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Henry Bukola Ezekiel, Duncan Sharp, Maria Marti Villalba, James Davis. Laser anodised carbon fibre - Coupled activation and patterning of sensor substrates. *Journal of Physics and Chemistry of Solids*, 2010, 69 (11), pp.2932. 10.1016/j.jpcs.2008.06.137 . hal-00612402

**HAL Id: hal-00612402**

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Submitted on 29 Jul 2011

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## Author's Accepted Manuscript

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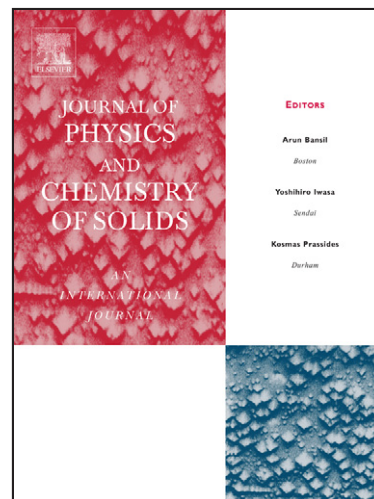
PII: S0022-3697(08)00338-7  
DOI: doi:10.1016/j.jpcs.2008.06.137  
Reference: PCS 5641

To appear in: *Journal of Physics and Chemistry of Solids*

Received date: 14 May 2008  
Accepted date: 21 June 2008

Cite this article as: Henry Bukola Ezekiel, Duncan Sharp, Maria Marti Villalba and James Davis, Laser anodised carbon fibre – Coupled activation and patterning of sensor substrates, *Journal of Physics and Chemistry of Solids* (2008), doi:10.1016/j.jpcs.2008.06.137

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## Laser Anodised Carbon Fibre – Coupled Activation and Patterning of Sensor Substrates

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### Abstract

The use of laser ablation as a method through which the simultaneous patterning and activation of carbon fibre electrodes can be achieved has been investigated. Laser induced exfoliation of the carbon fibre substrates was observed leading to creation of edge plane sites that enhance electrode performance. The laser mediated surface modification is compared to that attainable using conventional surface anodisation using electrochemical means.

### Keywords

Electronic materials; polymers; interfaces; microstructure; electrochemical properties

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## 1.0 Introduction

The large variety of physical forms that carbon can take allows for considerable versatility in the design of the sensor substrates used in electroanalytical applications. Glassy carbon, aerogels, fibre, graphitic felts and pastes are but a few of the more common [1]. Highly orientated pyrolytic graphite (HOPG) offering edge plane (eppg) and basal plane (bppg) morphologies are frequently used to explore the more fundamental side of electron transfer processes but have found increasing application in analytical contexts. The basal and edge plane possess different properties with the latter tending to exhibit considerably faster electrode kinetics and, as a consequence, possesses the potential for greater detection sensitivities [2-5]. The aim of the present communication has been to investigate a method through which the surface reactivity of a conventional carbon fibre electrode can be enhanced through laser patterning of the substrate.

The surface of carbon can be modified by mechanical [4-6], electrochemical [7-14], chemical [14-21] or thermal [22] means. There are typically three different levels of surface modification: alteration of the functionalities already present on the surface; the covalent attachment of hitherto exogenous species onto the electrode surface and, in the last level, the intercalation of species between the graphene layers of the base substrate. Altering the surface composition is amongst the more facile and can usually be achieved through the electrochemical pre-treatment/fracturing of the carbon substrate [7, 12, 17] as indicated in **Figure 1**. This typically involves the electro-oxidation of the carbon surface by applying a fixed anodic or cyclic potential. The oxidation increases the proportion of oxygen species such as hydroxyl, carbonyl, carboxyl and quinones at the electrode surface [14]. These are well known to influence the wettability, surface reactivity, porosity and conductivity of the electrode [1, 7, 8, 10]. It can also have the beneficial effect of increasing the availability of edge sites as a consequence of exfoliation / fracturing process that can, as with eppg electrodes, serve to increase electrode sensitivity towards particular analytes.

Laser patterning of carbon encapsulated composites have been shown to provide a quick and versatile method of producing electrode sensor assemblies but the ability of the laser to positively influence the surface characteristics of the underlying fibre has yet to be evaluated. The adoption of the electrochemical anodisation

approach requires the introduction of a separate/discrete step in the construction of the electrode sensor and it is clear that combining the patterning/activation process would represent a considerable simplification in the development process. In the present investigation, the use of laser ablation as a means of removing protective polymer encapsulants to expose and activate the sensor surface in a single step is assessed.

