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COMMUNICATION

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

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

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A synthetic mimic of Fe-Fe hydrogenase (H_2ase) is reported which bears a terminal alkyne group in the ligand. Using a terminal azide bearing organic linkers, this complex could be covalently attached to various electrode surfaces (e. g. – Edge Plane Graphite, reduced Graphene oxide etc.). The electrocatalytic hydrogen evolution (HER) efficiency of these construct is investigated and the results show that EPG – H_2ase mimic construct is able to produce H_2 from acidic water efficiently with over 90% selectivity.

The increasing global energy demand and depleting fossil fuel-reserves has generated keen interest in the development of hydrogen (H_2) based clean energy economy.[1-3] There are several molecular catalysts that are quite efficient to generate H_2 in water and most of them are directly adsorbed/deposited on various electrodes and used as heterogeneous electrocatalysts.[4-6] Only a few catalysts have been covalently attached onto electrode surfaces in a site specific manner.[7-11] Site specific attachment allows better replication of molecular catalysis under heterogeneous condition.

In nature, H_2ases are a class of enzyme that interconverts proton (H^+) to H_2 efficiently.[12, 13] The electrochemical investigations of H_2ases are generally performed by thin film voltammetry where the enzymes are attached on the electrode surfaces and such approach has been proved to be an efficient technique for investigating the reactivities of these enzymes.[14-16] Following the original reports, several groups have demonstrated the suitability of Fe-Fe H_2ase mimics as efficient H_2 evolution reaction (HER) in acidic aqueous medium by physiadsorbing them on electrode surfaces.[4, 17] Unfortunately, this often leads to excessive catalyst loading, slower electron transfer kinetics between the electrode and the catalyst and gradual leaching of the adsorbed catalyst.[18] Additionally charged molecules do not physiadsorb on neutral graphite surfaces well. Thus covalent attachment, without compromising the catalyst structure, can help to resolve these problems associated with physiadsorption.

Covalent attachment of catalysts to electrode surfaces can be achieved by Cu (I) catalysed 1,3-cycloaddition of azides to terminal alkyne, a reaction popularly referred as the ‘click’ reaction.[19-22] The advantage of covalent attachment via click reaction has been amply demonstrated in O_2 reduction catalysts.[23] Functional models of cytochrome C oxidase and mono nuclear Cu complex bearing a terminal alkyne group have been covalently attached on electrode surfaces. But widely accepted gold-thiol electrode construct is suitable for electro catalytic investigations spanning mild potential ranges (0.5 to -0.5 V vs Ag/AgCl), and is limited due to the instability of thiol SAM at highly oxidizing/reducing potentials where the thiols gets desorbed. Graphite on the other hand is a stable electrode material at highly oxidizing and reducing potentials as well as over a wide range of pHs. Thus covalent attachment of HER catalysts to graphite electrodes is desirable. Till date there are only reports of covalent attachment of H_2ase mimic onto Au surface by Artero *et. al*.[10, 24, 25] The mimic investigated lacks the azadithiolato (ADT) bridge which is proved to be necessary for enzymatic activity of Fe-Fe H_2ases.[26] Here we are reporting the synthesis of an ADT bridged *p*-alkynylbenzeneazadithiolate diironhexacarbonyl complex (**A**) and its covalent attachment onto various (e. g. - rGO) electrode surfaces. Prior to complex **A** attachment, the electrodes have been modified with an azide terminated amine linker so that the catalyst can be tethered on to the electrode surface by “click” reaction. The inherent advantage of this modular approach is the ability to modify the length of the linker and attune the rate of electron transfer from the electrode to the catalyst. This modified electrodes exhibit stable HER activity over prolonged periods. This is the first report of direct covalent attachment of an azadithiolate (ADT) bridged mimic of Fe-Fe H_2ase active site to an electrode.

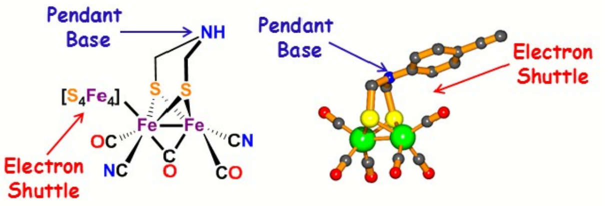

Fig. 1 (left) The active site of Fe−Fe hydrogenase, (right) Crystal structure of *p*-alkynylbenzeneazidodithiolate diironhexacarbonyl complex (**A**).

