# Electronic Supplementary Information

# Nanoscale Mapping of Catalytic Hotspots in Fe, N -modified HOPG by Scanning Electrochemical Microscopy – Atomic Force Microscopy

Srikanth Kolagatla, Palaniappan Subramanian, Alex Schechter*
Department of Chemical Sciences, Ariel University, Ariel 40700, Israel

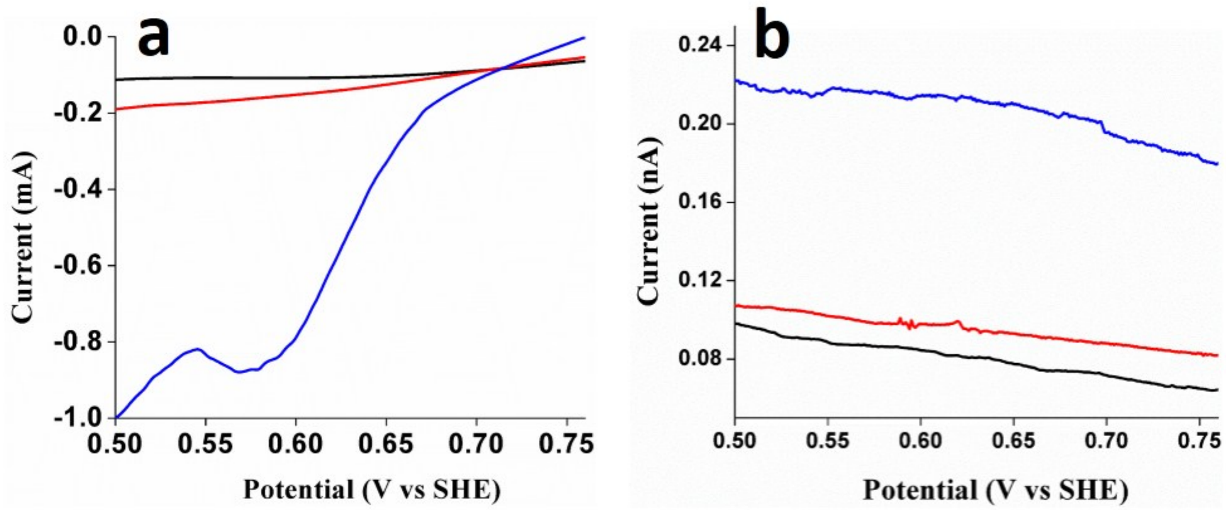

**Fig. S1** Steady state ORR polarization curve (a) and peroxide oxidation current (b) collected at the probe tip on HOPG (black), N-HOPG (red), Fe-N-HOPG (blue); Electrolyte: $O_2$ saturated 0.1 M $HClO_4$

The polarization curves were obtained in $O_2$ gas purged electrolyte. The potential for oxygen reduction reaction is chosen as 0.7 V (Fe-N-HOPG) and 0.68 V for HOPG and N-HOPG which are close to the onset potentials mentioned above. These values are well within the activation potential region of ORR. The peroxide oxidation current observed at 0.75 V is due to small background currents generated at 0.75V noticed in Fig. ESI 1a, known to occur on nano-electrodes mostly from solution impurities in the ppm level[1]. Nevertheless, the increasing oxidation current with the lowering of the working electrode potential can only be explained by $H_2O_2$ formation, as directly seen in the AFM-SECM measurements.

Further the Pt tip (secondary working electrode) which is used for probing the peroxide is place at 150 nm (out of feedback) above the HOPG electrode which is close enough to detect the byproduct-peroxide.

