Direct Electron Transfer From Single Enzymes to Single Wall Carbon Nanotubes

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The reported enzymatic biofuel cell, where the coupled conversion of glucose and oxygen using glucose oxidase (GOx) and laccase generated 1 Volt in an external circuit through a pair of single wall carbon nanotubes (SWCNT) spaced 2 μm apart offers a platform to investigate the functionality of enzymes when immobilized in this special geometry.[1] The directed self-assembly process that was used to attach the enzymes to the SWCNTs is new and unique and therefore needs careful study of the nature of the attachment mechanism and dynamics and how the catalysis of enzyme targets is affected. Understanding these effects is essential for the eventual nanofabrication of enzyme enabled sensor arrays on the SWCNT platform. The attachment process is summarized in Figure 1. Briefly, the substrate contains SWCNTs deposited on metal at the base of nanoscale windows using electrophoresis.[2] The enzymes are attached using cyclic voltammetry (CV) with the SWCNT as the target electrode in a three-electrode cell. The free end of the SWCNT has dangling bonds with attached -COOH groups. Any -COOH can react with any number of amines within the enzyme and form a covalent bond. The point of attachment to the enzyme will depend on its orientation as it is drawn towards the SWCNT during CV. The immobilized enzyme can catalyze target molecules and in some cases generate electrons that can be transferred directly to the SWCNT where they can be detected in an external circuit.

The specific site where the carboxyl group attaches to the enzyme may affect the electron transfer during catalysis of a target molecule. Also, the orientation and degrees of freedom of the enzyme may affect the probability (and rate) of catalysis. Studies of the immobilization effects on enzyme catalysis have only been performed on large systems.[3] An array of addressable single SWCNTs with attached enzymes offers an opportunity to possibly isolate effects from single enzymes. Since the diameter of the SWCNTs are only 1 nm and the GOx molecule is nearly 8 nm, there is a high probability that only one can be attached at the free end. Then measurements of electron transfer rates during catalysis from different sites within an array may include affects due to both the orientation and the attachment site of the enzyme. The example in Figure 2 shows the electron transfer rates by the catalysis of glucose by GOx from 6 different GOx/SWCNT electrodes in an array. Methods to uncouple enzyme immobilization effects from others will be discussed.

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[2] A. Goyal, S. Liu, Z. Iqbal, L. A. Fetter and R. C. Farrow, J. Vac. Sci. Technol. B **26**, 2524-2528 (2008).
[3] A. de Poulpiquet, A. Ciaccafava, E. Lojou, Electrochimica Acta **126**, 104-114 (2014).

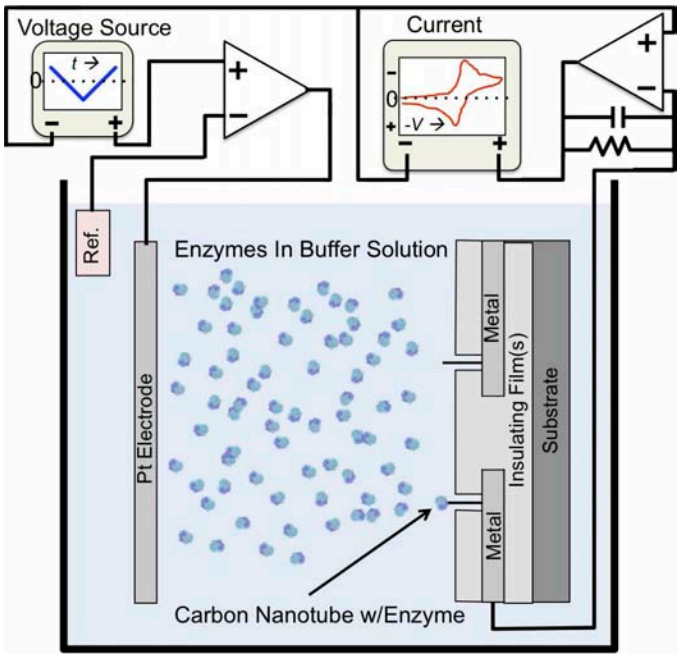

Figure 1 Diagram of cyclic voltammetry deposition of enzymes on selected carbon nanotubes in nanoscale windows with an electrical connection to an underlying metal. The reference electrode allows for measurement of the potential(s) that correspond to redox reactions at the working electrode (carbon nanotube). By convention the scan starts from a positive voltage and records the reduction of the electrode before the oxidation that may follow. The voltage separation between corresponding reduction and oxidation peaks can indicate whether the process is reversible.

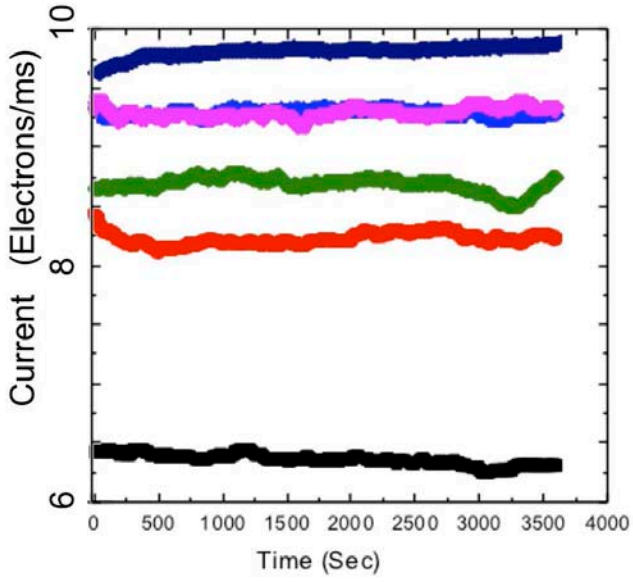

Figure 2 Plot of current generated by the reaction of glucose with glucose oxidase attached to six different carbon nanotubes in an array using a platinum counter electrode. The measurements were recorded as the voltage across a 200 TOhm load.