Complex **B** is synthesized by slight modification of procedure reported by Sun *et. al.*[24] as shown in Scheme 1. Condensation of dilithium salt of disulphidodiironhexacarbonyl precursor with N,N-bis(chloromethyl)-4-iodoaniline in tetrahydrofuran yields *p*-iodobenzeneazaidodithiolate diironhexacarbonyl complex (**B**).[27]

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Electronic Supplementary Information (ESI) available: X-Ray structure, FTIR, ESI MS, ^1H NMR and additional electrocatalytic data]. See DOI: 10.1039/x0xx00000x

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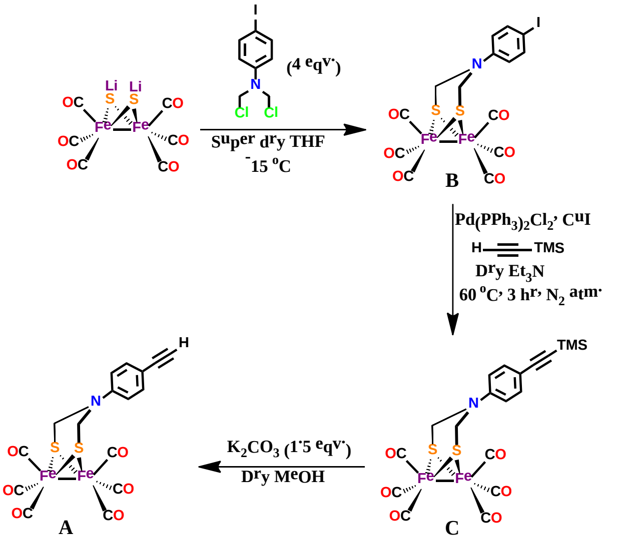
Palladium catalysed Sonogashira coupling of **B** (scheme 1) with trimethylsilylacetylene gives *p*-trimethylsilylacetyleno benzeneazidodithiolate diironhexacarbonyl complex (**C**) with high yields.[28] The deprotection of the trimethylsilyl group could not be carried out following the standard literature protocol (potassium fluoride and sodium hydroxide) as it resulted in formation of unknown degraded products. The deprotection was finally carried out by treating complex **C** with K_2CO_3 in dry MeOH to afford *p*-alkynylbenzeneazadithiolate diironhexacarbonyl complex (**A**) that bears a terminal alkyne group (Scheme 1). Suitable crystal for XRD of the complex **A** was grown by slow evaporation of dichloromethane solution (Fig. 1, right). This reveals the $d_{Fe\text{-}Fe}$ is 2.503 Å and $d_{Fe\text{-}S}$ is 2.208-2.276 Å. These values are consistent with previous reports on similar complexes. The FTIR data of the complex **A** in CH_3CN solution shows the carbonyl stretching frequencies at 2076, 2032, 1998 cm^{-1}. The additional peak at 2298 cm^{-1} represents the C≡CH stretching frequency of the alkyne group in complex **A** (^1H NMR of C≡C-H at 3.042 ppm (SI)).



Scheme 1 Scheme for single synthesis of complex *p*-alkynylbenzeneazadithiolate diironhexacarbonyl complex (**A**).

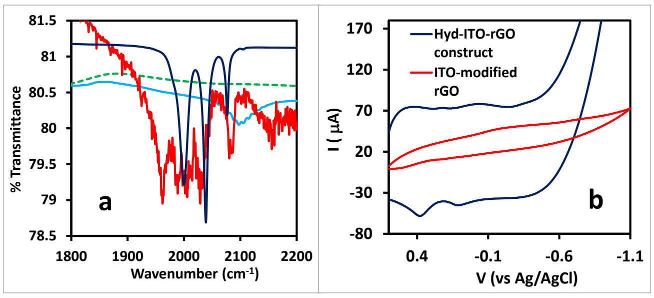
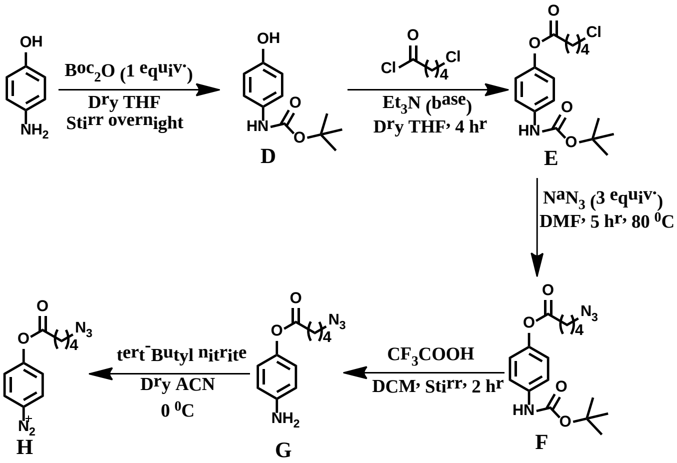


