Supporting Information

H_2 Evolution Catalyzed by FeFe-Hydrogenase Synthetic Model Covalently Attached to Graphite Surface

Md Estak Ahmed, Subal Dey, Biswajit Mondal and Abhishek Dey*

Department of Inorganic Chemistry

Indian Association for the Cultivation of Science

2A & 2B Raja SC Mullick Road, Kolkata, India, 700032

E-mail: icad@iacs.res.in

General procedure

Syntheses of all the compounds were performed under N_2 atmosphere. Compound **C** was synthesized in standard Schlenk technique. Anaerobic experiments were performed within MBRAUN glove box. The solvents used were purchased from Merck Specialities, Pvt. Ltd. (India), Spectrochem Pvt. Ltd. (India), RFCL Ltd. (India), Avra S2 synthesis Pvt. Ltd. (India). *p*-iodoaniline and thionyl chloride ($SOCl_2$) was purchased from Spectrochem Pvt. Ltd. (India), *p*-formaldehyde and superhydride ($LiBEt_3H$, 1 M in THF) was bought from Sigma-Aldrich chemicals Pvt. Ltd. and anhydrous Na_2SO_4 and sulfuric acid (98%) was purchased from Merck Specialities, Pvt. Ltd. (India). SiO_2 (60- 120) was purchased from SISCO Pvt. Ltd. (India). The column chromatography was performed on SiO_2 (60-100 mesh). Edge Plane Graphite (EPG) discs were purchased from Pine Instruments. The FT-IR data are measured on the Shimadzu FTIR 8400S instrument. All the NMR spectra were recorded on the Bruker DPX-300 or DPX-500 spectrometer at room temperature. The mass spectra are recorded by QTOF Micro YA263 instrument. X-ray single crystal data was collected at 120 K using radiation on a SMART APEX diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution refinement were carried out using the software package of APEX II. The structure was solved by direct method and refined in a routine manner. The nonhydrogen atoms were treated anisotropically. All the hydrogen atoms were located on a difference Fourier map and refined.

Electrochemical Measurements

Cyclic Voltammetry

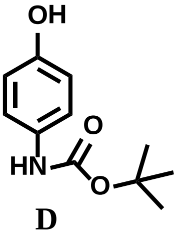
All electrochemical experiments were performed using a CH Instruments (model CHI710D Electrochemical Analyzer). Biopotentiostat, reference electrodes, Teflon® plate material evaluating cell (ALS Japan) were purchased from CH Instruments. The rotating ring disk electrochemical (RRDE) set up from Pine Research Instrumentation (E6 series Change Disk tips with AFE6M rotor) was used to obtain the RRDE data. A Pt wire was used as a counter electrode. The measurements were made against an Ag/AgCl aqueous reference electrode. Anaerobic CV experiment was performed in Glove Box or within a 5 neck S3 electrochemical cell brought from PINE Instruments by thoroughly degassing the whole set up. The EPG electrode was freshly polished with silicon carbide paper to get rid of all the contaminations out for each single use.

Synthesis

Synthesis of Complex B, [(μ-SCH_2N(4-Iodophenyl)CH_2S)$Fe_2(CO)_6$:[1] Complex **B** was synthesized according to the literature procedure using a standard Schlenk technique. The bis-N-chloromethylated ligand *p*-$IC_6H_4N(CH_2)_2Cl_2$ was synthesized by chloromethylation of *p*-Iodoaniline with paraformaldehyde and $SOCl_2$ by following reported procedure. 440 mg of $Fe_2S_2(CO)_6$ (1 mmol) was dissolved in 20 mL of dry tetrahydrofuran (THF). 2 mL of $LiBEt_3H$ (1 M in THF) was added dropwise to the red solution at −78 °C. The solution immediately turned to deep green. Then, ligand *p*-$IC_6H_4N(CH_2)_2Cl_2$ was added to the reaction mixture at −15 °C. The color immediately changed to red. The reaction mixture was stirred for further 1 h at room temperature. Removal of the solvent produces a dark brown precipitate. A crystalline red solid product was obtained after column chromatography with hexane-toluene (4:1) mixture. Single crystal was grown by slow evaporation of dichloromethane. ^1H NMR ($CDCl_3$): δ 7.42 (2H, d), 6.65 (2H, d), 4.28 (s, 4H); IR (CH_3CN): 2076 cm^{-1} (s), 2038 cm^{-1} (s), 1998 cm^{-1} (s).

