



Original article

Polystyrene–graphene oxide modified glassy carbon electrode as a new class of polymeric nanosensors for electrochemical determination of histamine



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ABSTRACT

A simple and rapid protocol for the synthesis of polystyrene–graphene oxide nanocomposite (PS/GONC) was achieved for first time using an *in situ* polymerization method. PS/GONC modified glassy carbon electrode (PS/GONC/GCE) has been employed as an efficient nanosensor for the electrooxidation of histamine. The PS/GONC/GCE is used as an electrochemical nanosensors for monitoring histamine using differential pulse voltammetry techniques (detection limit 0.03 $\mu\text{mol/L}$). In addition, the prepared nanosensor was successfully applied to determine histamine in fish samples, yielding satisfactory results. The spiked recoveries were in the range of 98.2%–103.1%.

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1. Introduction

Graphene, a novel material consisting of a monolayer of honeycomb-like crystal lattice of sp^2 -hybridized carbon atoms, has today become one of the hot spots of nanotechnology-oriented material science. Due to its 2D structure, graphene has versatile properties, such as high electron mobility, large surface area and robust mechanical strength. Graphene provides the greatest sensing area per unit volume because each atom of graphene is a surface atom [1]. Therefore, electron transport through graphene is highly dependent on electron donating or accepting molecules adsorbed on its surface, rendering graphene based materials as excellent candidates used in room temperature chemiresistor-type sensing applications [2]. Single graphene flakes have been produced with the traditional micromechanical cleaving technique [3] and thermal or plasma enhanced chemical vapor deposition methods [4,5]. However, the production of high-quality, single-layered graphene sheets as well as their deposition to a specific spot on a substrate is still challenging tasks, at least on a large scale. Graphene oxide (GO), on the other hand, can be produced on a

large scale and processed in solution [6–8]. GO, as a basic material for the preparation of individual graphene sheets in bulk-quantity, has attracted great attention in recent years. Additionally, the incredibly large specific surface area (two accessible sides), the abundant oxygen containing surface functionalities, such as epoxide, hydroxyl, and carboxylic acid groups, and the high water solubility afford GO sheets great promise for many more applications [6–8]. Its amazing characteristics, include a large surface area, extraordinary electrical [9–11], thermal [12], mechanical [13], and structural properties [14a–d], make graphene a highly versatile carbon species with promising applications in composites [15a–d], transparent conducting films [1,16], sensors [17], supercapacitors [18a and b], nanoelectronics [19], batteries [20a–d], catalyst supports [21], and biotechnology [22].

On the other hand, polymer composites are valued as strong, durable, and multifunctional species with potential applications as high performance materials. Yet, the cost of nanoparticles, their availability and the challenges that remain to achieve good dispersions pose major obstacles in their production [23]. One way to produce high performance composites is filling polymers with nanotubes [24]. A better alternative is dispersing of just a small amount of graphene in polymers which often turns them into tough, lightweight composites with good electrical conductivity and thermal stability. However, this option requires production of graphene sheets on an acceptable scale followed by their homogeneous incorporation into the polymers [25].

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Polystyrene (PS) is one of the most widely used commercial polymers. The integration of GO in a PS matrix produced nanocomposite thin films that are semiconducting and exhibit an ambipolar field effect [25]. The dispersion of graphene into a PS matrix has stimulated considerable research, including the preparation of graphene-PS composite thin films by adding linear mono-dispersed PS functionalized GO dispersion in DMF by Eda *et al.* [25]. Furthermore, there are some studies on the preparation of PS-graphene nanocomposite by polymerization where styrene monomer is dispersed in the water phase and polymerized with a water soluble radical initiator in the presence of GO. For example, fabrication of PS/graphene nanocomposite by microemulsion polymerization was reported by Ahn *et al.* [26]. Also, Ding *et al.* [27] synthesized the PS intercalated GO nanocomposite via polymerization in the presence of sodium laurel sulfate as emulsifier. To conclude, Hu *et al.* [28] prepared the graphene nanosheets-PS nanocomposites by *in situ* polymerization and reduction of GO using hydrazine hydrate.

In order to upgrade the properties of styrene and reach the desired PS/GO interaction, we decided to synthesize GO incorporated into PS. After the nanocomposite has been synthesized, we used PS/GONC for studying the electrochemical behavior of histamine. To the best of our knowledge, this is the first report of the determination of histamine based on its direct electrochemical oxidation by a PS/GONC modified glassy carbon electrode (PS/GONC/GCE). Using this system, detection of sensitive quantities of histamine was realized using differential pulse voltammetric method. The electrode has an ultra low detection limit of 0.03 $\mu\text{mol/L}$ during histamine electrooxidation, as compared with previous reports (Table 1) [29–34]. The excellent capacity of the electrode for histamine electrooxidation has demonstrated its excellent performance. Furthermore, the proposed polymeric sensor (PS/GONC/GCE) was successfully used to detect histamine in fish samples.

