Laser Induced Graphitic Carbon on Kevlar Cloth: a Promising Material for Electrochemical Sensing

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***Abstract*— In this study, we demonstrate the fabrication of Laser-Induced Graphitic Carbon (LIGC) electrodes on flexible Kevlar cloth for showing their potential use as wearable electrochemical sensors. Kevlar was converted into LIGC using an inexpensive hobbyist 450 nm laser, highlighting a cost-effective method for creating graphitic carbon on cloth. Laser parameters were optimized to achieve low sheet resistance. Morphological and spectroscopic characterization revealed that LIGC had an intricated 3D porous morphology and confirmed the formation of sp² hybridized carbon. Electrochemical analysis in $[Fe(CN)_6]^{4-}$, $Fe^{2+/3+}$ showed a quasi-reversible electron transport mechanism on the surface of graphitic carbon, primarily controlled by mass diffusion processes.**

Keywords—Kevlar cloth, laser writing, electrochemical sensor, and Laser-induced graphitic carbon

I. Introduction

The growing demand for lightweight, flexible and robust materials in wearable electronics has driven significant research into the development of novel electrode materials [1]. Conventional electrodes, typically made from rigid and fragile substances, are impractical for flexible applications because of their low mechanical durability [2]. Kevlar, an artificial fiber recognised for its high strength and thermal stability, has been identified as a suitable substrate for the development of flexible electrode materials [3].

Recent research highlights that carbon-based materials, especially graphitic carbon, possess exceptional mechanical robustness, chemical stability and electrical conductivity making them highly suitable for a wide range of electrochemical applications [4]. Nonetheless, a significant challenge remains in devising a simple and scalable method to transform Kevlar into a conductive material while preserving its inherent mechanical properties.

Laser-induced graphitization has become a cutting-edge technique for converting polymeric materials into conductive carbon. This method involves precisely exposing the material to a high-energy laser, which selectively transforms the polymer into graphitic carbon [5]. A notable advancement in this field is the fabrication of LIGC directly on Kevlar cloth. To date, LIGC fabricated on Kevlar cloth has primarily been employed in strain sensor [6], electrocardiogram electrodes, NO_2 gas sensors [3] and electrothermal application [7]. However, the potential of LIGC on Kevlar for electrochemical sensing or electrochemical studies has not yet been fully explored, despite its promising applications in wearable electronics. Given its ability to combine the mechanical strength and flexibility of Kevlar with the conductive properties of graphitic carbon, LIGC on Kevlar holds significant potential for electrochemical sensors.

In this work, we investigated the laser-induced graphitization of Kevlar cloth by using a hobbyist 450 nm visible laser, evaluating its potential as a flexible electrode material for electrochemical applications. The ability to convert Kevlar into a conductive material while retaining its flexibility and strength, opens up new possibilities for the development of advanced wearable electronics and sensors.

II. Materials and Methods

A. Materials

Commercial Kevlar (1500D, 250 g/m²) was sourced from Zhongfu Carbon Fiber Products Co., Ltd. KCl, PBS tablet and $K_4Fe(CN)_6$ were purchased from Sigma-Aldrich, a 5 mM solution of $[Fe(CN)_6]^{4-}$ in 1M KCl was used for the redox systems. All solutions were prepared using deionized (DI) Milli-Q water, which has a resistivity of 18.2 MΩ.cm and nitrogen gas was employed to eliminate oxygen.

B. Fabrication of electrodes

A KKmoon Portable Automated Desktop Laser Engraving Machine was utilized to produce graphitic carbon electrodes onto Kevlar by employing raster scanning customized electrode patterns. This machine was fitted with a laser with a wavelength of 450 nm and a power output of 3 W [8]. The Kevlar cloth was supported by a solid base made of glass slide. Acetone, isopropanol, and DI water were used sequentially for the cleaning of the electrodes to eliminate any laser engraving residue.

