



In-situ electro-polymerization of graphene nanoribbon/polyaniline composite film: Application to sensitive electrochemical detection of dobutamine



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ABSTRACT

The present paper demonstrates the capability of narrow graphene nanoribbons (GNRs) in constructing new sensing platforms. Graphene nanoribbons have been synthesized via a simple solvothermal route through unzipping of carbon nanotubes, which was confirmed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy analysis. These narrow carbon sheets were used to form a composite film by in-situ electro-polymerization with aniline. The produced graphene nanoribbon/polyaniline (GNR/PANI) composite film showed impressive performance in electrochemical determination of dobutamine (DBT). Under optimal conditions, in comparison to bare glassy carbon electrode a significant increase in peak current was observed on the surface of GNR/PANI modified glassy carbon electrode (up to 10 times), which is ascribed to the higher specific surface area induced by GNRs in combination with the electrocatalytic effect of polyaniline layer. We believe that such a composite film has a great potential in different applications including sensors, supercapacitors and etc.

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1. Introduction

Fabrication of rapid, selective, sensitive and cost effective sensing platforms, especially based on carbon nanomaterials, has attracted a great interest [1–3]. Although a considerable part of researches has been allocated to carbon nanotubes in the last decades [4–6], fascinating properties of graphene, single-layered graphite sheet, brought it very rapidly in the focus of attention in the realm of carbon nanostructures due to its outstanding electrical, mechanical and chemical properties [7–9]. In spite of the fact that graphene has potential applications in sensors [10], composites [11] and energy storage devices such as supercapacitors [12], the application of graphene in the field of nanoelectronic, especially field-effect transistors (FET), is limited due to the lack of band gap in it. In other words, the major challenges for graphene transistors include opening a sizeable and well-defined band gap in it [8]. In order to overcome this problem and open up a band gap in such

a 2D carbon sheet, one way is to reduce the width of graphene nanosheets [13]. These thin elongated strips of graphene, named graphene nanoribbons (GNRs), display a band gap as a function of ribbon widths meaning by decreasing the ribbon width, the band gap increases gradually and the ribbons transform from semimetals to semiconductors [14,15].

Several approaches have been developed to obtain GNRs including lithographic patterning [16], chemical vapor deposition (CVD) [17] and chemically derived techniques [18]. Very recently, a new method based on lengthwise unwrapping of multi-walled carbon nanotubes (MWCNTs) side walls has been introduced for the synthesis of GNRs [19–25]. This technique will allow the production of narrow GNRs with controllable widths and given edge configurations with respect to the diameter and chirality of the nanotubes. Various physical approaches have been proposed in the literature to synthesis GNRs from carbon nanotubes (CNTs) such as plasma etching [21], electrically unwrapping CNTs [22] and anisotropic etching by metallic nanoparticles [25]. Although these methods give us the opportunity of accurate control over the GNR widths, they all need high-tech instrumentations and cannot produce GNRs in a large scale.

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In the present research we use a simple yet effective chemical method for synthesis of GNRs from MWCNTs through a solvothermal route. The oxidation reaction is performed in a sealed autoclave in the presence of KMnO_4 as an oxidizing agent in an acidic medium ($\text{H}_2\text{SO}_4:\text{HNO}_3$, 3:1 v/v). The key is to use the created high pressure in a sealed autoclave vessel as a result of high temperature to split pristine MWCNTs. As a result the $\text{C}=\text{C}$ cleavage initiated at structural defects, but subsequent unzipping only take place in the bonds having enough strain. On the other hand, due to the high pressure produced in the medium, the time of reaction diminishes dramatically in comparison with the other chemical techniques.

It is noteworthy to mention that, the GNRs prepared by chemical methods is not a good candidate for electronic applications due to the structural defects and/or holes produced in the basal plane which resulted in the loss of electronic properties in the GNR sheets. In other words, the produced GNRs by chemical routes still contain residual defect sites due to the incomplete re-aromatization (even after intense reduction) and hence, their electronic conductivity is not as high as that observed in their counterparts produced by physical methods. Meanwhile, the produced graphene nanoribbons in this way are great candidates for electrochemical purposes since they have numerous edge atoms (especially in comparison with CNTs) which act as active electron transfer sites for fast electrochemical reactions.

