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Amine Functionalized polyaniline grafted to exfoliated graphite oxide: Synthesis, characterization and multi-element sensor studies

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ABSTRACT

An amine functionalized polyaniline (AMPANI) derivative has been grafted onto exfoliated graphite oxide (EGO). The synthesis involved the in-situ chemical oxidative polymerization of functionalized aniline monomer in the presence of EGO with diaminobenzene acting as a bridging ligand to yield EGAMPANI. The synthesized compound was characterized by FT-IR and FT-Raman spectroscopy as well as thermogravimetric and X-ray diffraction analysis. The EGAMPANI was then used to modify a carbon paste electrode (CPE), which was applied for multi-elemental sensing of Pb^{2+}, Cd^{2+} and Hg^{2+} ions using differential pulse anodic stripping voltammetry. The limits of detection achieved using the EGAMPANI modified CPE were 2.2×10^{-6} M for Hg^{2+} ion, 1.2×10^{-6} M for Cd^{2+} ion and 9.8×10^{-7} M for Pb^{2+} ion.

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1. Introduction

Exfoliated graphite oxide (EGO) is generally regarded as a key material for the preparation of functional materials for diverse applications. EGO carries various oxygen containing functional groups, such as the carboxyl, hydroxyl and epoxy groups, on its surface [1], which are distributed on the basal planes and edges. These groups facilitate the chemical functionalization of the EGO with both simple compounds [2] and high molecular weight polymers [3,4,5]. Another important property of EGO is its ability to adsorb simple and macromolecules through non-covalent electronic interactions. Depending upon the nature of functionalization, modified EGO exhibits different physical and chemical properties which in turn determine its applications for electronic devices and electrochemical sensors [6,7,8,9], surface modified electrodes [10], and others. Studies have also been reported on the functionalization of EGO intended to make it more lyophilic in nature [11,12]. Chemical functionalization has the advantage of very good polymer layer adhesion and long term performance [13] compared to physical deposition by non-covalent interaction.

EGO in its native form has already been reported for use in metal ion sensors [14]. EGO which is surface modified with an amine is expected to show sensor properties that are different from those of pure EGO. A convenient way of achieving amine carrying EGO surfaces is to graft amine containing polymers, such as functionalized polyaniline, onto them. It has been reported in an earlier investigation that functionalized polyaniline possesses an improved metal uptake capacity compared to its native form [15]. It is therefore likely that this property can be effectively used in metal ion sensors consisting of an EGO substrate and surface grafted polyaniline. A distinct advantage of using EGO as the substrate for metal ion sensors is its surface functional groups which will provide extra metal chelation in addition to the polymer.

In this investigation, the synthesis and characterization of EGO modified with amine functionalized polyaniline (EGAMPANI) have been performed, and its application in a multi-elemental electrochemical sensor for selected metal ions has been assessed. Initially, the EGO has been synthesized by following a modified procedure [16] of that

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Abbreviations: EG, exfoliated graphite; EGO, exfoliated graphite oxide; DAB, 1,4-diaminobenzene; EGO-DAB, exfoliated graphite oxide modified with 1,4-diaminobenzene; AMPANI, amine functionalized polyaniline; EGAMPANI, amine functionalized polyaniline grafted onto exfoliated graphite oxide; DCC, N,N′-dicyclohexylcarbodiimide; DMAP, dimethylaminopyridine; APS, ammonium persulfate.

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originally reported by Hummers and Offeman [17], and then the EGO surface has been enriched with diaminobenzene (DAB) to obtain EGO-DAB. Subsequently, the amine functionalized polyaniline (AMPANI) has been grafted onto the EGO-DAB surface by in-situ chemical oxidative polymerization, yielding EGAMPANI as the reaction product. In each step of the synthesis, the structure of the intermediary product formed has been confirmed by using NMR or FT-IR and FT-Raman techniques. The synthesized EGAMPANI has then been characterized with regard to its compositional, thermal, structural and topographic properties by means of CHNO analysis and TGA, XRD, SEM and microanalytical techniques. The differential pulse anodic stripping voltammetry (DPASV) technique has been adopted for Pb^{2+}, Cd^{2+} and Hg^{2+} metal ion sensing with an EGAMPANI modified carbon paste electrode (CPE).

2. Experimental

2.1. Chemical syntheses and analytical methods

The chemical synthesis work involved several parts, (i) the preparation of the amine functionalized aniline monomer starting from 2-hydroxyaniline, (ii) the preparation of exfoliated graphite oxide (EGO) from crushed commercial graphite, and (iii) the formation of the desired EGAMPANI by in-situ chemical oxidative graft polymerization of the AMPANI monomer onto the EGO surface with 1,4-diaminobenzene (p-phenylenediamine) (DAB) as the bridging ligand. Details of the individual synthesis protocols, the results from the NMR analysis of the intermediary products, and the suppliers of the chemicals used are provided in the Supplementary data.

