# High Surface Area Carbon Supports for Biocatalytic Electrodes

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## Introduction

• Biocatalytic fuel cells using enzyme as catalysts offer several advantages over conventional fuel cells, such as low manufacturing cost and superior selectivity. But one fundamental limitation is the low current density.

• Previous study has employed a carbon paper consisting of ~10 μm diameter carbon fibers as the support and increased current density by a factor of five.[1] Carbon nanotubes have been applied to catalyst support materials due to their unique structural, mechanical, and electrical properties.[2]

• We want to combine the attractive properties of nanoscale and microscale materials: enhance the current density of biocatalytic electrodes by increasing the electrode surface area via carbon nanotubes as well as maintaining high rates of species transport and excellent structural stability via microscale carbon fibers.

## Materials and Methods

• Using a chemical vapor deposition technique,[3] the iron nanoparticles catalyze the growth of single-walled nanotubes (SWNTs) on Toray carbon paper from E-Tek. The same process is used for growth of multi-walled carbon nanotubes (MWNTs) on Ohmically heated carbon fibers except electrodes are attached on either end of the paper and current is passed across the paper to heat it.[4]

• Morphological characterization consists of scanning electron micrograph (SEM), surface area measurements using the BET technique and porosity and pore size distribution from mercury porosimetry.

• Electrochemical measurements are conducted by means of a mediated glucose oxidase electrode. The enzyme composite electrode is prepared as previously reported.[1] Composition of a typical electrode is given in the caption to Figure 4. The electrode is immobilized on a glassy carbon rotating disk electrode, which is then polarized in the presence of glucose. We use two redox polymers as mediators which differ in their redox potential. The structures of these polymers are shown in Figure 1 and Figure 2.
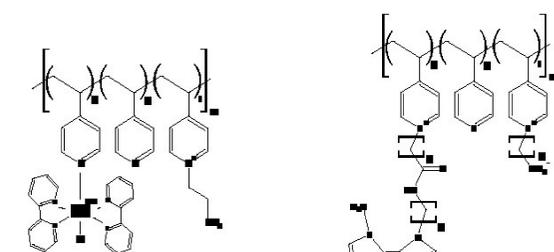


Figure 1. PVP-[Os(bipyridine)$_2$Cl]$^{2+/+}$ redox polymer mediator.[6] Redox potential: 0.28 V re: Ag|AgCl.



Figure 2. PVP-[Os(dialkylated-biimidazole)$_3$]$^{3+/2+}$ redox polymer mediator.[7] Redox potential: -0.19 V re: Ag|AgCl.

## Results



(a) Bare carbon fibers  (b) Iron-catalyzed nanotube growth  (c) Nanotube growth catalyzed by Fe/Al2O3  (d) Nanotube growth on Ohmically haeted fibers
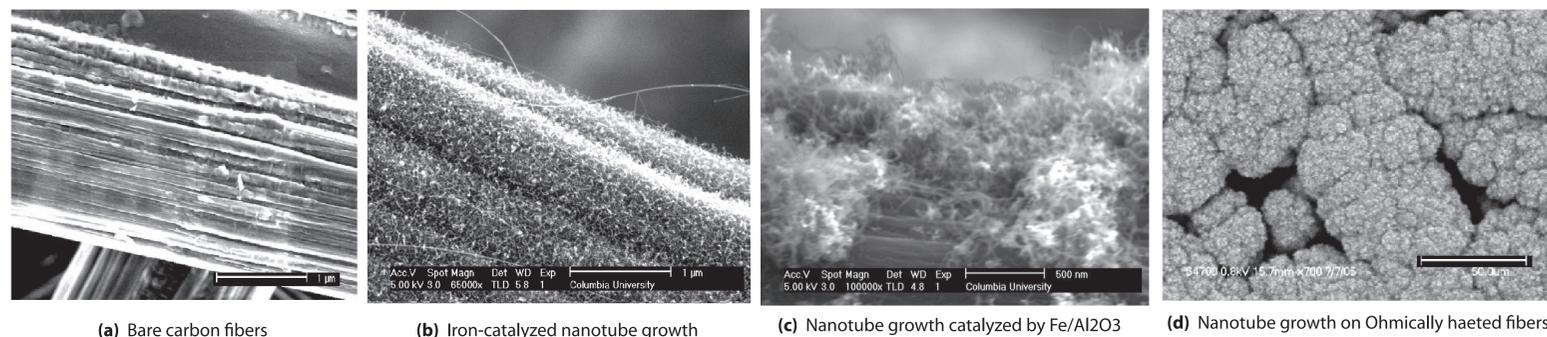
Figure 3. Scanning electron micrographs of carbon paper supports untreated **(a)** and modified for high surface area using various techniques **(b-d)**.
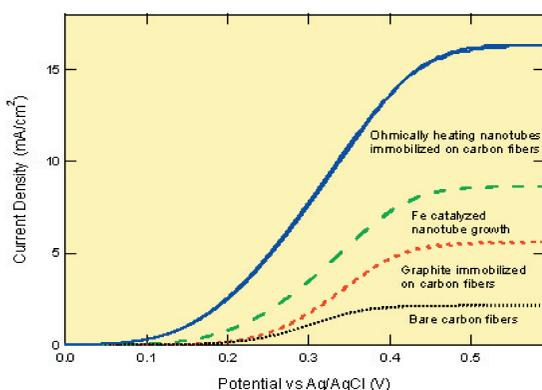