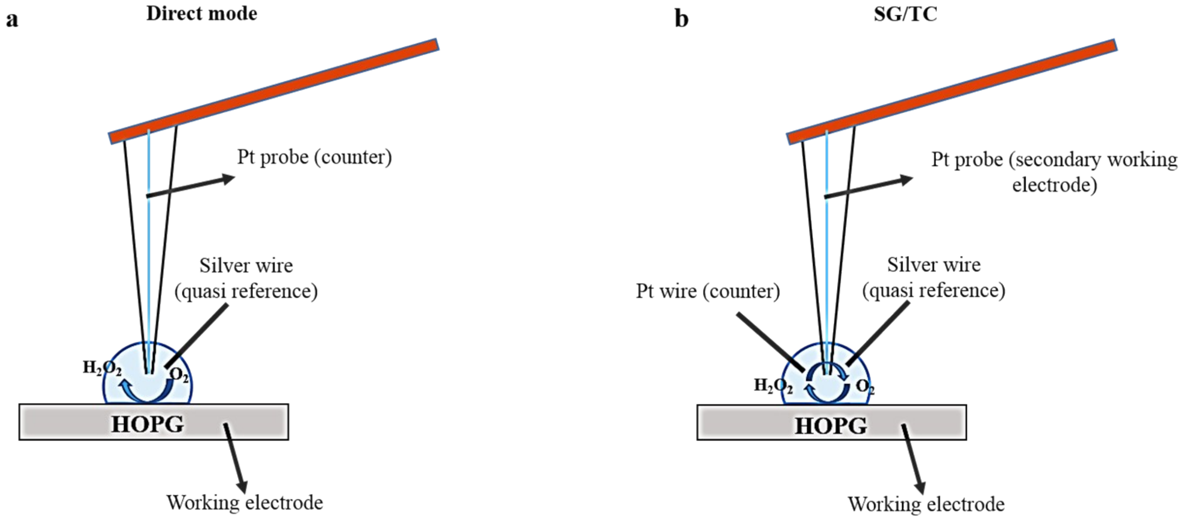

**Fig. S2** Schematics of experimental setup for performing oxygen reduction current mapping (a) and peroxide oxidation current mapping (b) on HOPG surface using SECM-AFM technique.

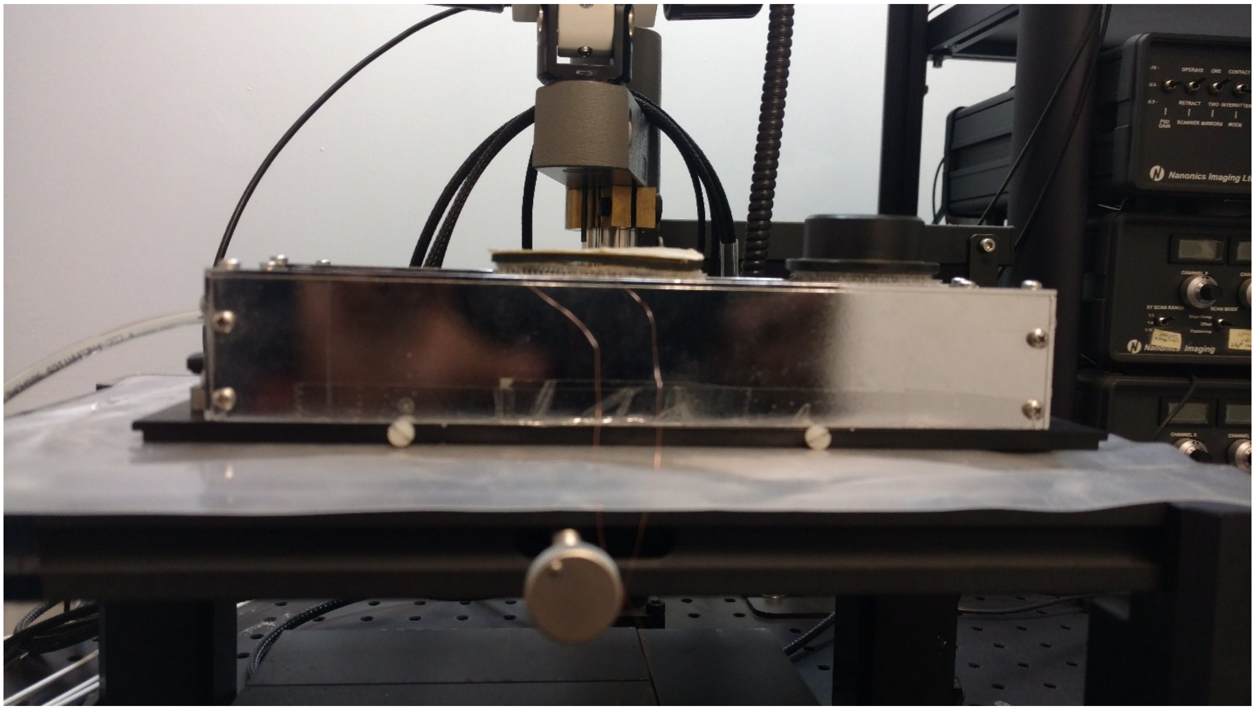

**Fig. S3** Photograph of closed set-up used with gas purging system for studying electrochemical reactions by EC-AFM technique.

The experiments were performed in an air tight closed Faraday cage which was attached to a gas flow controller for maintaining the constant follow of pure $O_2$ gas (see Fig. ESI S3). This set-up helps in reducing the evaporation rate of electrolyte, such that the O2 concentration in the droplet stays constant throughout the experiment time (50 min.). However, the electrolyte is refilled for repeated measurements due to reduction in the volume after more than 1 hour.

## REFERENCES

1. Physical Electrochemistry, Eliezer Gileadi, pp 213-219, Wiley-VCH; 1 edition (February 21, 2011), ISBN-10: 3527319700