Air plasma treatment of laser-induced electrodes for enhanced antioxidant determination

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ABSTRACT

Laser scribing techniques have been extensively explored for the large-scale fabrication of low-cost sensors with high reproducibility in laboratory environments, using a variety of substrates such as polyimide. In this study, laser-induced graphene (LIG) electrodes were fabricated by the photothermal conversion of sp^3 carbon within the polymeric matrix into sp^2 carbon using a CO_2 laser cutter. We investigated the surface modification of LIG electrodes by air plasma treatment, which enhanced their electrochemical activity. The cyclic voltammetric response using the $[Fe(CN)_6]^{3-/4-}$ redox couple exhibited a 3.6-fold increase in current after surface modification. The modified sensor associated with differential pulse voltammetry (DPV) showed a good linearity (R^2>0.99) in the range from 0.3 to 5.0 0.09 µmol L^{-1} with a limit of detection of 0.09 µmol L^{-1} for electrochemical oxidation of butylated hydroxyanisole (BHA). These results highlight the potential of plasma-treated LIG electrodes as a low-cost, efficient platform for antioxidant analysis in biofuel samples.

Key-words: butylated hydroxyanisole, Laser scribing, *biodiesel*,

Introduction

Low oxidation stability is the main drawback of biodiesel, which is overcome by using antioxidants [1,2]. Quality control can be assessed by monitoring oxidation stability through the quantification of antioxidant content in biofuels [3]. To address this challenge, the development of low-cost analytical methods for sensing antioxidant in biofuel samples is necessary. Laser scribing is a fast, cost-effective, and single-step technique for producing electrodes. This process involves the photothermal conversion of sp^3 carbon atoms present in a substrate (polyimide, PI) to sp^2 carbon atoms (graphene), under ambient conditions [4]. The electrochemical performance of LIG electrodes can be improved by modifying the ablated surface to meet analytical requirements. In this work, we demonstrate that a robotic air plasma system can be used to enhance the electrochemical activity of LIG electrodes and expand their applicability in biofuel analysis.

Experimental

Fabrication and modification of LIG electrodes

After developing the electrode layout in RDWorks 8.0 software, the LIG electrodes were produced using a CO_2 infrared laser source and commercial polyimide sheets The machine operated at a power of 2.3 W, a speed of 80 mm s^{-1}, a scan gap of 0.1 mm, and a working distance of 10 mm between the substrate and the laser output. The fabrication process for 10 electrodes was completed in 2.5 minutes. The following optimized treatment conditions were used to activate the LIG electrode surface using the lab-made robotic plasma system: a plasma power of 3000 mW, a working speed of 250 mm min^{-1}, a height of 1.5 mm between the electrode and the plasma source, and a line spacing of 0.1 mm (~5 seconds for 0.07 cm^2).

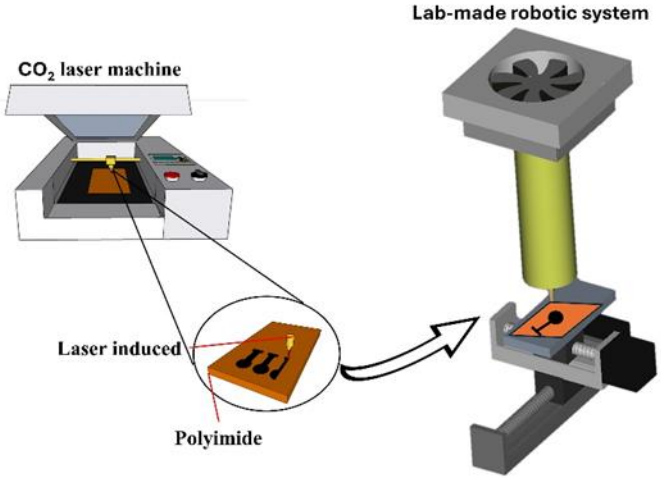

Figure 1. Schematic representation of the fabrication and modification of the LIG electrodes

