Redox cycling at nanowire-based interdigitated comb electrodes: Enhanced electrochemical sensitivity and electrode kinetics

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Typically, nanowire electrodes demonstrate enhanced performance, when compared to microelectrodes, due to improved mass transport occurring at the nanoelectrode [1, 2], thereby offering the potential for faster and more sensitive electroanalysis. Further enhancements are expected at nanowire electrode arrays. However, a critical factor in the design of nanowire electrode arrays is the inter-electrode distance and hence the objective is to assess the separation required between adjacent nanowires to maximise the electrochemical response. To this end, we simulated diffusion profiles existing at nanowire electrode arrays with various inter-electrode distances. Experiments show that nanowires that are sufficiently spatially resolved (diffusionally independent) demonstrate superior electrochemical performance, when employing sweep voltammetric techniques such as cyclic voltammetry, compared to nanowires that are relatively close to each other (overlapping diffusion profiles), which is in good agreement with the simulated results. By contrast, arrays with diffusionally overlapping profiles exhibit enhanced performance when employing step voltammetric techniques such as square wave voltammetry, see Figure 1. To date, to the best of our knowledge, this has not been seen or reported in literature. Fully integrated devices exhibited enhanced current amplification when employed in a collector generator format. Electrochemical responses are excellently described by classical Butler - Volmer kinetics, displaying a fast, heterogeneous electron transfer kinetics.

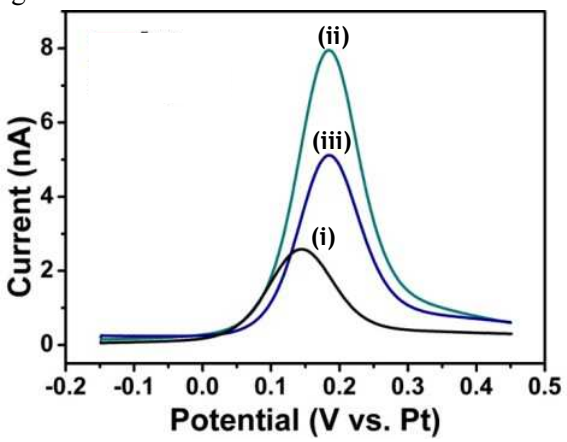

Figure 1: Typical square wave voltammograms of 5 mM FcCOOH in 10 mM PBS at (i) a single nanowire electrode, (ii) three nanowire electrodes in array separated by 5 µm and (iii) three nanowire electrodes in array separated by 15 µm.

1. Trevor J. Davies and Richard G. Compton, The cyclic and linear sweep voltammetry of regular and random arrays of microdisc electrodes: Theory, *Journal of Electroanalytical Chemistry*, 2005. **585**(1), p. 63-82.

2. Karen Dawson, Amélie Wahl, Richard Murphy and Alan O'Riordan., Electroanalysis at single Gold Nanowire Electrodes, *Journal of Physical Chemistry C*, 2012. **116**(27), p. 14665-14673.