Supporting Information

[Submitted to *Analyst]*

Multifunctional Carbon Nanoelectrodes Fabricated by Focused Ion Beam Milling

Rahul Thakar, Anna E. Weber, Celeste A. Morris and Lane A. Baker*

Department of Chemistry

Indiana University

800 E. Kirkwood Avenue

Bloomington, Indiana 47405

*Author to whom correspondence should be addressed.

E-mail: lanbaker@indiana.edu; Phone: (812) 856-1873; Fax: (812) 856-8300

Carbon electrode fabrication

Quartz rods or capillaries were pulled with a P-2000 laser-puller (Sutter Instruments, Novartis, CA) with the following parameters.

Parameters listed in program #1 were used to pull quartz rods.

heat = 680, filament = 5, velocity = 45, delay = 195, pull = 195 (#1)

Platinum electrodes were fabricated as described previously. Briefly, a 25 µm platinum wire was inserted inside a quartz capillary and sealed under vacuum with program #2. The platinum wire/quartz glass assembly was pulled with program #3.

heat = 685, filament = 4, velocity = 120, delay = 120, pull = 0 (#2)

heat = 630, filament = 3, velocity = 35, delay = 170, pull = 150 (#3)

Quartz capillaries were pulled into nanopipets with ~50 nm pore openings from parameters listed in program #4.

heat = 650, filament = 4, velocity = 45, delay = 170, pull = 190 (#4)

Fabrication of conical electrodes

Cone shaped electrodes were fabricated from pulled quartz rods as described previously. Briefly, pulled quartz rods were coated with parylene, and pyrolyzed inside a high temperature furnace to convert into PPC. Carbon electrodes were soaked in an adhesion promoter solution and placed end on inside a home built device fitted with a micromanipulator to lower the carbon electrodes into PDMS. The entire assembly was placed inside the parylene deposition chamber. After the final insulation with parylene, electrodes were carefully drawn out of PDMS with the help of a micromanipulator to obtain a conical carbon electrode as shown in the text (Figure 1b).

SECM-SICM instrumentation and data collection

A four-electrode set-up for SECM-SICM was conducted with a ScanIC SICM (Ionscope, Ltd, London, UK) as described previously[1]. In brief, the FIB-milled carbon ring/nanopore electrode was filled with 0.1 M KCl and a Ag/AgCl QRE inside the pipette served as the working electrode. Another Ag/AgCl electrode in the bath solution served as a QRE and a Pt wire served as a counter electrode, connected to the reference and working electrode through a home-built counter-electrode driver[2]. Conductive carbon tape was utilized to make electrical contact to the carbon ring electrode through the underlying PPC film, which was also referenced to the Ag/AgCl QRE. Faradaic current was recorded through an auxiliary channel. For SECM-SICM experiments, +100 mV potential was applied to the Ag/AgCl working electrode and -600 mV potential was applied to the PPC electrode, both with respect to the Ag/AgCl (QRE). The bath electrolyte consisted of 2 mM $Ru(NH_3)_6Cl_3$/ 0.1 M KCl

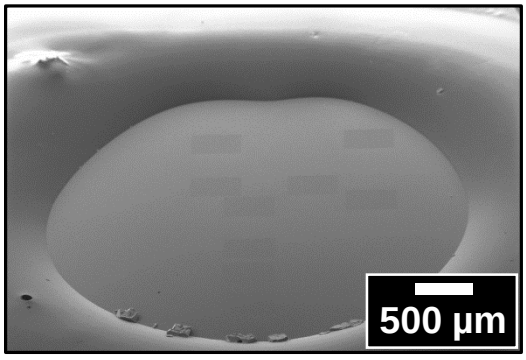

Figure S1. SEM micrograph of a fabricated carbon macroelectrode. An area was isolated with a tape mask and sealed with epoxy.

