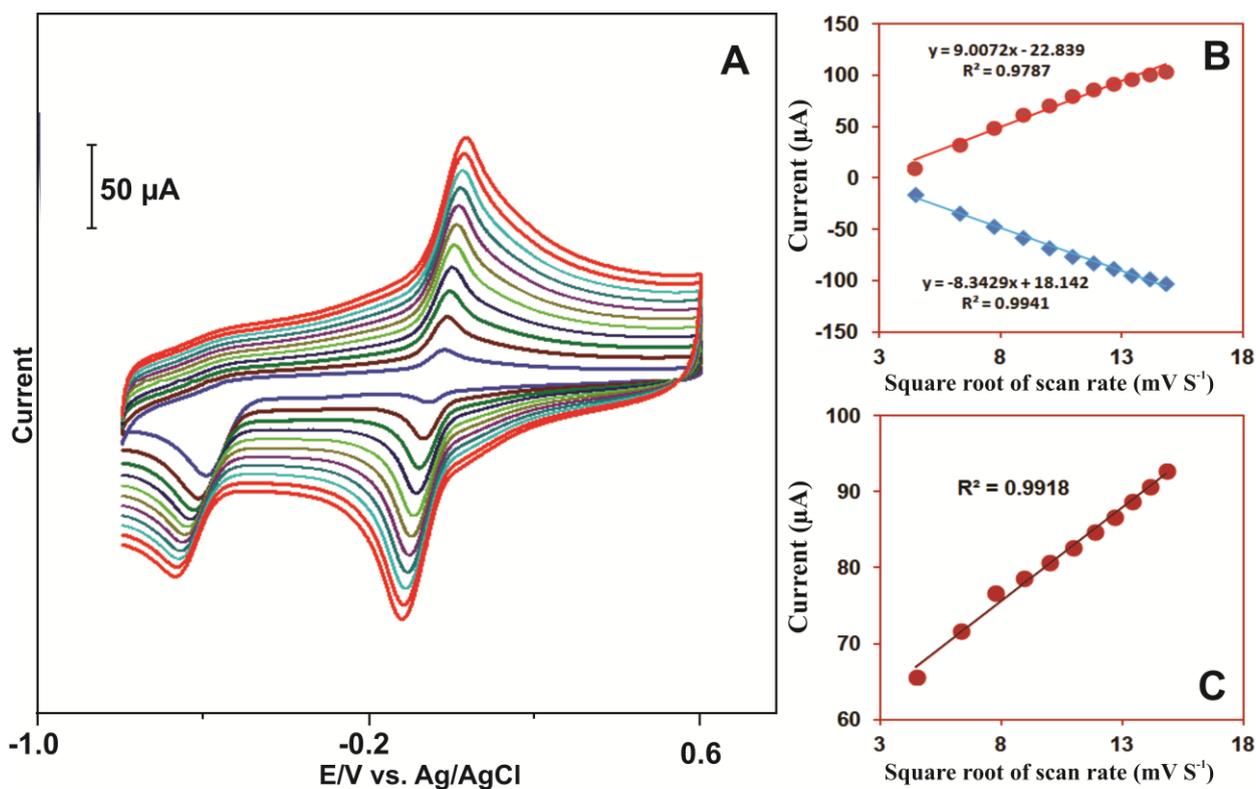


Figure 3. A) Cyclic voltammograms obtained at EAG/SPCE for 500 μM NB containing PBS at different scan rates range from 20 to 220 mVs⁻¹ (inner to outer). B) The calibration plot of redox couple (I_{pa} and I_{pc}) vs. square roots of scan rates. C) The calibration plot of I_{pc} vs. square roots of scan rates.

Fig. 3 show the CV response of EAG/SPCE in 500 μM NB containing PBS at different scan rates range from 20 to 220 mVs⁻¹ (inner to outer). It can be seen that the redox peak current and reduction peak current of NB increased with increasing the scan rates from 20 to 200 mVs⁻¹ and the oxidation and reduction peak potential is also shifted towards positive and negative potential directions. Moreover, the redox peak current (Fig. 3B) and reduction peak current (Fig. 3C) of NB had a linear dependence with the square root of scan rates with the correlation coefficient of 0.9787/0.9941 and 0.9918, respectively. The result indicates the electrochemical direct reduction of NB at EAG/SPCE is a typical diffusion controlled irreversible process; while the electrochemical redox reaction of phenyl hydroxylamine to nitrosobenzene is a typical diffusion controlled reversible electrochemical process [21]. The electrochemical behavior of NB is further evaluated by CV at EAG/SPCE in the presence of 500 μM NB containing different pH solutions (pH 3–9) and the results are shown Fig. 4. It can be seen that the redox peak current and reduction peak current increases with increasing the pH from 3 to 9. Moreover, the reduction peak potential of NB shifted towards negative and positive directions upon increasing and decreasing the solution pH (Fig. 4B), indicating that the electrochemical behavior of NB is pH dependent. Moreover the reduction product of NB (phenyl hydroxylamine) is more active in neutral or high pH [22]. Hence, pH 7 is selected as an optimum pH for further studies.