Results and Discussion

Figure 2A shows the expected voltammograms for $Fe(CN)_6^{3-/4-}$, and the electrochemical profile reveals a significant increase in the current response for electrodes treated with air plasma (approximately 3.6-fold). Additionally, the peak-to-peak separation (ΔEp) decreased from 126 mV to 66 mV after surface modification. Initially, the redox behavior of BHA was assessed by cyclic voltammetry (CV) in 0.1 mol L^{-1} $HClO_4$. As noticed, three electrochemical responses were observed in this study (O_{x1} at around +0.56 V, R_{ed1} at +0.25 V and O_{X2} at +0.40 V) (Figure 2B). The consistent and well-defined response of the Ox2 and R_{ed1} suggests that an indirect detection strategy may provide a more reliable alternative. Therefore, further voltammetric investigations were carried out on these processes to better understand its potential for analytical applications. Under the optimized experimental conditions, a linear relationship was observed between the peak current and the concentration of BHA. For Ox2, the linear range was 0.3 to 5.0 µmol L^{-1}(R^2 = 0.995) with a sensitivity of 4.3 µA L µmol^{-1}, while for Red1, the linear range extended from 0.3 to 6.0 µmol L^{-1} (R^2 = 0.993), with sensitivity of 3.7 µA L µmol^{-1}. Table 1 summarizes some analytical features of DPV method for determination of BHA.

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Table 1. Analytical features of the DPV method for BHA detection on air plasma-treated LIG electrode

Analytical features	Ox1	Red1
Linear range (µmol L^{-1})	0.3 – 5.0	0.3 – 6.0
Sensitivity (µA L µmol^{-1})	4.3	3.6
Intercept / (µA	0.2	0.5
LOD (µmol L^{-1})	0.09	0.09
LOQ (µmol L^{-1})	0.3	0.3
R^2	0.995	0.993

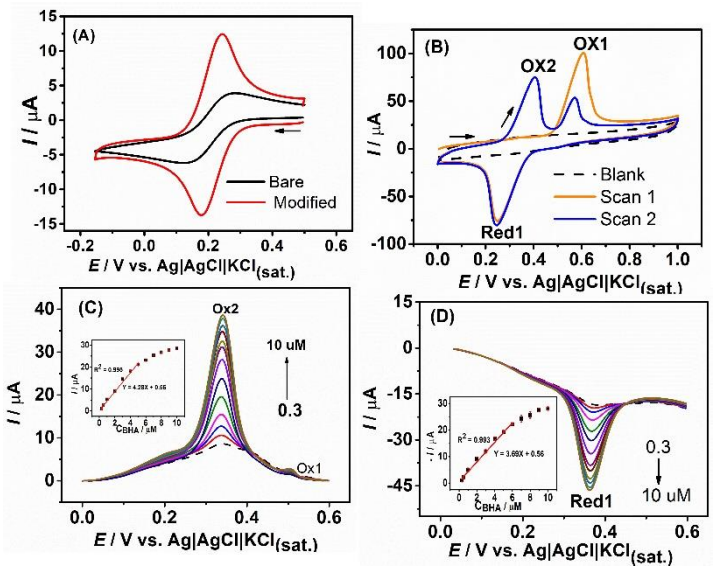

Figure 2. (A) CVs recorded in presence of 1.0 mmol L^{-1} $Fe(CN)_6^{3-/4-}$ in 0.1 mol L^{-1} KCl solution; (B) Cyclic voltammograms obtained for 1.0 mmol L^{-1} of BHA in 0.1 mol L^{-1} $HClO_4$; (C and D) DPV responses (n=3) for concentrations of SFL on modified electrode (0.3 to 10.0 µmol L^{-1}). Inserts: respective calibration curves.

Conclusions

The laser scribing technique can provide affordable electrodes through a large-scale and precise fabrication process. Here, we show for the first time that applying a robotic air plasma system to the surface of LIG electrodes significantly enhances their electrochemical activity. We also demonstrate the potential of the modified electrodes for the detection of BHA. These findings suggest that the modified LIG electrodes hold great promise for the advancement of electrochemical sensing platforms in biofuel analysis.

Acknowledgments

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