



Graphene–epoxy composite electrode fabricated by in situ polycondensation for enhanced amperometric detection in capillary electrophoresis



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ABSTRACT

This report describes the development and application of a novel graphene–epoxy composite electrode as a sensitive amperometric detector of capillary electrophoresis. The composite electrode was fabricated on the basis of the in situ polycondensation of a mixture of graphene and 1,2-ethanediamine-containing bisphenol A epoxy resin in the inner bore of a piece of fused silica capillary under heat. The structure of the material was investigated by scanning electron microscopy, thermogravimetric analysis, X-ray diffraction, and Fourier transform infrared spectroscopy. The results indicated that graphene sheets were well dispersed and interconnected throughout the composite to form an electrically conductive network. The performance of this unique electrode was demonstrated by separating and detecting two naturally occurring phenolic compounds in rosemary in combination with capillary electrophoresis. The graphene-based detector offered significantly lower operating potentials, higher sensitivity, satisfactory resistance to surface fouling, and lower expense of operation, indicating great promise for a wide range of applications.

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1. Introduction

Since Novoselov and Geim successfully isolated graphene in 2004, it has attracted tremendous scientific and technological attention because of its unique nanostructure and properties [1–3]. Graphene is an important allotrope of carbon with a two-dimensional nanostructure of sp^2 -bonded carbon atoms that are arranged in a chicken wire or honeycomb pattern [2]. It indicates great promise for a variety of applications such as electronics, sensors, drug delivery, batteries, fuel cells, solar cells, supercapacitors, hydrogen storage and functionalized materials because of its excellent electrical and thermal conductivity, strong mechanical strength, and high surface area [4–11].

As an important carbon-based nanomaterial, graphene has been employed to fabricate electrochemical sensors and biosensors because of its excellent conductivity and electrocatalytic activity [12–16]. It was demonstrated that graphene exhibited strong electrocatalytic activity when it was employed to improve the electrochemical response of some bioactive substances [17–21]. The

ability of graphene to promote the electron-transfer reactions suggests great promise for electroanalytical chemistry.

To date, a variety of approaches have been developed for the fabrication of graphene-based electrodes for electrochemical sensing. Among them, surface modification was the commonly used method. Graphene was usually dispersed in solvents [22] or polymer solutions [23,24] that were subsequently modified on the surface of electrodes. In addition, electrochemical polymerization [25] and electrodeposition [26] was also employed to modify graphene sheets on electrodes. Another method based on in situ polymerization was developed for the fabrication of graphene–polymer composition electrodes for amperometric detection (AD) [27,28]. Recently, graphene–copper nanoparticle hybrid prepared by in situ chemical reduction was mixed with paraffin oil and packed into one end of a piece of fused silica capillary to fabricate microdisc electrodes for measuring carbohydrates in combination with capillary electrophoresis (CE) [11]. In 2012, Sheng et al. assembled graphene sheets on anion exchange resin (AER) spheres via electrostatic interaction and chemical reduction [29]. The prepared electrically conductive spheres were embedded in the bores of polypropylene pipette tips to fabricate disposable graphene ball electrodes for CE–AD. More recently, graphene–nickel nanoparticle hybrid was prepared by the far infrared-assisted reduction of a mixture containing graphene oxide,

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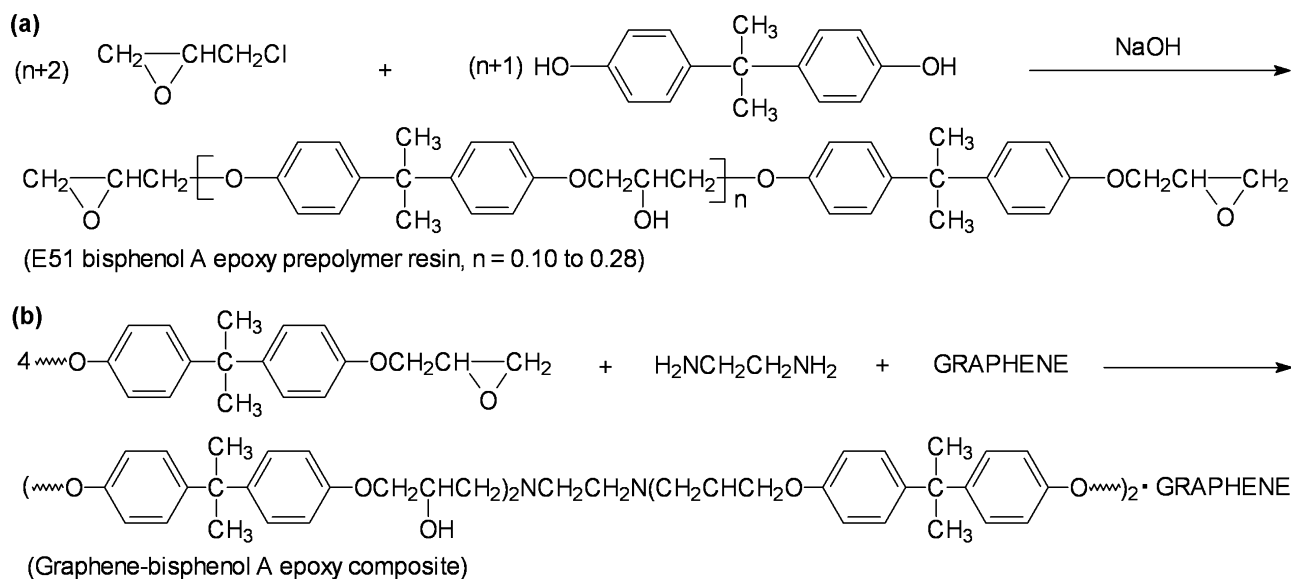


