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Supporting Information

Ammonium Tetrathiomolybdate as a novel electrode material for Convenient Tuning of Kinetics of Electrochemical O_2 Reduction by Iron Porphyrin Catalysts

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Experiment details

Materials

All reagents were of the highest grade commercially available and were used without further purification. Sodium molybdatepentahydrate ($Na_2[MoO_4].5H_2O$), and potassium hexaflurophosphate (KPF_6) were purchased from Sigma-Aldrich. Disodium hydrogen phosphate dihydrate (Na_2HPO_4. $2H_2O$), potassium chloride (KCl), hydrochloric acid (HCl), aqueous NH_3 (98%), and ethanolwere purchased from Merck.Sodium sulphide nonahydrate (Na_2S. $9H_2O$) was purchased from Rankem, India. Au wafers were purchased from Platypus Technologies (1000 Å of Au on 50 Å of Ti adhesion layer on top of a Si (III) surface).

Instrumentation

All electrochemical experiments were performed using a CH Instruments (model CHI710D Electrochemical Analyzer). Biopotentiostat, and electrodeswere purchased from CH Instruments. The rotating ring disk electrochemical (RRDE) set up was obtained from Pine Research Instrumentation (E6 series ChangeDisk tips with AFE6M rotor). The AFM data were recorded in a Veecodicp II (Model no: AP-0100) instrument bearing a phosphate doped Si cantilever (1-10 ohm.cm, thickness 3.5-4.5 μm, length 115-135 μm, width 30-40 μm, resonance frequency 245-287 KHz, elasticity 20-80 N/m). The surface morphology of the assembled layers were observed through a field-emission scanning electron microscope (FE-SEM, JSM-6700F), purchased from JEOL LTD, JAPAN. X-ray Photoelectron Spectroscopy (XPS) data were collected using an instrument from Omicron Nanotechnology GmbH, Germany (serial no.-0571).

Synthesis

Ammonium tetrathiomolybdate (ATM)

ATM was prepared from $Na_2MoO_4.2H_2O$ according to reported procedure.[1]

α_4-meso-tetra(2-(4-ferrocenyltriazol)phenyl)porphyrinatoiron (III) (α_4-FeFc$_4$) bromide

The α_4-FeFc$_4$ complex was synthesized as reported in literature.[2]

Construction of Electrodes: Formation of self assembled adlayer

Au wafers were cleaned electrochemically by sweeping several times between 1.5 V to -0.3 V in 0.5 M H_2SO_4. Immersing solutions of ATM were prepared by simply dissolving solid ATM crystals in triple distilled water. Freshly cleaned Au wafers were rinsed with triple distilled water, purged with N_2 gas and immersed in the solutions for the formation of self assembly. The immersion time has been varied according to requirement and has been clearly stated in the respective experiments.

Characterization of the modified surfaces

Atomic Force Microscopy (AFM)

Freshly cut Au wafers were taken for each AFM analysis where ATM modified surfaces were made as described above. The surfaces were thoroughly rinsed with triple distilled water before analysis. AFM data were obtained at room temperature in a Veecodicp II instrument bearing a phosphate doped Si cantilever (1-10 ohm.cm, thickness 3.5-4.5 μm, length 115-135 μm, width 30-40 μm, resonance frequency 245-287 KHz, elasticity 20-80 N/m).

Field Emission Scanning Electron Microscopy (FE-SEM)

Samples were prepared in a similar way like AFM. The surfaces were dried at room temperature and were then observed through FE-SEM applying an accelerating voltage of 5 kV after the surfaces were platinum coated. For all the FE-SEM experiments a working distance of 8 mm was used.

X-ray Photoelectron Spectroscopy (XPS)

XPS was performed on the ATM modified surfaces using Mg Kα radiation (1253.6 eV) for excitation. High resolution scans, with a total energy resolution of about 1.0 eV, were recorded with pass energy of 20 eV, step size of 0.2 eV. Base pressure of the chamber initially was 1×10^{-10} mbar and during the experiment was $\sim 3 \times 10^{-10}$ mbar. Binding energy spectra were calibrated by the Ag $3d_{5/2}$ peak at 368.2 eV. An error of ±0.1 eV was estimated for all the measured values.

Physiadsorption of α_4-$FeFc_4$ catalyst on the self assembled ATM layer

$FeFc_4$ was dissolved in chloroform to make a 1 mM solution. ATM modified surfaces were prepared as described in previous section. The wafers were taken out of the depositing solutions, washed thoroughly with triple distilled water and dried before every experiment. These were then inserted in the plate testing material. The chloroform solution of the catalyst was added over the surfaces after rinsing with triple distilled water and ethanol and then the catalyst solution was allowed to physiadsorb for 40 min. After 40 min, the surfaces were rinsed with chloroform followed by ethanol and triple distilled water.

Electrochemical measurements:

Cyclic Voltammetry (CV)

All CV experiments were done in pH 7 buffer (until otherwise mentioned) containing 100 mM $Na_2HPO_4.2H_2O$ and 100 mM KPF_6 (supporting electrolyte) using Pt wire as the counter electrode and Ag/AgCl as the reference electrode. The electrochemical data are adjusted to RHE scale (unless otherwise stated) using the standard equation:

$$E^0 \text{ (RHE)} = E^0 \text{ (Ag/AgCl)} + 0.2 \text{ V} + 0.059 \text{ X pH}.$$

All electrochemical experiments were performed at room temperature and under ambient conditions.

