Supporting Information for

# Single Molecular Imaging of Iron-Phthalocyanine Catalyzed Oxygen Reduction Reaction by *in situ* Scanning Tunneling Microscopy

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[§]These authors contributed equally.

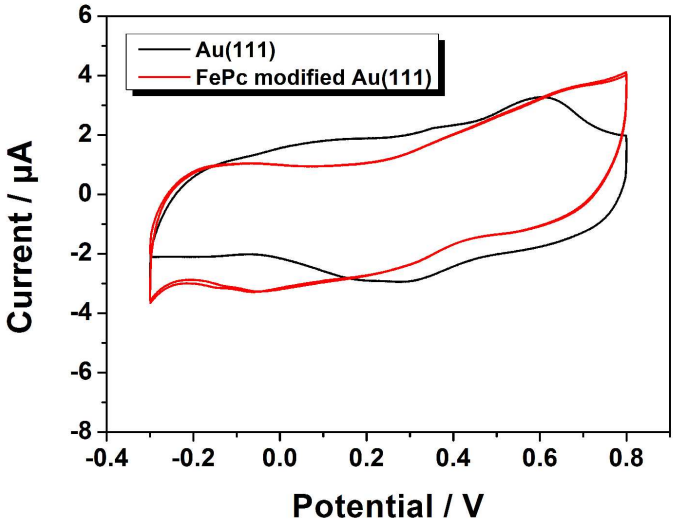


Figure S1. Typical cyclic voltammograms of bare (black line) and FePc-modified (red line) Au(111) electrodes in 0.1 $HClO_4$ saturated by nitrogen. Scan rate is 50 mV/s.

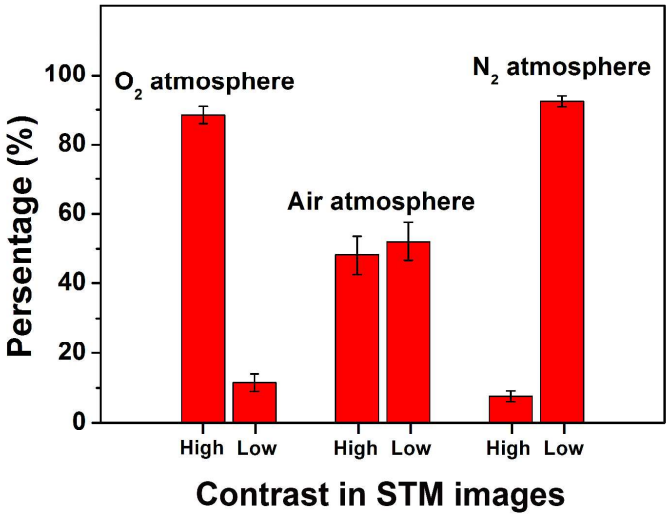


Figure S2. Histograms of the percentage of high-contrast spots and low-contrast spots in 0.1 M $HClO_4$ saturated by air, $O_2$ and $N_2$.

