



# A synergistic combination of reduced graphene oxide and antimony nanoparticles for estriol hormone detection



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## ABSTRACT

In this study, the modification of reduced graphene oxide (rGO) with antimony nanoparticles (SbNPs) for determination of estriol in natural water is presented for the first time. The morphology and the electrochemical performance of the rGO–SbNPs composite were characterised by scanning electron microscopy and cyclic voltammetry, respectively. The synergistic combination of rGO sheets and Sb nanoparticles yielded a limit of detection (LOD) of  $0.5 \text{ nmol L}^{-1}$  ( $0.14 \mu\text{g L}^{-1}$ ) for estriol hormone, the lowest LOD for estriol reported in the literature to our knowledge. The proposed device was successfully applied in the determination of estriol in a natural water sample, and is a promising platform for a simple, rapid, direct and ultrasensitive analysis of estriol.

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## 1. Introduction

Estriol (1,3,5,(10)-estratriene-3,16 $\alpha$ ,17 $\beta$ -triol) is one of the essential steroid estrogens that exhibit a critical impact on reproductive and sexual functioning, bone structure and some organs. Estriol is found as a pollutant in environmental waters and it is a member of a class of chemicals known as endocrine disruptors that have adverse effects by interfering with the function of hormones in the human body and on aquatic organisms [1,2]. These endocrine disruptors can persist after water purification treatments and even at low concentrations can potentially exert biological effects [3]. The monitoring of endocrine disruptors in the aquatic environment is progressively becoming a priority for government and regulatory agencies as well as the general public. Thus, the development of modern strategies of analysis to measure these endocrine disruptors, e.g. estriol, at low concentration levels is very important.

Quantification of estriol has been proposed using several methods including various chromatographic techniques [4–6], immunoassays [7–9], electrophoresis [10,11] and electroanalytical methods [1,12,13]. Owing to its operational simplicity, low expense, fast response, high sensitivity, potentiality for

miniaturisation and automation, and in-field/on-site monitoring, the electroanalytical method is of great interest.

Since its discovery in 2004, graphene has led to an explosion of interest in the field of electrochemistry due to its extraordinary electronic transport properties, high electrocatalytic activities and large surface area [14,15]. Similar to carbon nanotubes (CNTs), graphene can also be employed as a support that can be modified with different species. The modification of graphene with antimony nanoparticles (SbNPs) offers great opportunities for new functions due to the synergistic effects of the component materials and may expand the application area of graphene.

Electrodes based on antimony are widely used in electrochemical stripping analysis since they possess similar properties to bismuth and can act as a “mercury-free” electrode for measuring trace heavy metals and other species of interest that are associated with environmental monitoring [16,17]. Recently, our research group proposed the use of a nanocomposite based on CNTs modified with SbNPs for electrochemical sensing [18], and the application of a paraffin composite electrode modified with CNT–SbNPs for the simultaneous determination of sulfamethoxazole and trimethoprim in natural water [19].

In this study, we present a synergistic combination of reduced graphene oxide (rGO) and SbNPs. The rGO–SbNPs composite was synthesised, characterised and applied, for the first time, in the determination of estriol in natural water. The proposed electrode is promising, allowing for the fast, simple and sensitive determination of estriol in environmental samples.

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## 2. Materials and methods

### 2.1. Apparatus and procedures

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed using a model PGSTAT30 Autolab electrochemical system (Eco Chemie, Utrecht, Netherlands) equipped with GPES software (Eco Chemie, Utrecht, Netherlands). The cell was assembled with a conventional three-electrode electrochemical system: bare glassy carbon (GC), GC/graphene oxide (GO), GG/rGO or GC/rGO-SbNPs as a working electrode (diameter: 3 mm); Ag/AgCl/KCl (3.0 mol L<sup>-1</sup>) as a reference electrode; and a Pt plate as an auxiliary electrode. All experiments were carried out at a 25 °C. Electrochemical characterisation of the GC/rGO-SbNPs electrode was performed using CV in 0.5 mol L<sup>-1</sup> HCl with a scan rate of 50 mV s<sup>-1</sup>. DPV measurements were obtained with a scan rate of 10 mV s<sup>-1</sup>, pulse amplitude of 100 mV, and a step potential of 2 mV in a 0.1 mol L<sup>-1</sup> phosphate buffer solution (PBS) pH 9.0, containing 50.0 μmol L<sup>-1</sup> of estriol standards.

The surface morphology of each material was characterised using a field-emission gun scanning electron microscope (FEG-SEM) and the images were recorded using a model FEI Inspect F50 microscope (FEI Company, Hillsboro, USA).

### 2.2. Chemicals and solutions

All solutions were prepared with water purified from a Barnstead Nanopure system, resistivity ≥ 18 MΩ cm (Thermo Scientific, USA). All reagents used in this study were of analytical grade and were used without further purification. Graphite powder of 1–2-μm particle size, antimony chloride (SbCl<sub>3</sub>) and estriol were purchased from Sigma-Aldrich (Germany).

