FABRICATION OF ADVANCED CARBON ELECTRODES FOR ENERGY GENERATION AND STORAGE APPLICATIONS

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Abstract: Biofuel cells have emerged as a potential answer towards powering implantable biomedical devices that overcome several drawbacks associated with conventional batteries. However they are still challenged by their low power output and short operational lifetime impeding their commercial adoption. This paper presents carbon micro-nanofabrication technique that can form the basis for advanced enzymatic biofuel cell electrodes with fractal-like geometry to reduce internal resistance and maximize enzyme loading. The techniques use CMEMS (Carbon Micro Electro Mechanical System) fabrication technology which allows us to create 3-dimensional microstructures out of carbon and optimize the interfacial area per footprint of the electrode. The CMEMS carbon microfabrication technique can be further applied to create more complex fractal-like structures. The present paper first presents multi-scale carbon manufacturing routes for fabrication of biofuel cell electrodes and then focuses on functionalization approaches for these Carbon based electrodes using Glucose Oxidase as the anodic enzyme, and 2,4 Dihydroxy-Benzaldehyde (Hydroquinone) as the mediator which facilitates the electron transfer between the enzyme and the electrode surface. The enzyme-mediator system was shown to participate in mediated electron transfer.

Keywords: Electrodes, Carbon, MEMS, Biofuel Cells

INTRODUCTION

Modern day research on Implantable Biomedical Devices (IBD) is focused on building micro devices that consume lower levels of power while performing a multitude of life saving tasks, ranging from heart stimulation in a pacemaker to localized drug delivery. Although design improvements in IBDs are impressive, one challenge still exists; conventional electro-chemical batteries are limited when it comes to safety and longevity and most IBDs even today have to be powered by chemical batteries like Lithium Ion or Ni-Cd batteries. Replenishment of chemical batteries is only possible through replacement which requires surgical procedure in case of Implantable Biomedical Devices. Biofuel cells on the other hand use biologically safe enzymes that can be easily injected into the electrode region for replenishment. A fusion of natural power sources have the potential to change the way IBDs are fueled, allowing for the development of more powerful implantable microdevices to maintain and monitor health. Examples include implantation of self-powered Drug Delivery Devices which will go on to reducing drug side effects by minimizing concentration spikes (which are the major cause of drug side effects but are inevitable when drugs are administered in the form of pills).

Carbon has been used as an electrode material due to its wide window of electro-chemical stability and its ability to combine with itself to form varying structural forms (allotropes). This ability (called catenation) allows us to develop novel fabrication routes to create carbon platforms starting from most organic precursor or polymers on hand. Utilization of this property gives us the freedom to develop different geometries and patterns of three dimensional carbon structures using electrical, chemical, and photonic means to create a base structure using resins or polymers as precursors and then pyrolysing them in a reducing environment thus giving the final carbonaceous structure. Our research strategy is to ultimately fabricate fractal electrodes that we have been shown to be one of the most efficient electrode geometries due to its low internal resistance and high surface area [1, 2].We intend to utilize the high surface area of such fractal electrodes to functionalize them with a high density of biocatalysts and maximizing the transmitted electrical energy through a continuously connected branched topography inherent in fractal geometry allowing the electrons to flow along the least-resistance path .

In the spirit of this research approach, we will show in the present report the major developments we have made in the fabrication of fractal like three dimensional carbon electrodes and different derivitization approaches we have developed and tested to maximize the enzyme loading on these electrodes.

ELECTRODE FABRICATION

The electrodes were manufactured using two main techniques namely Carbon Micromachining and Far Field Electrospinning using PAN as precursor polymer.

Carbon MEMS

Carbon Micromachining using CMEMS is a carbon microfabrication technique based on the

patterning of a UV sensitive epoxy resin or photoresist like SU8 (Figure 1). SU8-50 was patterned using Photolithography to produce posts with a height of 150μ and diameter 30μ. The resulting microstructures were then pyrolysed at a temperature of 900 ^{0}C or higher maintaining a ramp rate such that at any given time the temperature of the furnace is lower than the glass transition temperature of the crosslinked epoxy [3, 4]. The heat leads to the vaporization of the non-carbonaceous components of the crosslinked epoxy leaving behind the carbon in a mixed sp^2/sp^3 hybridized state.