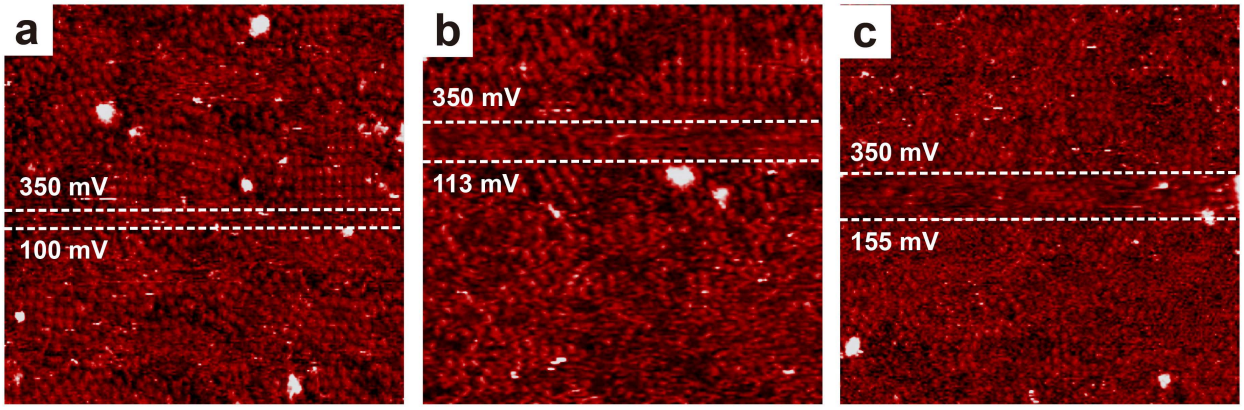


Figure S3. Sequential STM images of the FePc monolayer on Au(111) in 0.1 M $HClO_4$ saturated by nitrogen at different potential. Image conditions: (a) Upper region: E = 350 mV, $E_{bias}$ = −278.0 mV, $I_t$ = 1.000 nA, data scale = 500.0 pm. Lower region: E = 100 mV, $E_{bias}$ = −278.0 mV, $I_t$ = 1.000 nA, data scale = 500.0 pm; (b) Upper region: E = 350 mV, $E_{bias}$ = −278.0 mV, $I_t$ = 1.000 nA, data scale = 500.0 pm. Lower region: E = 113 mV, $E_{bias}$ = −278.0 mV, $I_t$ = 1.000 nA, data scale = 500.0 pm; (c) Upper region: E = 350 mV, $E_{bias}$ = −278.0 mV, $I_t$ = 1.000 nA, data scale = 500.0 pm. Lower region: E = 115 mV, $E_{bias}$ = −278.0 mV, $I_t$ = 1.000 nA, data scale = 500.0 pm.

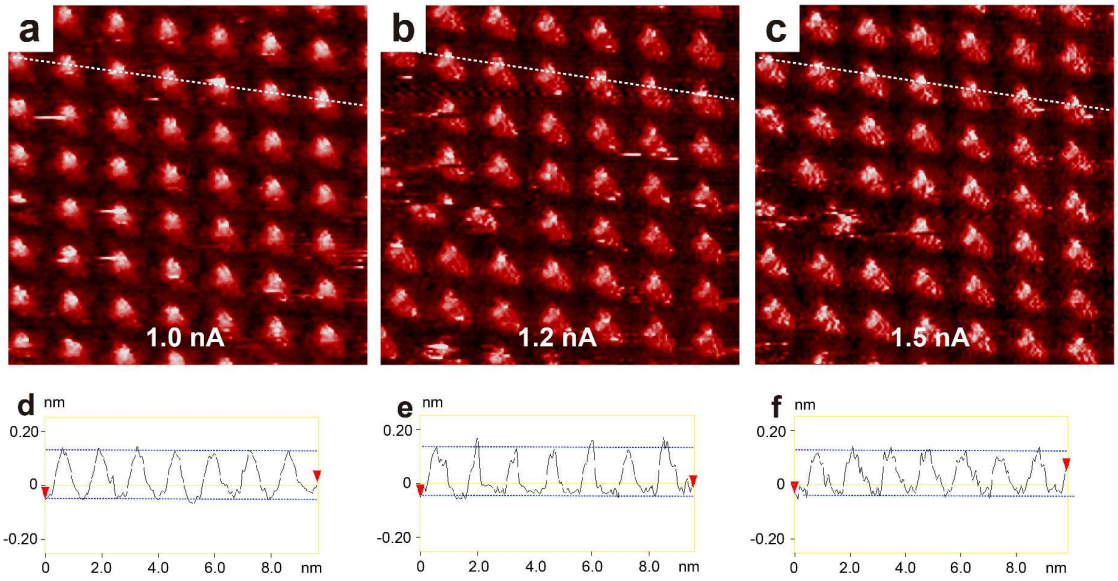


Figure S4. Sequential STM images and cross-section profiles of the FePc monolayer on Au(111) in 0.1 M $HClO_4$ saturated by oxygen at different set-current. (d – f) are cross-section profiles along the white dotted line in (a – c). Image conditions: (a) E = 306 mV, $E_{bias}$ = −184.0 mV, $I_t$ = 1.000 nA, data scale = 500.0 pm; (b) E = 306 mV, $E_{bias}$ = −184.0 mV, $I_t$ = 1.200 nA, data scale = 500.0 pm; (c) E = 306 mV, $E_{bias}$ = −184.0 mV, $I_t$ = 1.500 nA, data scale = 500.0 pm.