NMR spectra were recorded using a Bruker 400 MHz spectrometer. Molecular mass of compounds was determined with a Waters Q-TOF micro-mass spectrometer. For Fourier transform infrared (FT-IR) studies, samples were pressed into pellets using KBr and scanned in the range of 4000 to 400 cm^{-1} in a Perkin Elmer FT-IR spectrometer. FT-Raman spectra were acquired in a LabRAM HR spectrometer with Ar ion laser of wavelength 514 nm as source at magnification 100× and using a CCD camera ranging from 0 to 3000 cm^{-1} as detector. CHNO contents were determined using an EA Flash 1112 series instrument. Thermograms of the samples were recorded using a Netzsch STA 409 instrument at heating rate 2 °C min^{-1}. X-ray diffraction (XRD) patterns of powdered samples were recorded with a PANalytical X-ray diffractometer ranging from 6 to 70° with Cu anode K-α radiation of wavelength 1.54 Å as source. For the morphological studies, an FEI Quanta 200 scanning electron microscope was used. X-ray photoelectron spectroscopic (XPS) studies were carried out using a SPECS GmbH Phoibos 100 MCD Energy Analyzer with AlK radiation of energy 1486.6 eV. The electrochemical studies were carried out using a CHI 660D electrochemical workstation.

2.2. Preparation of EGAMPANI modified carbon paste electrode (CPE) and differential pulse anodic stripping voltammetry (DPASV) test procedure

A carbon paste electrode (CPE) modified with EGAMPANI was prepared by mixing 5 wt.% of EGAMPANI to a blend of 4:1 ratio of carbon black and paraffin oil. This paste was then filled into a glass tube of inner diameter 4 mm, into which a copper wire was inserted for electrical contact. All stripping voltammetric analyses were conducted in a three terminal cell, which contained a CPE as the working electrode, a calomel electrode as the reference electrode, and a platinum wire of 1 mm diameter as the counter electrode. Individual solutions of Pb^{2+}, Cd^{2+} and Hg^{2+} ions as well as mixed equimolar solutions of these metal ions were used for analysis. All solutions were prepared from the respective nitrate salts, using an acetate buffer to maintain a constant pH of 5. Volumes of 10 ml were used in each experiment, and the solutions were purged with argon to remove dissolved oxygen prior to investigation. The deposition of metal onto the CPE surface was performed at a constant potential of − 1.3 V for about 10 min, and the stripping of the deposit from the electrode surface was achieved by sweeping from − 1.1 to + 1.0 V with a scan rate of 25 mV s^{-1}. The stripping analysis was carried out with step potential of 0.004 V, amplitude of 0.05 V, pulse period of 0.5 s, pulse width of 0.2 s and sampling width of 0.0167 s. A neat CPE was prepared and used under the same conditions in order to distinguish the response of the EGAMPANI modified CPE from that of the neat one. All electrochemical studies were carried out under nitrogen atmosphere. The limit of detection (LoD) has been determined according to its definition given in the literature [18], using the relation $LoD = LoB + 1.645\ S_{D\ (\mathrm{low\ concentration\ sample})}$, where $LoB = Mean_{\ (\mathrm{blank})} + 1.645\ S_{D\ (\mathrm{blank})}$ and S_D is the standard deviation of three determinations.

3. Results and discussion

3.1. Synthesis of EGAMPANI

The synthesis of the aniline monomer is depicted in Scheme 1. The synthesis was initiated from 2-hydroxyaniline, in which the amine functional group was protected by reacting it with acetic anhydride to form the corresponding acetanilide (1). This was followed by the reaction with epichlorohydrin in the presence of a weak base to produce compound (2). The epoxide ring introduced in step 2 was then reacted with dimethylamine so that compound (3) was formed. Finally, the acetanilide moiety in compound (3) was deprotected to obtain the monomer (4). This was later used for chemical oxidative grafting.

The further reaction pathway to EGAMPANI is illustrated in Scheme 2. EGO prepared according to Hummers' method was used as the starting material. As it is well known, EGO is a good adsorbing agent for organic molecules and macromolecules by π–π stack interactions [19] and, beyond this, the oxygen containing functional groups on the EGO surface enable grafting polymers onto it through the formation of covalent bonds [1,20,21]. Taking advantage of both these properties of EGO, the EGO surface has been enriched with DAB. Chemical linking was achieved by amide bond formation in the presence of DCC as the coupling agent and DMAP as a base. Grafting of AMPANI was then accomplished through reaction of EGO-DAB with monomer (4) by in-situ chemical oxidative polymerization using APS as the oxidizing agent. This produced the desired EGAMPANI. One of the advantages of using AMPANI in the synthesis of EGAMPANI is that it is highly water soluble at all pH, which facilitates washing off any ungrafted excess AMPANI that may have formed during the in-situ polymerization.

3.2. Characterization of EGAMPANI

To study the type of bonding of the AMPANI to the EGO surface, the synthesized EGAMPANI and its intermediate compounds were analyzed using FT-IR spectroscopy. The spectra recorded for EGO, EGO-DAB and EGAMPANI are compiled in Fig. 1.

The spectrum of EGO (Fig. 1a) shows major bands at 1064, 1234, 1457, 1622 and 1733 cm^{-1}, which correspond respectively to the vibrational modes of C–O stretching, C–OH stretching of phenolic group, C=C phenyl ring stretching, and carbonyl group stretching at the edge of layer planes or in conjugate functional groups. The intense band observed at 3456 cm^{-1} is due to O–H stretching vibration of graphite oxide. These results confirm that EGO has a large number of oxygen containing functional groups on its surface. At both 2926 and 2857 cm^{-1} the C–H stretching vibrations of substituted aromatic compounds of EGO are observed, which is in line with earlier findings [3]. After the reaction of EGO with DAB to EGO-DAB, the carboxylic stretching frequency previously observed at 1733 cm^{-1} for EGO is shifted to 1709 cm^{-1} (Fig. 1b), indicating the formation of an amide bond. The amide bond is further confirmed by the stretching vibrations

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