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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 characterization 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 toward NB than other modified electrodes due to the combined unique properties of exfoliated GR and CHI. The GR-CHI composite modified electrode can be 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 is evaluated in the presence of nitroaromatic, biologically active and dihydroxybenzene compounds. The sensor shows appropriate practicality and good repeatability toward detection of NB in lab water samples.

1. Introduction

Over the past decades, the detection of toxic nitroaromatic compounds has received significant attention owing to their dentrimental health effects in human beings [1]. In particular, nitrobenzene (NB), a 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 been 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 and electrochemical methods are considered simpler and more 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. However, unmodified carbon electrodes are not suitable due to poor selectivity and less sensitivity toward NB [9,10]. Hence, the selective and sensitive determination of NB with low detection limit is of interest to sensor development.

Graphite (GR) is an anisotropic abundant carbon material, containing high numbers of active edge planes and inert basal planes [11]. Due to the closer arrangement of each GR sheets, it has shown poor electrochemical behavior and sensitivity in electroanalysis when compared to other GR forms such as pyrolytic and edge plane GR [12,13]. Hence, different modifications or pretreatments have been used to improve the electrochemical properties and selectivity of GR [11,14]. Recently, we have reported that carbohydrate polymers entrapped GR have higher electron transfer ability than pristine GR and its performances have been found similar to graphene analogs [15–17]. For instance, the β-cyclodextrin, chitosan and chitin (CHI) stabilized GR has shown enhanced electrocatalytic activity and a higher surface area than GR, and its electrochemical behaviors have been 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 leads to the exfoliation of GR sheets and

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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 (μA/μM/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_2O_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_2O_3/GCE—γ-Al_2O_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.

results in 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 toward 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, USA 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) 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) 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) 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 are shown in Fig. 1. The SEM image of GR clearly reveals the flake morphology with bundles 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 a dense, uniform covering of CHI on the GR microsheets, resulting from the strong interaction between CHI and GR microsheets.

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

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