



Synthesis of poly(sodium 4-styrenesulfonate) functionalized graphene/cetyltrimethylammonium bromide (CTAB) nanocomposite and its application in electrochemical oxidation of 2,4-dichlorophenol



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ABSTRACT

Poly(sodium 4-styrenesulfonate) (PSS) intercalated graphene (PSS-GN) was prepared via in situ reduction of exfoliated graphite oxides in the presence of PSS, and then mixed with CTAB to form a stable PSS-GN-CTAB nanocomposite through electrostatic self-assembly. The prepared composites were characterized by Fourier transform infrared spectrometry (FT-IR), ultraviolet and visible spectrometry (UV-vis) and X-ray diffraction (XRD). A novel 2,4-dichlorophenol (2,4-DCP) electrochemical sensor was fabricated based on a PSS-GN-CTAB modified glassy carbon electrode. It was found that the composite of PSS-GN-CTAB exhibited excellent electrocatalytic activity towards the oxidation of 2,4-DCP. Linear sweep voltammetry (LSV) was used for the quantitative determination of 2,4-DCP. Under the optimum conditions, the peak current of 2,4-DCP was proportional to its concentration at the range of 1.0×10^{-8} to 2.0×10^{-6} mol L⁻¹ with a detection limit 2.0×10^{-9} mol L⁻¹. The newly developed method was successfully applied for the determination of 2,4-DCP in the waste water with good recoveries. The proposed electrode system represents a new platform for designing excellent electrochemical sensors with water-dispersed graphene.

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1. Introduction

2,4-DCP is a representative chlorophenol compound that is widely employed as an important intermediate in the manufacture of some commonly used phenoxy herbicides, pharmaceuticals, fungicides, and insecticides. It poses a serious ecological problem as an environmental pollutant due to the high toxicity, strong odor emission and persistence in the environment, and suspected carcinogenic, and mutagenic properties [1]. The highly hazardous and toxic characteristics of 2,4-DCP require the development of simple, fast, sensitive, and accurate analytical methods for its detection and quantification. Many analytical methods have been established to determine 2,4-DCP, such as high performance liquid chromatography [2], gas chromatography [3], spectrophotometry [4], chemiluminescence [5], and electrochemical methods [6–11]. Among them, electrochemical methods are preferable over other methods due to the advantages of fast response, cheap instrument, low cost, simple operation, small size that affords a portable sensor for on-site detection. However, the reported detection limits of

2,4-DCP for other electrochemical methods were too high to meet the regulatory limits. Furthermore, the electrode modified materials in these reports are usually based on bio-enzymes, which are difficult to immobilize on electrode surfaces, require a chemical mediator such as hydrogen peroxide, and can be easily denatured if the pH, ionic strength, or temperature are not carefully controlled. All these factors have encouraged us to investigate novel electrode materials for the determination of 2,4-DCP.

Graphene (GN) is a one-atom-thick hexagonal array of sp²-bonded carbon atoms packed into a two-dimensional honeycomb structure. Ever since its discovery in 2004, graphene has been having a profound impact for many areas of science and technology due to its unique nanostructure and extraordinary properties, including high conductivity, high surface area, and low manufacturing costs [12,13]. These unique properties make graphene a promising component for potential applications in fabricating electrochemical sensors [14–20]. Unfortunately, graphene is hydrophobic and tends to agglomerate irreversibly or even restack to form graphite through van der Waals interactions and strong π-π stacking, which will not only ruin the advantage of the high surface area of graphene, but also sacrifice the outstanding single-layer electrical properties of graphene [21]. The propensity to agglomerate may limit its further applications, particularly in electrochemical

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sensors, because most of its unique properties are only associated with individual sheets [22].

A great effort has been made to improve the dispersion of graphene via chemical modification [23,24], covalent [25,26] or noncovalent functionalization [27–31]. Among them, a most exciting example is the surface functionalization of graphene with poly(sodium 4-styrenesulfonate) (PSS) (PSS-GN). The negatively charged poly(sodium 4-styrenesulfonate) units assist the dispersion of graphene in water by electrostatically preventing the restacking of graphene, and thus preserving the intrinsic electronic and structural properties of graphene. PSS-GN has been proven to show good stability, high conductivity, efficient electron transfer and good electrocatalytic activities [32–34]. It is believed that PSS-GN based films will have great application for electrochemical sensors and are worthy of further exploration.

Cetyltrimethylammonium bromide (CTAB), a type of cationic surfactant, is often used as an absorbent for phenols due to the strong hydrophobic interaction between the long alkyl chain of CTAB and aromatic ring of phenols [35]. In this case, CTAB can be employed to enrich the phenols on the electrode surface. Considering the positive charge of CTAB which allows it to easily assemble with the negatively charged PSS-GN, and its strong noncovalent interaction with phenols, in this work, the nanocomposite of PSS-GN and CTAB was prepared by self electrostatic assembly to yield an electrode material for the determination of 2,4-DCP. The PSS-GN-CTAB electrode gave extraordinary electrocatalytic activity towards the oxidation of 2,4-DCP and sensitive determination of 2,4-DCP was achieved. The proposed PSS-GN-CTAB electrode system represents a new platform for designing novel electrochemical sensors with water-dispersed graphene.

