Green-synthesized gold nanoparticles supported on reduced graphene oxide for chronoamperometric sensing of nitrite in environmental and food samples

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ABSTRACT

Nitrite is a chemically reactive and environmentally persistent anion found in aquatic ecosystems, posing carcinogenic and ecological risks. This work presents a sensor based on a glassy carbon electrode modified with a green-synthesized nanocomposite of gold nanoparticles (AuNPs) anchored on reduced graphene oxide (rGO). The material was synthesized via an one-step green co-reduction process, in which an aqueous extract of *Camellia sinensis* acted simultaneously as a reducing agent for both the gold precursor (Au^{3+}) and graphene oxide (GO), which was previously obtained from graphite recovered from spent Zn–C batteries. Chronoamperometric detection showed a linear range of 49.3–607.5 µM (R^2 = 0.990), LoD of 0.21 µM, and LoQ of 1.00 µM. The sensor's applicability was assessed in tap water, mineral water, and synthetic water samples representing two Brazilian aquifers. The proposed sensor represents a reliable platform for nitrite detection in environmental and food matrices.

Keywords: chronoamperometric nitrite sensor; gold nanoparticles; reduced graphene oxide; tea mediated co-reduction; green chemistry.

Introduction

Nitrite (NO_2^-) is a hazardous contaminant requiring sensitive detection. Electrochemical sensors modified with nanomaterials like gold nanoparticles (AuNPs) and reduced graphene oxide (rGO) have shown high sensitivity. Electrochemical detection offers a sensitive, low-cost alternative for nitrite monitoring (1), especially when combined with nanomaterials such as rGO and metallic nanoparticles (2). Among them, AuNPs are notable for their catalytic activity and biocompatibility (2). In line with green chemistry principles, plant extracts have been explored as eco-friendly reducing agents in nanomaterial synthesis (3). This study reports a green-synthesized electrochemical sensor based on a glassy carbon electrode (GCE) modified with a nanocomposite of AuNPs anchored onto rGO, derived from spent battery graphite rods. The nanocomposite was produced via an one-step green co-reduction using an aqueous extract of *Camellia sinensis*, and the sensor demonstrated effective performance in environmental and food samples.

Experimental

Green synthesis of AuNPs–rGO nanocomposite

A total of 25 mg of GO was dispersed in 25 mL of distilled water (1 mg mL^{-1}) and sonicated for 1 hour. Simultaneously, a black tea extract was prepared by boiling 200 mg of *Camellia sinensis* (Matte Leão®) in 12 mL of water at 80 °C for 5 minutes, followed by filtration. The GO dispersion was mixed with 0.25 mL of $HAuCl_4$ solution (1 mM) and 6 mL of the tea extract. The mixture was heated under reflux at 90 °C for 6 hours. The resulting black precipitate (AuNPs–rGO) was washed with distilled water, centrifuged three times at 4000 rpm for 5 minutes, dried at 80 °C, and stored.

Fabrication of the modified electrode

A glassy carbon electrode (GCE) was polished sequentially using alumina slurries (1.0, 0.3, and 0.05 µm) and sonicated in ethanol and ultrapure water. Then, 6 µL of the AuNPs–rGO suspension (0.5 mg mL^{-1}) was drop-casted onto the GCE surface and dried under an infrared lamp for 20 minutes.

Electrochemical measurements

Electrochemical experiments were performed using a PGSTAT204 potentiostat (Metrohm) with NOVA 2.1.5 software, in a conventional three-electrode setup: Ag/AgCl (3.0 mol L^{-1} KCl) as reference, platinum wire as auxiliary, and AuNPs–rGO/GCE as the working electrode. Chronoamperometry (CA) and cyclic voltammetry (CV) were performed in 0.1 mol L^{-1} phosphate buffer solution (pH 5.0). All measurements were conducted in triplicate to ensure reproducibility.

Results and Discussion

Elemental and structural characterization

The nanocomposite obtained via green co-reduction was characterized using structural, elemental and morphological analysis. Elemental analysis (CHNS) was employed to evaluate the carbon content and infer the extent of GO reduction. The carbon percentage increased from 62.3% in GO to 68.2% in rGO, indicating effective removal of oxygenated functional groups during the green co-reduction process. The AuNPs–rGO nanocomposite presented similar elemental composition to rGO, suggesting that gold nanoparticle incorporation did not significantly alter the overall carbon framework. Trace levels of nitrogen and sulfur may be

attributed to the residual biomolecules organic components of the *Camellia sinensis* extract.