## 2.0 Experimental Details

Electrochemical measurements were conducted using a  $\mu$ Autolab type III computer controlled potentiostat (Eco-Chemie, Utrecht, The Netherlands) using a three electrode configuration consisting of a glassy carbon working electrode (3mm diameter, BAS Technicol, UK), a platinum wire counter electrode and a 3 M NaCl Ag | AgCl half cell reference electrode (BAS Technicol, UK). Modification of carbon fibre electrodes was investigated using a 30W CO<sub>2</sub> air-cooled computer controlled laser-cutter (FB400 series CadCam Technology Ltd, Nottingham, UK). Directional control over the laser, raster/vector speed and output power was achieved by means of the proprietary software (ApS-Ethos). The resolution of the laser beam is 25  $\mu$ m. Electrochemical anodisation of carbon fibres was conducted using the procedures described previously [23,24] and typically involved amperometric oxidation (+2V, 15 minutes) in 0.1M sodium hydroxide solution.

## 3.0 Results and Discussion

Carbon fibres were encapsulated within a polyester resin laminate as described in previous work by the authors [23, 24]. An electrode window was then created by rastering the laser across a pre-selected area of the polymer-fibre composite. This has the effect of removing the polymer and exposing the fibre which can, in principle, be used as the working electrode in a sensor assembly. Cyclic voltammograms detailing the response of unmodified and electrochemically anodised carbon fibres (of similar geometrical area) towards uric acid (2 mM, pH 7, 50 mV/s) are detailed in **Figure 2**. It can be seen that the oxidation of the purine (**I**→**II**, **Inset Figure 2**) at the unmodified fibre is barely visible and is characteristic of poor electron transfer

kinetics at a substrate that is largely basal plane in structure. The voltammogram recorded at the anodised fibre, in contrast, displays a well defined and easily quantifiable oxidation process. The change in profile is dramatic but is in keeping with previous work where electrochemical anodisation has been shown to aid both the resolution and the sensitivity of voltammetric processes [23,24]. The key question, however, is whether a similar effect could be achieved simply as a consequence of exposing the carbon surface to the laser.

Cyclic voltammograms highlighting the response of the laser etched composite structure towards urate (2 mM, pH 7, 50 mV/s) are detailed in **Figure 3**. In all cases, the area of polymer (0.03 cm<sup>2</sup>) removed is the same – the only difference between the scans is the power applied to that defined area. The greater the laser intensity – the greater the magnitude of the apparent surface activation. The capacitive background current observed with the laser etched system is however significantly smaller than that obtained with the electrochemical pre-treatment and may reflect a greater propensity of the latter to introduce surface charge to the fibre through the generation of greater numbers of oxygen species.

Application of the more extreme laser settings can however have a deleterious effect on the electrode surface and there is a sustained decrease in the peak height where maximum power is applied or where multiple passes are used. This effect was further investigated with ferrocyanide as the model analyte. Cyclic voltammograms detailing the response of the various laser anodised (60 and 100%) fibres to ferrocyanide (2 mM, 50 mV/s) are compared in **Figure 4**. It can be seen that the unmodified fibre exhibits little response to the redox probe. Laser activation provides a superior response but the definition of the peak processes can be seen to degrade at the higher power setting with an increase in noise observed on the voltammetric trace.

It is clear that the response of the laser activated surface is similar to that observed after electrochemical anodisation and clearly provides an enhancement in performance over that attainable at the unmodified carbon. Scanning electron micrographs of the carbon fibre before and after laser treatment are detailed in **Figure 5A** and **5B**. Exfoliation of the laser treated fibre can be observed even at moderate power settings (60%) and can be seen as striations along the fibre which will lead to a substantial increase in the electrode surface area – especially as a consequence of the nanofracturing at the surface. This is seen more clearly in **Figure 5C** where laser induced damage to the core fibre is observed at maximum power.

It is important to note that the enhancement in peak resolution, however, is not simply a result of the increased area - as increasing the exposed and hence the “nominally active” area of the unmodified fibre did not lead to the behaviour exhibited by the either electrochemical or laser ablated fibres shown in Figures 2 and 3. The main difference between native and modified fibre lies in the relative population of the edge plane sites and oxygen functionalities. It is the increase in both these feature that would lead to the increase in electrode sensitivity and it can be seen from both the electrochemical and morphological characterisations that the laser option provides a viable alternative to the electrochemical process.

