ELECTROCHEMICAL SENSING WITH A SUSPENDED SINGLE NANOWIRE

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ABSTRACT

The use of nanoscale electrodes is beneficial in microfluidic sensing applications, as a high sensitivity and efficient mass transport can be achieved. Facile preparation of millimeter-long gold nanowires is possible using nanoskiving. Single nanowires were suspended over a glass microchannel, which was closed with a complementary PDMS microchannel. Using the nanowire as an electrode, cyclic voltammograms of ferrocene were recorded, with the electroactive solution flowing through the channel at different rates. Nanowires suspended in the center of the flow profile exhibit higher current responses than nanowires on the bottom of microchannels, due to efficient analyte transport towards the electrode surface.

KEYWORDS: Nanoelectrochemistry, nanowires, nanoskiving

INTRODUCTION

Employment of electrochemical detection in microfluidic systems is of great interest to analytical chemists and biological researchers. This is due to direct signal transduction, as well as the ease with which these techniques can be miniaturized. Moreover, the sensitivity of electrochemical detection is not compromised when employed in miniaturized systems; (sub)micron-scale electrodes often outperform their macroscale counterparts as a result of improved mass transport. Here we demonstrate electrochemical sensing with a single Au nanowire (NW) bisecting the cross-section of a microfluidic channel. The NWs were fabricated by nanoskiving, which allows straightforward and simple preparation of millimeter-long wires using edge lithography [1]. Placing the detection element in the center of a microchannel – in the region of fastest flow – facilitates the most immediate response to changes in solution composition. Due to efficient analyte transport to the wire, signal amplification is higher compared to nanowires positioned on a channel wall or surface [2].

EXPERIMENTAL

The fabrication of microfluidic channels bisected by gold NWs was performed as described earlier [1]. In brief, 200 nm by 200 nm by 1.5 mm Au NWs were nanoskived; after thin-film Au deposition and embedding in epoxy resin, an ultramicrotome was used to create well-defined sections containing single wires. A single epoxy section containing a NW was placed over a 70-µm-wide, 30-µm-deep glass channel, and the surrounding epoxy was etched off using O_2 plasma (see Fig. 1). A complementary polydimethylsiloxane (PDMS) channel was aligned and bonded on top of this glass part to create a 1-cm-long sealed channel with a suspended nanowire. The PDMS part also featured ports that allow electrical contact to the NW using pads of silver paste (see Fig. 2). A solution of 1 mM ferrocene in acetonitrile (with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte) was used as electroactive species. Using a syringe pump, the microchannel was perfused via tubing inserted into the PDMS. A Ag/Ag^+ reference electrode was placed in a reservoir downstream of the microchannel (see Fig. 2). Cyclic voltammograms (CVs) were recorded at a scan rate of 20 mV/s and different flow rates using a LabVIEW-controlled FEMTO DDPCA-300 transimpedance amplifier as a potentiostat.

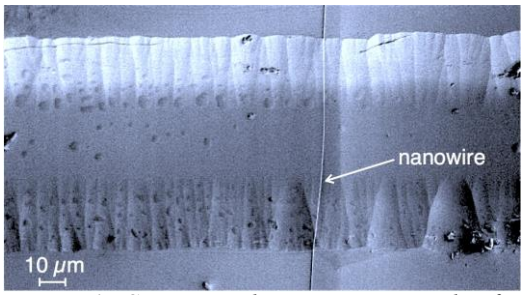

Figure 1: Scanning electron micrograph of a nanoskived gold nanowire suspended over a glass microchannel.

RESULTS AND DISCUSSION

In Fig. 3 (insets), CVs recorded with a single NW, either suspended in a channel or placed on the channel bottom, are shown for flow rates ranging from stagnant solution up to 20 µL/min. The current increases with flow rate. The limiting current (at 0.6 V) is expressed as a function of the flow rate. The current increases sublinearly and monotonically, which was also observed for conventional microelectrodes [3]. This is observable both in suspended nanowires, and nanowires placed on the bottom of a channel. However, even under stagnant flow, the detected current is approximately 5 times larger as compared to a nanowire placed at the bottom of the microchannel. This is the result of the improved mass transfer to the wire placed in the *center* of the flow profile.