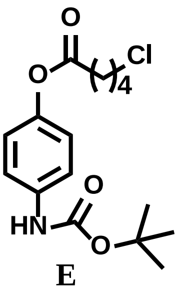
Synthesis of Complex C, [μ-SCH_2N(4-Trimethylsilylethynylphenyl)CH_2S][$Fe(CO)_3$]$_2$:[1] Complex **B** (100 mg, 0.17 mmol), Pd(PPh3)$_2$Cl$_2$ (11.86 mg, 0.017 mmol) and CuI(3.38 mg, 0.017 mmol) were dissolved in 20 mL triethylamine in a two way round bottom flask in argon atmosphere. Then trimethylsilyl iodide (33.9 mg, 0.34 mmol) was added to it and the reaction mixture was heated at 60 °C for 3 hr. The solution turned to black. The solvent was evaporated to get the dark-brown precipitate. The red solid was obtained after column chromatography with toluene-hexane mixture (1:4). ^1H NMR ($CDCl_3$): δ 7.41 (2H, d), 6.64 (2H, d), 4.29 (s, 4H); IR (CH_3CN): 2076 cm^{-1} (s), 2036 cm^{-1} (s), 2000 cm^{-1} (s).

Synthesis of Complex A, [μ-SCH_2N(4-Ethynylphenyl)CH_2S][$Fe(CO)_3$]$_2$: Complex **C** was taken in 10 mL dry and degased methanol and potassium carbonate (1.5 equiv.) was added to it and the reaction mixture was stirred for 2 hour at room temperature. Methanol was evaporated and the red solid product was obtained after column chromatography with toluene-hexane mixture (3:7). The Single crystal was grown by slow evaporation of dichloromethane. . ^{1}H NMR ($CDCl_3$): δ 7.46 (2H, dd), 6.69 (2H, dd), 4.33 (s, 4H), 3.04 (s, 1H); IR (CH_3CN): 1998 cm^{-1} (s), 2032 cm^{-1} (s), 2073 cm^{-1} (s), 2298 cm^{-1}; ESI$^+$ Mass (TOF) $[M + H]^+ = 493.89$; Calculated [m/z] = 492.90.



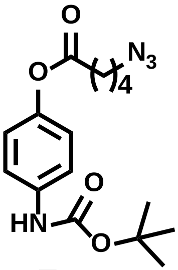
D

Synthesis of D: 4-Aminophenol (1.09 g, 10.0 mmol) was dissolved in 60 mL of dry THF. Boc_2O (2.18 g, 10.0 mmol) was added dropwise, and the mixture was stirred overnight at room temperature. After removal of the solvent the pure compound **D** was isolated by column chromatography with EtOAc/Hexane mixture (1:4) as a white solid. Yield: 1.86 g (88 %). ^{1}H NMR ($CDCl_3$): δ 1.51 (s, 9H), 4.96 (s, 1H), 6.45 (br s, 1H), 6.75 (d, 2H), 7.18 (d, 2H); GC-MS, m/z = 209.11; FTIR (KBr): 1696 cm^{-1} (C=O, amide).



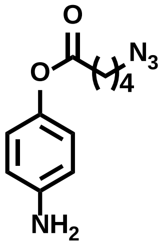
E

Synthesis of E: Compound **D** (1.05 g, 5.0 mmol) and triethylamine (TEA, 1.05 mL, 7.5 mmol) were dissolved in 40 mL of dry THF. 5-Chlorovaleroyl chloride (775 µL, 6.5 mmol) in 10 mL dry THF was added drop wise at 0 °C and then the mixture was stirred for 4 hr. After removal of the THF, 50 ml of dichloromethane was added to the reaction mixture. The organic layer is washed with water (2 x 30 ml). The organic phase was dried over anhydrous Na_2SO_4 and removal of the solvent gives the crude product which was purified by column chromatography with EtOAc/Hexane (1:5) to afford compound **E** as oily liquid. Yield: 1.15 g (80 %). ^{1}H NMR ($CDCl_3$): δ 1.51 (s, 9H), 1.90 (m, 4H), 2.58 (m, 2H), 3.58 (t, 2H), 6.48 (br s, 1H), 7.00 (d, 2H), 7.35 (d, 2H); FTIR (KBr): 1709 cm^{-1} (C=O, amide), 1742 cm^{-1} (C=O, ester).