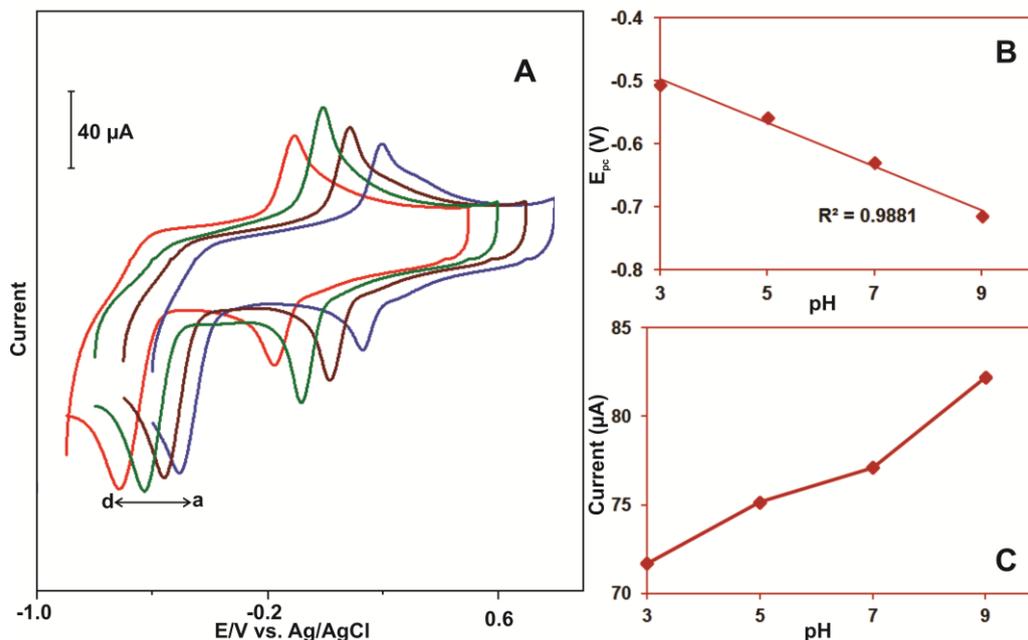


Figure 4. A) Cyclic voltammograms for 500 μM NB containing different pH solutions (3–9, a-d) at EAG/SPCE. B) The corresponding calibration plot of E_{pc} vs. pH. C) Calibration plot of I_{pc} vs. pH.