Coverage calculation

The coverage for a particular redox couple is estimated by taking the average of the integrated area under the corresponding oxidation and reduction currents of the respective species obtained from their reversible voltammogram. The experiments were repeated thrice and an average value with standard deviation has been presented.

Time dependence experiments with ATM modified Au surfaces

Au wafers were cleaned as mentioned in previous section. Separate surfaces were used for each experiment. During time dependent studies the wafers were immersed into 1 mM aqueous solution of ATM for 10 min, 20 min, 30 min, 40 min upto 400 min. The electrode surfaces were then taken out and rinsed with triple distilled water and dried under N_2 atmosphere. These surfaces were then subjected to electrochemical and AFM studies.

Details of RDE and Koutecky-Levich (K-L) analysis:

The electrocatalytic O_2 reduction at different rotation rates (RDE) have been performed for $FeFc_4$ immobilized on ATM modified Au. This technique not only helps in determining the number of electrons involved in ORR but also provides a direct proof of the stability as well as durability of these catalysts on the electrode surfaces (Figure 2A, main text). The O_2 reduction current increases with increasing rotation rates following the Koutecky–Levich equation, $I^{-1} = i_K^{-1} + i_L^{-1}$, where i_K is the potential dependent kinetic current and i_L is the Levich current.[3,4] i_L is expressed as $0.62nFA[O_2](D_{O2})^{2/3}\omega^{1/2}v^{-1/6}$, where n is the number of electrons transferred to the substrate, A is the macroscopic area of the disc (0.096 cm^2), $[O_2]$ is the concentration of O_2 in an air saturated buffer (0.22 mM) at 25 °C, D_{O2} is the diffusion coefficient of O_2 (1.8×10^{-5} cm^2 s^{-1}) at 25 °C, ω is the angular velocity of the disc and v is the kinematic viscosity of the solution (0.009 cm^2 s^{-1}) at 25 °C.[3,4] The plot of I^{-1} at multiple rotation rates *vs.* the inverse square root of the angular rotation rate ($\omega^{-1/2}$) is linear. The slopes obtained from the experimental data for $FeFc_4$ closely matches with the theoretical slope predicted for a $4e^-$ process (Figure 2B, main text).

Rotating Ring Disk Electrochemistry (RRDE): Partially Reduced Oxygen Species (PROS) detection and calculation

The platinum ring and the Au disk were both polished using alumina powder (grit sizes: 1 µm, 0.5 µm and 0.03 µm) and electrochemically cleaned and inserted into the RRDE tip which was then mounted on the rotor and immersed into a cylindrical glass cell equipped with Ag/AgCl reference and Pt counter electrodes. In this technique, the potential of the disk is swept from positive to negative and when O_2 is reduced, any H_2O_2, i.e., a $2e^-$ reduction product of O_2, produced in the working disk electrode is radially diffused to the encircling Pt ring, which is held at a constant potential and oxidizes the H_2O_2 back to O_2. The ratio of the $2e^-/2H^+$ current (corrected for collection efficiency) at the ring and the catalytic current at the disk is expressed as PROS and it provides an *in-situ* measure of the $2e^-/2H^+$ reduction side reaction. The collection efficiency (CE) of the RRDE set-up was measured in a 2 mM $K_3[Fe^{III}(CN)_6]$ and 0.1 M KNO_3 solution at a 10 mV/s scan rate and 300 rpm rotation speed. A 20±2% CE was generally recorded during these experiments. The potential at which the ring was held during the collection experiments at pH 7 for detecting H_2O_2 was obtained from literature reported by Zhang *et al.* in *J. Electroanal. Chem.* **1993**, *345*, 253.

Equation for PROS calculation, PROS (%) = i(ring)/[i(disc)xCE]x100

Details of Laviron's method to determine k_{ET}:

The apparent rate of heterogeneous electron transfer (k_{ET}) from the electrode to the redox active site of the physiadsorbed iron porphyrin complex has been determined using Laviron's method where the separation between the cathodic and anodic peak potentials (ΔE_p) at different scan rates is utilized to measure the k_{ET} (Figure S11, ESI).[5,6] The value of transfer co-efficient (α) can be determined using equations 1 and 2, respectively.

$$E_{pc} = E^0 - (RT/\alpha nF)\ln(\alpha nF\nu/RTk_{ET}) \quad (1)$$

$$E_{pa} = E^0 + [(RT/(1-\alpha)nF)\ln[(1-\alpha)nF\nu/RTk_{ET}) \quad (2)$$

Where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively, E^0 is the apparent midpoint potential of the redox active species, ν is the scan rate, n is the number of electron transferred (n=1 for both $Fe^{III/II}$ and Fc/Fc^+ couples) and R, T, F have their usual meaning. The potentials for cathodic and anodic peaks varied linearly with ln(ν) as shown in figure S12A, C and E, ESI.[7] The ratio of the slopes of the plots has been analysed to evaluate the average values of α.

The k_{ET}(s) between the electrode and the complex $FeFc_4$ physiadsorbed on the ATM assemblies having different lengths have been determined from the following equations 3 and 4, respectively

$$\log k_{ET} = \alpha\log(1-\alpha) + (1-\alpha)\log\alpha - \log(RT/nF\nu) - \alpha(1-\alpha)nF\Delta E_p/2.3RT \quad (3)$$

$$\Delta E_p = 2.3RT/nF\alpha(1-\alpha)\,[\alpha\log(1-\alpha) + (1-\alpha)\log\alpha - \log(RT/nF\nu) - \log k_{ET} \quad (4)$$

The plot of ΔE_p versus log(ν) produces a straight line alongwith an intercept (figure S12B, D and E, ESI). K_{ET} is determined from the intercept of this line.

