

A disposable and low-cost laser-scribed graphene electrochemical sensor for simultaneous detection of hydroquinone, paracetamol and methylparaben

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INTRODUCTION

Laser-scribing technology has been used as an alternative method for scalable fabrication of graphene-based devices in a single step (LSG), employing different substrates such as polyimide (PI)[1], paper[2], phenolic paper[3], among others. The LSG technique enables the controllable fabrication of electrodes onto several surfaces with the geometry of interest without the use of templates/stencils and additional chemicals commonly used to manufacture electrochemical devices[2].

Electrochemical sensors based on the LSG technology have aroused the interest of many research groups due to low-cost, simple, and easy manufacturing approach, not requiring sophisticated instrumentation and processes. Benefitting from these characteristics, the development of disposable, portable, and miniaturized sensors employing inexpensive and new precursor substrates is an exciting approach for the (bio)sensing field[4].

Human activities have resulted in the contamination of water resources with a plethora of emerging pollutants (EP) (pharmaceuticals, endocrine disruptors, hormones, toxins, etc). Given the environmental problems and potential adverse effects of EP on human health, it is important the continuous monitoring of EP in different water supply systems. In this sense, the development of portable, sensitive, and low-cost methods for simultaneous determination of several EP species in water samples is of utmost importance for in-field analysis and in resource-limited settings. Thus, in this work, we used polyetherimide (PEI) as a novel polymeric substrate to manufacture a low-cost, disposable, and portable LSG sensor for the simultaneous determination of three important emerging contaminants (HQ, PA, and MP) in the water samples.

EXPERIMENTAL

A CO₂ pulsed laser (Router VS4040C, Visutec, São Paulo/Brazil) with a 10,5 % power and a scan rate of 40 mm/s was employed to manufacture the PEI-LSG devices in a three-electrode design (counter electrode (CE), reference electrode (RE) and working electrode (WE)). The laser output device surface was positioned at a distance of 10 mm from the PEI platform. Silver ink was used to paint the connections and the RE. Double-sided tape (3M®) was used to delimit the electrode area.

The morphologic characterization of the PEI substrate and PEI-LSG was carried out by scanning electron microscopy (SEM, model TM3000) with an applied acceleration voltage of 15 kV. Raman spectroscopy was performed on a Horiba T64000 confocal microscope with a 532 nm laser, 30 mW power, 100x objective, 200 μm aperture, 100 μm slit, 15 s of exposure, and 5 scans accumulation. The cyclic voltammetry(CV) and electrochemical impedance spectroscopy(EIS) were employed to characterize the electrochemical behavior of the PEI-LSG sensor using 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M KCl.

RESULTS AND DISCUSSION

The laser irradiation on the PEI substrate provides devices with high definition in a single step of manufacture (Figure 1a). The graphene-like material formed by the laser engraving was electrochemically characterized by CV varying the scan rate values from 5 to 200 mV/s resulting in a peak potential separation (ΔE_p) equal (56.3 ± 8.9) mV and the peak current ratio (I_{pa}/I_{pc}) of 0.90 ± 0.09 , which is correlated to a reversible process (Figure 1b). Also, the anodic and cathodic peak currents present a linear behavior to the square root of the scan rate ($v^{1/2}$) (Figure 1c), indicating a diffusion-controlled nature of the mass transport described by the Randles-Sevcik equation [5]. Using this equation and the slope of the anodic curve obtained in Figure 1c, we calculated the electroactive area of the electrode, which was equal to 0.17 cm^2 , corresponding to a 3.4-fold enhancement of the geometric area (0.05 cm^2).

Figure 1d-f shows the micrographs obtained of PEI sheet and PEI-LSG device in different magnifications. The micrographs illustrate that the PEI sheet is a flat polymeric surface (Figure 1d) and that the localized carbonization using CO_2 laser radiation provides a graphene film with high porosity and cavities (Figure 1e), which contributed to the increased electroactive area[3]. Besides, a cross-section image shown in Figure 1f demonstrates a delimitation between the PEI substrate and the LSG film.

Raman spectroscopy was used to characterize the graphene-like material formed by the photothermal laser irradiation on PEI substrate. As shown in Figure 1g, the Raman spectrum of PEI-LSG material shows a D band at 1341 cm^{-1} (corresponding to defects and/or functional groups present in the graphene structure), and the G band at 1572 cm^{-1} (corresponding to the sp^2 hybridization), which is described due to the two-photon lattice vibrational process in graphene structure[6]. The ratio of D and G band intensities (I_D/I_G) was 0.87, indicating a high disorder material, which can provide catalytic and high electron-transfer properties[2].