Fig. 1. (a) Reaction routine for the preparation of bisphenol A epoxy resin and (b) reaction mechanism of the polycondensation between epoxy resin and 1,2-ethanediamine in the presence of graphene.

nickel (II) ions, and hydrazine. It was successfully loaded on the surface of a magnetic electrode for sensing carbohydrates [30].

Since the pioneering work of Jorgenson and Lukacs [31,32], CE has been applied in the separation and determination of a variety of samples because of its minimal sample volume requirements, short analysis time, and high separation efficiency, indicating great promise for biomedical and pharmaceutical analysis, clinical diagnostics, and environmental monitoring [33,34]. Amperometric detection offers great promise for CE, with features that include high sensitivity, low cost, low-power demand, and inherent miniaturization of the detector and control instrument [35]. The performance of CE–AD is strongly influenced by the detection-electrode material. Usually, the detection electrode should provide favorable sensitivity and reproducibility. It is interesting to develop some novel graphene-based electrodes for the sensitive and reproducible amperometric detection of CE.

As an important thermosetting polymer, epoxy has been widely used in the fields of adhesive, coating, construction, aerospace, automobile and electronics because of its outstanding mechanical and thermal properties and excellent processability. Epoxy resins are composed of epoxide group-containing prepolymers that can react with hardeners to form solids. The most commonly used epoxy resin is the diglycidyl ether of bisphenol A (DGEBA) formed from the reaction between bisphenol A and epichlorohydrin (Fig. 1A). As a rigid and water-insoluble polymer, epoxy is a promising material in the fabrication of graphene-based composite electrodes because it can be facilely produced by in situ polycondensation [36]. Graphene–epoxy composites have been prepared by in-solution polycondensation [37–39], UV-initiated polymerization [40], and freeze drying [36]. Previous investigations mainly focused on its mechanical strength and electric conductivity [37–40,36]. Because the content of graphene in the prepared composites was less than 4% (w/w), they were not suitable for the fabrication of electrodes owing to their low electric conductivity. To the best of our knowledge, there is no early report on the preparation and application of graphene–epoxy composite electrodes.

In this work, a simple approach based on the in situ polycondensation was developed for the fabrication of graphene–epoxy composite electrode for enhanced amperometric detection. To prepare the electrode, a mixture of graphene and hardener-containing bisphenol A epoxy resin was packed into a piece of fused silica

capillary and was allowed to polycondense under heat. The preparation details and characterization of the composite as well as the feasibility and performance of the fabricated electrode are reported in the following sections in combination with the measurement of two phenolic compounds by CE.

2. Experimental

2.1. Reagent and solutions

Graphite powder, sodium nitrate, potassium permanganate, hydrogen peroxide solution (30%, w/w), hydrazine hydrate (85%, w/w), 1,2-ethanediamine, and sulfuric acid (98%, w/w) were purchased from SinoPharm (Shanghai, China). Bisphenol A epoxy resin (designation, 618(E51); epoxy equivalent weight, 185–210 g/mol; mean degree of polymerization, 0.10–0.28) was obtained from Shanghai Resin Factory Co. Ltd. (Shanghai, China). It was manufactured from epichlorohydrin and bisphenol A in the presence of NaOH (Fig. 1A). Carnosol and carnosic acid were supplied by Sigma (St. Louis, MO, USA). Other chemicals were all of analytical grade. Stock solutions of carnosol and carnosic acid (10 mM each) were prepared in methanol. The running buffer for CE separation was 50 mM borate buffer (pH 9.2).

2.2. Apparatus

The surface morphology of the materials was observed by using a scanning electron microscope (PHILIPS XL 30, Eindhoven, The Netherlands). Thermogravimetric analysis (TGA) was performed in air at a heating rate of 10 °C/min by using a PerkinElmer Pyris 1 DTA-TGA instrument. A Rigaku D/max-rB diffractometer (Rigaku, Tokyo, Japan) with CuK- α 1 radiation (40 kV, 60 mA) was employed to perform X-ray diffraction (XRD) measurements. Fourier transform infrared spectroscopy (FT-IR) spectra of graphene, graphene–epoxy composite and epoxy were measured using a FT-IR spectrometer (NEXUS470, NICOLET).

The CE–AD system used in this work has been described in our previous reports [11]. A ± 30 kV high-voltage dc power supply (Shanghai Institute of Nuclear Research, China) provided a separation voltage between the two ends of the capillary. The inlet of the capillary was held at a positive potential while the outlet of

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