Supporting Figures and Tables:

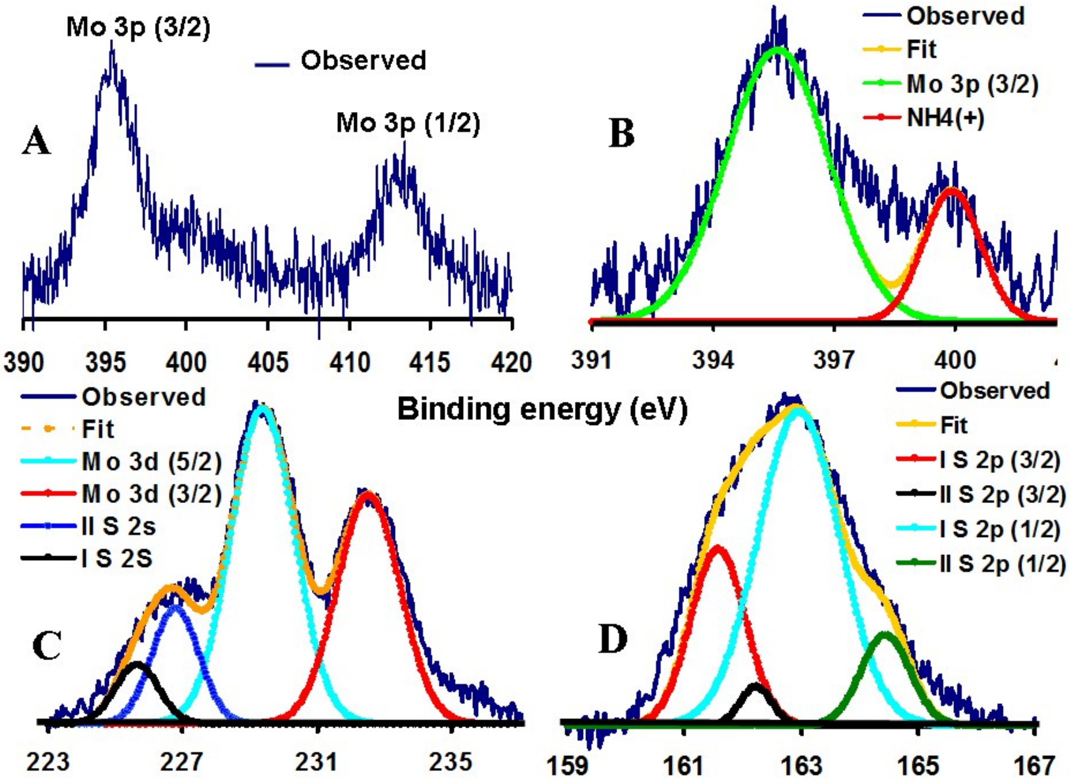
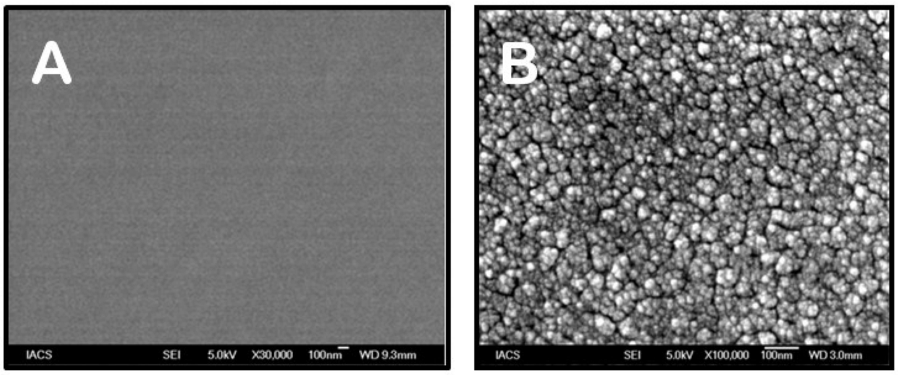


Figure S1. XPS data of ATM modified Au electrode showing different regions along with their best fits showing the various components.



Bare Au

ATM modified Au

Figure S2. FE-SEM images of (A) bare Au and (B) ATM modified Au.

