Supporting Information

# **Magnetically Gated Microelectrode**

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### Microelectrode fabrication

Electromagnetic microelectrodes were fabricated from electromagnetic micropores previously developed.<sup>[1]</sup> Briefly, the electromagnetic micropores were fabricated by etching backside wells and frontside pore wells. A photolithographic process is then used to produce a patterned seed layer for gold deposition. Gold was electrodeposited onto this seed layer, followed by an etch through the pores from the backside, and finally the trap was insulated with silicon oxide. To fabricate microelectrodes, polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) was spin coated (90 s @ 3000 rpm) onto the electromagnetic pores (trap diameter = 100  $\mu$ m) and the entire device was placed in a two compartment cell in which a backside air pressure (10 psi) was applied while curing the PDMS at room temperature for 24 hours (figure S1a). This backside air pressure was present to ensure that the micropores remained open during the curing process. The PDMS layer acts not only to insulate the microelectromagnetic traps, but also provides the desired insulator thickness needed to produce a maximum magnetic field in the center of the traps.<sup>[1b, 2]</sup> Insulator thickness has been previously investigated by our group and is shown to produce a maximum magnetic field in the center of a 100 µm trap at distances between 15 and 20 µm above the trap. This field distribution is critical to reversibly pull magnetic material on and off of the microelectrode surface. Next, paraylene c was deposited (~ 1 µm) onto the entire device through chemical vapor deposition (figure S1b). Deposition was completed in two steps (1.5 g and 0.5 g) to insure that no pin hole leaks formed. This insulation layer was applied to insulate the backside silicon wells to reduce interference between the trap current and electrochemical measurements. Next, several coats of colloidal silver liquid (silver epoxy, Electron Microscopy Sciences) were painted and dried onto the backside of the device (figure S1c). Once the backside wells were filled with dried silver epoxy, another layer was painted onto the device and a thin piece of copper tape (epoxy on tape removed) was attached to the wet silver epoxy and allowed to dry. This copper tape served as connection between the silver epoxy and a power supply. The device was then mounted in a glass u-tube apparatus where a gold platting solution (Orotemp 24 RTU rack, Technic inc.) was placed in the compartment exposed to the frontside of the device. A stainless steel electrode, stir bar, and temperature probe were also place in this compartment and the solution was stirred and heated to 65 °C. A potential difference (between -0.1 and -1 V) was applied between the copper/silver (active) and stainless steel (ground) electrodes to achieve a current density between 0.1 - 1.0 amps/decameter<sup>2</sup> with a picoammeter (keithly 6487). Plating was continued until a rise in current was observed, which signified that the pore was completely plated with gold (figure S1d). Figure S1e shows a schematic of the completed device.

## Reversible gating protocol

The entire device was mounted in a two compartment cell. This test cell allowed application of a potential difference (CHI660C, CH Instruments) between the working (gold microelectrode), reference (Ag/AgCl), and auxiliary (Pt) electrodes while simultaneously energizing the microelectromagnetic trap via contact pads and a secondary power source (1786B, BK Precision) connected to an H-bridge. In a typical experiment, a solution of 5 mM hexaamineruthenium (III) chloride (Strem Chemicals) and 100 mM potassium chloride (Mallinckrodt Chemicals) was added to the top compartment and cyclic voltammogram (CV) was recorded at a scan rate of 10 mV/s. The limiting current of the CV was then used to calculate the approximate electrode radius.

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A clockwise or counterclockwise current of 300 mA was then passed through traps while recording CVs. Magnetic particles (300 nm<sub>OD</sub>, 02130, Ademtech) were placed in the top compartment and a 300 mA clockwise current was used to direct particles to the electrode surface. This current, in combination with an external magnet, was previously determined (simulated) to be <10 mT.<sup>[1b]</sup> Once particles were over the electrode, a CV was recorded and a counterclockwise current of the same magnitude was used to remove the particles from the electrode surface at which time a final CV was taken. Current-time plots were performed by applying constant potential difference of -0.35 V for approximately 70 s. Optical micrographs were taken of the traps and magnetic particle manipulation with a CCD camera (Exi Aqui, Qlmaging). All experiments were conducted in a copper mesh faraday cage.