F

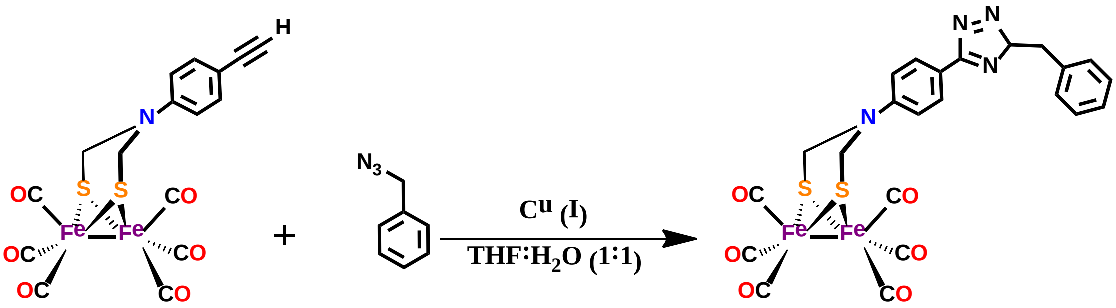
Synthesis of F: Compound **E** (0.86 g, 3 mmol) was dissolved in 8 mL DMF and warmed at 80 °C for 5 hr with excess sodium azide (3 equiv.). After 5 hr the reaction was cooled down to room temperature and 20 mL water was added. The compound was extract with DCM and the pure compound was obtained by column chromatography with EtOAc/Hexane (1:5). Yield: 0.74 g (83%). ^{1}H NMR ($CDCl_3$): δ 1.51 (s, 9H), 1.73 (m, 2H), 1.82 (m, 2H), 2.58 (t, 2H), 3.34 (t, 2H), 6.48 (br s, 1H), 7.00 (d, 2H), 7.35 (d, 2H); FTIR (KBr): 1697 cm^{-1} (C=O, amide), 1738 cm^{-1} (C=O, ester), 2097 cm^{-1} (azide).



G

Synthesis of G: Compound **F** (293 mg, 1 mmol) was dissolved in DCM (10 ml). Then, trifluoroacetic acid (160 μl) was added to it at 0 ^{0}C and the mixture was stirred for 2 hr at room temperature. Then 10 ml DCM was added and the organic layer was washed with water (15x2). The organic phase was dried over anhydrous Na_2SO_4 and removal of the solvent gives the crude product which was purified by column chromatography with EtOAc/Hexane (1:4) to afford the pure compound. Yield: 175 mg (91 %). ^{1}H NMR ($CDCl_3$): δ 1.40-1.86 (m, 4H), 2.35 (t, 2H), 3.30 (t, 2H), 6.65 (d, 2H), 6.85 (d, 2H); GC-MS, m/z= 192.11; FTIR (KBr): 1738 cm^{-1} (C=O, ester), 2100 cm^{-1} (azide).

Click reaction with benzyl azide: Complex C (20 mg, 0.04 mmol) and benzylazide (8 mg, 0.06 mmol) were taken in 5 mL THF and then Cu(I) catalyst prepared in situ using $CuSO_4$ and (+)-sodium L-ascorbate was added to it and the reaction mixture was stirred at rt for 6 hr. The reaction was monitored by TLC time to time and after 6 hr it showed the complete conversion of complex **C.** The solvent was removed by evaporation, and the residue was purified by column chromatography to afford the pure compound. ^{1}H NMR ($CDCl_3$): δ 4.34 (s, 4H), 5.56 (s, 2H), 6.76 (d, 2H), 7.25 (s, 1H), 7.33 (s, 2H), 7.38 (s, 2H), 7.59 (s, 1H), 7.74 (d, 2H). ESI$^+$ Mass (TOF) $[M + H]^+$ = 625.827.



Scheme S1: Click reaction of complex **C** with benzyl azide in presence of Cu(I) catalyst

Modification of EPG surface with azide terminated linker: The EPG surface was modified using 4-(5-azidopentanoate) benzenediazonium perchlorate. 4-aminophenyl 2-azidoacetate (20.4 mg, 10 mmol L^{-1}) was taken in 10 mL dry acetonitrile and the temperature was lowered to 0 °C. Then *tert*-butyl nitrite (13 µL, 1.1 equiv.) was added to it at 0 °C and stirred the solution for 10 mins. Then electrode modification was optimally achieved by recording three CVs between 0.5 and -0.8 V vs Ag/AgCl. Throughout the reaction and electrode modification the temperature was kept at 0 °C.