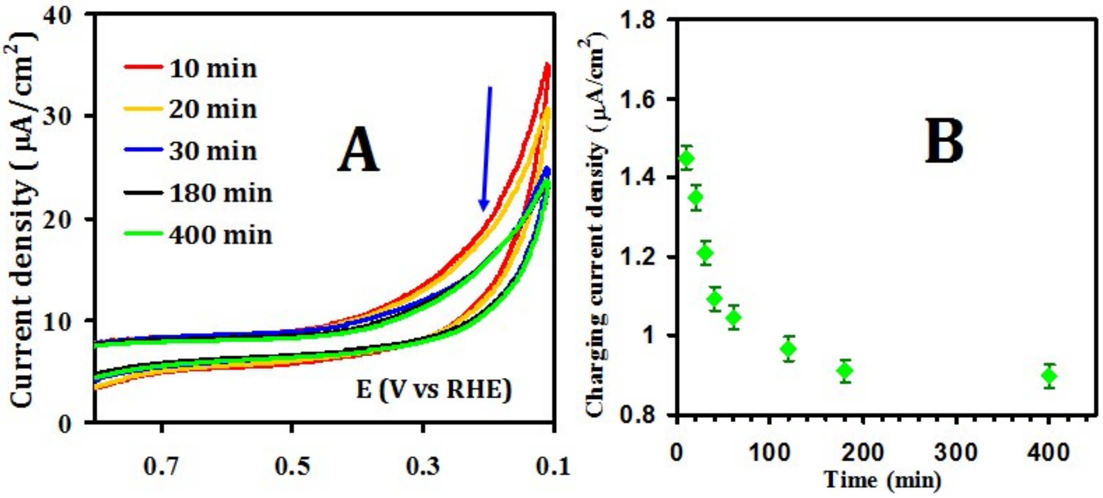


Figure S3. (A) CV data of 1 mM ATM modified surfaces subjected to various time of deposition in air saturated pH 7 buffer at a scan rate of 50 mV/s using Ag/AgCl as reference and Pt wire as counter electrodes respectively. All the data are not shown. (B) A plot of the corresponding charging current values of the respective CV curves as a function of immersion time where the currents are calculated at 0.61 V (vs. RHE) potential.

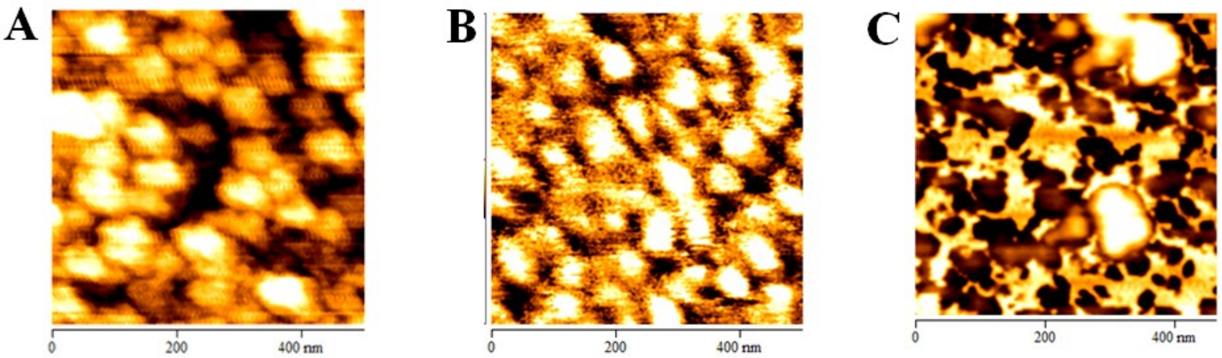


Figure S4. (A), (B), and (C) are the 2D topology AFM images of ATM modified surfaces incubated for 10 min, 40 min and 400 min, respectively.