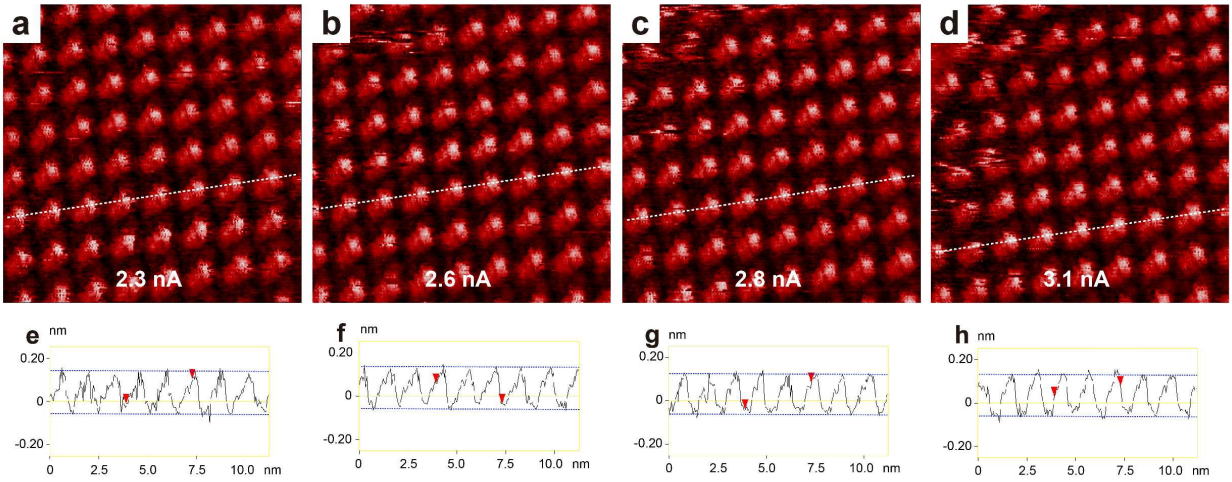


Figure S5. Sequential STM images and cross-section profiles of the FePc monolayer on Au(111) in 0.1 M $HClO_4$ saturated by oxygen at different set-current. (e – h) are cross-section profiles along the white dotted line in (a – d). Image conditions: (a) E = 306 mV, $E_{bias}$ = −339.0 mV, $I_t$ = 1.000 nA, data scale = 500.0 pm; (b) E = 306 mV, $E_{bias}$ = −339.0 mV, $I_t$ = 1.200 nA, data scale = 500.0 pm; (c) E = 306 mV, $E_{bias}$ = −184.0 mV, $I_t$ = 1.500 nA, data scale = 500.0 pm; (d) E = 306 mV, $E_{bias}$ = −339.0 mV, $I_t$ = 1.200 nA, data scale = 500.0 pm.

