Supporting Information for

Light Activated Electrochemistry for the Two Dimensional Interrogation of Electro-active Regions on a Monolithic Surface with Dramatically Improved Spatial Resolution

Ying Yang,[†] Simone Ciampi,[‡] Ying Zhu,[†] and J. Justin Gooding[*,†]

[†]*School of Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia*

[‡]*Intelligent Polymer Research Institute, University of Wollongong, Wollongong, NSW 2522, Australia*

Corresponding Author

[*]justin.gooding@unsw.edu.au

Ph: +61-2-9385 5384

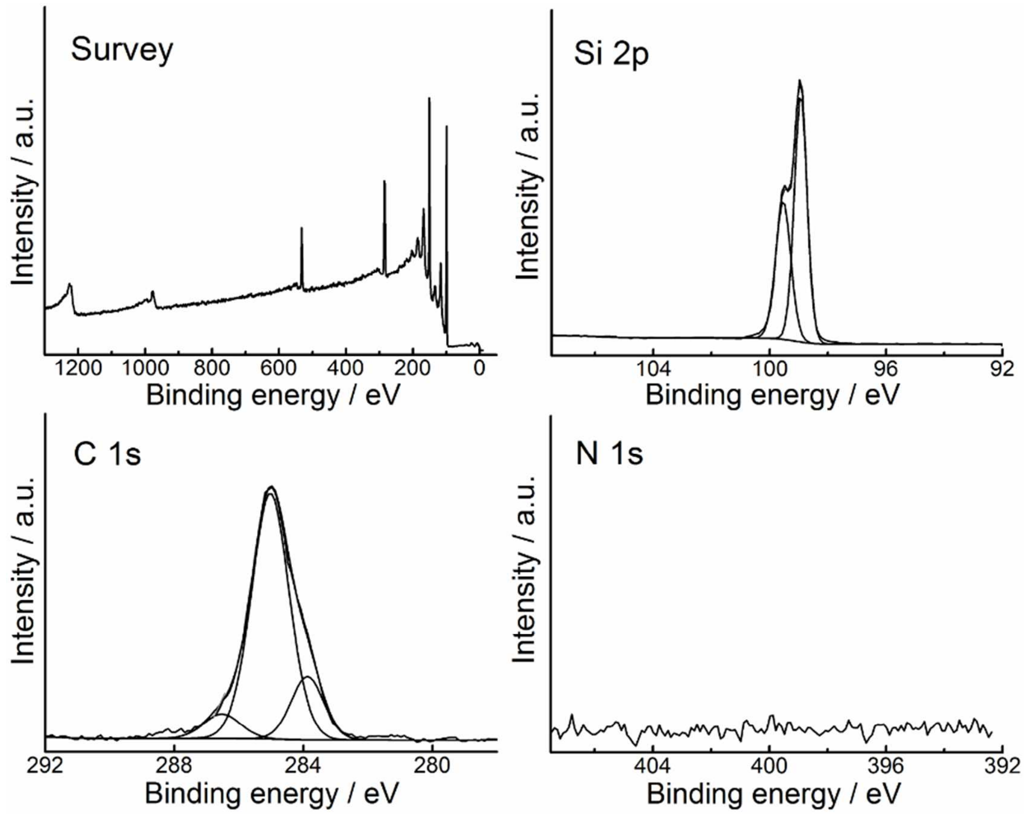

Figure S1. XPS spectra and high-resolution Si 2p, C 1s, and N 1s narrow spectrographs of alkyne terminated silicon surface.

The electrocatalytic property of anthraquinone for oxygen reduction was characterized using cyclic voltammetry curves. As shown in Figure S2, with the concentration of O_2 increased, there is significant increase in the magnitude of the cathodic current value. These results indicate anthraquinone modified silicon is good at catalyzing O_2 reduction[1-2]. Hence, in the chronoamperometric experiments there was no other oxidized state but O_2 in the electrolyte to contribute to the reduction current. The buffer solution was leaved in air atmosphere to maintain constant O_2 concentration.

