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Supporting Information

Effect of channel height and electrode aspect ratio on redox cycling at carbon interdigitated array nanoelectrodes confined in a microchannel

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Electrode system fabrication

The 1:1 aspect ratio carbon IDA nanoelectrode chip was designed to consist of four pairs of IDA carbon electrodes and a single PDMS channel connecting all of the electrodes. The carbon nanoelectrodes were fabricated through a single photolithography process and a pyrolysis process. These nanoelectrodes were covered with a PDMS channel following an insulation layer deposition process, as shown in Fig. S2. First, a 6-in silicon wafer was insulated with a 1-μm-thick layer of thermal oxide. The wafer was spin-coated with a 3-μm-thick negative photoresist (SU-8, Microchem, Corp., USA), after which micrometer-sized IDA structures were patterned using UV lithography. The long and narrow polymer patterns (width = 1.5 μm, gap = 1.5 μm) were converted into carbon nanoelectrodes (width = 650 nm, thickness = 650 nm, gap = 2.35 μm) through pyrolysis at 900 °C in a vacuum condition, because the pyrolysis is accompanied by a dramatic reduction in volume. Although the volume reduction in pyrolysis is approximately isometric, its rate depends on the dimensions of the original polymer. In this experiment, the micro-sized polymer IDA structures shrank more in the vertical direction, reducing the aspect ratio of the structure to ~1. The pyrolyzed carbon structures were selectively insulated with multiple RF-sputtered insulating layers (100-nm-thick SiO_2/100-nm-thick Al_2O_3/100-nm-thick SiO_2) using a lift-off process so that only carbon nanoelectrodes collect the redox current. The PDMS microchannel was patterned using soft lithography from an SU-8 polymer mold pre-patterned by photolithography. Finally, the carbon chip coated with SiO_2/Al_2O_3/SiO_2 layers and the PDMS microchannel were bonded together after oxygen plasma treatment.

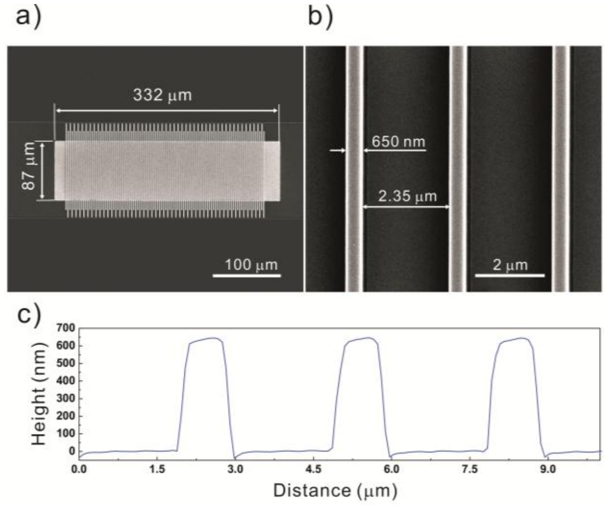

Fig. S1 (a) An SEM image of 1:1 aspect ratio carbon IDA nanoelectrodes passivated with multiple insulation layers except for an open sensing area (width = 87 μm, length = 332 μm), (b) a magnified SEM image of the carbon nanoelectrodes (width = 650 nm, thickness = 650 nm, gap = 2.35 μm), and (c) a side profile of the carbon nanoelectrodes measured using atomic force microscopy.

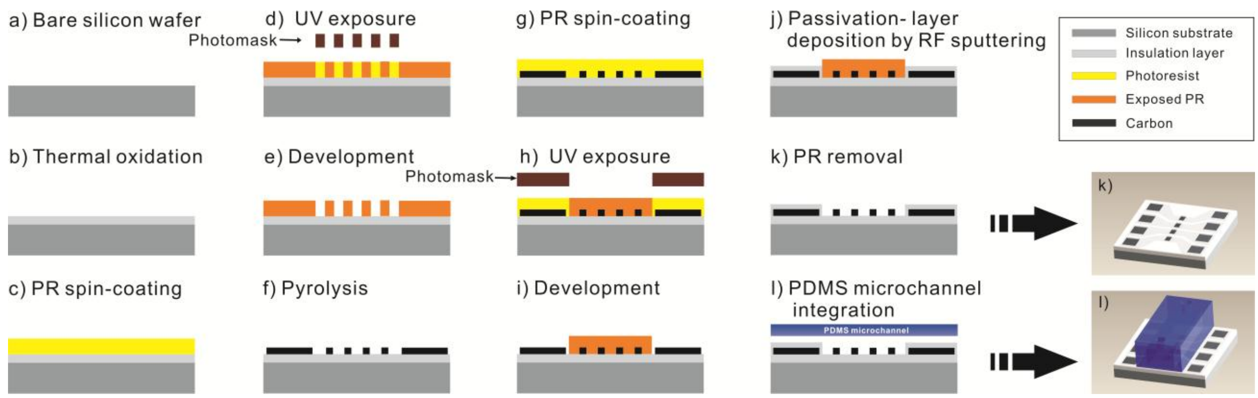

Fig. S2 Schematic diagram of fabrication steps for carbon IDA nanoelectrodes integrated in a PDMS microchannel: (a) a bare silicon wafer, (b) thermal oxidation, (c)–(e) first photolithography process for SU-8 IDA microelectrodes and polymer pads, (f) pyrolysis, (g)–(i) second photolithography process for patterning passivation layers, (j) passivation-layer deposition by RF sputtering, (k) photoresist (PR) removal, and (l) integration of a PDMS microchannel.

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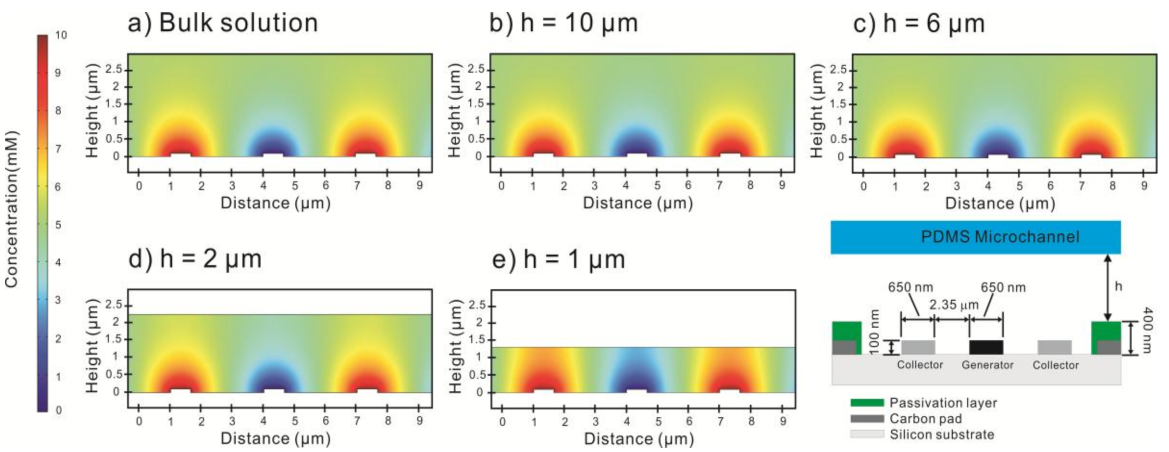

Fig. S3 Simulation results of the concentration profiles of ferrocyanide in the dual mode for thin-band carbon nanoelectrode sample (electrode width = 650 nm, height = 100 nm, gap = 2.35 μm, number of electrode pairs = 50, insulation thickness = 300 nm) in various microchannels.