Preparation of hybrid nanocatalysts containing enzymes and gold nanoparticles for ethanol/O<sub>2</sub> biofuel cell

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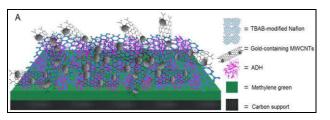
#### Introduction

The biofuel cell provide a means to obtain clean, renewable energy and have great potential for maybe in the future be used as alternative energy source for low power devices. Even with some promising characteristics, enzymatic biofuel cell still have many challenges to be faced for a future application of this system. Some key issues in the development of this device, such as lifetime, stability of enzymes, achievement of higher power densities, overcoming difficulties in the electron transfer between enzymes and electrodes, and the improvement of techniques for enzyme immobilization are still important objects of research [1, 2]. Some new trends in biocatalysts for biofuel cell include the incorporation of nanoscale materials such as carbon nanotubes, nanofibers, nanocomposites, and the incorporation of nanoparticles in bioelectrodes [3].

Previously works by our research team showed that both polyamidoamine (PAMAM) dendrimers and tetrabutylammonium bromide (TBAB) modified-Nafion® membrane can effectively immobilize dehydrogenase enzymes [4-6]. Based on the most recent works and developments, this work focus the development of hybrid nanocatalysts containing enzymes, carbon nanotubes and gold nanoparticles for enzymatic biofuel cell EtOH/O<sub>2</sub>, employing two platforms for immobilization of enzymes, PAMAM dendrimers and TBAB-modified Nafion®.

# Experimental

Two different strategies were employed to prepare the metallic gold nanoparticles. In a first methodology, the synthesis involved the insertion of gold nanoparticles inside PAMAM structure. The metal nanoparticles encapsulation method involves complexation of the respective metal ion with the internal tertiary amine groups of the dendrimer, followed by chemical reduction using formic acid (Figure 1) [7]. The other method is based on nanoparticles synthesis on multi walled carbon nanotubes (MWCNTs) by microwave-assisted heating [8]. The bioelectrodes were fabricated by using two already described techniques: passive adsorption and layer by layer (LbL) [4]. In a first situation, the bioelectrodes was prepared by passive adsorption immobilizing the enzyme alcohol dehydrogenase (ADH) along with gold nanoparticles supported onto MWCNTs and (TBAB) modified-Nafion® membrane onto a carbon cloth platform. In a second situation, the gold-containing PAMAM dendrimers were employed to prepare the LbL electrodes in a carbon paper platform. Figure 1 A and B illustrates both designed bioelectrodes.



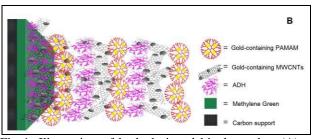


Fig 1. Illustration of both designed bioelectrodes. (A) = passive adsorption employing TBAB modified-Nafion<sup>®</sup>. (B) = LbL employing gold-containing PAMAM.

### Discussion

results indicated that both bioelectrodes were able to provide enhanced catalytic performance compared to the control samples (without addition of any gold nanoparticle); in fact, the addition of gold nanoparticles provided both higher power density values as well as higher current density. Considering that driving electronics is a very important issue in enzymatic devices, the enhanced performance towards ethanol oxidation obtained is an indication of better electron transfer through the bioelectrode structure. Based on this data, it can be inferred that both ADH and nanocatalyst can be effectively immobilized onto carbon platforms using PAMAM dendrimers and TBAB modified-Nafion. Also, the combined use of small amounts of nanocatalyst with enzyme can satisfactorily enhance the bioanode performance.

# Acknowledgements

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