On the other hand, nanocomposites of graphene/polyaniline have attracted considerable attention in different areas including solar cells [26], supercapacitors [27,28] and sensors [29] particularly electrochemical biosensors [30,31]. In comparison to graphene sheets these composites are more suitable for electrode modification, show more compatibility for bio-functionalization and improve the sensitivity of the biosensors. In order to investigate the capability of the produced GNRs in construction of composite film for sensing applications, we fabricate graphene nanoribbon/polyaniline film through in-situ electro-polymerization on the surface of glassy carbon electrode (GNR/PANI-GCE) in acidic medium. As a model, the obtained composite film was used for the electrochemical investigation of dobutamine, an important catecholamine, which is a drug acts on the sympathetic nervous system and used for the treatment of heart failure and cardiogenic shock and yet there are only a few articles around its electrochemical determination [32–34]. Zhang introduced an adsorptive stripping voltammetry method for the determination of DBT on poly(acridine orange) film modified glassy carbon electrode with the detection limit of 2.0×10^{-9} M for 200 s open circuit accumulation [32]. Pletnev and co-workers used screen-printed electrodes modified with carbon paste that consisted of graphite powder dispersed in ionic liquids (IL) for electrochemical determination of catecholamines including dobutamine [33]. Recently, Wei et al. developed a modified glassy carbon electrode based on a magnesium oxide microflowers–nafion composite film for electrochemical oxidation of DBT with a detection limit of $0.092 \mu\text{M}$ [34]. Here, we used an electrochemical polymerization process for fabrication of a uniformly distributed composite layer of graphene nanoribbons/polyaniline film on the surface of glassy carbon electrode for electrochemical determination of dobutamine. Our results showed a considerable enhancement in the electrochemical performance of the modified electrode: the anodic peak current increased dramatically (up to 10 times) and a slight decrease in peak potential observed on the surface of GNR/PANI-GCE. We ascribed these results to the high surface area introduced by GNRs as well as electrocatalytic behavior of polyaniline. The results obtained for clinical samples are in good agreement with experimental ones revealed that the prepared sensing composite layer with this method can be used in electrochemical determination of catecholamines such as dobutamine.

2. Experimental details

2.1. Synthesis of graphene oxide nanoribbons

In order to synthesis graphene nanoribbons, 50 mg MWCNTs (OD: 30–50 nm, L: 1–10 μm , purity >95 wt%, PlasmaChem GmbH, Germany) were suspended in 16 mL of concentrated acid mixture ($\text{H}_2\text{SO}_4:\text{HNO}_3$, 3:1 v/v) and stirred for 6 h. KMnO_4 (300 mg) was then added and the mixture was transferred to an autoclave. The sealed autoclave was heated in an oven to 120°C for 1 h and after that allowed the mixture to cool to room temperature. Then, the reaction mixture was poured onto 50 mL of iced DI water containing 2.5 mL H_2O_2 (30%). The resulting light brown colored graphene oxide nanoribbons (GONRs) precipitate was collected on a 200 nm pore size poly-tetrafluoroethylene (PTFE) membrane. The product was washed with DI water until a neutral pH level was achieved and allowed to dry under vacuum at 50°C for 6 h.

2.2. Preparation of graphene nanoribbon/polyaniline composite film

GNR/PANI composite film was synthesized based on the method proposed by Huang et al. for graphene sheets [35]. Briefly, 5 mg of graphene oxide nanoribbons (GONRs) were dispersed in 5 mL of H_2SO_4 (1 M) and then 50 μL aniline monomer was added to this mixture. The reaction mixture was stirred for 30 min allowing electrostatic adsorption to occur between positively charged monomer and negatively charged GONR. After that, the dispersion was centrifuged and rinsed with DI water. The resulting mixture was re-dispersed in 5 mL DI water and sonicated until a homogeneous dispersion (1 mg mL^{-1}) resulted.

The GNR/PANI composite film was synthesized through a one-step electro-polymerization process. For this aim, 5 μL of GNR/aniline suspension was casted on the surface of a glassy carbon electrode and the potential scanned between -1.3 and $+0.8$ V (versus Ag/AgCl) at a scan rate of 50 mVs^{-1} for a total of 10 cycles. During the scanning process graphene oxide nanoribbons was electrochemically reduced at cathodic potentials, while aniline monomer polymerized at anodic potentials on the surface of graphene sheets.

2.3. Materials characterization

The morphologies of GNRs and GNR/PANI composite film were characterized with a field emission scanning electron microscope (Zeiss, SIGMA VP) and a transmission electron microscope (Philips CM10HT-100KV). The Raman spectra were obtained with a Senterra Raman microscope (Bruker Optics Inc., Germany) equipped with a 785 nm He–Ne laser as an excitation source. X-ray powder diffraction (XRD) spectra were recorded on an X'Pert MPD (Philips) instrument using $\text{CuK}\alpha$ (1.5405 Å) radiation.

An ABB-Bomem MB-100FT-IR spectrophotometer was used for recording FTIR spectra. Cyclic voltammetry (CV) analysis were performed on an Autolab PGSTAT 302-potentiostats. A conventional three-electrode system was used for all electrochemical measurements: a glassy carbon electrode (GCE, modified or unmodified) with a diameter of 2 mm as the working electrode, Ag/AgCl as the reference electrode, and a platinum wire as the auxiliary electrode.

3. Results and discussion

3.1. Synthesis of graphene nanoribbons

To obtain optimum conditions for unzipping pristine MWCNTs, the effect of reaction conditions that is the amount of KMnO_4 ,

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