2. Experimental

2.1. Apparatus

Electrochemical experiments were performed with a computer-controlled Autolab modular electrochemical system (Eco Chemie Ultecht, The Netherlands), driven with GPES software (Eco Chemie). A conventional three-electrode cell was used with an Ag/AgCl (Methrom, The Netherlands) as a reference electrode and a Pt wire as a counter-electrode. The working electrode was PS/GONC/GCE. All measurements were conducted at a thermostated temperature of 20 ± 1 °C. The transmission electron microscope (TEM) images were obtained at JEOL-1200 EX TEM (Japan). The images of scanning electron microscope (SEM) were obtained at Hitachi S-4800 (Japan).

2.2. Chemical and reagents

All chemicals used were analytical grade from Merck (Darmstadt, Germany) and were used without further purification. Briton

Robinson buffers were prepared by initially dissolving 10 mL concentrated orthophosphoric acid, 8.7 mL glacial acetic acid and 9.27 g boric acid in water and diluting to 1.0 L in a volumetric flask. This solution was subsequently used to prepare appropriate buffers by addition of 7.5 mol/L NaOH to reach the desired pH value. Voltammetric experiments of histamine were carried out in 0.15 mol/L Briton Robinson buffer of pH 4.00. Histamine was purchased as hydrochloride salts from Sigma (USA). Dansyl chloride for dansylation was obtained from Sigma-Aldrich (Switzerland).

Stock solutions of the histamine were prepared separately to concentrations of 1 mg/mL in 0.1 mol/L hydrochloric acid (HCl). A working solution was prepared by diluting 1 mL of each stock solution in 0.1 mol/L HCl to a final volume of 10 mL. The Dansyl chloride solution (5 mg/mL) was prepared by dissolving 500 mg of Dansyl chloride in 100 mL of acetone. All solutions were kept at a temperature of 4 °C prior to use.

Histamine extraction from the samples was carried out according to the procedures developed by Mah *et al.* [35] with a little modification. A 3 g slurry of each sample was transferred into a centrifuge tube containing 10 mL of 5% (w/v) trichloroacetic acid (TCA) and 200 μL of 1,7-diaminoheptane. The mixture was vortexed for 15 min and then centrifuged at $5000 \times g$ for 10 min at 4 °C. The supernatant was collected and the residue was extracted again with the same volume of TCA. Both supernatants were filtered through Whatman paper No. 1 and combined. The final volume was adjusted to 25 mL with TCA.

2.3. Synthesis of the PS/GONC

Initially, the GO was prepared according to our previous works [36,37]. In brief, pure graphite (1.0 g) and potassium chlorate (8.0 g) were mixed in fuming nitric acid (20 mL) at room temperature without subsequent aging and stirred for 24 h. The following processes, such as washing, filtration and cleaning, were carried out as in the Brodie method. The synthesized graphite oxide (10 mg) was dispersed in aqueous NaOH solution (30 mL) at pH 10. The prepared graphite oxide was sonicated by a bath type sonicator (Sonoswiss SW3-H, 38 kHz, Switzerland) for 1 h. After ultrasonication, samples were immediately precipitated by a centrifuge at 15,000 rpm for 10 min. The graphene oxide sheets were extracted carefully.

Then, 1.5 mL octanol was added to an aqueous solution containing 75 mL distilled water and 250 mg sodium dodecyl sulfate. Then 50 mg of GO was added. The mixture was sonicated for 1 h minimum and transferred to a three necked round bottom flask (rbf), cooled in an ice bath and equipped with a condenser, dripping funnel, and nitrogen inlet. Then a mixture of 2.5 g styrene and 0.025 g benzoyl peroxide was added under a stream of N_2 in 30 min. The resulting mixture was homogenized by sonication at 0 °C for another 30 min. Then polymerization was carried out by increasing the temperature of the mixture in an oil bath to 80 °C for 4 h under an inert nitrogen blanket. Polymerization rendered a stable gray colored PS/GO emulsion from which excess surfactants and residual monomers were washed away by methanol and water

Table 1
Analytical parameters for detection of histamine at several electrochemical sensors.

Type of electrode	Method	Linear range	LOD	Ref.
PS/MWCNT/DOx/HRP/Fc	Amperometric	0.3–20 $\mu\text{mol/L}$	0.17 $\mu\text{mol/L}$	[29]
SPCE	Amperometric	10–300 $\mu\text{mol/L}$	3.0 $\mu\text{mol/L}$	[30]
Nickel-GCE	Chronopotentiometric	0.5–110 mmol/L	0.11 mmol/L	[31]
DOx/HEMA/SPE	Amperometric	0–60 $\mu\text{mol/L}$	0.65 $\mu\text{mol/L}$	[32]
DOx/Pt	Amperometric	–	305.5 $\mu\text{mol/L}$	[33]
DOx/nylon-net membrane/glutaraldehyde/Pt	Amperometric	1–50 $\mu\text{mol/L}$	50 $\mu\text{mol/L}$	[34]
PS/GONC/GCE	DPV	0.1–3 $\mu\text{mol/L}$	0.03 $\mu\text{mol/L}$	This work

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