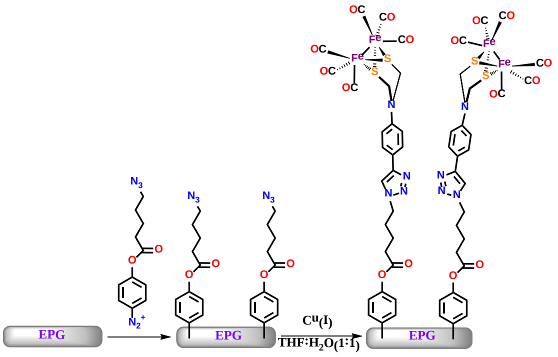
Fig. 2 (a) Overlay of the ATR-IR data of GO (in green), reduced GO modified with azide terminated amine linker (in sky blue) and Hyd-ITO-rGO construct (in red). The solution IR data of complex **A** is shown in blue. (**b**) Cyclic voltammogram of Hyd-ITO-rGO construct in pH7 phosphate buffer (scan rate 100 mV/s).

Using a benzyl azide, it was found that complex **A** underwent 1,3-dipolar Huisgen addition in THF/H_2O (1:1) solvent mixture in the presence of Cu(I) catalyst in 6 hours. The product formation was confirmed by ^1H NMR and mass spectra (Scheme S1). An azide terminated alkyl amine linker[4] is refluxed in CH_3CN along with GOs followed by reduction with aqueous NH_3 gives the desired azide terminated rGOs. This modified rGOs was then deposited on ITO surfaces and complex **A** is clicked to this ITO-modified rGOs surface (Hyd-ITO-rGO construct) following the conditions mentioned above. This Hyd-ITO-rGO construct is characterized by FTIR and X-ray photoelectron spectroscopy (XPS). The CO vibrations in the IR data at 2084, 2031, 2001, 1990 and 1963 cm^{-1} indicates an complex **A** and the absence of azide vibration at 2098 cm^{-1} (present in the ITO-modified rGOs) (Fig. 2**a**) suggest successful 1,3 cycloaddition of complex **A** to the ITO-modified rGOs. XPS is a convenient tool to establish the immobilization of complex (**A**) as binding energies are not only specific to element but also sensitive to its chemical environment (charge, oxidation state etc.). The peaks at 711.3 eV and 724.5 eV correspond to the $2p_{1/2}$ and $2p_{3/2}$ ionization of Fe(I) centre and the peak at 162.4 eV correspond the ionization of 2p of thiolate sulphur. Peaks at 399.8 eV and 402.1 eV represent N_{1s} ionization of the triazole nitrogens and the tertiary nitrogen, respectively. A weak peak at 404.1 eV indicates the presence of some residual azides nitrogen (Fig. S2).

The CV of the Hyd-ITO-rGO construct showed two reduction waves at 450 mV and -30 mV and two oxidation waves at 380 mV and 95 mV vs Ag/AgCl (Fig. 2**b**). The scan rate dependence of the CV current (Fig. S3a) shows that with the increasing of the scan rate the splitting between two waves increase. The current vs scan rate gives a linear curve (Fig. S3b) which confirms the catalyst is attached on the surface not in solution. Unfortunately these modified rGO surfaces are not amenable to prolonged electrolysis under acidic aqueous conditions (Fig. S10). Thus the Hyd-EPG construct which is stable is used for electrocatalytic HER investigations.



Scheme 2 Schematic diagram for the synthesis of the linkers with azide and amine at the terminal.



Scheme 3 Schematic presentation of covalent attachment for Fe-Fe H_2ase model complex (**A**) on the modified EPG.

Edge Plane Graphite (EPG) electrode surfaces were functionalized with complex **A** as well. The original procedure for EPG

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modifications developed by Saveant *et. al.* is implemented here with some modifications to construct the azide terminated modified EPG[29, 30] (Fig. S1). The azide terminated aromatic amine linkers are synthesized as shown in Scheme 2 and experimental details are provided in SI. The modified EPG electrode with a phenylene layer bearing aliphatic azide group (Scheme 3) is stable over a wide range of potential even under strong acidic conditions where these H_2ase mimic are known to work.[9] This procedure ensures the grafting of a maximum amount of azide moieties without totally passivating the surface.