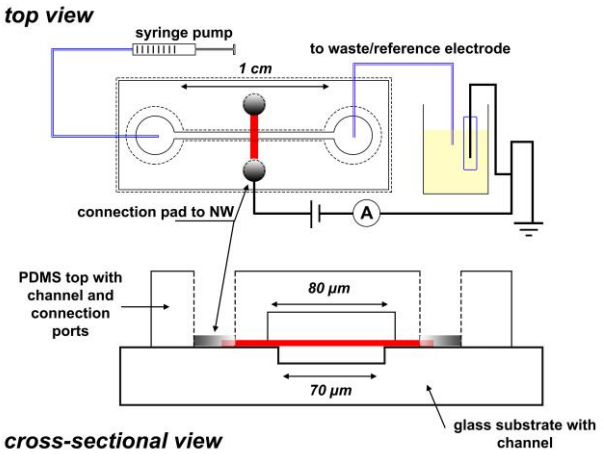

Figure 2: Top and cross-sectional schematic of the glass-PDMS device. The NW is depicted as a red stripe. Electrical contact is established with the NW through ports punched in the PDMS.

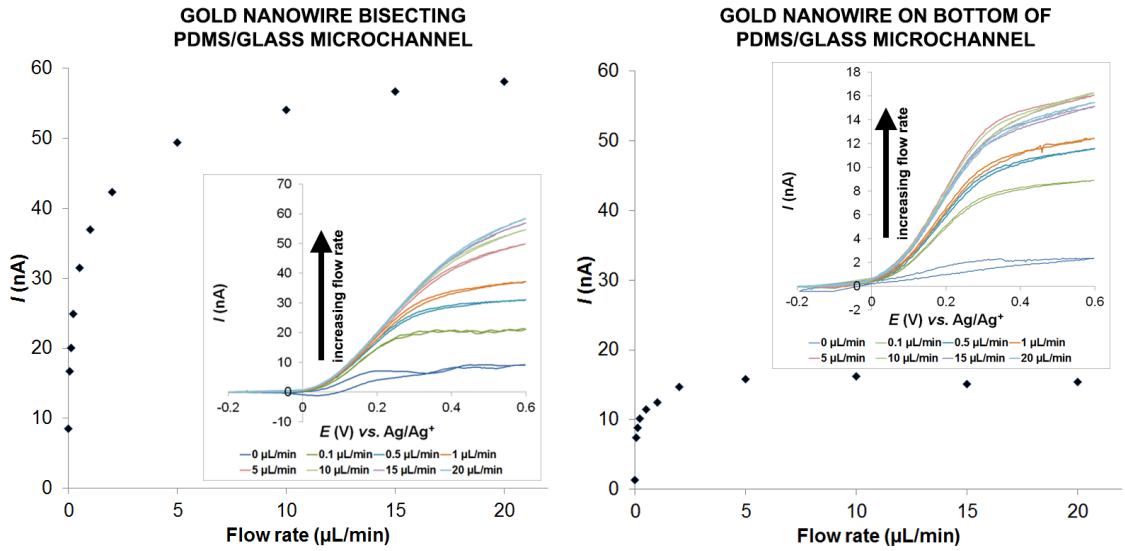

Figure 3: Limiting current (at 0.6 V) as a function of the syringe pump flow rate, generated at Au NWs in the center of the flow profile (left) or on the bottom of a microchannel (right). Insets: CVs of single gold NWs, suspended or on a flat substrate, for different flow rates (scan rate of 20 mV/s for all CVs).

CONCLUSION

This is the first report of integrated suspended nanowire sensors being used for electrochemical voltammetry in a microchannel under flow. The method enables probing in the center of the channel without disturbing the flow pattern. Thus, it enables fast and accurate sensing.

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