The electrochemical performance of the PEI-LSG sensor was compared with LSG devices fabricated in other polymeric substrates, such as PI and phenolic paper. CVs plots for the redox probe using PI, PEI, and phenolic paper-based electrodes exhibited peak-to-peak separation of 95.8 ± 9.7 mV, 56.3 ± 8.9 mV, and 104.8 ± 11.4 mV, respectively (Figure 1h). Besides, k° was calculated using Nicholson's and Lavagnini's equations [7]. The k° values obtained for PI, PEI, and phenolic paper were $4.76 \times 10^{-3} \text{ cm/s}$, $3.20 \times 10^{-2} \text{ cm/s}$ and $3.64 \times 10^{-3} \text{ cm/s}$, respectively. To further characterize the electrochemical behavior, EIS was employed to obtain the resistance to charge transfer (Rct). According to the Nyquist plots (Figure 1i), the Rct values for PI, PEI, and phenolic paper were, $0.566 \pm 0.098 \text{ k}\Omega$, $0.089 \pm 0.008 \text{ k}\Omega$, and $0.735 \pm 0.137 \text{ k}\Omega$, respectively. The higher k° values and lower Rct indicate that the PEI-LSG device is an excellent alternative material to be applied as a disposable and portable electrochemical sensor.

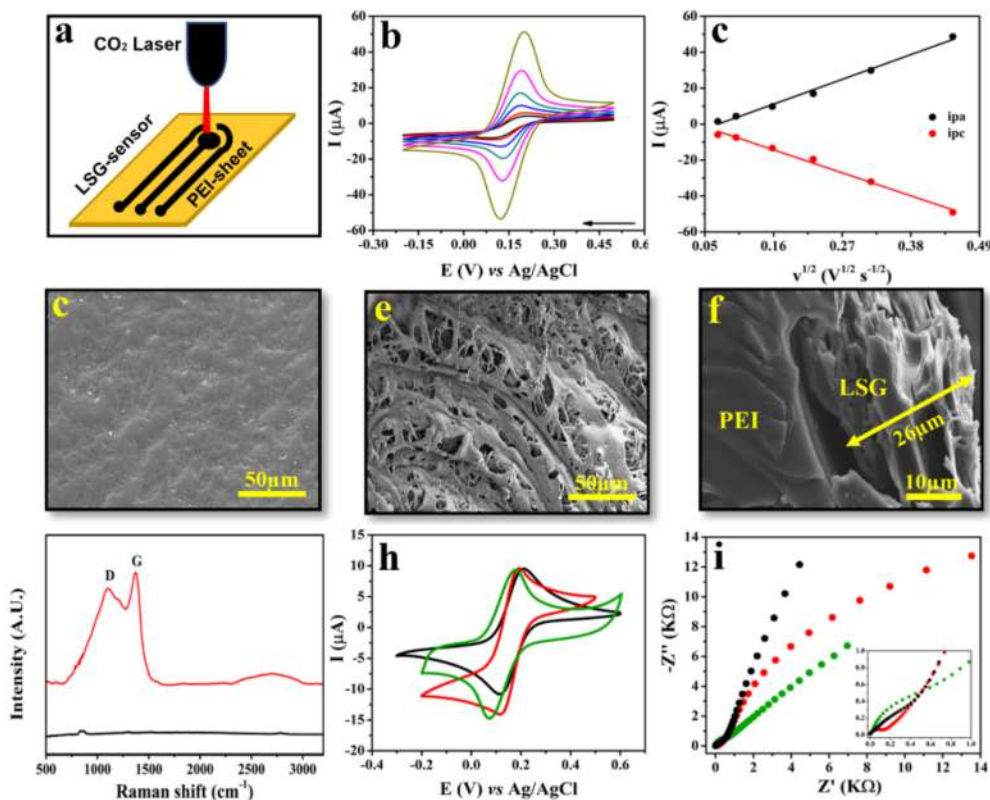


Figure 1:(a)Schematic representation for PEI-LSG manufacture. (b)CVs recorded using the PEI-LSG electrode in the medium of 5.0 mM $[\text{Fe}(\text{CN})_6]^{-3/-4}$ containing 0.1 M KCl at different scan rate (v) values (5-200 mV/s). (c) Peak current for both anodic and cathodic processes as a function of $v^{1/2}$. (d-f) SEM images with different magnifications (1,000x and 4,000x) of PEI-LSG surface. (g) Raman spectra of the (●) PEI substrate, (●) PEI-LSG. (h) CVs recorded using different LSG devices ((●) PI, (●) PEI, and (●) phenolic paper) in a solution of 5.0 mM $[\text{Fe}(\text{CN})_6]^{-3/-4}$ containing 0.1 M KCl at 50 mV/s. (i)Nyquist plots were obtained in the same conditions of part h and the inset shows a zoomed view of the plots at high-frequency regions.

The PEI-LSG electrochemical device was employed to evaluate the voltammetric behavior of each EP (HQ, PA, and MP). For that, CVs were recorded with scan rate values ranging from 10.0 to 200.0 mV/s in 0.1 M BR buffer solution (pH=8.0). It was possible to note good linearity between the logarithm of the anodic peak current ($\log i$) versus the logarithm of the scan rate ($\log v$), which provided slopes of 0.99, 1.09, and 0.82 for HQ, PA, and MP, respectively, indicating that the reaction was entirely controlled by adsorption[5]. Following, to characterize the pH dependence in the redox processes and the best analytical condition for simultaneous analysis, a square wave voltammetry (SWV) was used for pH study in the range of 3 to 9, which demonstrated optimal peak potential separation and higher peak current for all species at pH=8.0. Thus this condition was used for analytical applications.