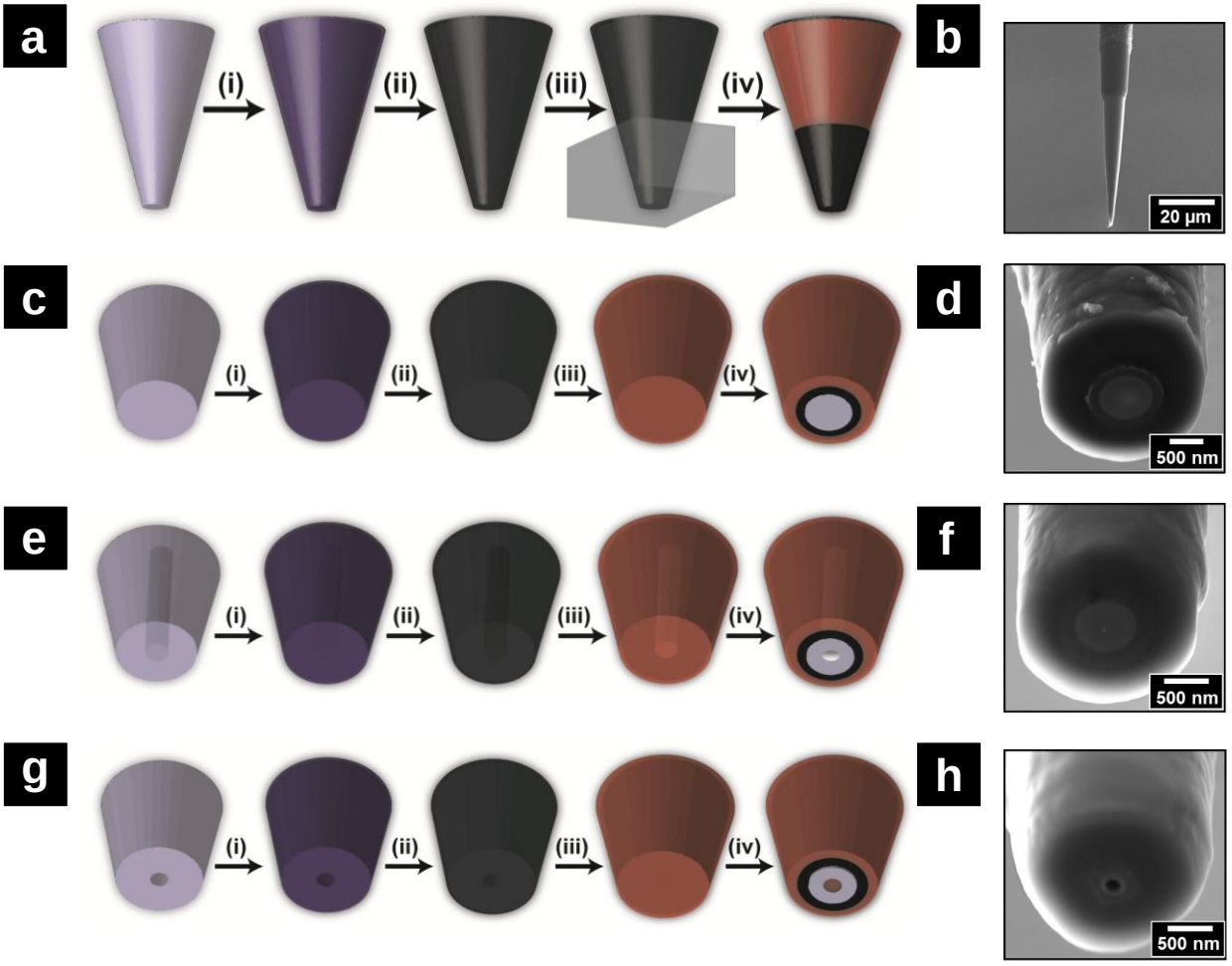

Figure S2.. Scheme for fabrication of multifunctional carbon electrodes. **a)** Fabrication of cone-shaped carbon electrodes. (i) a bare pulled quartz rod is coated with parylene (ii) parylene coated quartz rod is converted into conductive carbon, upon pyrolysis at 900 ^{0}C (iii) carbon coated quartz rod is masked in PDMS to isolate a defined area before the final insulation step (iv) parylene insulation of conductive carbon probe to reveal a cone-shaped geometry. **b)** Electron micrograph of a cone-shaped electrode with base radius of 4.25 µm, and 49.2 µm in length **c)** Fabrication of carbon ring electrodes (i) a bare pulled quartz rod is coated with parylene (ii) parylene coated quartz rod is converted into conductive carbon, upon pyrolysis at 900 ^{0}C (iii) carbon coated