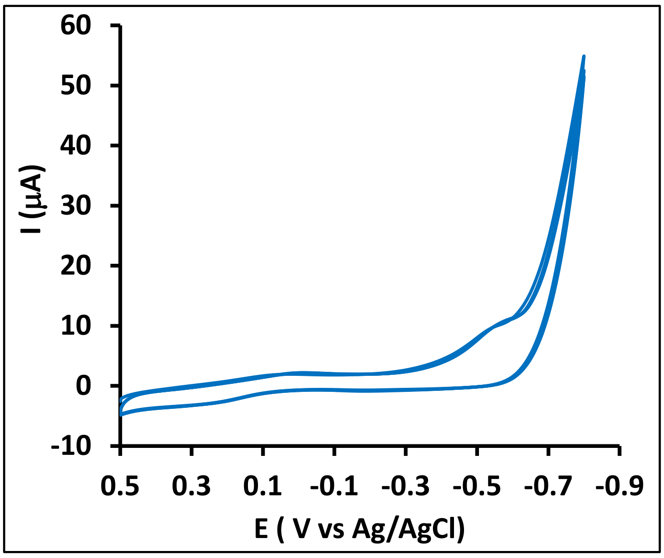


Figure S1: Cyclic voltammetry of a solution of 4-(5-azidopentanoate) benzenediazonium perchlorate (10 mmol L^{-1}) in MeCN. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte (100 mmol).