Tethering of the complex **A** on the modified EPG surface (Hyd-EPG construct) was further achieved by following the same protocol as described for the Hyd-ITO-rGO construct (Scheme 3). The XPS data obtained (Fig. 3) on the resultant electrode confirm the covalent attachment of complex **A** on the modified surface. The two sharp peaks centred at 710.9 and 724.5 eV correspond to the ionization of the $2p_{1/2}$ and $2p_{3/2}$ levels of the Fe (I) centre respectively (Fig. 3**a**). The peak centred at 162.5 eV represent the ionization of 2p orbital of the thiolate sulphurs (Fig. 3**b**). A broad peak centred at 399.4 eV and a shoulder at 402.1 eV indicates the ionization of 1s orbital of the triazole nitrogen atoms and tertiary amine nitrogen atoms, respectively (Fig. 3**c**). The data does not show any N_{1s} ionization at ~ 404 eV suggesting absence of free azides upon completion of the click reaction. The ratio of area under the peaks for the triazole N_{1s} and tertiary N_{1s} is ~3:1, consistent with the stoichiometry of Hyd-EPG construct.

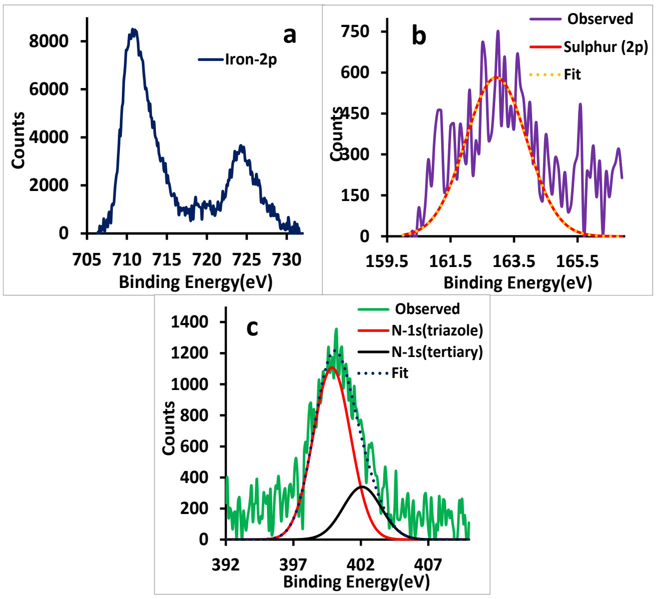

Fig. 3 X-ray photoelectron spectra of modified EPG electrode (Hyd-EPG construct). Fe 2p (**a**), S 2p (**b**), and N 1s (**c**) are shown here.

Cyclic Voltametry (CV) of Hyd-EPG construct yields weak and broad features. So an estimation of the amount of catalyst is difficult. Ethynyl ferrocene is covalently attached instead of complex **A** to the azide modified EPG electrode. The CV data of this construct shows the Fc/Fc⁺ process at 0.36 V vs Ag/AgCl in 1N $HClO_4$ (Fig. 4**b**). The area under the curve yields a coverage of 1.43 x10^{14} molecules/cm^2. This is two orders of magnitude higher than the value obtained using physiadsorbtion and clearly demonstrates the advantage of covalent attachment over physiadsorbtion.[4]

The electrocatalytic hydrogen production by the Hyd-EPG construct is investigated in degassed dilute H_2SO_4 solution using a rotating ring disc electrochemistry (RRDE) setup (Fig. 4**a**). The polarisation curve, when swept from positive to negative potentials, shows a large catalytic current (I_{cat}) with onset potential at -0.72 V vs Ag/AgCl (the modified EPG electrode only, green line). As the acid concentration is increased, the catalytic current density increases and the onset shifts to more positive potential (Fig. 4**c**). These results are consistent with our previous reports, where a similar type hydrogenase mimic was physiadsorbed on EPG electrodes.[4] This large catalytic response is confirmed to be due to HER *in situ* RRDE where a Pt ring encircles the EPG disk and is held at a constant potential (0.9 V) to re-oxidize the H_2 produced to H^+.[4] A constant rotation speed of 300 rpm is maintained to generate the hydrodynamic force due to which the hydrogen generated at the disk is diffused out to the Pt ring where it is detected. The blue line is (Fig. 4**a**) indicates the catalytic H_2 production on Hyd-EPG construct and the red line (Fig. 4**a**) indicates the oxidation of H_2 on the Pt ring establishing H^+ reduction at dilute acid concentrations. The H_2 generation is further confirmed by Gas Chromatography (GC).