Table 1. CHNS elemental composition of the samples used in the development of the AuNPs–rGO sensor

Amostras	C (%)	H (%)	N (%)	S (%)
Residual graphite from spent Zn–C batteries [a]	100,14	–1,3438	–0,27688	–0,1483
Battery waste-derived GO [b]	62,332	1,194	1,683	1,5828
Green rGO [b]	68,181	1,596	1,1282	0,91245
AuNPs–rGO verde[b,c]	69,448	1,5336	0,33658	0,25247

Notes: [a] Precursor for GO synthesis; [b] Synthesized via green tea-mediated reduction using *Camellia sinensis* extract; [b,c] Modifier used in the proposed electrochemical sensor.

Electrochemical performance of the sensor

Differential pulse voltammetry (DPV) results (Figure 1a) confirmed that the AuNPs–rGO/GCE electrode exhibited a significantly enhanced anodic peak current and a more favorable (lower) oxidation potential for the detection of 500 µmol L^{-1} sodium nitrite ($NaNO_2$), attributable to the synergistic electrocatalytic effect between reduced graphene oxide (rGO) and gold nanoparticles (AuNPs).

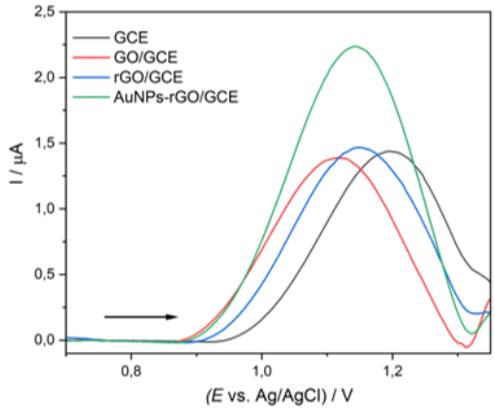

Figure 2 (a). DPV responses of GCE, GO/GCE, rGO/GCE, and AuNPs–rGO/GCE electrodes toward nitrite detection in 0.1 mol L^{-1} phosphate buffer (pH 5.0).

Chronoamperometric measurements (Figure 3), conducted in 0.1 mol L^{-1} phosphate buffer solution at pH 5.0, demonstrated a rapid and stable amperometric response, with a wide linear dynamic range (49.3–607.5 µM; R^2 = 0.990), a limit of detection (LOD) of 0.2 µM, and a limit of quantification (LOQ) of 1.0 µM.

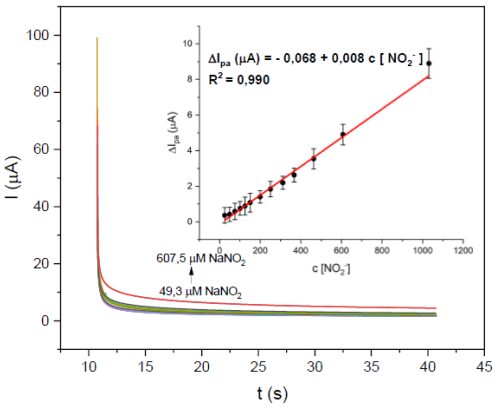

Figure 3 Chronoamperometric response of AuNPs–rGO/GCE to increasing concentrations of NO_2^- (inset: calibration curve).

Fabrication reproducibility and stability and analysis of samples

The inter-day fabrication reproducibility of AuNPs–rGO/GCE electrodes was evaluated by measuring the response to 300 µmol L^{-1} of NO_2^- in 0.1 mol L^{-1} phosphate buffer (pH 5.0) at an applied potential of +1.1 V. The relative standard deviation (RSD) ranged from 5.13% to 13.80% across six independently prepared electrodes (n = 6). The standard addition method was applied to quantify nitrite in all samples and to assess potential matrix effects.

Table 2. Real samples analyzed for nitrite detection using the proposed AuNPs–rGO/GCE sensor.

Sample	Added (µM)	Found (µM)	Recovery (%)
Sausage extract	510	614.96	120.58
Simulated Alter do Chão aquifer water	510	492.59	96.59
Simulated Guarani Aquifer Water	510	605.47	118.72

Conclusão

The fabricated sensor exhibited excellent analytical performance, including a limit of detection (LoD) of 0.2 µmol L^{-1}, a linear concentration range of 49.3 to 607.5 µmol L^{-1}, and satisfactory fabrication reproducibility and operational stability, as evidenced by a global RSD of 16.63% (n = 6). Its successful application to real samples confirms the sensor's potential for use in food quality control and environmental monitoring

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