quartz rod is completely insulated with parylene (iv) carbon ring electrode was exposed with FIB milling. **d)** Electron micrograph of a typical carbon ring electrode with an outer radius of 550 nm and an inner radius of 350 nm. **e)** Fabrication of carbon ring/platinum disk dual electrodes. A 25 µm platinum wire is sealed inside a quartz capillary and the platinum/quartz capillary assembly is pulled to fabricate platinum electrodes (the platinum electrode is not exposed at this stage). (i) platinum electrode is coated with parylene (ii) parylene coated platinum electrode is converted into conductive carbon, upon pyrolysis at 900 ^{0}C (iii) conductive carbon platinum electrode is completely insulated with parylene (iv) dual electrode with a carbon ring and platinum disk is exposed with FIB milling. **f)** Electron micrograph of a dual electrode with a 40 nm platinum disk (diameter) and a carbon ring with an outer radius of 488 nm and an inner radius of 335 nm. **g)** Fabrication of a carbon ring/nanopore electrode. (i) pulled nanopipette is coated with parylene (ii) parylene coated nanopipette is converted into conductive carbon, upon pyrolysis at 900 ^{0}C (iii) conductive carbon nanopipette is completely insulated with parylene (the pore is blocked with parylene at this stage) (iv) carbon ring electrode with a nanopore in the center is exposed with FIB milling. h) Electron micrograph of a carbon ring/nanopore electrode with a 165 nm (diameter) nanopore. Outer radius of the carbon ring electrode is 278 nm and inner radius is 135 nm.

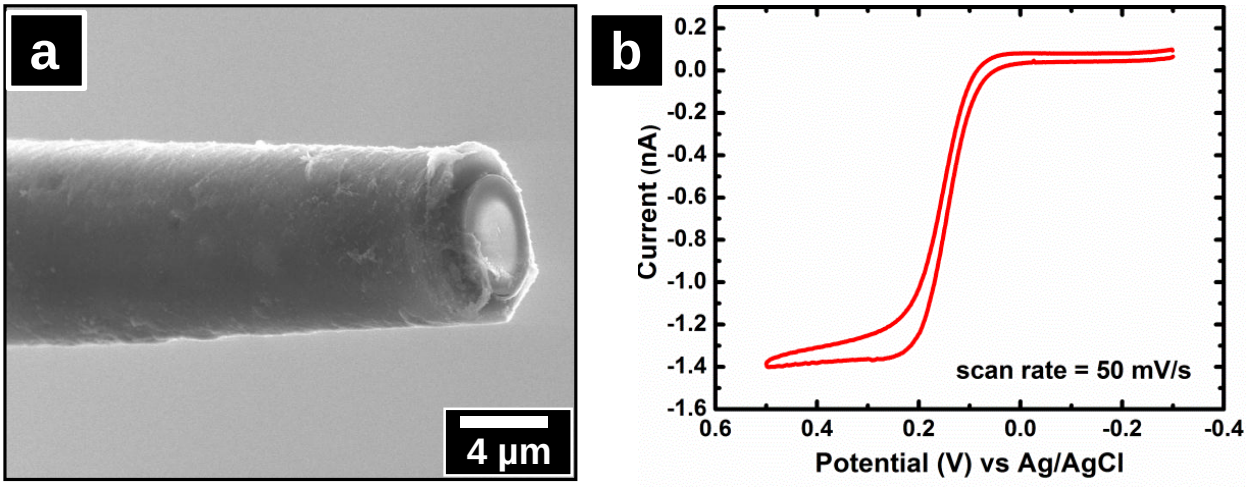

Figure S3. **a)** SEM micrograph of a mechanically polished carbon ring electrodes and **b)** the corresponding voltammetric response in $FcTMA^+$ solution with 0.1 M KCl.