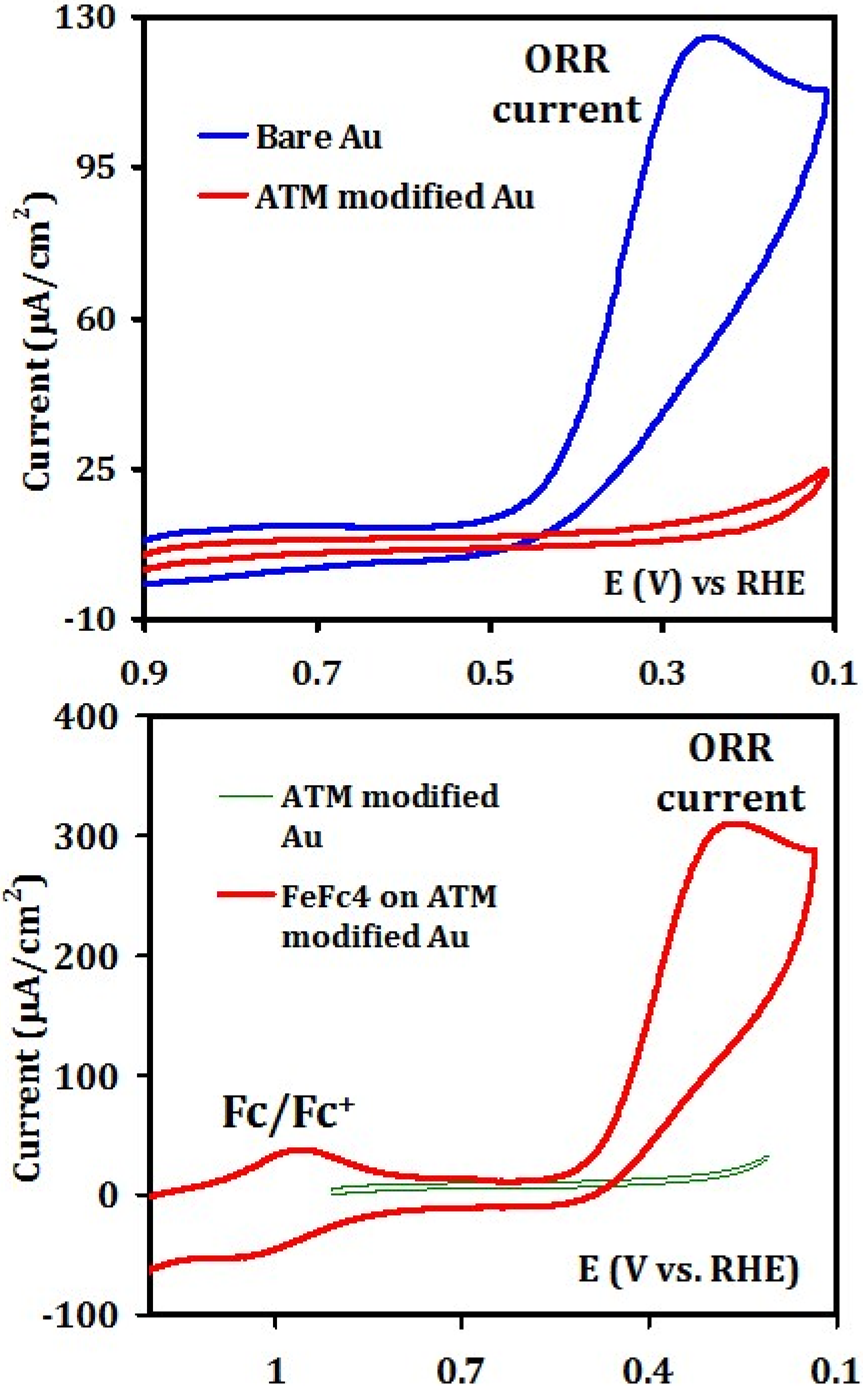


Figure S5. TOP: Overlay of CV data of bare Au wafer (blue) and the ATM modified Au surface (red) in air saturated pH 7 buffer at a scan rate of 50 mV/s using Ag/AgCl as reference and Pt wire as counter electrodes respectively. **BOTTOM:** Overlay of CV data of ATM modified Au surface before physiadsorbing (green) iron porphyrin and after physiadsorbing (red) iron porphyrin ($FeFc_4$).

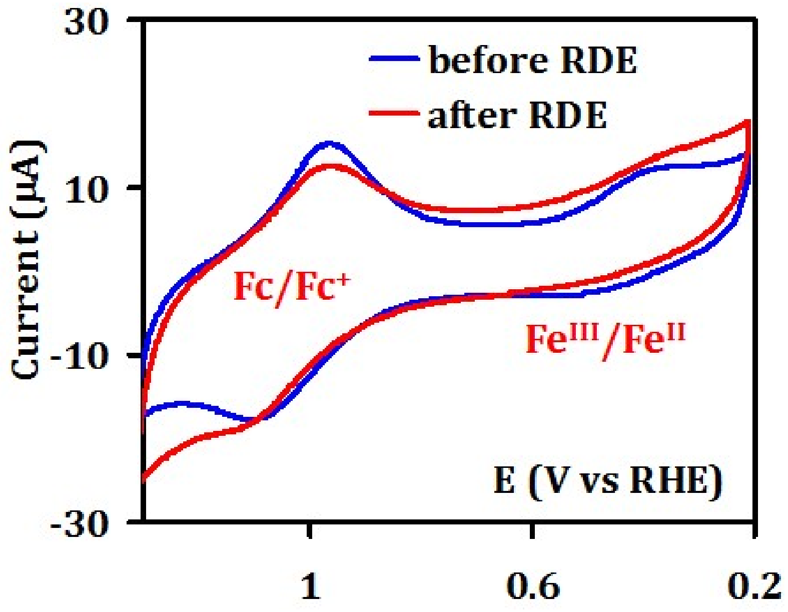


Figure S6. CV data of $FeFc_4$ immobilized on ATM modified Au before (blue) and after (red) RDE experiment in pH7 under anaerobic conditions.

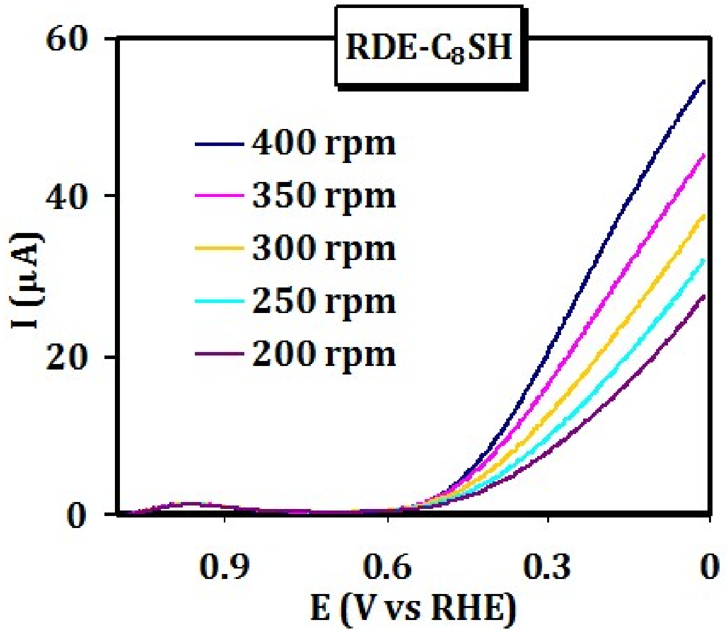


Figure S7. RDE data of $FeFc_4$ immobilized on ATM modified Au (for 40 mins) in pH7.