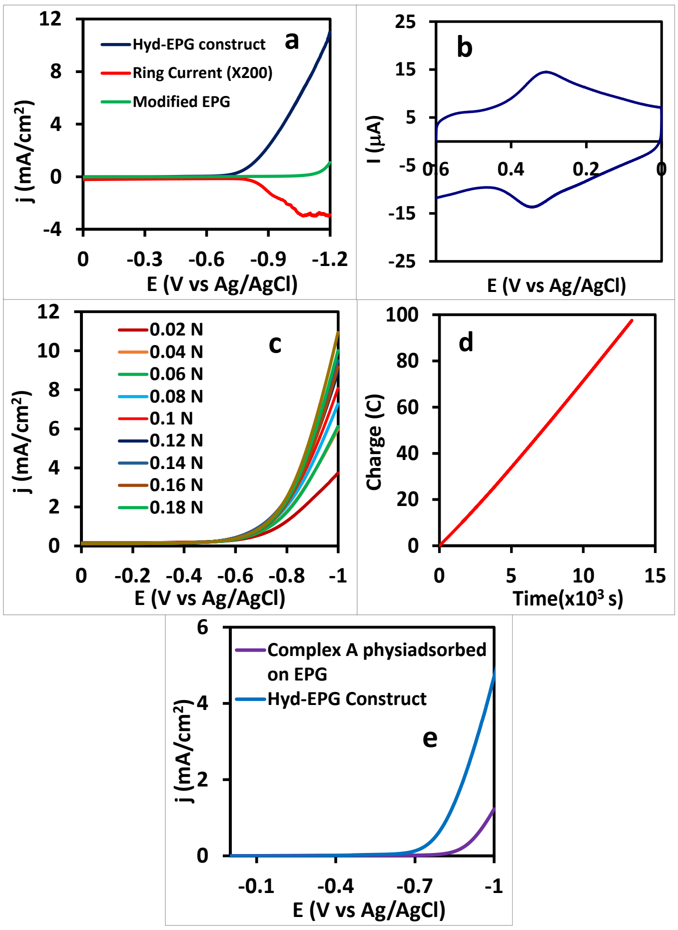

Fig. 4 (**a**) RRDE data of Hyd-EPG construct (blue line, indicating H_2 generation and the corresponding Pt-ring current red line, indicating H_2 detection); the ring held at a constant potential of 0.9 V in aqueous 0.1 N H_2SO_4 (**b**) CV of ethynyl ferrocene covalently attached to the electrode in 1 N $HClO_4$ at 100 mV/s using Pt as counter and Ag/AgCl (satd. KCl) as reference(**c**) LSV of Hyd-EPG construct for electrochemical hydrogen generation with increasing acid concentration(**d**) Controlled potential bulk electrolysis at −0.9 V vs Ag/AgCl in aqueous 0.20 N H_2SO_4 **(e)** LSV of Hyd-EPG construct(blue) and complex **A** physiadsorbed on EPG.

Bulk electrolysis of the Hyd-EPG construct in 0.20 N H_2SO_4 at -0.9 V shows steady consumption of charge at a constant rate indicating stability of the covalently attached catalyst under long term electrocatalytic conditions (Fig. 4**d**). The total charge dissipated during the process is 7.67 C over 1200 s and the amount of hydrogen gas collected is 0.8 mL through vertical

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displacement of water in an inverted burette. The Faradaic yield (FY) is thus calculated to be 90.7%. The head space gas was analysed in GC further confirming hydrogen production (Fig. S4). The advantage of covalent attachment is clear when the HER currents for the Hyd-EPG construct (Fig. 4**e** blue) is compared to that of complex **A** physiadsorbed (Fig. 4**e**, purple) on the EPG electrodes. The substantially enhanced HER current in the former is due to higher coverage attained due to covalent modification.

Conclusions

In conclusion a novel Fe-Fe H_2ase model having an ADT bridge and a terminal alkyne is synthesized and attached to graphite electrode via an azide group bearing linker grafted to the graphite electrode. The strategy for covalent attachment developed is modular and amenable to structural modification of the linker as well as the complex. Using this strategy complex **A** is attached to rGO as well as EPG surfaces. The EPG electrode bearing covalently attached Fe-Fe H_2ase model is found to retain it's HER activity and stable over several hours of electrolysis and no leaching of the catalyst is observed. The covalent attachment offers two orders of magnitude greater catalyst coverage without compromising the inherent catalytic properties of the catalyst.

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Notes

All the potentials mentioned in the manuscript are reported with respect to Ag/AgCl (sat. KCl) electrode. The Authors declares no conflict of interest. The modified complex **A** after clicking on to surface is denoted as "Hyd".

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