### 2.3. Synthesis of the GO, rGO and rGO-SbNPs composite

The graphene oxide (GO) was prepared by an improved Hummers' method [20]. Typically, 10 g of graphite and 10 g of NaNO<sub>3</sub> was mixed with 450 mL of H<sub>2</sub>SO<sub>4</sub> (98%) in a 2500-mL flask. The mixture was then stirred for 30 min in an ice bath, followed by the addition of 60 g of KMnO<sub>4</sub> under vigorous stirring. The reaction mixture was then held under refrigeration at 4 °C for 24 h. Next, the mixture was stirred at 35 °C followed by the addition of 450 mL of H<sub>2</sub>O, also under vigorous stirring. After that, the reaction temperature was rapidly increased to 98 °C and a further 450 mL of H<sub>2</sub>O was added, followed by 300 mL of 30% H<sub>2</sub>O<sub>2</sub> aqueous solution. The reaction mixture was again held under refrigeration at 4 °C for 24 h. The obtained GO solution was centrifuged for 30 min at 8000 rpm and washed several times with 5% HCl and distilled water until the pH of the filtrate was neutral. Finally, the GO obtained was lyophilised for 24 h.

The synthesis of the rGO-SbNPs composite was performed using sodium dodecyl sulphate (SDS) as a surfactant. A suspension containing a ratio by weight of 10:4 GO/SDS was prepared in 15 mL of ethanol (pure grade) and then sonicated for 20 min. An excess of sodium borohydride was then added, and this suspension was sonicated for another 20 min. A solution containing 40% SbCl<sub>3</sub> in relation to the amount of GO was slowly dropped into the rGO solution, which was kept under constant stirring. Once the reaction was complete, the rGO-SbNPs composite was dispersed using an ultrasonic probe for 1 h. The rGO-SbNPs obtained were centrifuged for 10 min at 3000 rpm and washed several times with distilled water until the solution became colourless. After that, 5 mL of ethanol (pure grade) was added to the resulting composite and then the rGO-SbNPs were dried at 60 °C.

To evaluate the synergistic effect of rGO and SbNPs, the chemical synthesis of rGO was also performed as above, but without adding SbCl<sub>3</sub>.

### 2.4. Electrodes preparation

Prior to modification, the GC electrode surface was polished with 0.3-μm alumina slurries, rinsed thoroughly with double-distilled water, sonicated for 5 min in ethanol and 5 min in water, and then dried in air. A suspension containing 0.3 mg of rGO-SbNPs and 1.0 mL of water was dispersed using ultrasonic stirring for 20 min. A 10-μL aliquot of this dispersion was dropped onto the GC electrode surface, and dried at room temperature. For comparison, the GC/GO and GC/rGO electrodes were also prepared as described above.

### 2.5. Sample preparation and analysis of estriol in natural water

Known amounts of the standard estriol solution were added to a 10-mL aliquot of natural water from a dam located in São Carlos (São Carlos/SP—Brazil), giving a final concentration of 5.0 μmol L<sup>-1</sup> estriol. This sample was mixed with 10 mL of 0.1 mol L<sup>-1</sup> PSB pH 9.0. No further sample treatment was done. The estriol content was determined by three successive additions of aliquots of the standard estriol solution.

### 2.6. HPLC measurements

Estriol spiked into natural water was determined quantitatively by HPLC using a Shimadzu (Kyoto, Japan) DGU-14A modular system comprising two LC-10A pumps, a CTO-10A oven, and an SPD-10AV variable wavelength detector. Separations were carried out on an Ascentis C-18 HPLC column (25 cm × 4.6 mm, i.d.: 5 μm), protected by an Ascentis C-18 guard column (2 cm × 4.0 mm, i.d.: 5 μm), eluted with a mixture of methyl alcohol, water and formic acid (65:35:0.2 v/v) with a flow rate of 1 mL min<sup>-1</sup> under isocratic conditions. The monitored wavelength was 280 nm.

## 3. Results and discussion

### 3.1. Surface morphology and electrochemical characterisation of the rGO-SbNPs composite

The surface morphology of the GO, rGO and rGO-SbNPs composite samples was characterised by FEG-SEM. A drop of ethanolic suspension of these materials was applied onto the Si substrate and the FEG-SEM micrographs of the GO, rGO and rGO-SbNPs are shown in Fig. 1. Fig. 1A displays typical images of GO where it is evident that the material consists of a mixture of single layers and multi-layer graphene sheets. GO as two-dimensional materials tend to stack together through π-π interactions, which causes the blocking of catalytically active sites [21]. On the other hand, Fig. 1B presents the images of rGO, in which the graphitic material displayed a typical wrinkled structure with plenty of corrugations. The reduction of graphene oxide causes the unstacking of sheets and, consequently, the unblocking of active sites. The inset in Fig. 1A exhibits typical Raman spectra for the GO sheets. It was observed that the synthesised GO presented two characteristic absorption bands in its Raman spectrum: the G band at 1590 cm<sup>-1</sup> and the D band at 1355 cm<sup>-1</sup>. The G band corresponds to bond stretching of sp<sup>2</sup> carbon pairs. The D band is associated with the breathing mode of aromatic rings with dangling bond in-plane terminations. The relationship between the intensity of the D band (*I<sub>D</sub>*) and G band (*I<sub>G</sub>*) is usually employed to evaluate the size of the in-plane sp<sup>2</sup> domains for carbon materials. The obtained value for the *I<sub>D</sub>*/*I<sub>G</sub>* ratio was 0.94 for obtained GO sheets. Already, the inset in Fig. 1B shows typical Raman spectra for the rGO sheets. The higher magnitude

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