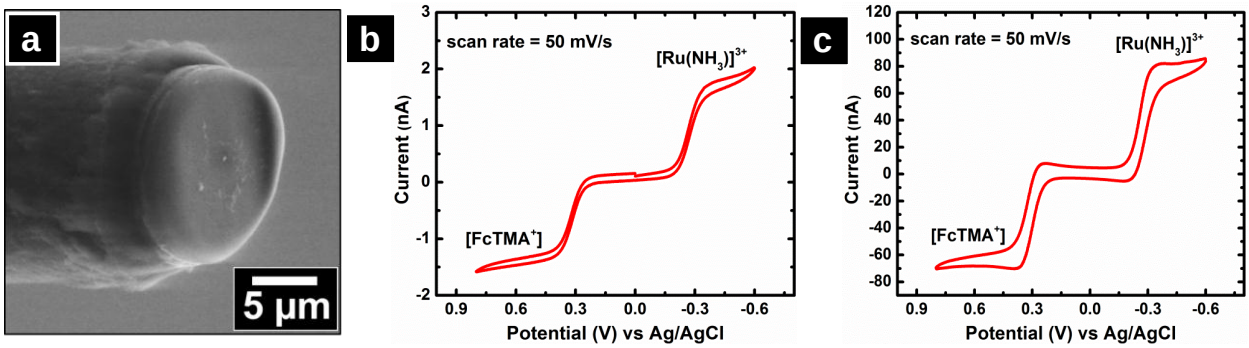

Figure S4. **a)** SEM micrograph of a mechanically polished dual electrode with a platinum disk and a carbon ring electrode. Corresponding voltammetric response obtained in a 1.25 mM solution of $FcTMA^+$ and $Ru(NH_3)_6Cl_3$ with 0.1 M KCl with the **b)** Platinum electrode and **c)** Carbon electrode

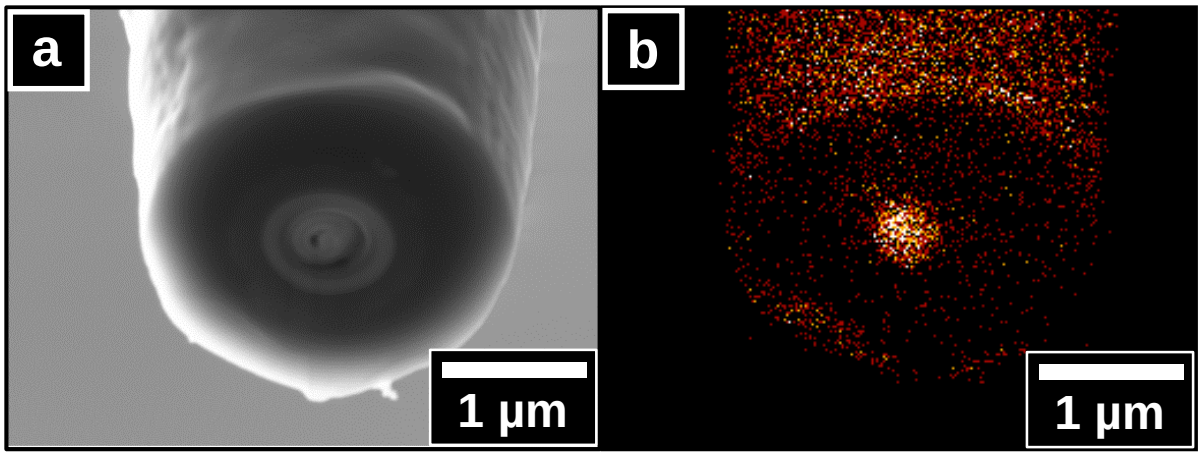

Figure S5.**a)** SEM micrograph of a carbon ring/nanopore electrode that was milled with the FIB. B) Energy dispersive X-ray (EDX) spectra recorded for the same electrode shows the Ga^{+} implantation observed, post FIB milling.