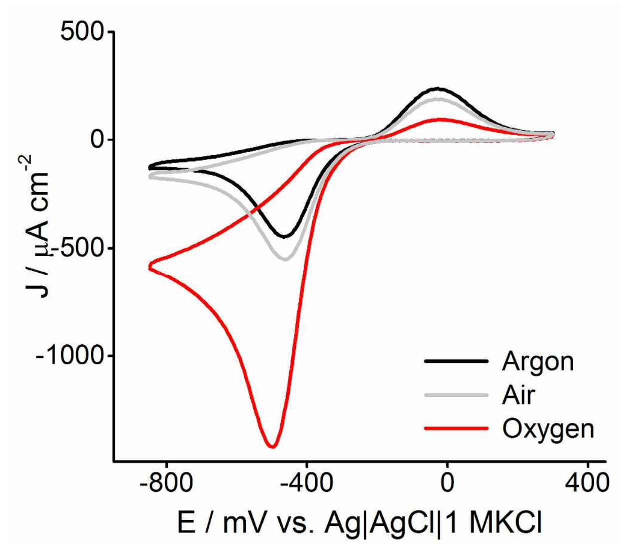

Figure S2. Cyclic voltammetry of anthraquinone modified poorly doped p-type silicon in B&R buffer solution (pH=7.02) at air atmosphere, and saturated with argon or oxygen.

The advantage of topside LAE was further demonstrated by light-assisted electrochemical "writing" conducting polymeric features on a homogeneous alkyne terminated n-type silicon (8–12 Ω cm resistivity, 200 μm thickness) electrode by simply scanning the laser beam (FWHM = 15 μm) along a straight line. It was achieved by electrodepositing polyaniline from aniline monomers on n-type silicon electrode by using cyclic voltammetry. Figure S3a represents the polyaniline patterning grows on the silicon surface. Figure S3b shows that the width of polymer pattern is smaller than 20 μm even though the polyaniline patterning is not uniform as expected. The morphology for polyaniline is characterized by SEM and shown in Figure S3c, from which it can be seen that the membrane shows typical fibrous and porous structure of polyaniline.[3-4] From the previous work in Gooding group, M. H. Choudhury and S. Ciampi presented that polypyrrole arrays could be deposited on n-type silicon upon the backside LAE, but showed a worse spatial resolution (~400 μm).[5] The comparison indicates the topside LAE shows a 20-fold improved resolution in mask-free electrochemical deposition.

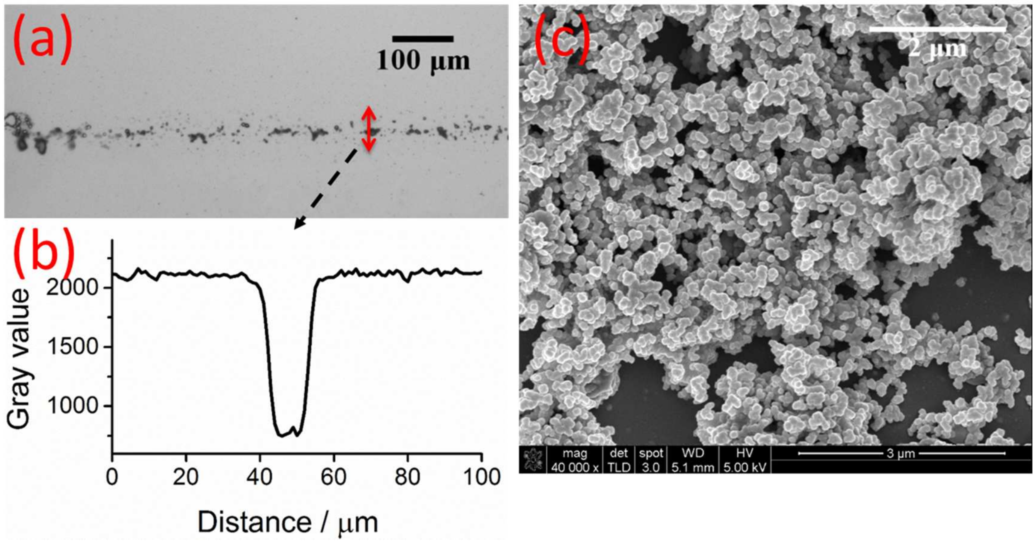

Figure S3. Topside LAE for polyaniline writing on a passivated poorly doped n-type silicon (8-12 Ω cm resistivity, 200 μm thickness). (a) Microscopy image of polymer pattern, achieved by light-assisted electrochemical growth of conductive polyaniline on silicon electrode by scanning light along a straight line at the topside. (b) Plot of Grayscale image across the polyaniline pattern. (c) Scanning electron microscope image of polyaniline pattern on silicon. Deposition of polyaniline was achieved by cyclic voltammetry in 0.5 M H_2SO_4 containing 0.1 M aniline, in which the potential range was between -0.2 V and 0.6 V and at a scan rate of 50 mV s^{-1}. The laser was scanned back and forth for 4 cycles with a raster rate of 20 μm s^{-1}.