C. Characterization

The structure of the graphitic carbon electrodes was studied using a FEI Quanta 650 scanning electron microscope (SEM, model Zeiss SUPRA 35 VP, Oxford Instruments) which operated at an acceleration voltage of 5 kV. Raman spectroscopy was conducted with a Horiba XploRA Raman microscope featuring with a 532 nm laser at 70 mW. The measurements were carried out using 10× objective, 2400 grating, 30-second sampling time, one accumulation, and a 10% filter.

D. Electrochemical Analysis

Cyclic voltammetry (CV) electrochemical measurement was carried out using an Autolab potentiostat/galvanostat electrochemical system. The graphitic carbon electrode was used as the working electrode (WE), an Ag/AgCl (1M KCl) electrode as the reference electrode (RE) and a platinum wire as the counter electrode (CE). The three electrodes were set up within a Teflon cell, exposing a circular area measuring 8 mm in diameter to the electrolyte. Prior to the measurements, the electrolyte solutions were treated with nitrogen gas for 30 minutes.

III. RESULTS AND DISCUSSION

A. Morphological characterization

Fig. 1a presents a schematic illustration of the direct laser writing technique employed to produce graphitic carbon electrodes. Fig. 1b displays a photograph of an individual electrode (length: 18 mm) produced by raster scanning the visible laser back and forth across the kevlar cloth surface.

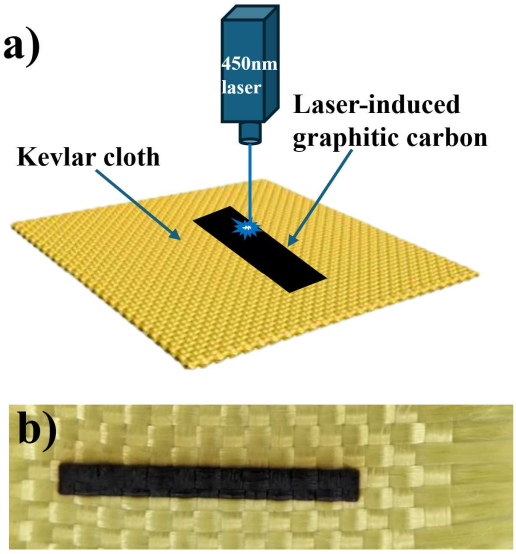

Fig. 1. (a) Schematic diagram of the laser graphitization process utilized for the production of graphitic carbon electrodes. (b) Photograph of graphitic carbon working electrode.

Various laser parameters were explored to optimize the sheet resistance of laser-induced graphitic carbon (LIGC) on Kevlar surface. It was observed that when laser power was below 70% of its maximum, the resulting LIGC exhibited high sheet resistance, rendering it unsuitable for electrochemical applications. At 70% laser power, the LIGC demonstrated an acceptable level of sheet resistance. However, increasing the power beyond 80% led to the ablation of the LIGC from the Kevlar surface. Therefore, laser powers of 70% and 80% were chosen for further optimization by adjusting the laser depth, as shown in Table 1. It was found that at 70% laser power, increasing the laser depth led to a rise in conductivity. In contrast, at 80% laser power, the sheet resistance showed fluctuations, initially increasing and then decreasing. Notably, at 80% laser power and 80% depth, the LIGC achieved a minimum sheet resistance of 18 Ω/sq, which was considered optimal for electrochemical studies.

Table 1: Laser parameter optimization data

Power	70				80				
Depth	40	50	60	70	40	50	60	70	80
Sheet resistance (Ω/sq)	46	42	38	30	22	26	25	30	18

Electron microscopy analysis (Fig. 2a) revealed that the fabricated line microstructure exhibited a consistent, flaky morphology characterized by a huge surface area and outstanding porosity, resembling carbon electrodes having graphene-like structure produced using different laser wavelengths. The SEM images also displayed an extensive three dimensional arrangement of overlapping graphitic carbon sheets, featuring a large number of available sides formed by kinked and wrinkled regions. This type of morphology, with a significant presence of "exploded" holes, has been documented previously for graphitic structures generated under laser illumination either visible or infrared [5], [8]. The proposed mechanism for converting kevlar into graphitic frameworks involves the uptake of laser photon energy, which is converted into heat, creating localized conditions of elevated temperature as well as pressure. Since the procedure was carried out in the air, the existence of ambient moisture and oxygen led to some carbon being ablated, which helped to develop the porous structure. These materials are well-suited for electrochemical sensing applications because of their porous 3D design, which is projected to provide a highly accessible electrochemical surface area, and their many edge planes, which are expected to promote electrochemical transfer.