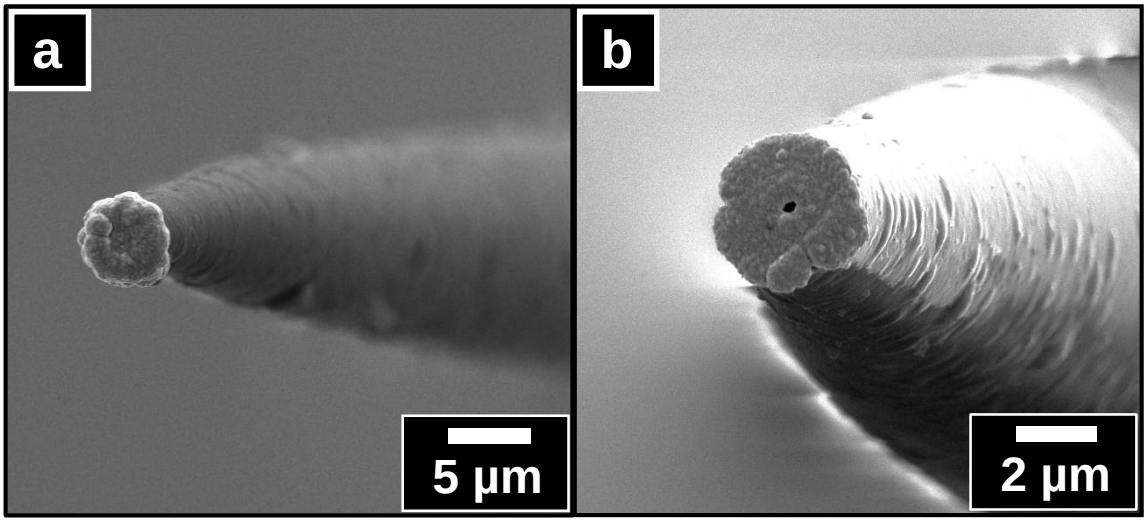

Figure S6 SEM micrograph of **a)** carbon ring electrode and **b)** carbon ring/nanopore electrode post copper deposition. Copper deposition was carried out in a solution of 50 mM $CuSO_4.5H_20$ in 0.25 M H_2SO_4. Deposition potential of -0.8 V vs Ag/AgCl was applied for 5 seconds. Copper deposition shows the origin of the electrochemical signal and the absence of pinhole leaks.

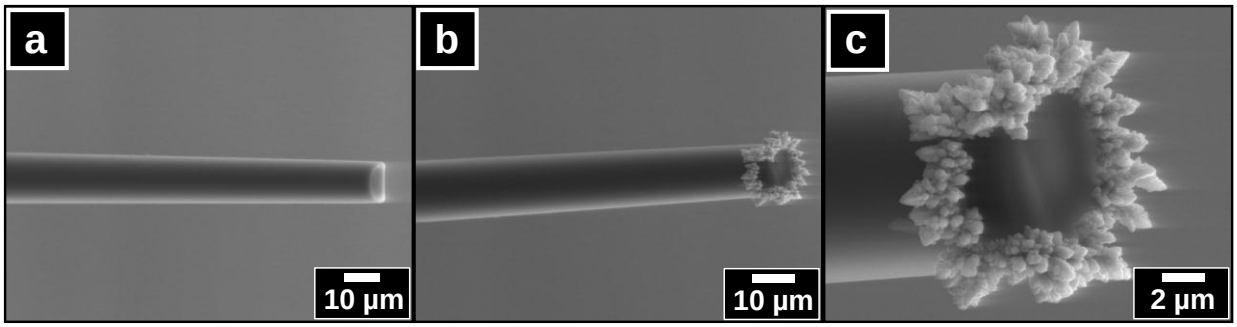

Figure S7 SEM micrograph of a polished carbon ring electrode **a)** before and **b)** after copper deposition. **c)** High-magnification SEM of the micrograph shown in (b). Copper deposition was carried out in a solution of 50 mM $CuSO_4.5H_20$ in 0.25 M H_2SO_4. Deposition potential of -0.8 V vs Ag/AgCl was applied for 8 seconds.

References

(1). Y. Zhou, C.-C Chen, L. Baker, *Anal. Chem.* 2012, **84**, 3003.
(2). C.-C. Chen, Y. Zhou, L. Baker, *ACS Nano* 2011, **5**, 8404.