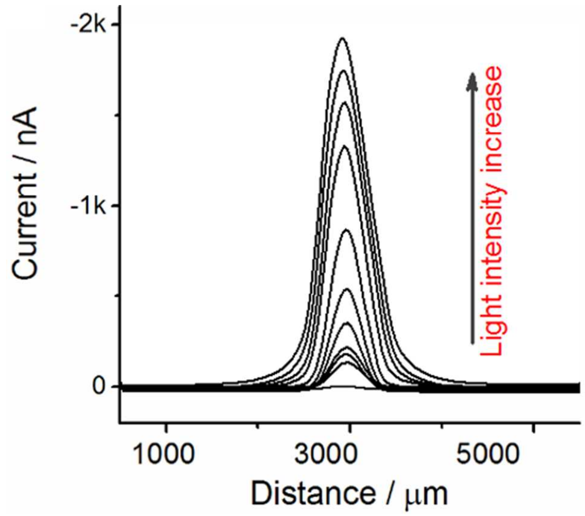

Figure S4. Current *versus* distance trace for a silicon electrode with an anthraquinone strip in B&R buffer (pH=7.03) under topside illumination and with different light intensities.

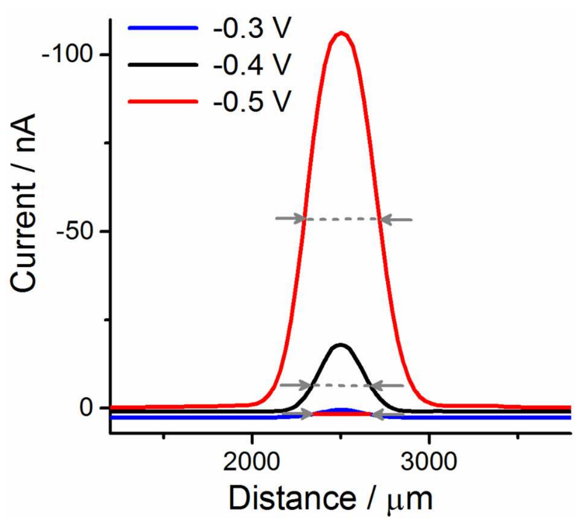

Figure S5. Current *versus* distance trace for a silicon electrode with an anthraquinone strip in B&R buffer (pH=7.03) under topside illumination and with different applied potentials. When light intensity is 1 W cm^{-2}.

References

1. Vaik, K.; Mäeorg, U.; Maschion, F. C.; Maia, G.; Schiffrin, D. J.; Tammeveski, K. Electrocatalytic oxygen reduction on glassy carbon grafted with anthraquinone by anodic oxidation of a carboxylate substituent. *Electrochim. Acta* **2005,** *50* (25–26), 5126-5131.
2. Kullapere, M.; Tammeveski, K. Oxygen electroreduction on anthraquinone-modified nickel electrodes in alkaline solution. *Electrochem. Commun.* **2007,** *9* (5), 1196-1201.
3. Gao, M.; Yang, Y.; Diao, M.; Wang, S.-g.; Wang, X.-h.; Zhang, G.; Zhang, G. Exceptional ion-exchange selectivity for perchlorate based on polyaniline films. *Electrochim. Acta* **2011,** *56* (22), 7644-7650.
4. Yang, Y.; Diao, M. h.; Gao, M. m.; Sun, X. f.; Liu, X. w.; Zhang, G. h.; Qi, Z.; Wang, S. g. Facile Preparation of Graphene/Polyaniline Composite and Its Application for Electrocatalysis Hexavalent Chromium Reduction. *Electrochim. Acta* **2014,** *132*, 496-503.
5. Choudhury, M. H.; Ciampi, S.; Yang, Y.; Tavallaie, R.; Zhu, Y.; Zarei, L.; Goncales, V. R.; Gooding, J. J. Connecting electrodes with light: one wire, many electrodes. *Chem. Sci.* **2015,** *6* (12), 6769-6776.