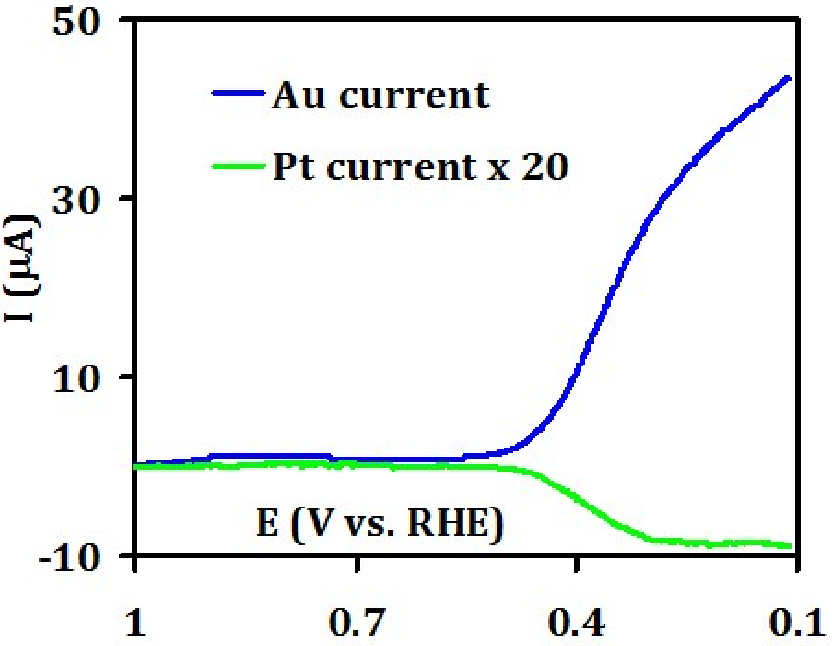


Figure S8. RRDE data of $FeFc_4$ physiabsorbed on ATM modified Au electrode, immersed for 10 min showing the disk and Pt ring currents, in air saturated pH 7 buffer at a scan rate of 10 mV/s and rotation speed of 300 rpm, using Ag/AgCl reference and Pt wire counter electrodes.

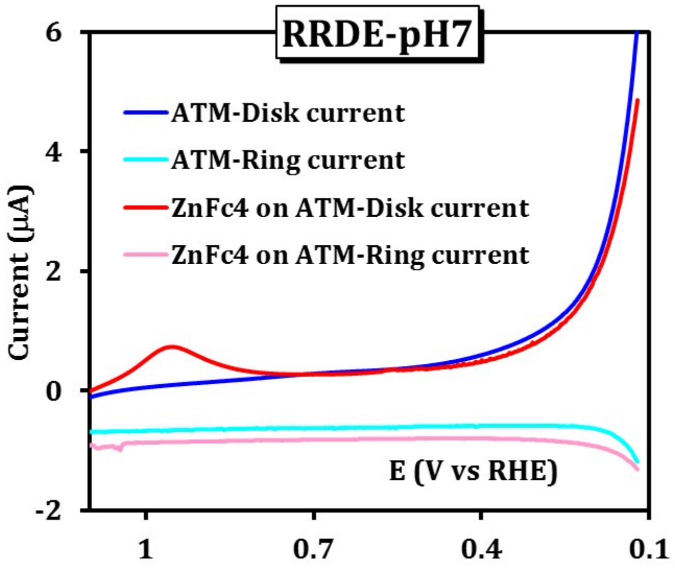


Figure S9. RRDE data of ATM modified Au electrode (without any catalyst) and $ZnFc_4$ physiadsorbed on ATM modified Au electrode, showing the disk and Pt ring currents, in air saturated pH 7 buffer at a scan rate of 10 mV/s and rotation speed of 300 rpm, using Ag/AgCl reference and Pt wire counter electrodes.

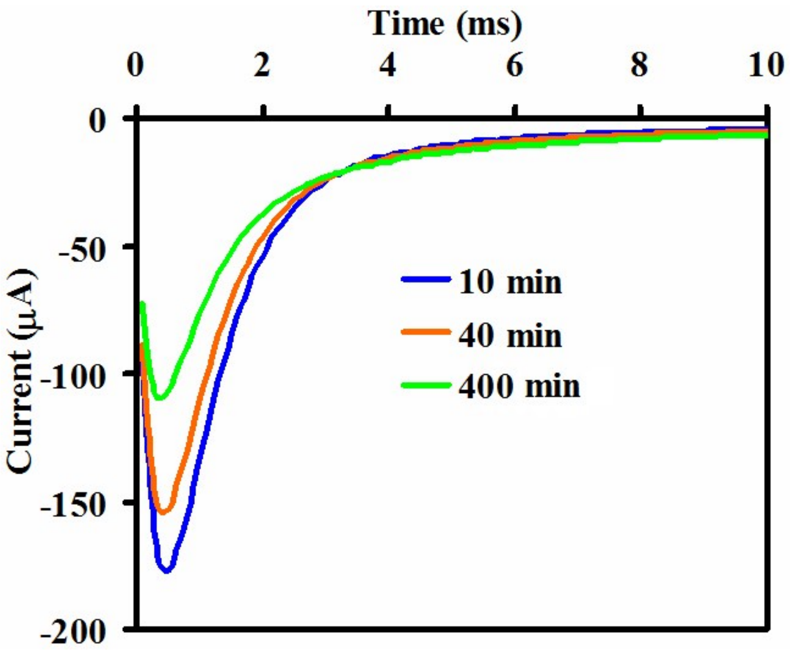


Figure S10. Chronoamperometric response of $FeFc_4$ complex physiadsorbed on Au surfaces modified with ATM for different time interval.