#### **4.0 Conclusions**

It is clear that carbon possesses considerable flexibility in its ability to be modified and effectively tailored to specific applications. In most cases however, acquiring sufficient sensitivity towards particular analytes has often required surface modifications that increase the complexity of the construction method. The approach advocated here highlights the possible replacement of the (electro) chemical anodisation stage with a reagentless instrumental process. The results between the different approaches are comparable but in adopting the latter - greater simplicity and control could be introduced to the sensor assembly process.

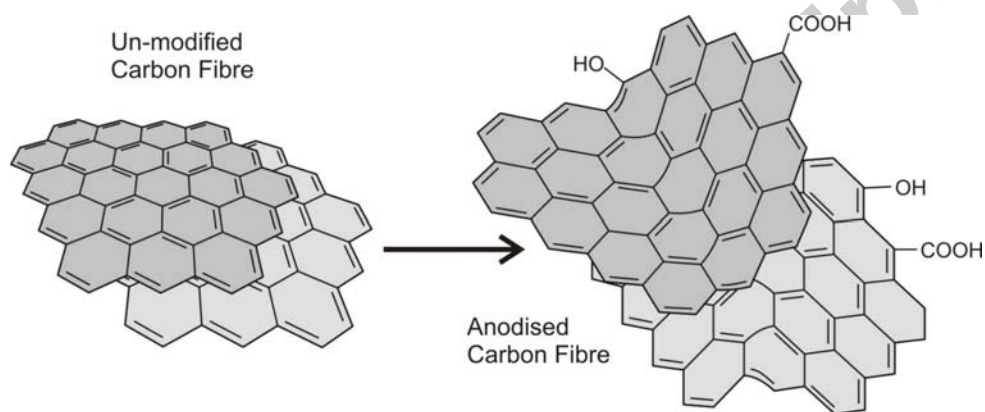
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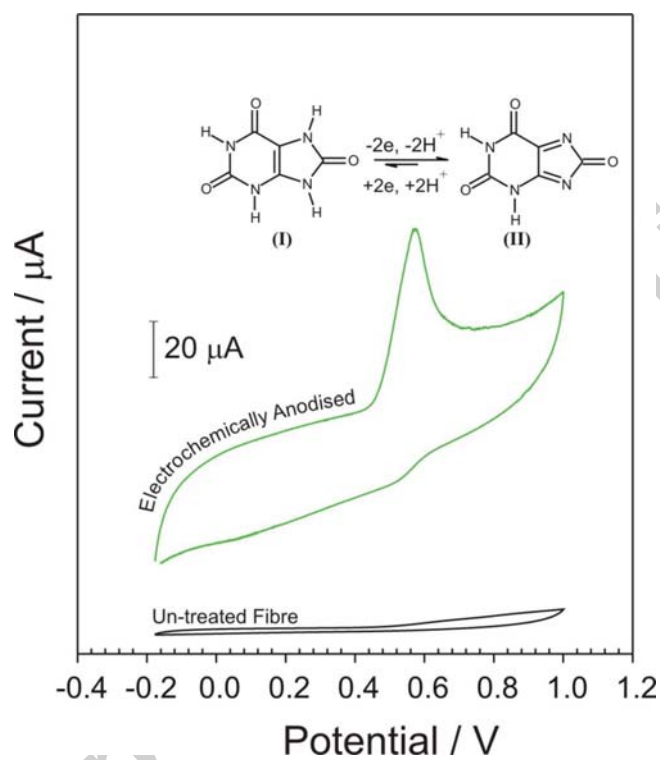