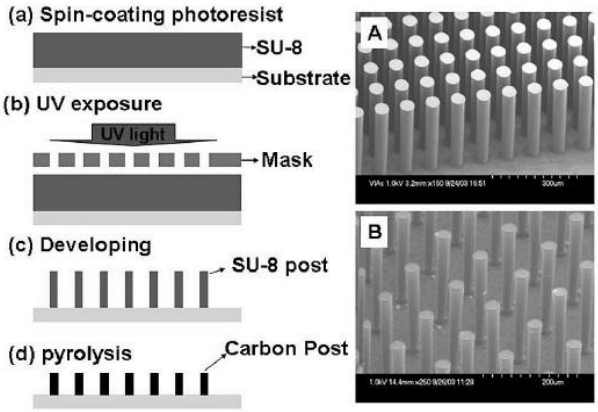

Figure 1. Schematic for the CMEMS fabrication process

Multiscale CMEMS-CNT Electrodes

SU8-50 was doped with catalyst particles to create nucleation sites on the microposts for the growth of carbon nanotubes. Iron acetyl acetonate was used as the CNT growth catalyst and was homogenized into the SU8 polymer before spinning onto the wafer. A low concentration of 0.05M of catalyst was found to be optimal. Any higher concentration of the catalyst blocked the UV light and obstructed the cross linking of SU8 during the exposure and post baking step. The SU8 posts after development were pyrolysed at 900^{0}C and then placed in a CVD tube for CNT growth. The growth took place in an acetylene reducing environment. The SEM images of the carbon microposts on the CMEMS electrode before and after the CNT growth are shown in Figure 2. The electrochemical activity of CNT flanked CMEMS electrode was compared against CMEMS electrode before CNT growth and the CNTs were found to participate in the electrochemical activity. The discussion of the electrochemical data is outside the scope of this paper. CNT conducts electrons into the CMEMS microposts and adds extra hierarchical dimensions to microposts in CMEMS electrode.

Carbon Nanofiber Electrodes

Preparation of porous carbon nanofibers was done by first electrospinning a blend of PAN-PMMA in different ratios wherein PMMA phase was used as a sacrificial polymer for generation of pores. We obtained thick mat like macro sheets of electrospun polymeric nanofibers that were folded over onto them-

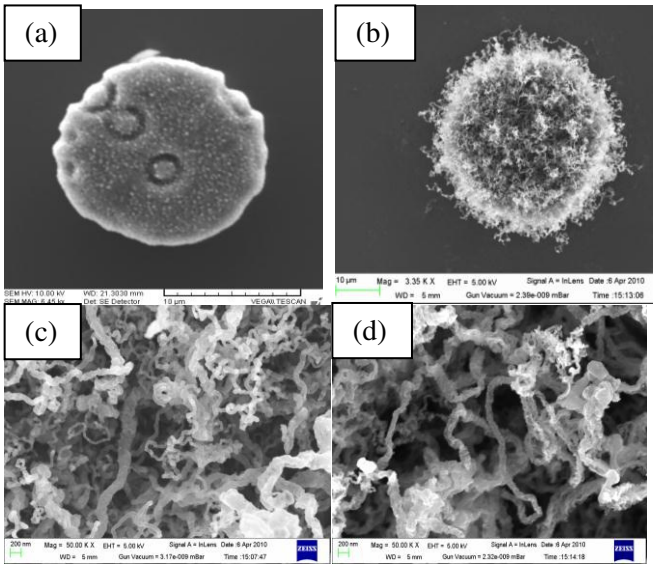

Figure 2. SEM image of the catalyst doped CMEMS electrode before CVD (a) and after CVD with carbon nanotube growth (b), Close up images of carbon nanotubes (c,d) which are believed to be multiwalled CNTs

-selves several times to create thick mats and then heat treated to decompose the PMMA phase leaving behind porous "islands" in the PAN bulk phase of the nanofiber. The heat treated mats were then pyrolysed in a reducing environment at 900 ^{0}C to obtain highly porous carbon nanofiber mats as a standalone electrode. Figure 3 reveals the PAN nanofibers and the carbon nanofibers after the pyrolysis of the electrospun nanofibers. These nanofibers mats were tested for their electrochemical activity and found to be highly active.