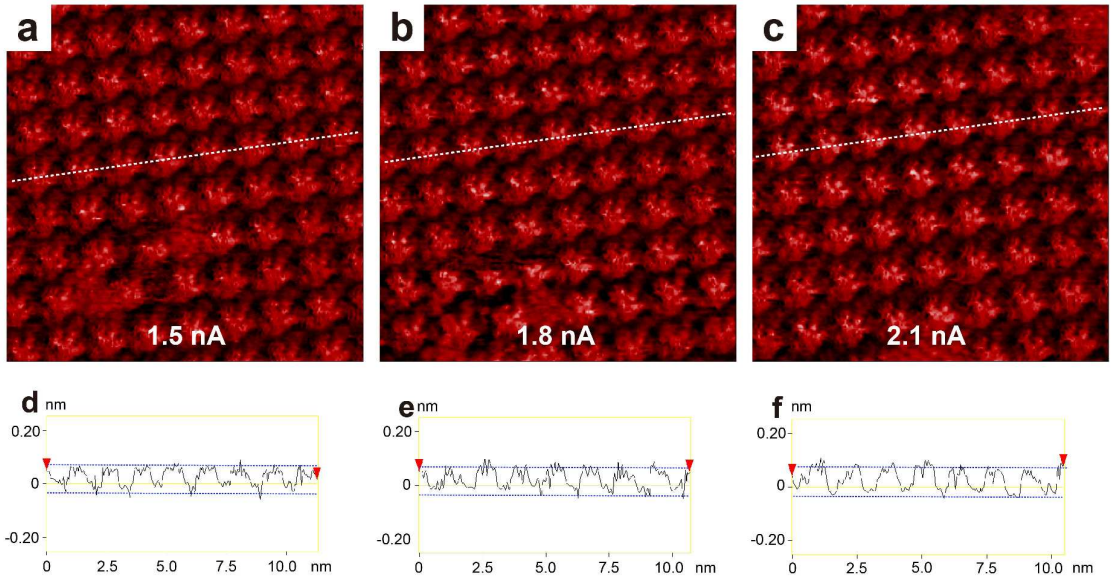


Figure S6. Sequential STM images and cross-section profiles of the FePc monolayer on Au(111) in 0.1 M $HClO_4$ saturated by nitrogen at different set-current. (d – f) are cross-section profiles along the white dotted line in (a – c). Image conditions: (a) E = 292 mV, $E_{bias}$ = −281.0 mV, $I_t$ = 1.500 nA, data scale = 500.0 pm; (b) E = 292 mV, $E_{bias}$ = −281.0 mV, $I_t$ = 1.800 nA, data scale = 500.0 pm. (c) E = 292 mV, $E_{bias}$ = −281.0 mV, $I_t$ = 2.100 nA, data scale = 500.0 pm.

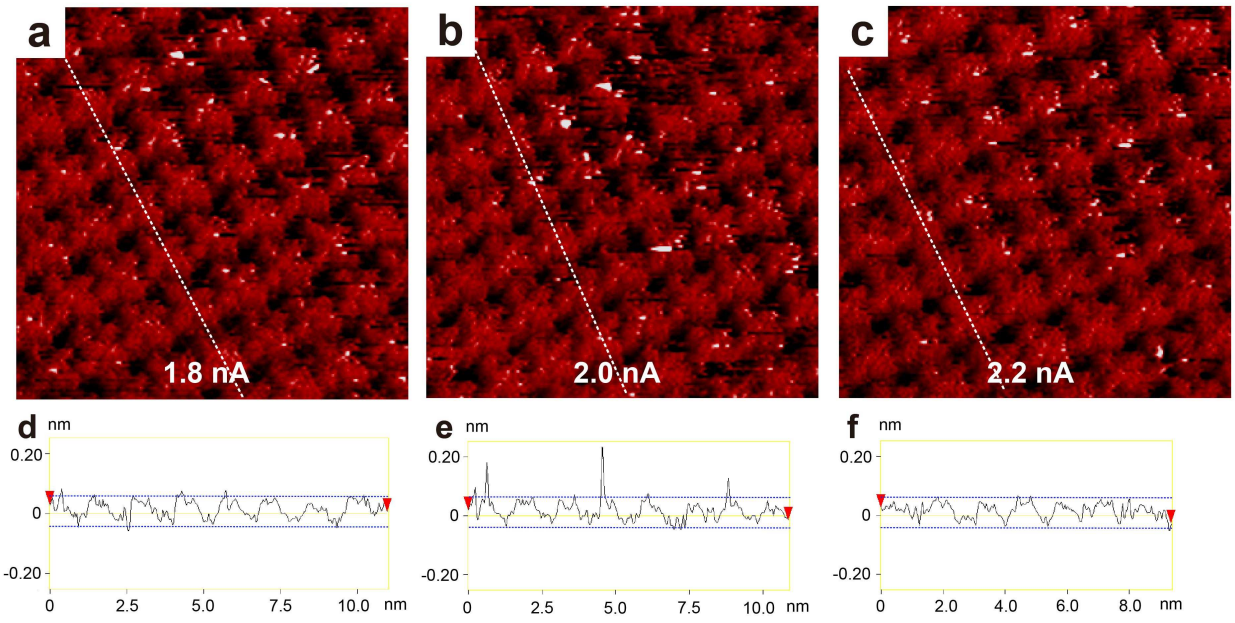


Figure S7. Sequential STM images and cross-section profiles of the FePc monolayer on Au(111) in 0.1 M $HClO_4$ saturated by nitrogen at different set-current. (d – f) are cross-section profiles along the white dotted line in (a – c). Image conditions: (a) E = 306 mV, $E_{bias}$ = −490.0 mV, $I_t$ = 1.800 nA, data scale = 500.0 pm; (b) E = 306 mV, $E_{bias}$ = −490.0 mV, $I_t$ = 2.000 nA, data scale = 500.0 pm; (c) E = 306 mV, $E_{bias}$ = −490.0 mV, $I_t$ = 2.200 nA, data scale = 500.0 pm.

