Discrete Gold Nanowire Sensor Arrays: Exploiting the diffusion regime
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A key advantage of employing nanoscale electrodes is that it enables high densities of sensors to be fabricated in a much smaller footprint at key substrates, such as on a silicon chip, thus yielding much higher information-generating capability per device. In electrochemistry, attempts to work at very small (sub-micrometer) electrode sizes at silicon substrates, particularly discrete individual nanowires have not been reported extensively in the literature [1]. This reflects the difficulty in both fabrication and integration of nanowire electrodes as functional sensing elements in functional devices. However, the drive to developing new sensor devices that exhibit increased sensitivity with the ultimate goal of achieving single molecule detection remains a key technological motivation in this area [2-3].

In this regard, increasing the number of sensing elements, by fabricating arrays of discrete nanowires, offers the potential to achieve enhanced sensitivity at a much lower foot print when compared to ultra-microelectrodes A critical challenge however is to ensure that wires are correctly spaced to exploit analyte diffusional regimes occurring between neighboring nanowire electrodes [4-5]. To this end, a key requirement is to understand the diffusional process occurring at electrodes and correlate this with the sensing application prior to sensor design and fabrication. In this manner a 'design for purpose' approach for electrochemical sensors at silicon chips will result in optimized sensitivity when compared to the 'one size – fits all' approach currently taken with, e.g., screen printed electrodes when considering the diverse range of electroanalytical methods currently being applied to a huge variety of target analytes. During analyte immobilization or sequestering methods, such as immunoassays or under-potential deposition, a concentration gradient is established at an electrode surface down which fresh analyte must flow from the bulk solution – to optimize sensitivity it would be therefore necessary to ensure that electrodes are sufficiently spaced so as to be diffusionally independent. By contrast, during cycling methods, such as steady-state ECL or redox cycling overlap in diffusion profiles should result in higher sensitivities.

Finite element analysis has been previously applied to arrays of nanoelectrodes with uniform dimensions such as nanopores and nanodiscs. In this work, we employed finite element diffusion domain simulation studies to assess the minimum separation between neighboring nanowire electrodes allowing diffusion independence. Therefore, we simulated diffusional mass transport at gold nanowire electrodes in array, separated by 5, 10, 15 and 20 μm. Simulation results suggested that radial diffusion to nanowires should be present at fast scan rates for a separation between 10 μm, where diffusional overlap of adjacent concentration profile is observed, and 15 μm, where the diffusion profiles of each nanowire is independent.

To confirm these simulations, silicon chip were designed

that comprised twelve separate electron beam fields containing either a single nanowire or nanowire arrays were designed and fabricated. The chips also contained on-chip counter electrodes, SiNx passivation and on-chip contact pads located at the chip periphery that facilitated direct electrical probing and thereby eliminated the requirement for time consuming microelectronic packaging approaches. Critical dimensions of nanowire and nanowire arrays were characterized using a combination of optical, probe and electron microscopy. Electrical and electrochemical characterization of the nanowire arrays was undertaken to explore the diffusional process occurring at arrays with increasing number of nanowires. Finally, application of pulse voltammetric techniques was used to explore future analytical possibilities employing nanowire arrays as sensor elements.
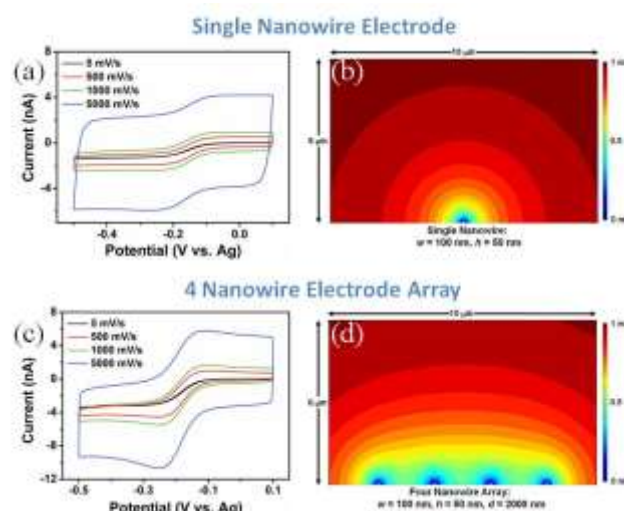

Figure 1: (a) CV measurements recorded at single nanowire electrode and an array 4 nanowires (c,) were based on 1 mM $Ru(NH_3)_6^{3+}$ in 10 mM PBS at a range of scan rates vs. Ag. Simulations are of a plane perpendicular to rows of nanowire electrodes. (B & D) In all cases bulk concentration is 1 mM and $D_O = 5.3 \times 10^{-6}$ $cm^2\ s^{-1}$ at a scan rate of 5000 mV s^{-1}.

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