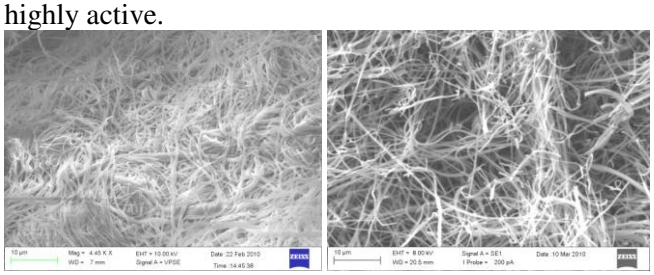

Figure 3. SEM images of PAN: PMMA nanofibers in the ratio 9:1 (left) and Carbon Nanofibers obtained from pyrolysis of PAN: PMMA nanofibers (right)

These carbon nanofiber mats can be combined with CMEMS electrode to create multiscale nanostructured fractal-like electrode. PAN nanofibers were electrospun onto Carbon Microposts arrays fabricated via CMEMS technique into multiscale fractal-like tree geometry as seen in Figure 4 below.

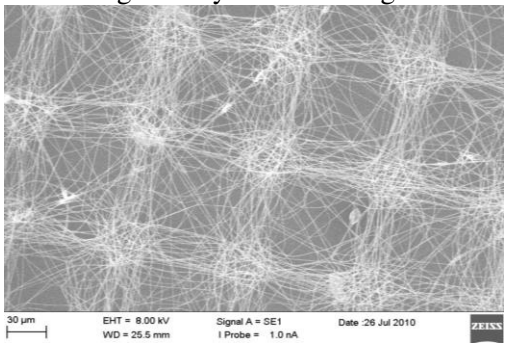

Figure 4. Multiscale CMEMS electrode with PAN nanofibers

ELECTRODE FUNCTIONALIZATION

The carbon electrodes were first activated with oxygen plasma to generate carboxylic functional groups on the surface of the carbon electrodes that can be used to conjugate it with amine terminated groups through the carbodiimide chemistry. The plasma treated electrodes were then treated with a solution of Ethylene Diamine linker in EDC (which was used as the coupling reagent) for up to 3-4 hours. The EDOA functionalized carbon surface was then treated with a solution of 2,4 Dihydroxy-Benzaldehyde (Hydroquinone)/ Sodium Borohydride to initiate coupling of the hydroquinone mediator molecule to the EDOA linker (see Figure 5 for the reaction).

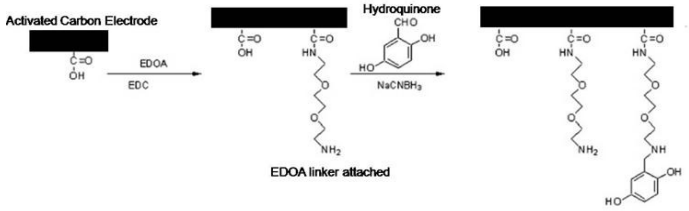

Figure 5. Reaction scheme for the attachment of hydroquinone mediator to the carbon electrode through EDOA linker

The 2% (w/v) solution of enzyme Glucose Oxidase in PBS buffer was then incubated on the mediator functionalized electrode surface for several hours in order to couple it to the remaining carboxylic groups via the amide linkage. The enzyme attachment to the electrode was further improved by a cross-linking reaction by incubating it in a 1% glutaraldehyde solution for up to 10 minutes.