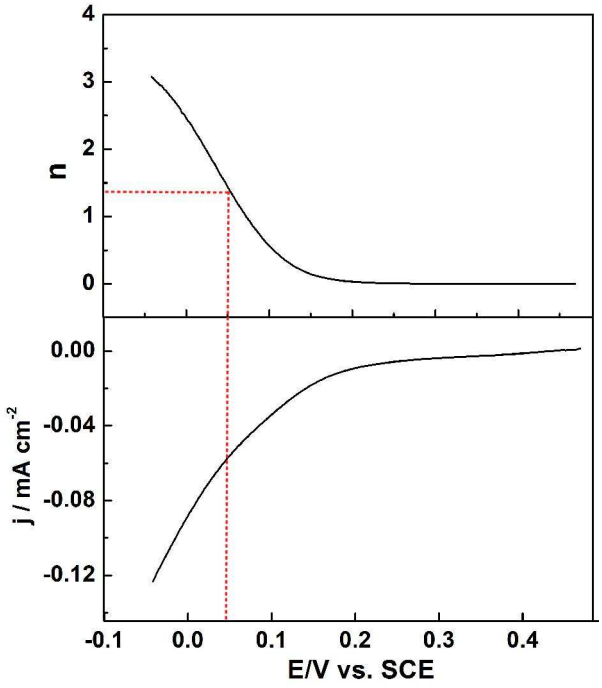


Figure S8. Steady-state ORR polarization curve (bottom) in $O_2$-saturated 0.1 M $HClO_4$ at a scan rate of 10 mV $s^{-1}$ and corresponding electron transfer number (n, top) during ORR process catalyzed by FePc modified Au(111) surface.

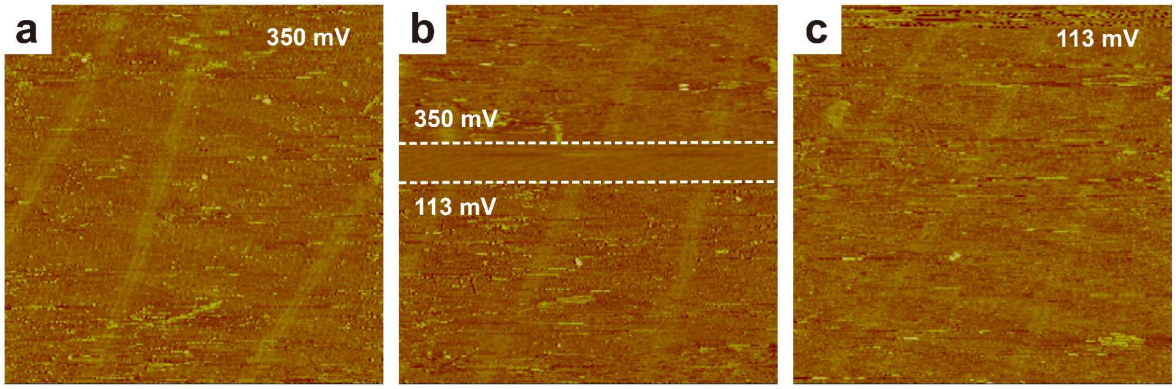


Figure S9. Sequential STM images of the Au(111) single-crystal substrate in 0.1 M $HClO_4$ saturated by oxygen at different potential. Image conditions: (a) E = 350 mV, $E_{bias}$ = −116.0 mV, $I_t$ = 1.000 nA; (b) Upper region: E = 350 mV, $E_{bias}$ = −116.0 mV, $I_t$ = 1.000 nA. Lower region: E = 113 mV, $E_{bias}$ = −55.3 mV, $I_t$ = 1.000 nA; (c) E = 113 mV, $E_{bias}$ = −55.3 mV, $I_t$ = 1.000 nA.