### Glucose sensor protocol

Glucose oxidase from *aspergillus niger* (Sigma and Aldrich) was attached to 300 nm amine functionalized magnetic particles (02230, Ademtech) through glutaraldehyde coupling. The entire device was mounted in the two compartment cell described above and a solutions which contained various concentrations of glucose (0.65- 20 Mm), 0.5 mM ferrocene carboxlic acid, and 50 mM phosphate buffer (pH 7.5) and 50 mM KCI were placed on the coil and microelectrode. The magnetic particles were then pulled to the center of the coil with a 300 mA clockwise current and the coil current was turned off and let sit for one minute to minimize heat production produced by the coil. A CV for ferrocene was then recorded (0.1 to 0.3 V at a rate of 10 mV/s) and the particles were pulled out of the center of the trap with a counterclockwise current of 300 mA. A final CV was taken after the coil current was turned off for one minute.



**Figure S1.** Fabrication of an electromagnetic microelectrode (a) PDMS coated onto the chip surface (b) paralyne c deposited onto chip (c) silver epoxy added to the backside of the chip (d) Au electroplated from frontside of the chip (e) Schematic representation of electromagnetic microelectrode



Figure S2 Characterization of various size microelectrodes. (a) CVs of 5 mM ruthenium hexamine produced by four microelectrodes fabricated in the center of a single-coil microlectromagnetic trap. (b-e) Optical micrographs of four electrodes (b) 10 µm<sub>OD</sub> pore within a 75 µm<sub>OD</sub> coil (c) 25 µm<sub>OD</sub> pore within a 100 µm<sub>OD</sub> coil (d) 25 µm<sub>OD</sub> pore within a 100  $\mu$ m<sub>OD</sub> coil where the pore is overplated (e) 25  $\mu$ m<sub>OD</sub> pore within a 100  $\mu$ m<sub>OD</sub> coil where the pore is overplated to a greater extent than is shown in d. Over plating pores were found to significantly increase the size of the electrode, not only increasing the radius of the electrode, but also changing the shape of the electrode from a disk to a hemisphere. This is because once gold is plated to the top of the pore, the gold starts to plate isotropically above the pore producing the hemisphereical shape which is apparent in d and e. The radius (r) is calculated with either the equation for steady state current at a disk electrod (b and c) (i<sub>ss</sub> = 4nFD<sub>o</sub>C<sub>o</sub>r) or steady state current of a hemispherical electrode (d and e) ( $i_{ss} = 2\pi FD_oC_or$ ). Though b and c are not entirely planer and d and e are overplated and clearly not perfectly hemispherical electrodes these equations are used as an approximation to show that various size electrodes can be fabricated through use of different size pores and degree of platting.



Figure S3 TEM of Ademtech magnetic particles



**Figure S4** Control experiments in 5 mM hexaammineruthenium (III) chloride and 100 mM potassium chloride that show that the coil current does not affect the limiting current produced by the electrode. In addition, when particles are not over the electrode there is no observable affect on the limiting current.



**Figure S5** Control Gox experiments that show that there is not a significant differences in the limiting current when Gox modified particles are not at the electrode surface (red trace, particles out) and not in solution at all (black trace, no particles). In both cases 0.5 mM ferrocence carboxylic acid and 10 mM glucose were present in solution.

### References

- (a) J. R. Basore, N. V. Lavrik, L. A. Baker, *Adv. Mater.* 2010, 22, 2759–2763; (b) J. R. Basore, N. V. Lavrik, L. A. Baker, *Langmuir* 2010, 26, 19239-11244.
- [2] H. Lee, A. M. Purdon, R. M. Westervelt, *IEEE Trans. Magn.* **2004**, *40*, 2991-2993.