3.3. Amperometric determination of NB

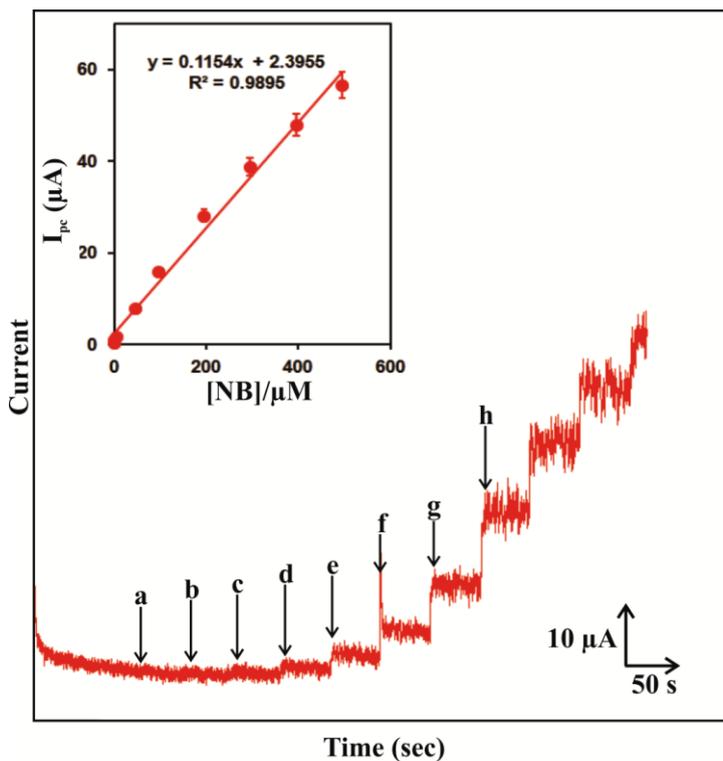


Figure 5. A) Amperometric $i-t$ response obtained at EAG/SPCE for the addition of 0.3 μM (a), 0.5 μM (b), 1 μM (c), 3 μM (d), 5 μM (e), 10 μM (f), 20 μM (g) and 50 μM NB (h) into the PBS. Applied potential: -0.624 V. B) Calibration plot for amperometric current response vs. [NB].

The electrochemical determination of NB was done at EAG/SPCE modified electrode in PBS by using amperometry. Fig. 5 shows the amperometric *i-t* response of EAG/SPCE for the successive addition of different concentration of NB in constantly stirred N₂ saturated PBS. The applied potential is held at -0.625 V. A sharp amperometric response is obtained for each addition of 0.3 μM (a), 0.5 μM (b), 1 μM (c) and 3 μM (d) of NB, which is attributed to the fast direct electrochemical reduction of NB to phenyl hydroxylamine on EAG/SPCE surface.

The response of the NB at the modified electrode is reached within 5 s, revealing the fast diffusion of NB on the electrode surface. Moreover, the amperometric response current increased with increasing the concentration of NB. The amperometric current response of NB increases linearly in the concentration range from 0.3 to 374.5 μM (Fig. 5B inset). The calibration plot for amperometric current response vs. different concentration of NB was found as $I_{pc} = 0.1154 \mu\text{M} + 2.3955$ with the correlation coefficient of 0.9895. The sensitivity was calculated as $1.445 \mu\text{A}\mu\text{M}^{-1} \text{cm}^{-2}$ with the limit of detection (LOD) of 0.06 μM (S/N=3). The analytical performance of the fabricated electrode (LOD, sensitivity, linear response range) of the sensor was compared with previously reported NB sensors and the comparative results are shown in Table 1.

Table 1. Comparison of analytical performance of the developed NB sensor with previously reported NB sensors.

Modified electrode	Analytical Method	Linear range	Sensitivity ($\mu\text{A}\mu\text{M}^{-1} \text{cm}^{-2}$)	LOD (μM)	Ref.
NiCu Alloy electrode	CA	up to 20 mM	0.298	0.4	[23]
MMPCMs/GCE	LSV	up to 40 μM	2.36	0.008	[24]
Pd-GG-g-PAM-silica/GCE	DPV	up to 1.9 mM	0.026	0.06	[25]
PEDOT/MWCNT/CPE	CA	up to 43 μM	–	0.083	[26]
silica-coated AgNPs/GCE	CA	up to 25 nM	114	0.025	[27]
PNMPC/Nafion/GCE	DPV	up to 200 μM	6.93	0.05	[28]
Ag/ATP/GCE	LSV	up to 30 μM	–	1.1	[29]
OMC/DDAB/GCE	LSV	up to 2.9 mM	–	10	[30]
C60/ MCPE	SDCV	up to 6 mM	–	30	[31]
silica-coated AuNPs/GCE	CV	up to 1 μM	0.102	0.025	[32]
EAG/SPCE	Amp	up to 374.5 μM	1.445	0.06	present work

Abbreviations;

LOD – Limit of detection; CA – Chronoamperometry; MMPCMs – Macro-/meso-porous carbon materials; GCE – Glassy carbon electrode; LSV – Linear sweep voltammetry; Pd-GG-g-PAM-Silica – palladium nanoparticles decorated on guar gum grafted polyacrylamide-silica; DPV – Differential pulse voltammetry; PEDOT – Poly(3,4-ethylenedioxythiophene); MWCNT – Multi-walled carbon nanotube; CPE – Carbon paste electrode; AgNPs – Silver nanoparticles; PNMPC – Pt nanoparticles ensemble on macroporous carbon; Ag – Silver; ATP – Attapulgit; OMC – ordered mesoporous carbon; DDAB – Didodecyldimethylammonium bromide; C60 – Carbon 60; MCPE – Modified carbon paste electrode; SDCV – Semi-differential cyclic voltammetry; AuNPs – Gold nanoparticles; CV – Cyclic voltammetry; EAG – Electrochemically activated graphite; SPCE – Screen printed carbon electrode; Amp – Amperometry.

