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Electrochemical fabrication and amperometric sensor application of graphene sheets

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ABSTRACT

Graphene sheets have been fabricated by applying two-step electrochemical processes in two-electrode cell system containing 0.1 M sodium dodecyl sulfate (SDS). First step is intercalation of SDS into graphite anode electrode and this process has been applied at different intercalation potential values of 1, 3, 5, and 7 V. Second step includes exfoliation of SDS-intercalated graphite electrode in the same medium by acting as cathode. Stable graphene dispersions are obtained after these two electrochemical steps. Characterization of graphene sheets have been carried out using scanning electron microscopy, electron dispersive spectroscopy, fourier transform infrared spectroscopy, UV–Vis. absorption spectroscopy, X-ray diffraction, and cyclic voltammetry techniques. Graphene sheets have been modified onto glassy carbon electrode (GCE) by drop-casting of graphene dispersion. Graphene/GCE having a good electrocatalytic activity has been used for amperometric determination of nitrite in both standard laboratory and real samples. The oxidation current density was linearly proportional to the nitrite concentration in a range between 1 and 250 μM. The sensitivity of the sensor was calculated as 0.843 $\mu A \mu M^{-1}$ cm^{-2} with a detection limit of 0.24 μM at a signal-to-noise ratio of 3.0.

1. Introduction

Graphene has been isolated by Novoselov and Geim by scotch-tape method in 2004 [1]. After this exploration, graphene has been focused by the researchers because of its high mobility, unique transport performance, high mechanical stability and high thermal and satisfied electrical conductivity. Electrochemistry is suitable technique for graphene production because it is economic, environmentally friendly, and simple. Upto date, some electrochemical routes have been performed to produce graphene flakes by applying electrochemical intercalation of various compounds e.g. ionic liquids [2–4], poly(sodium-4-styrenesulfonate) [5], acetamide-urea-ammonium nitrate melt [6], sodium dodecyl sulfate (SDS) [7–11], sodium dodecyl benzenesulfonate [11,12], cetyltrimethylammonium bromide [13,14], glycine based complex [15], tetrasodium pyrophosphate [16], and $NaOH/H_2O_2$ [17].

Nitrite is an important additive and extensively used for fish, meat and cheese products in food technology. Meat is generally not labeled as “cured” without addition of nitrite since it blocks toxins produced by the clostridium botulinum bacteria. Nitrite amount in food products must be under control because its high level causes to toxicity, which have cancer risk for human body. Therefore, quantitative analysis of nitrite in real samples is of great importance. Up to now,

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electrochemical quantification of nitrite has been applied on modified conductive substrates to decrease electrooxidation potential and increase electroactive surface area. For this purpose, conductive or semiconductive electrodes have been modified with dye polymers [18,19], dye polymer/graphene [20,21] metal nanoparticles/graphene [22,23]. Electrochemical quantification of nitrite has also been initially studied on flexible graphene-based paper electrode by our group [24].

This paper describes the synthesis of graphene sheets including two-step electrochemical processes in two-electrode cell system containing 0.1 M SDS. In the first step, SDS has been intercalated into graphite electrode by serving graphite as anode in the electrochemical cell. We have investigated effect of different intercalation potentials on the quality of produced graphene flakes. Second step includes exfoliation of SDS-intercalated graphite electrode by acting this electrode as cathode. Fabricated graphene sheets have been characterized by scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), fourier transform infrared spectroscopy (FTIR), UV–Vis. absorption spectroscopy, X-ray diffraction (XRD), and cyclic voltammetry techniques. Amperometric quantification of nitrite in both laboratory and real samples have been performed by using produced graphene sheets. For this purpose, graphene sheets have been supported onto glassy carbon electrode (GCE) by drop-casting of graphene dispersion.

2. Experimental section

2.1. Materials

All the chemicals used in this study were of analytical reagent grade and used without further purification. Milli-Q ultrapure water (conductivity: 5.5 $\mu S \cdot m^{-1}$) was used all through this study. Phosphate buffer solutions (PBS, 0.1 M) with different pH values were prepared by mixing stock solutions of 0.1 M H_3PO_4 and KH_2PO_4, and the pH of the buffer solution was adjusted to desired value by using a pH-meter (Hanna Instruments). The solutions were deaerated by passing dry nitrogen through the electrochemical cell for 15 min prior to each experiment.

2.2. Electrochemical fabrication of graphene sheets

Fabrication procedure was presented in Fig. 1. Synthesis procedure includes two step electrochemical processes in 0.1 M SDS (Sigma Aldrich, reagent grade) solution by using two-electrode system. First step is applied for intercalation of SDS into graphite electrode according to following reaction:

$$[C_X] + \left[DS^-\right] \rightarrow \left[C_X^+ DS^-\right] + e^-$$

To achieve this step, graphite rod (Goodfellow, England, 99.5% purity) is used as anode and Pt-fiol (Sigma Aldrich) served as cathode. Because intercalation conditions effect the quality of graphene sheets, this step is carried out at different intercalation potential values of 1, 3, 5, and 7 V. Second step is performed for exfoliation of SDS-intercalated graphite electrode in the

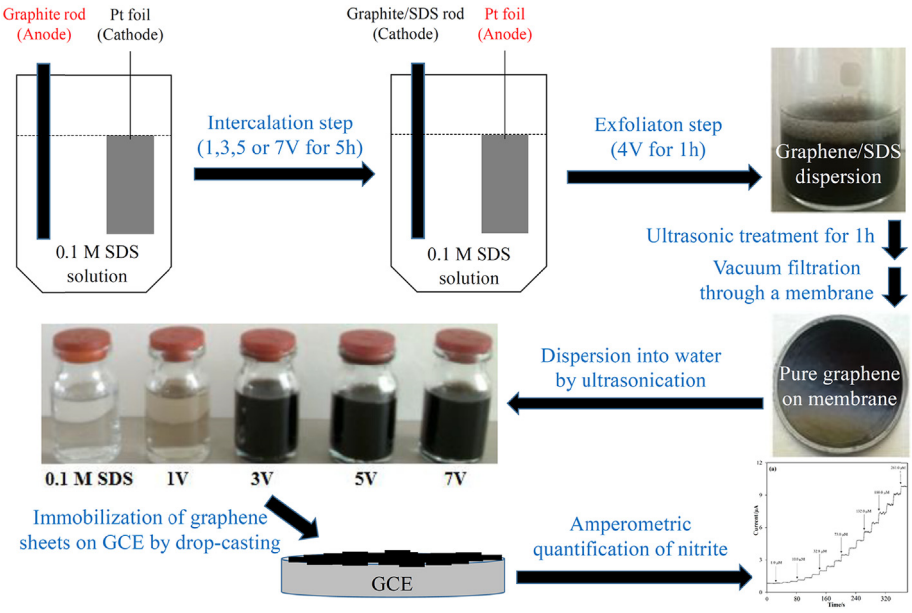

Fig. 1. Schematic presentation of the electrochemical preparation and amperometric sensor application procedure of graphene sheets.