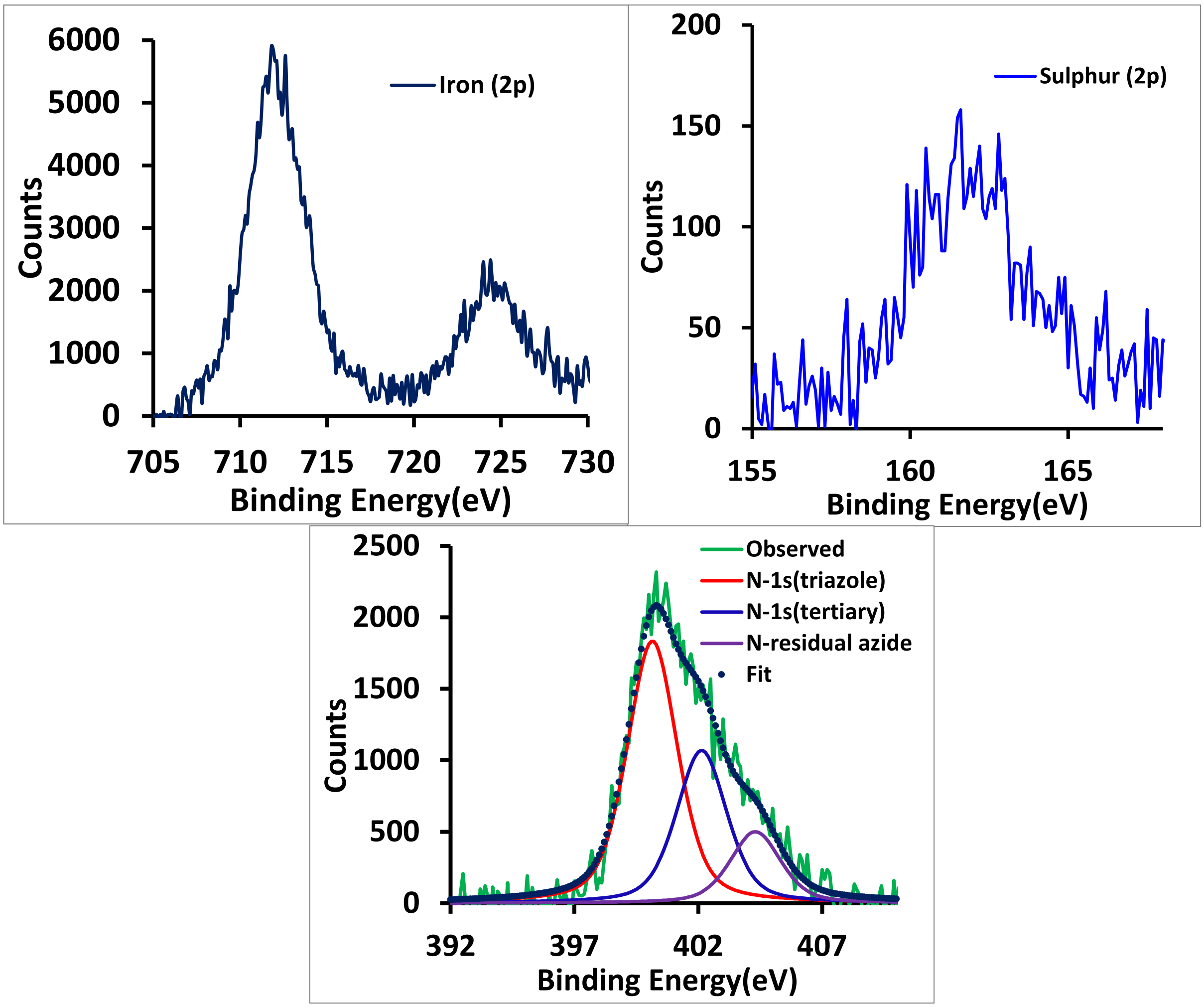


Figure S2: X-ray photoelectron spectra of Hyd-ITO-rGO construct

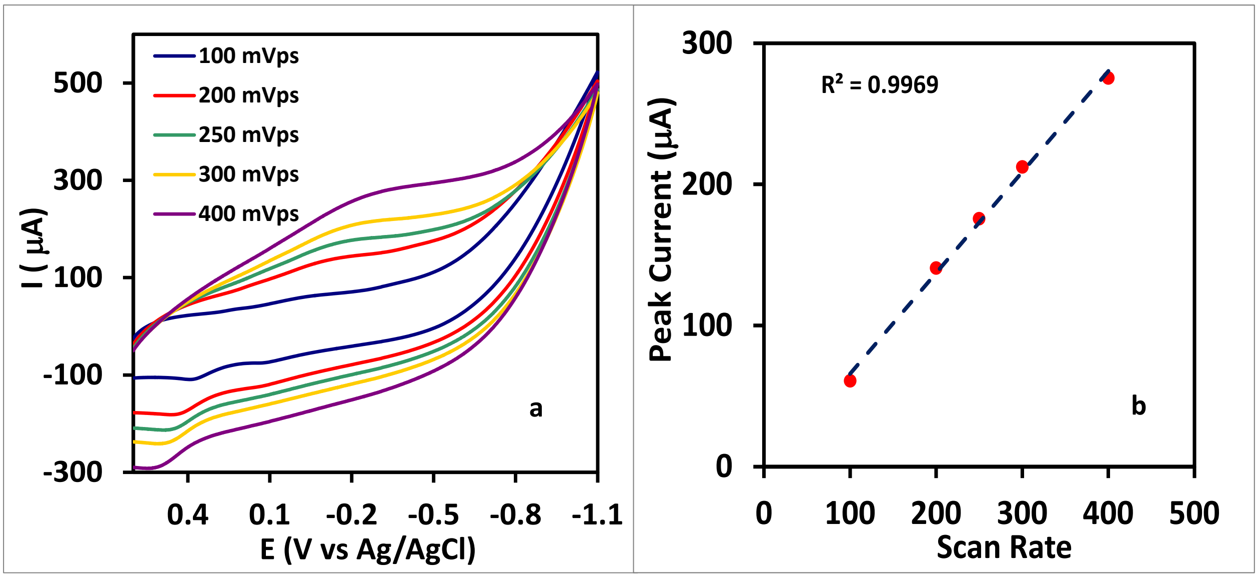


Figure S3: (a) Cyclic voltammogram of Hyd-ITO-rGO construct in pH7 phosphate buffer at different scan rates. (**b**) Scan rate vs Peak current plot of the same Hyd-ITO-rGO construct in pH7 phosphate buffer

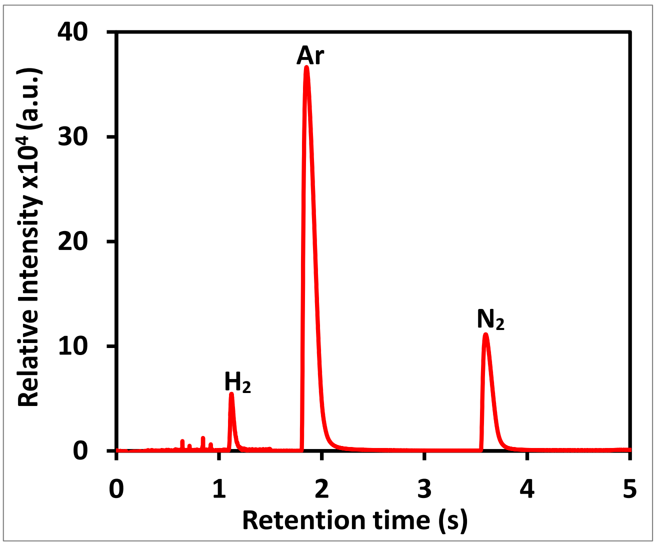


Figure S4: GC plot of the gas collected from the headspace during the bulk electrolysis.