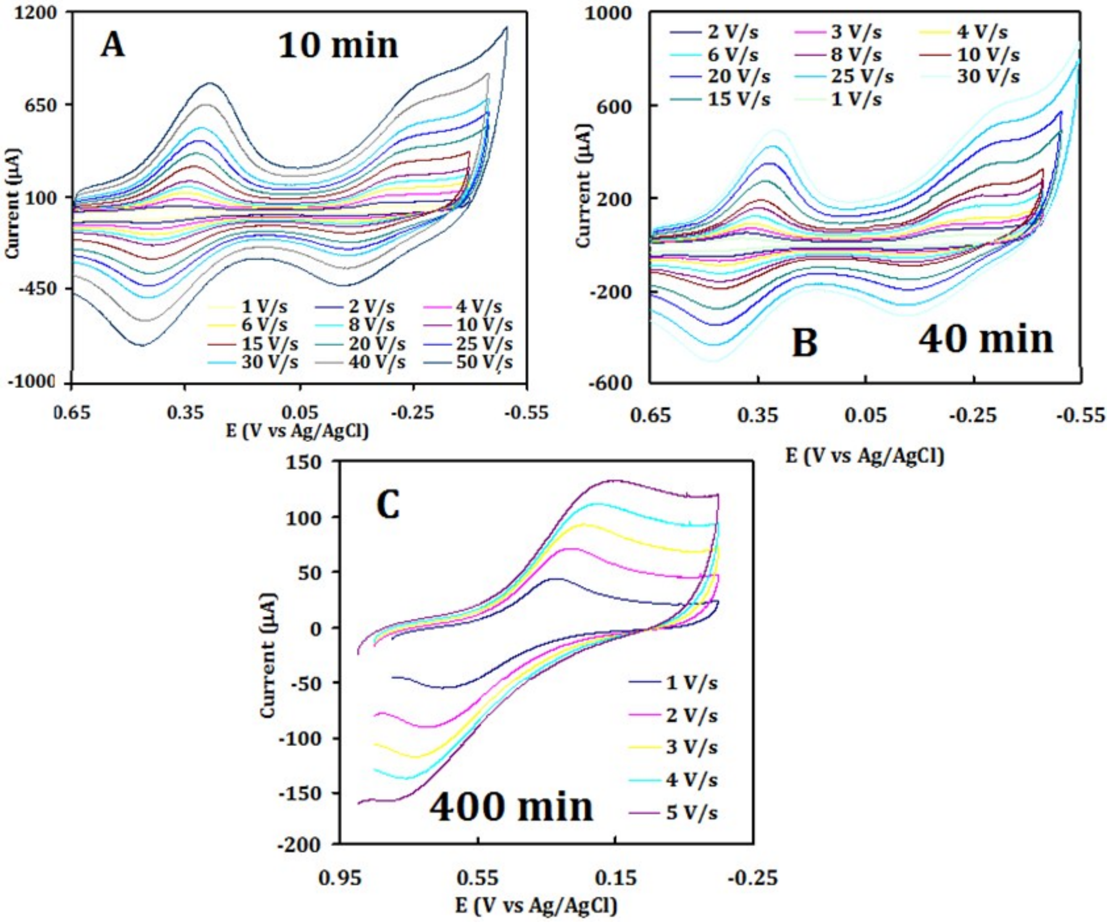


Figure S11. Cyclic voltammograms of $FeFc_4$ complex physiadsorbed on top of (A) 10 min, (B) 40 min and (C) 400 min ATM assembly on Au in different at scan rates recorded in pH 7 buffer under Ar atmosphere using Ag/AgCl as reference electrode and Pt wire as counter electrode. Note that, in case of 400 min assembly no CV for $Fe^{III/II}$ is obtained and therefore has not been shown in the plot.