## Figure Legends

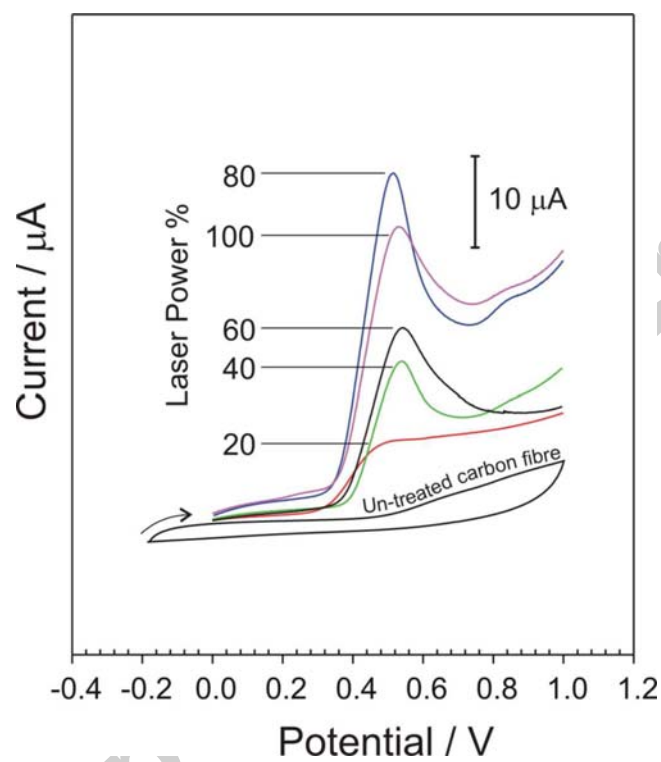
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- Figure 2.** Cyclic voltammograms detailing the response of untreated and electrochemically anodised fibres towards 2mM uric acid (Inset). Scan rate: 50mV/s
- Figure 3.** Linear sweep voltammograms detailing the influence of laser exposure on the activation (anodisation) of carbon fibre. Response to urate oxidation (2mM). Scan rate: 50mV/s
- Figure 4.** Cyclic voltammograms detailing the response of unmodified and laser anodised carbon fibres towards ferrocyanide (2 mM). Scan rate: 50mV/s
- Figure 5.** Scanning electron micrographs detailing the surface morphology of (A) untreated and (B) laser (power: 60%) anodised carbon fibres
- Figure 6.** Scanning electron micrograph of carbon fibre after repeated exposure (2 passes) to the laser at full power