Figure 4. Polarization of the glucose oxidase anode from different support morphologies. Experiment conducted under N$_2$ in pH 7.1 PBS buffer at 37.5°C, 50 mM glucose, on a rotating disk electrode at 4000 rpm rotation rate. Current densities were based on the area of the 4-mm carbon cloth disk (0.13 cm²), and 39.6 wt% GOx (with NaIO$_4$), 59.5 wt% PVP[(Os-bipy)$_2$Cl], 0.9 wt% PEGDGE at 0.32 mg/cm² GOx loading.



Figure 5. Dependence of maximum current density on glucose concentration. Electrode poised at 0.5 V vs Ag/AgCl. Glucose oxidase loading 0.37 mg/cm². All other conditions as in Fig. 4.



Figure 7. Polarization of the anode supported by Ohmically-heated carbon fiber, mediated by different redox species. Other conditions as in Fig. 4.

• Implementation of high surface area carbon substrates in glucose oxidase anodes has dramatic effect on glucose oxidation rates. Figure 4 shows that the MWNT-treated carbon cloth has the highest limiting current density, 16.3 mA/cm², about 7.4 times that of bare carbon paper.

| Material | Current Density (mA / cm²) | Surface Area (m² / g) | Median Pore Diameter (nm) |
|---|---|---|---|
| Bare Toray | 2.2 | 0.3 (0.42)[a] | 23408 (78%)[b] |
| GDL 10 | 5.5 | 2.2 (6.1) | 30258 (88%) |
| Fe catalyzed nanotubes | 8.4 | 19.5 (35.0) | 16 (75%) |
| Ohmically heated Toray | 16.3 | 16.7 (27.2) | / |

Table 1. Effect of carbon support structure on electrode surface area and maximum current density. Surface area measured by BET and capacitance (a). Median pore diameter and porosity (b) obtained by mercury porosimetry. Maximum current density obtained from Fig. 4.

• The higher current density on the nanopaper can be partially explained by the increased surface area. The Ohmically heated paper has a surface area lower than the iron-catalyzed because of the penetration problem though the activity on the surface is high.
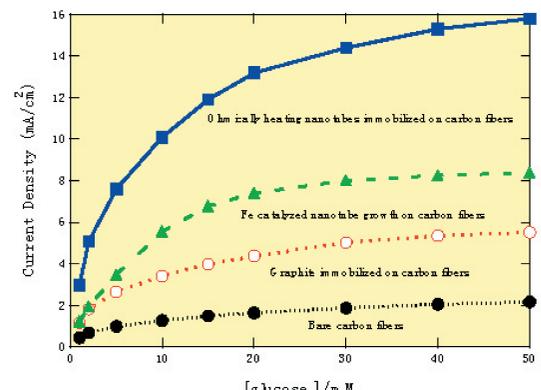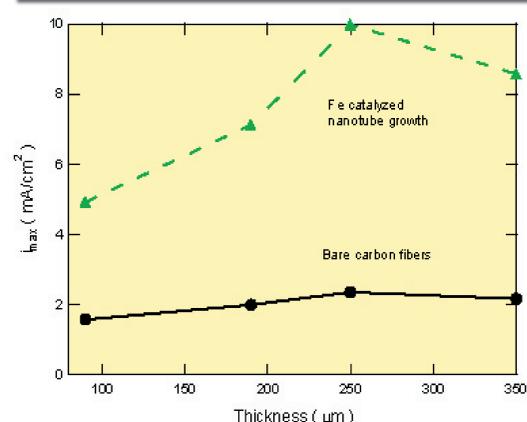