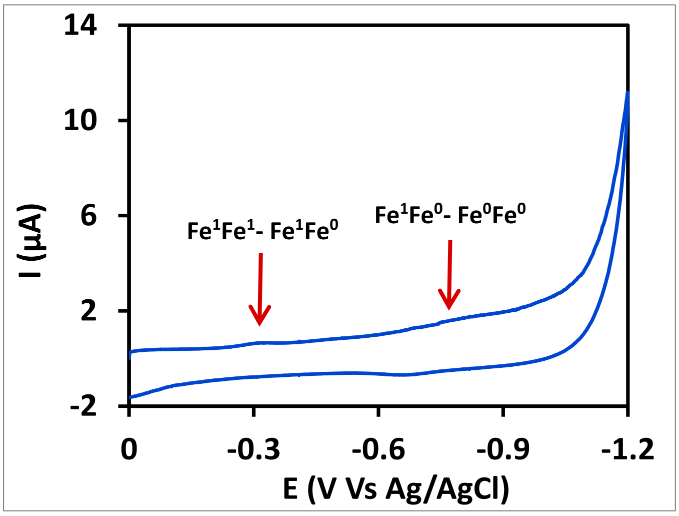


Figure S5: Cyclic voltammogram of Hyd-EPG construct in pH7 phosphate buffer (scan rate 100 mV/s, Pt as counter and Ag/AgCl as reference electrodes were used).

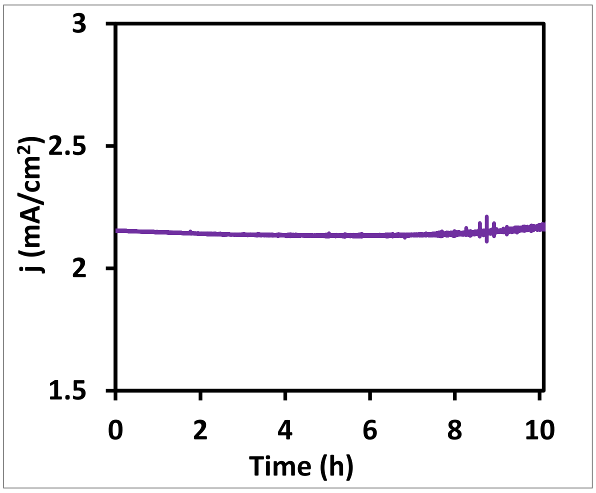


Figure S6: Controlled potential bulk electrolysis at −0.9 V vs Ag/AgCl in aqueous 0.20 N H_2SO_4.

TON and TOF calculation:

From the cyclic voltammetry of Fc^+/Fc couple after click we get the surface coverage is 1.43×10^{14} molecules/cm^2.

The controlled potential electrolysis experiments at −0.9 V vs Ag/AgCl in 0.2 N H_2SO_4 is indicate that 253 C charge is consumed in 10 h and the gas collected is 26.9 ml.

So in 10 h number of molecules of H_2 produced is ~0.75×10^{21}.

Therefore TON is ~0.5×10^{7} after 10 h and TOF is ~139 s^{-1}.

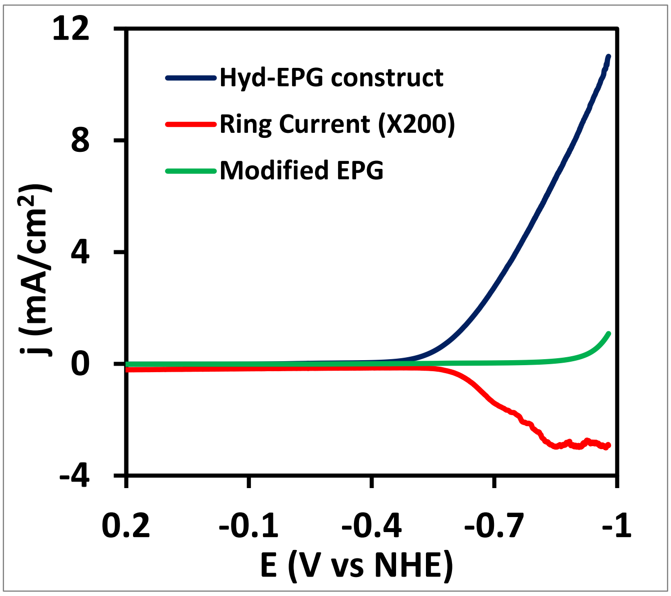


Figure S7: RRDE data of Hyd-EPG construct (blue line, indicating H_2 generation and the corresponding Pt-ring current red line, indicating H_2 detection); the ring held at a constant potential of 0.9 V in aqueous 0.1 N H_2SO_4.