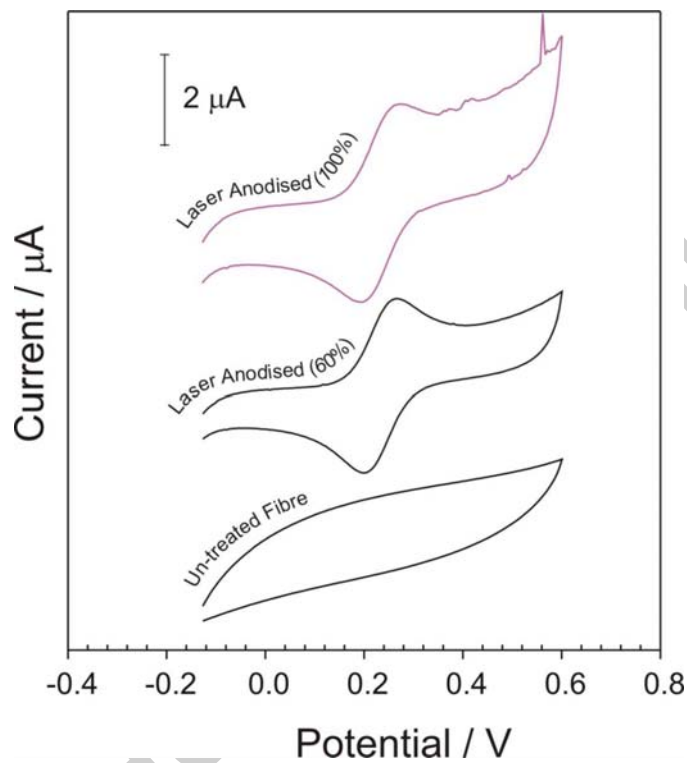
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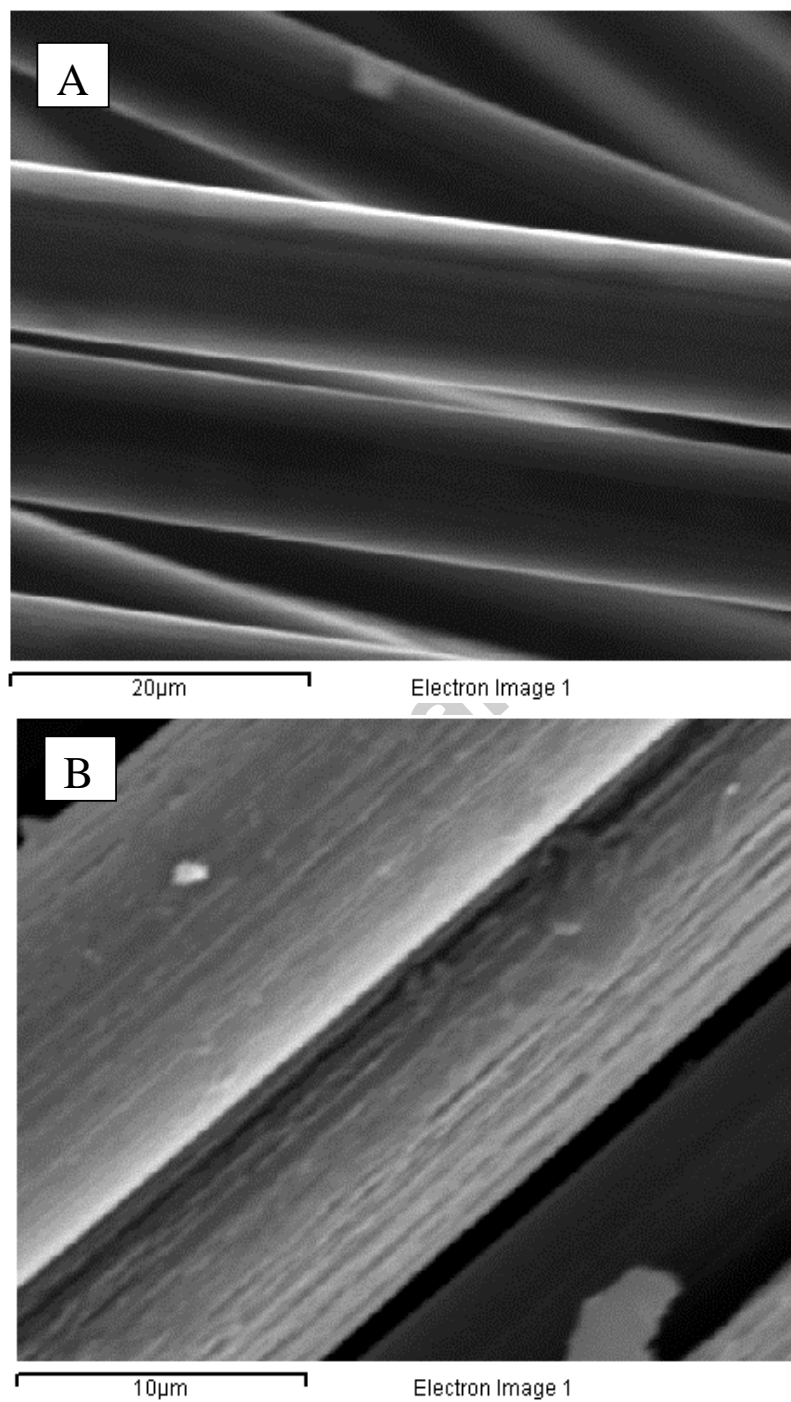
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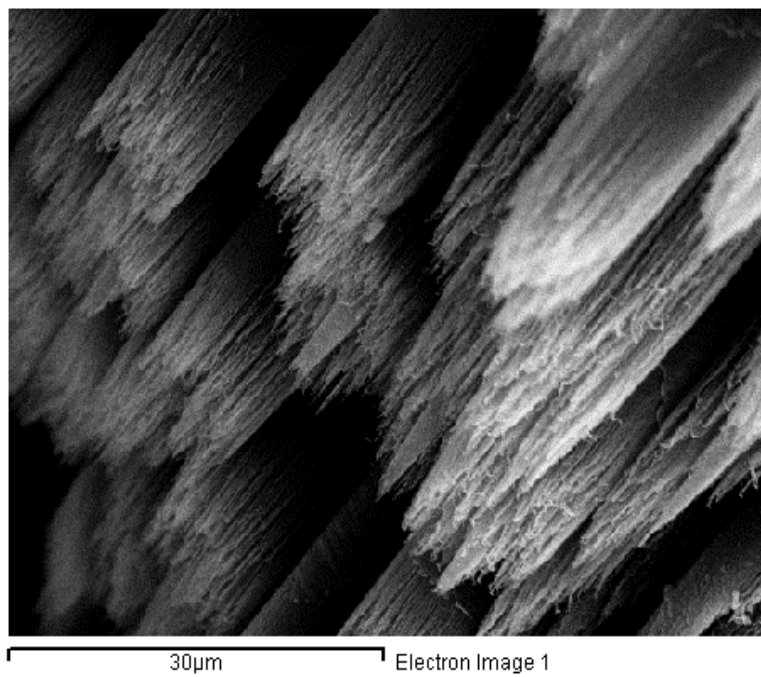
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