Enzyme functionalization Results

The mediated electron transfer was tested by Cylic Voltammogram of the enzyme-mediator functionalized electrode in PBS buffer with and without Glucose after deaerating the solution by bubbling N_2 for 30 minutes. Any traces of oxygen could lead to the competing reaction that leads to the production of H_2O_2 as the by-product. The Cyclic Voltammograms of the Mediator-Enzyme functionalized electrode revealed the phenomenon of mediated electron transfer through the appearance of redox peaks in the presence of Glucose which is illustrated in Figure 6. The CV revealed oxidation peaks when tested in 1M glucose in PBS solution. These peaks can be attributed to the mediated electron transfer since the absence of oxygen prohibits any H_2O_2 production peaks while no other interfering reactions are known to occur. The redox peaks for the Mediated Electron Transfer between the electrode and the enzyme are weak due to the low quantity of enzyme that got attached to the electrode surface since most of its functionality generated by the Plasma treatment is believed to have been used up for the attachment of mediator, which was attached first in the sequence of attachment.

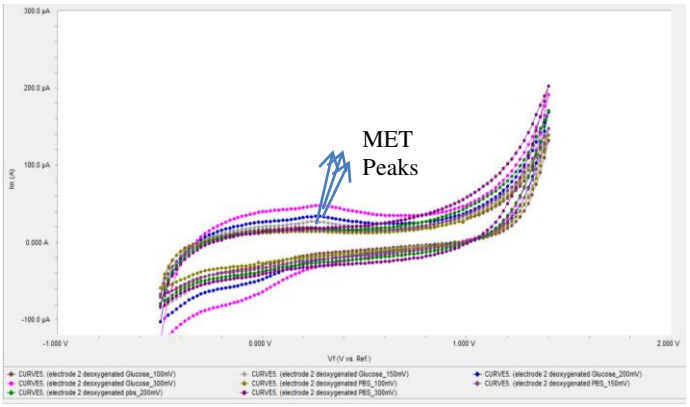

Figure 6. Cyclic Voltammogram of Enzyme functionalized carbon electrodes in the absence of glucose (flat curves) and presence of glucose (curved pointed with arrows) in 100mM PBS. The different CV curves are taken at different scan rates (100mV/s, 200mV/s, and 300mV/s)

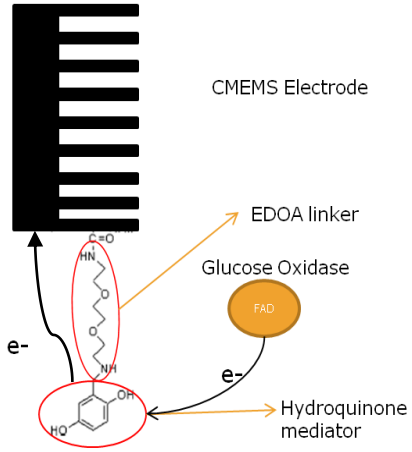

Figure 7. Proposed Mediated Electron Transfer pathway for the functionalized carbon electrode

CONCLUSION

CMEMS electrodes were nanostructured by growth of MWCNTS into a multiscale fractal-like structure. Further electrospinning was successfully used to fabricate Carbon Nanofiber Mat electrodes that were found to exhibit good electrochemical activity. It was further shown that the Carbon Nanofiber mats can also be integrated with CMEMS platform to create multiscale fractal-like tree geometry. It was also shown that Carbon MEMS based electrodes can be functionalized with enzymes and well as an enzyme-mediator system for future applications in biofuel cells as well as in glucose sensors. The CMEMS fabrication technique not only gives us the advantage of the ubiquity of carbon in biological coupling, but also allows us to control the geometry in a manner that minimizes interfacial electron transfer resistance. More complex electrode fabrication designs will have promising influence in the future of biofuel cells and biosensors.

ACKNOWLEDGEMENTS

Authors would like to thank NSF for Grant NIRT-0709065, supporting this project. Special thanks to Dr. Genis Turon Teixidor for continued guidance and Dr. Horacio Kido for his ideas & technical lab expertise.

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