

Glucose detection at single gold nanowiresK. Dawson., S. Barry, A. Wahl,
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Compared to traditional macroelectrodes, nanoscale electrodes have tremendous potential as electrochemical sensors exhibiting enhanced performance. As critical dimensions of the electrodes enter the nano regime, 3D analyte diffusion profiles to the electrode dominate with a corresponding increase in mass transport, higher current densities giving rise to an increase in the ratio of faradaic to charging current, higher signal to noise ratios, steady-state sigmoidal voltammograms, low depletion of target molecules, low supporting electrolyte concentration requirements and shorter RC time constant^{1,2}. A variety of different fabrication approaches of nanoelectrodes have been reported to date. However challenges arising from difficulty in fabrication pathways, lack of reproducibility and small electrochemical currents (<100 pA), are still prevalent. Recently 1-dimensional nanostructures based on bands and wires are being explored as nanoelectrodes to provide practical solutions. 1-dimensional nanoelectrodes, such as nanowires, benefit from nanoscale critical dimensions (width) ensuring enhanced mass transport, while the high aspect ratio permits higher measurable currents in the ≥ 1 nA regime and with uniform current densities.

In the work, we report the fabrication and in-depth electrochemical analysis of discrete gold nanowire electrodes for use in electrochemical applications. The single nanowire electrodes and nanowire electrode arrays were fabricated using a hybrid E-beam / photolithography approach, providing electrodes with well-defined and reproducible dimensions. Finite element diffusion domain simulation studies were employed to explore mass transport to nanowire electrodes. Simulation results suggested that radial diffusion to nanowires should be present at fast scan rates. This behavior was confirmed experimentally where CVs obtained in FcCOOH, were observed to be steady-state, with high currents (nA) and sigmoidal up to 5000 mV s⁻¹. The electrochemical responses of nanowires, in model redox mediators, were excellently described by Butler-Volmer kinetics. The nanowire electrodes are applied to reproducible determination of heterogeneous electron transfer-rate constants, k^0 , for three key model redox analytes, FcCOOH, Fe(II)(CN)₆⁴⁻, and Ru(NH₃)₆³⁺.

We explore the application of single on-chip gold nanowires for use as electrochemical sensors employing glucose as target molecule. For glucose sensing, ferrocene monocarboxylic acid was employed as a redox mediator, while also amplifying the electrochemical signal. The nanowire-based devices demonstrated rapid glucose detection across the linear concentration range of 10 μ M to 1 mM with a theoretical limit of detection of 3 μ M (S/N = 3)⁷. The wide dynamic range, high sensitivity and selectivity coupled with good the biocompatibility of the gold nanowire electrode opens up the possibility of employing nanowire electrodes as sensors in future non-invasive glucose diagnostic devices employing, for example, saliva or tears which typically has glucose present in ~100 – 500 μ M range; see Figure 1.

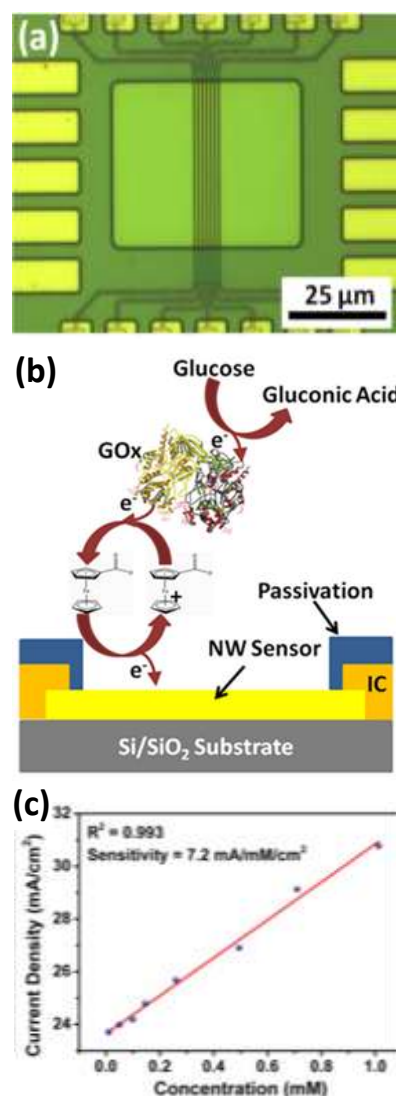


Figure 1: (a) optical micrograph of seven individually contacted nanowires fabricated at a silicon chip substrate. (b) Schematic of the glucose detection mechanism and (c) calibration plot for micromolar glucose detection.

References

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