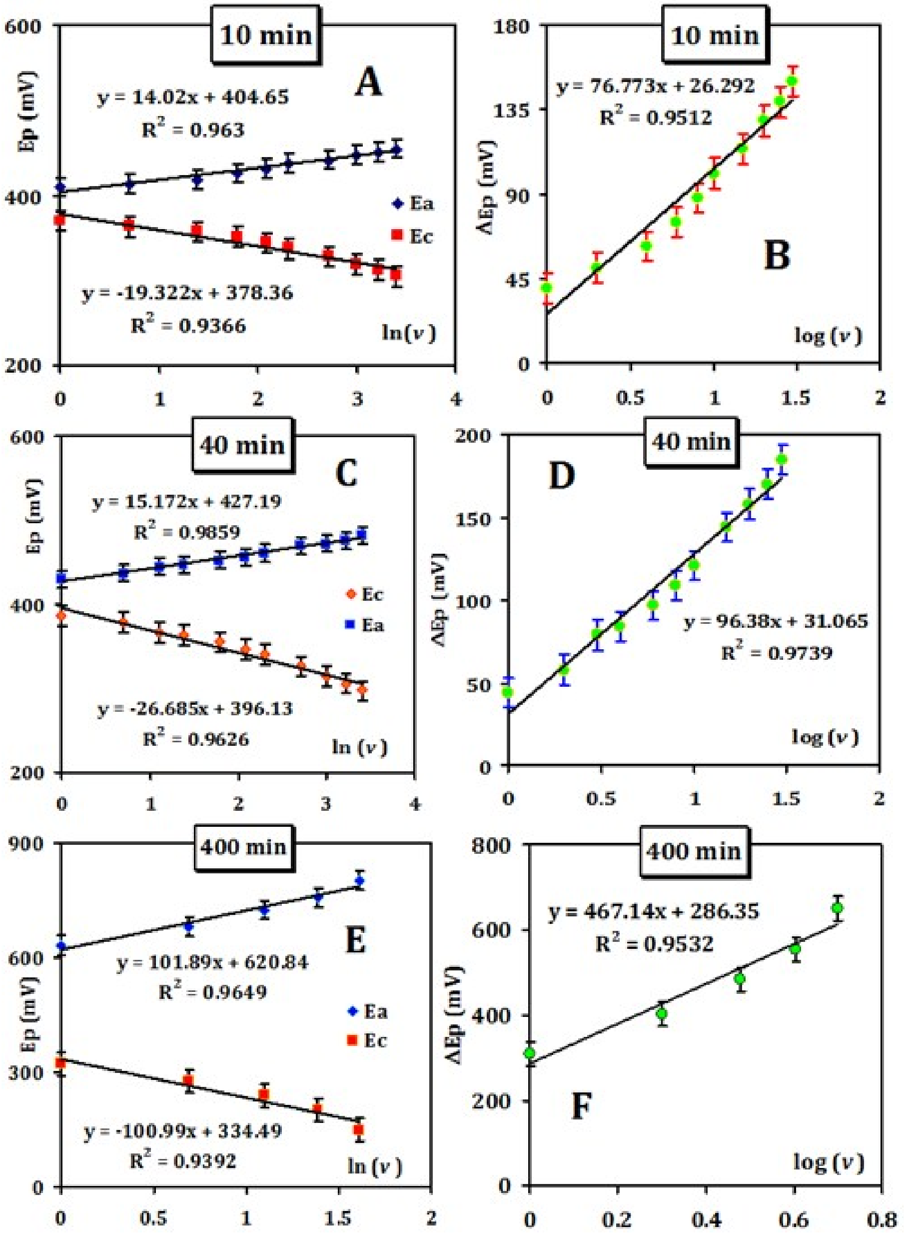


Figure S12. Plot of peak potential (E_p) vs ln(ν) for Fc/Fc$^+$ocouple of FeFc$_4$ complex physiadsorbed on top of (A) 10 minutes, (C) 40 minutes and (E) 400 minutes ATM assembly on Au in pH 7 buffer under anaerobic conditions. Plot of ΔE_pvs log (ν) for Fc/Fc$^+$ couple of FeFc$_4$ complex physiadsorbed on top of (B) 10 minutes, (D) 40 minutes and (F) 400 minutes ATM assembly on Au at similar conditions. E_a and E_c are anodic and cathodic potentials vs Ag/AgCl, respectively.

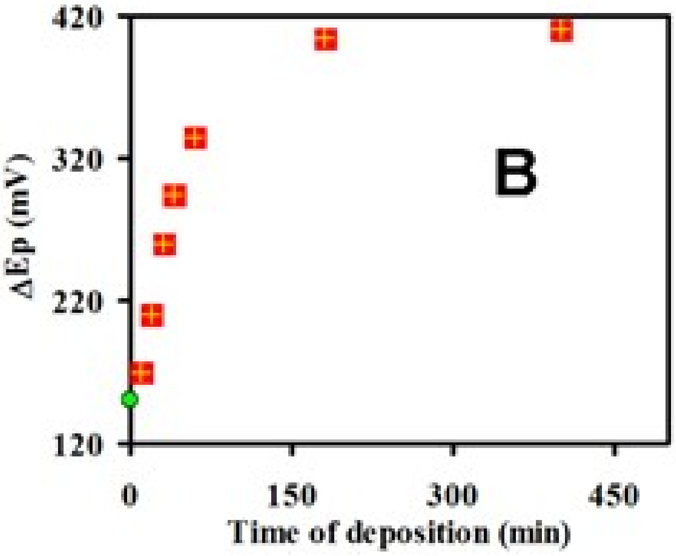


Figure S13. A plot of ΔE_p vs time of deposition of the corresponding CVs obtained in figure 3A. The green point in this plot corresponds to the bare electrode i.e. in the absence of any ATM on the Au surface.

Table S1: Comparison of peak splitting for bare Au and ATM modified gold surfaces after different time of immersion using redox couple $K_3[Fe(CN)_6]$ in 0.1 M KNO_3

Samples	**Peak splitting (mV)**
Bare Au	***150***
10 min immersion	***170***
20 min immersion	***210***
30 min immersion	***260***
40 min immersion	***295***
60 min immersion	***335***
180 min immersion	***404***
400 min immersion	***410***

Notes and References:

1. J. W. McDonald, G. D. Friesen, L. D. Rosenhein, and W. E. Newton, *Inorg. Chim. Acta,* 1983, **72**, 205-210.
2. S. Samanta, K. Sengupta, K. Mittra, S. Bandyopadhyay, and A. Dey, *Chem. Commun.* 2012, **48**, 7631-7633.
3. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications* 2nd ed.; John Wiley & Sons, Inc.: New York, 2001.
4. J. –M. Saveant, *Elementss of Molecular and Biomolecular Electrochemistry;* Wiley-Interscience: Hoboken, NJ, 2006.
5. E. Laviron, *J. Electroanal. Chem. Interfacial Electrochem.* 1979, **101**, 19-28.
6. S. Bandyopadhyay, A. Rana, K. Mittra, S. Samanta, K. Sengupta, and A. Dey, *Inorg. Chem.* 2014, **53**, 10150-10158.

7. In case of 10 and 40 min assembly, ΔE_p is taken from both the Fc/Fc$^+$ and Fe$^{III/II}$ couple at different scan rates to calculate k_{ET}. However, in case of 400 min assembly, only Fc/Fc$^+$ couple is taken into consideration to calculate k_{ET} because Fe$^{III/II}$ CV has not been observed in this assembly presumably due to very slow ET rate.