The Raman spectrum of the graphitic carbon electrode (Fig. 2b) revealed three prominent peaks, identified as the D, G, and 2D peaks, were seen at around 1345, 1575, and 2680 cm^{-1} respectively. The D peak, resulting from distorted sp^2 carbon bonds, indicates structural defects. The E_{2g} vibrational mode of graphitic carbon is represented by the G. Together with the 2D peak, these verify that a graphite-like carbon structure has formed [9]. Two additional smaller peaks were detected at approximately 2437 cm^{-1} and 2925 cm^{-1}, corresponding to the D + D″and D + D′ combination modes, respectively. The D peak displayed

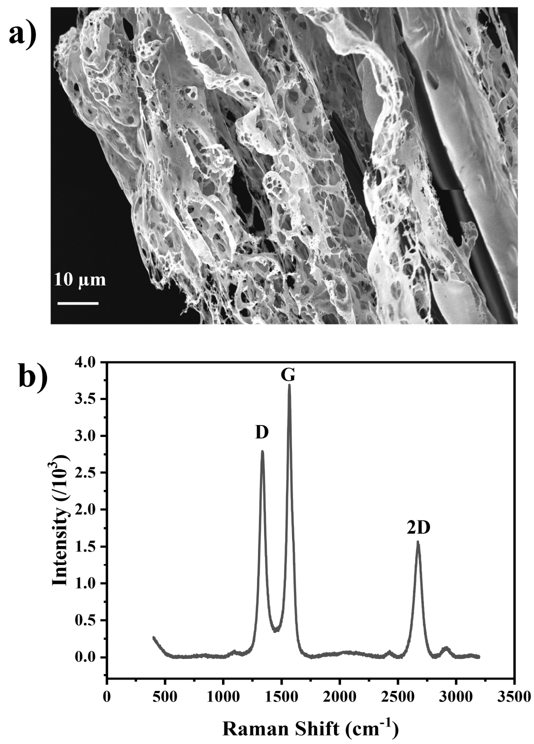

Fig. 2. (a) SEM image of graphitic carbon electrode, (b) Raman spectra of graphitic carbon electrode.

a single, sharp Lorentzian profile having a full width at half maximum (FWHM) of around 54.14 cm⁻¹, which is indicative of relatively low structural disorder. The G peak, a first-order Raman mode, appeared as a convolution centered at 1575 cm⁻¹. The intensity ratio (I_D/I_G) between the D peak and the G peak was around 0.85, signifying that the laser-ablated surface possesses a crystalline nature with highly ordered graphitic regions and nanocrystalline area within a disorganized carbon framework [8]. Moreover, the comparatively large I_{2D}/I_G proportion suggests that the material consists of only a few graphene layers. The 2D peak was centered at 2680 cm⁻¹, accurately represented by a single Lorentzian profile, exhibiting a full width at half maximum (FWHM) of 68.04 cm⁻¹. This ratio, combined with the observed Raman peaks, suggests that the laser-induced graphitic carbon on Kevlar cloth has a mixed structure with both defective and ordered graphitic regions, making it suitable for applications requiring a balance of conductivity and mechanical flexibility.

Table 2 shows a comprehensive comparison of the characteristics of laser-induced graphitic carbon (LIGC) derived from Kevlar cloth using various laser types with other LIGC reported in literature. The Raman spectral features, specifically the intensity proportions of the D/G and 2D/G peaks, exhibited minimal variation when LIGC was fabricated using a visible laser. The sheet resistance reported is line with values between 2 and 20 Ω/sq, generally reported. In this regard, the study outlined in this paper shows that LIGC structures of comparable characteristics to those obtained with costly femtosecond and infrared systems can be produced with low-cost visible lasers.