The simultaneous detection of HQ, PA, and MP was performed by SWV in the concentration ranging from 10 μM to 50 μM (Figure 2a). The analytical curves showed a high linear behavior ($n=3$ replicates), providing R^2 of 0.997, 0.991, and 0.999 for HQ, PA, and MP, respectively (Figure 2b-d). The limit of detection (LOD) was calculated according to

parameters obtained from the analytical curve ($LOD=3\sigma/S$), where σ is the standard deviation of the intercept and S is the slope. We obtained LODs of 9.42×10^{-8} , 3.23×10^{-7} , and 2.95×10^{-7} mol/L for HQ, PA, and MP, respectively. It is important to highlight that the individual calibrations were performed and demonstrated no significant difference in the sensitivity compared to simultaneous analyses of HQ, PA, and MP.

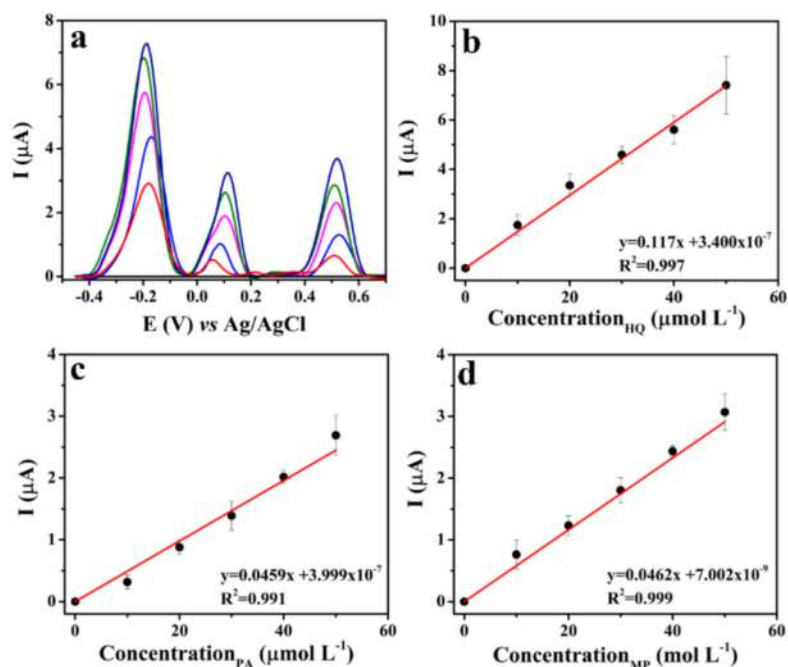


Figure 2:(a)Baseline-corrected SWV plots recorded for different concentrations of HQ, PA and MP (0.0-50.0 μM) in 0.1 M BR buffer solution (pH=8.0). (b-d)Analytical curves obtained using the peak current as a function of HQ, PA, and MP concentrations, respectively.

The selectivity studies were carried out to evaluate possible interfering species (environmental and anthropogenic origins) such as carbonate, diazepam, caffeine, nitrate, Cu^{2+} , and Pb^{2+} in the presence of HQ, PA, or MP. All species concentration was given at 50 μM . In this study, no significant interference (<12% current variation) was obtained in HQ, PA, and MP detection, demonstrating the adequate selectivity of the sensor. The reproducibility assays were evaluated using 10 different electrodes in the presence of 50.0 μM HQ, PA, and MP, resulting in a relative standard deviation (RSD) of 3.44%, 6.56%, and 4.19%, respectively.

The PEI-LSG sensor was employed to detect HQ, PA, and MP in tap water and river water samples with spiked concentrations ranging from 10 to 40 μM , resulting in recoveries from 94.8% to 117.6% for tap water and 93.1% to 118.0% to river water. These values demonstrate the adequate accuracy and robustness of the proposed method for simultaneous detection of HQ, PA, and MP. The analytical parameters obtained for quantification of HQ, PA, and MP using our LSG sensor were compared to the literature. From the summarized information, we can highlight that the low-cost PEI-LSG sensor presents low LOD values, and excellent manufacturing reproducibility features, allowing it to be applied as a single-use device.

CONCLUSIONS

A novel disposable and low-cost LSG electrochemical sensor was fabricated using CO₂ laser on PEI substrate, providing a high-performance electroanalytical device. The LSG sensor presented a porous graphene-like material with high electron transfer features that enable the development of a sensitive and accurate determination method for HQ, PA, and MP in tap and river water samples. The proposed method presented adequate selectivity and reproducibility, allowing us to indicate it as an excellent alternative for emerging pollutants detection.

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