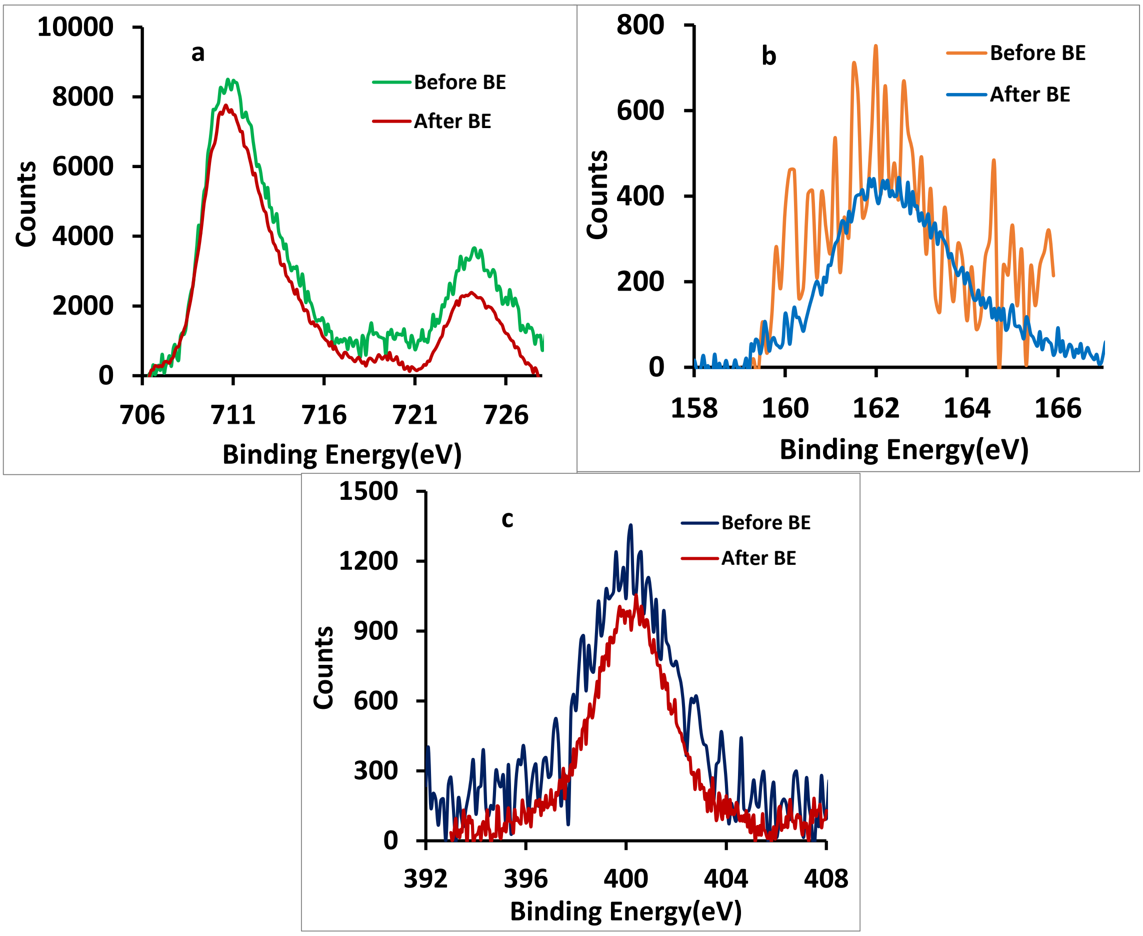
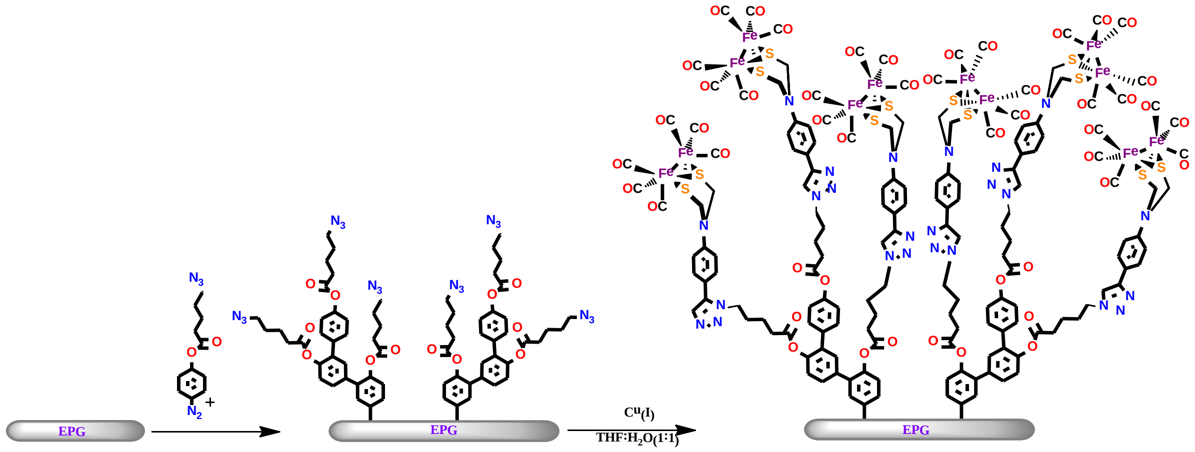
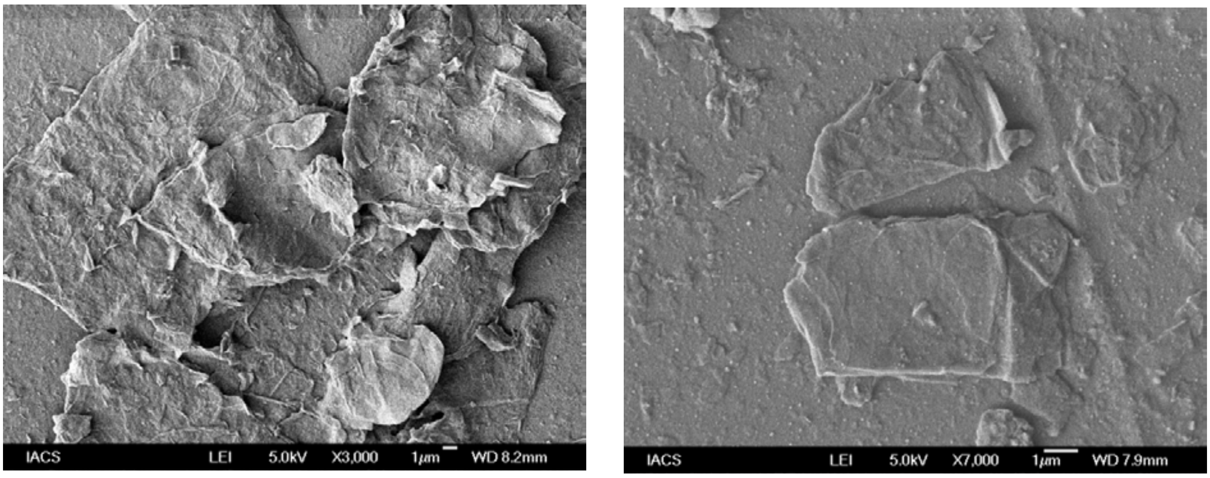