2. Experimental

2.1. Reagents and apparatus

Natural graphite flakes with the average diameter of 200 mesh were purchased from Sigma-Aldrich. Poly(sodium 4-styrenesulfonate) (PSS) (70000 g/mol) was purchased from Sigma-Aldrich. Concentrated hydrochloric acid (HCl), concentrated sulphuric acid (H_2SO_4), hydrogen peroxide (H_2O_2 30%), hydrazine hydrate (N_2H_4 : 80%) and potassium permanganate (KMnO_4) were analytical grade reagent received from Tianjin Chemical (Tianjin, China), and used without further purification. Pentachlorophenol (PCP, 99.0%), 2-chlorophenol (2-CP, 99.0%), 2,4-dichlorophenol (2,4-DCP, 99.0%), pyrocatechol, hydroquinol, and hydroxyphenol were purchased from Sigma-Aldrich. Nafion and CTAB were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. All the other chemicals and reagents used in the experiments were of analytical grade and used without further purification. Redistilled water was used throughout.

A Bruker IFS 66 v/s infrared spectrometer was used for acquiring the IR spectra. UV–vis spectra were obtained from a Lambda 35 UV–vis spectrometer (Perkin Elmer, USA). The X-ray diffraction (XRD) patterns were acquired on a Rigaku D/max-III A diffractometer (Japan). An RST 5000 electrochemical system (Suzhou Risetech Instrument Co., Ltd., China) was employed for all voltammetric measurements. AC impedance spectroscopy was implemented on a CHI660E electrochemical workstation (Shanghai Chenhua Co., China). A conventional three-electrode system was used, including a bare glassy carbon electrode (GCE) (diameter of 4 mm) or a Nafion/PSS-GN-CTAB/GCE as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire electrode as the auxiliary electrode. All of the pH values were measured with a PHS-3 C precision pH meter (Leici Devices Factory of Shanghai, China).

2.2. Preparation of PSS-GN-CTAB nanocomposite

Graphene oxide (GO) was synthesized from graphite powder according to the modified Hummer's method [36]. 1.0 g graphite was added into 98% H_2SO_4 (69 mL) in an ice bath with stirring, and KMnO_4 (8.0 g) was added slowly. The above mixture was kept at 35 °C overnight. Then distilled water (280 mL) was gradually added into the reaction system and continued stirring until the solution turned yellowish brown. After another 2 h of vigorous stirring, 25 mL of 30% H_2O_2 was added and the solution turned golden yellow immediately. Lastly, the mixture was washed with distilled water until the solution became acid free. The reaction mixture was filtered and dried under vacuum at 65 °C. The GO was obtained as a gray powder and used for the further experiments.

The water-soluble sulfonated graphene sheets were prepared from GO by the following three steps [37]. First, 0.2 g GO and 2.0 g PSS were added into 200 mL of redistilled water and sonicated for 30 min to form a stable supernatant suspension. Second, 10 mL of hydrazine monohydrate was added into the mixture. Third, after heating at 95 °C for 3 h, the mixture was centrifuged to remove excess hydrazine and PSS. The obtained black product is named as PSS intercalated graphene sheets (PSS-GN).

PSS-GN-CTAB composite was obtained by adding 1.0 mg PSS-GN into 1 mL CTAB ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) and sonicating for 2 h to yield a uniform suspension.

2.3. Preparation of the working electrode

Before modification, the bare GCE was polished to a mirrorlike finish with a 0.05 μm alumina slurry then washed successively with 1:1 $\text{HNO}_3/\text{H}_2\text{O}$ (v/v), anhydrous alcohol, and redistilled water in an ultrasonic bath, then dried. The working electrode was prepared as follows: first, 7 μL of PSS-GN-CTAB mixture was dropped onto the freshly prepared GCE surface and dried. Then, 5 μL Nafion (0.5%, w/v) solutions were coated onto the PSS-GN-CTAB/GCE and dried under an infrared lamp. Lastly, the electrode surface was washed with doublely distilled water to remove unbound materials from the electrode surface. The obtained electrode is henceforth referred to as Nafion/PSS-GN-CTAB/GCE.

2.4. Electrochemical measurements

Known aliquots of 2,4-DCP stock solution and 5 mL of 0.1 mol L^{-1} PBS (pH 3.0) were added into an electrochemical cell, and then the three-electrode system was installed in it. Cyclic voltammetry (CV) was employed between 0.3 and 1.2 V (vs SCE) with a scan rate of 0.05 V s^{-1} . Linear sweep voltammetry (LSV) was recorded from 0.3 to 1.2 V. AC impedance was performed in a $1.0 \times 10^{-3} \text{ mol L}^{-1}$ $\text{Fe}(\text{CN})_6^{3-/4-}$ (1:1) solution containing 0.1 mol L^{-1} KCl. The parameters were as follows: frequency range from 0.01 to 10^5 Hz; initial potential, 0.2 V; amplitude, 0.01 V, and quiet time of 2 s.

3. Results and discussion

3.1. Characterization of PSS-GN composite

In Fig. 1A (left), the r-GO prepared in the absence of PSS easily precipitated and settled down to the bottom of the bottle. However, the as-prepared PSS-GN dispersion with a concentration of 1.0 mg mL^{-1} is very stable and hardly any precipitate appeared after several months of standing (right).

The FTIR spectra of GO and PSS-GN composite are given in Fig. 1B. Obviously, the GO spectrum has typical FTIR absorptions of oxygen-containing functional groups, such as broad absorption of the stretching vibrations that correspond to carboxylic acids

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