Table 2: Comparison of LIGC quality with literature data

Laser Type	Raman (I_D/I_G)	Raman (I_{2D}/I_G)	Sheet Resistance (Ω/sq)	Reference
CO_2 laser	0.85	0.60	10.8	[3]
Femtosecond laser	0.73	0.66	2.86	[10]
CO_2 laser	0.49	0.57	--	[11]
CO_2 laser	~0.71	~0.52	19	[12]
450nm visible laser	0.85	0.60	18	This work

B. *Electrochemical characterization*

The suitability of LIGC generated from Kevlar cloth as an electrode material for future electrochemical applications was assessed by analyzing its electrochemical performance. This characterization was conducted using a standard three-electrode setup, where LIGC was used as WE, an Ag/AgCl (1M KCl) electrode as RE, and a platinum wire as CE, as depicted in Fig. 3a. The conventional redox pair $[Fe(CN)_6]^{3-/4-}$, known for its reversible one-electron transfer, was employed as the redox probe in this study. Electron transfer kinetics at the LIGC electrode was analyzed using cyclic voltammetry (CV) technique. Prior to measurement, the electrode surface underwent electrochemical cleaning in a 0.01M phosphate buffer solution. As shown in Fig. 3b, this cleaning process resulted in a noticeable enhancement of the

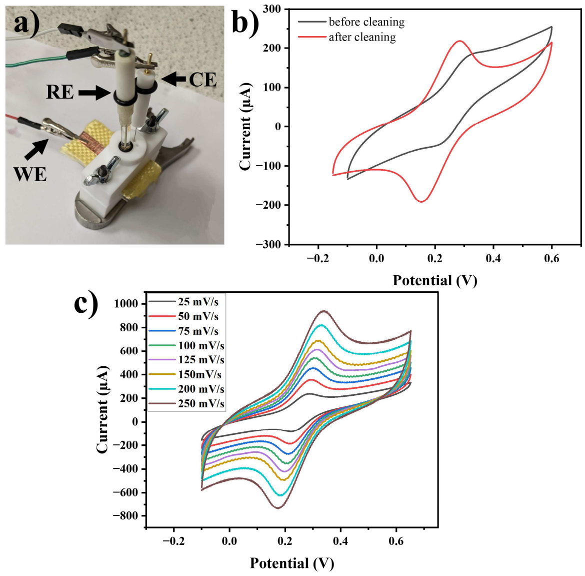

Fig. 3. (a) Electrochemical setup, (b) Cyclic voltammogram in 5 mM $[Fe(CN)_6]^{3-/4-}$ before and after cleaning the electrode, (c) Cyclic voltammogram at different scan rates for 5 mM $[Fe(CN)_6]^{3-/4-}$ in 1M KCl.

oxidation and reduction peak currents for $[Fe(CN)_6]^{3-/4-}$. Furthermore, the peaks became more defined, and the reduced peak-to-peak spacing indicated improved electrode performance. Fig. 3c shows the typical cyclic voltammetry curves obtained in 5 mM $[Fe(CN)_6]^{3-/4-}$ in 1M KCl for the 3 mm wide graphitic carbon electrode at a scan rates of 25 to 250 mVs^{-1}. Despite quick scan rates of 250 mVs^{-1}, ΔE_P values less than 200 mV were retained. For three electrodes, the average ΔE_P measured at 100 mVs^{-1} scan rate was 93 mV, demonstrating a quasi-reversible response.

Conclusions

The successful conversion of laser induced graphitic carbon on Kevlar cloth has been presented using a cost-effective hobbyist 450 nm visible laser. The resulting LIGC electrode showed quasi-reversible behavior, with further improvement obtained with the incorporation of an electrode surface cleaning step. For the first time, the LIGC derived from Kevlar showed potential as electrochemical sensor. This work opens new horizons for wearable sensing applications.

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