Figure S9: Overlay of X-ray photoelectron spectra of modified EPG electrode (Hyd-EPG construct) before and after long time bulk electrolysis. Fe 2p (**a**), S 2p (**b**), and N 1s (**c**) are shown here.



Scheme S2: Schematic presentation of covalent attachment for Fe-Fe H_2ase model complex (**A**) on the modified EPG.



Before Electrolysis

After Electrolysis

Figure S10: FE-SEM images of Hyd-ITO-rGO construct before and after Control Potential Electrolysis (CPE), which shows that the Hyd-ITO-rGO construct is not stable after long time CPE.

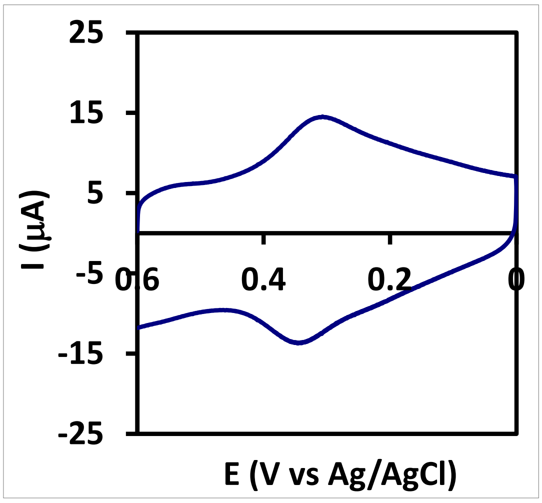


Figure S11: CV of ethynyl ferrocene covalently attached to the electrode in 1 N $HClO_4$ at 100 mV/s using Pt as counter and Ag/AgCl (satd. KCl) as reference.

Table S1: List of covalently attached molecular catalyst on modified electrode surface.

Catalyst	η (mV)	Electrolyte	TON	Ref.
Diimine–dioxime cobalt catalyst-CNT	350	pH 4.5	$4X10^4$	2
A dithiolate-bridged hexacarbonyldiiron complex-Au & Carbon	~600-700	pH~0.96	…..	3
Nickel-bisdiphosphine complex-CNT	Very Low overpotential	0.5 M H_2SO_4	10^5	4
Co-P^3-ITO	360	pH3	…..	5
{2Fe3S}Subsite of Fe-Fe Hydrogenase-Pt & Carbon	>800	Organic acidic medium	…..	6

Complex **A-**EPG	440 mV	0.05 M H_2SO_4	~10^7	

References:

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