Figure 6. Dependence of the glucose oxidation current density on carbon paper thickness. Electrode poised at 0.5 V vs Ag/AgCl. All other conditions as in Fig. 4.



Figure 8. Temperature dependence of maximum current density on 190 μm nanotube-treated carbon paper. Electrodes poised at 0.5 V vs Ag/AgCl for PVP[(Os-bipy)$_2$Cl], 0.0 V vs Ag/AgCl for PVP[Os(da-biimidazole)$_3$]. Other conditions as in Fig 4

• The current densities increased with the glucose concentration until the concentration reached 50 mM (Fig. 5). The apparent Michaelis constant is not found to be effected by the carbon support, suggesting that mass transfer rates are independent to support. A maximum is found in the electrode thickness dependence (Fig. 6), believed to be related to the trade-off between film thickness on the fibers and bulk enzyme concentration at constant area loading.
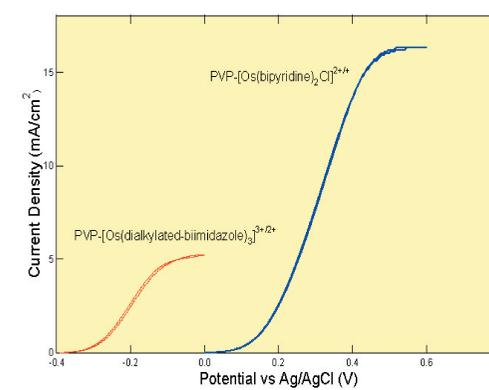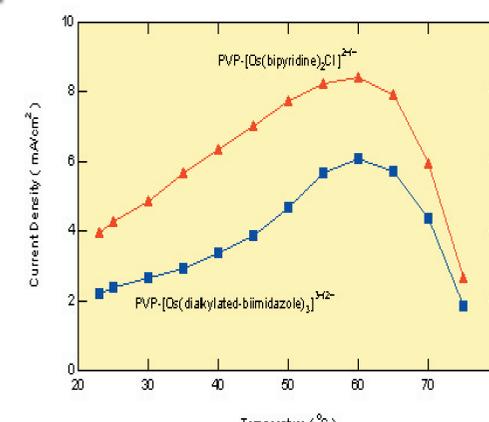
• The two redox mediators differ in their redox potential, which determines the potentials at which glucose oxidation takes place, and also determines the rate of enzyme-mediator electron transfer. Figure 7 illustrates the inherent trade-off in these properties. The effect of temperature are shown in Figures 8. Peak activity is observed at 60°C for both mediators (Fig. 8).

## Conclusions

• High surface area carbon materials such as nanotubes immobilized on micron-scale carbon fiber substrates provide an effective way to dramatically improve electron transfer in biocatalytic electrodes without compromising structural strength.

• Glucose oxidase electrodes have been demonstrated with seven-fold improvements in current density due to these multiscale, carbon-based materials.

• Current density can be over 16 mA/cm² c if other conditions are optimized.

## Future Work

• Approach ideal nanotube morphology, possibly by catalyzing nanotube growth throughout the void space of the carbon fiber paper.

• Implement these electrodes in a flow-through electrode system, investigating effects of fuel composition, electron mediation, and stability.

• Synthesis of carbon nanofibers by electrospining. We have previously shown that polymer nanofibers as small as 30 nm in diameter, can be easily synthesized by an electrospinning.[5]

## Acknowledgment

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