It can be seen that the developed NB is comparable with the previously reported NB sensors [23–32], hence it can be used for sensitive detection of NB. The good analytical performance of the EAG/SPCE towards NB is attributed to the large surface defects and high electrochemical surface area of EAG.

3.4. Anti-interference study

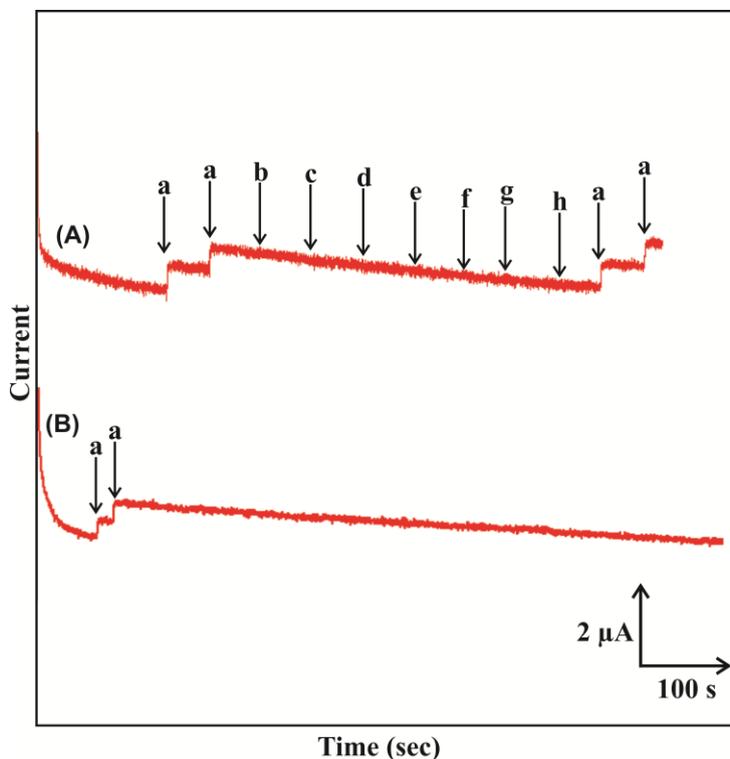


Figure 6. A) Amperometric *i-t* response obtained at EAG/SPCE for the addition of 5 μM NB (a) and 100 μM addition of 3-nitroaniline (b), 4-bromo nitrobenzene (c), 4-chloro nitrobenzene (d), 4-nitroaniline (e), 2-nitroaniline (f), resorcinol (g) and phenol (h) into the PBS. Applied potential: -0.624 V . B) Amperometric stability of EAG/SPCE for 5 μM NB (a) containing PBS up to 1000 sec.

The selectivity of the fabricated sensor is more important in amperometric sensors especially for the compound has a similar structural property. Hence, it is necessary to study the selectivity of the modified electrode towards NB in the presence of nitroaromatic and phenolic compounds. In order to evaluate the selectivity of the fabricated sensor, amperometric *i-t* response of EAG/SPCE was studied for 5 μM NB (a) in the presence of 100 μM addition of 3-nitroaniline (b), 4-bromo nitrobenzene (c), 4-chloro nitrobenzene (d), 4-nitroaniline (e), 2-nitroaniline (f), resorcinol (g) and phenol (h) and shown in Fig. 6A. The experimental conditions are similar to the aforementioned section. It can be seen that a good amperometric response is observed for the each addition of 5 μM NB, whereas the other potentially electroactive species do not show any response at the modified electrode. However, the response current of NB decrease slightly upon the addition of nitroaromatic compounds. The above

results indicate that the fabricated EAG/SPCE is more suitable for selective determination of NB in the presence of other nitroaromatic and phenolic compounds.

The operational stability of the EAG/SPCE towards the response current of 5 μM NB was examined up to 1000 s by amperometric measurement and shown in Fig. 6B. The response current of NB lost is only 10.1 % of its initial current response when it is continuously run up to 1000 s in 5 μM NB containing constantly stirred PBS. The result indicates a good operational stability of the EAG/SPCE towards the detection of NB.

4. CONCLUSIONS

In conclusion, an amperometric NB sensor has been fabricated using the EAG modified SPCE. The EAG modified SPCE exhibited a high sensitivity and lower overpotential for the detection of NB compared with other modified SPCEs. The EAG modified SPCE showed a high sensitivity, wider linear response along with lower LOD for the detection of NB. The developed sensor also has good selectivity for NB determination in the presence of other nitroaromatic and phenolic compounds. As a future perspective, the developed sensor can be used for the sensitive detection of NB in environmental samples.

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