Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary information

Task-Specific functionalization of graphene for CO_2 conversion applications

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ESI 1: Proton exchange membrane (PEM) CO_2 conversion cell fabrication

The supported electrocatalysts are used without any further modification to construct the PEM cell. The construction of PEM CO_2 conversion cell is similar to that of conventional PEM fuel cell. The cell contains proton exchange membrane (Nafion 117®) electrolyte, catalyst layers, gas diffusion layers, anode and cathode reservoirs and current collectors. Here, catalyst coated carbon cloth as cathode (or anode)-gas diffusion layer- backing layer assembly. Stainless steel sheets associated with graphite plates are used as current collectors. Carved channels of 3 mm width on graphite function as cathode (or anode) reservoirs. The synthesized cathode electrocatalysts were dispersed in isopropanol by ultrasonic irradiation with 5 wt % Nafion® solution. The slurry was coated on carbon cloth (11.56 cm^2, SGL Germany), by simple brush coating technique. Anode also made by the similar method using commercially available Pt/carbon (Pt/C, 20 wt% Pt) catalyst. The Pt loading was maintained to be 0.5 mg cm^{-2} at anode and 1 mg cm^{-2} at cathode for all the experiments.

On the other hand, Nafion® 117 membranes were treated according to the standard procedure. At first, the membranes were treated in a 5 wt% H_2O_2 solution for an hour at 353 K and then washed with deionized (DI) water to remove traces of H_2O_2 from the surface. In the second step, the membranes were rinsed in hot deionized (DI) water (353 K) for an hour. Then the membranes were transferred to an 8 wt.% H_2SO_4 solution and treated for an hour at 353 K. The treated membranes were washed and stored in DI water before use. A thin layer of Nafion® was coated on the electrodes and dried before make the membrane-electrode assembly (MEA) in order to improve the contact between electrode and electrolyte. Treated Nafion® 117 membrane was sandwiched between the prepared anode and cathode at 403 K with 2 ton load for 4 min as shown in Fig. S1.

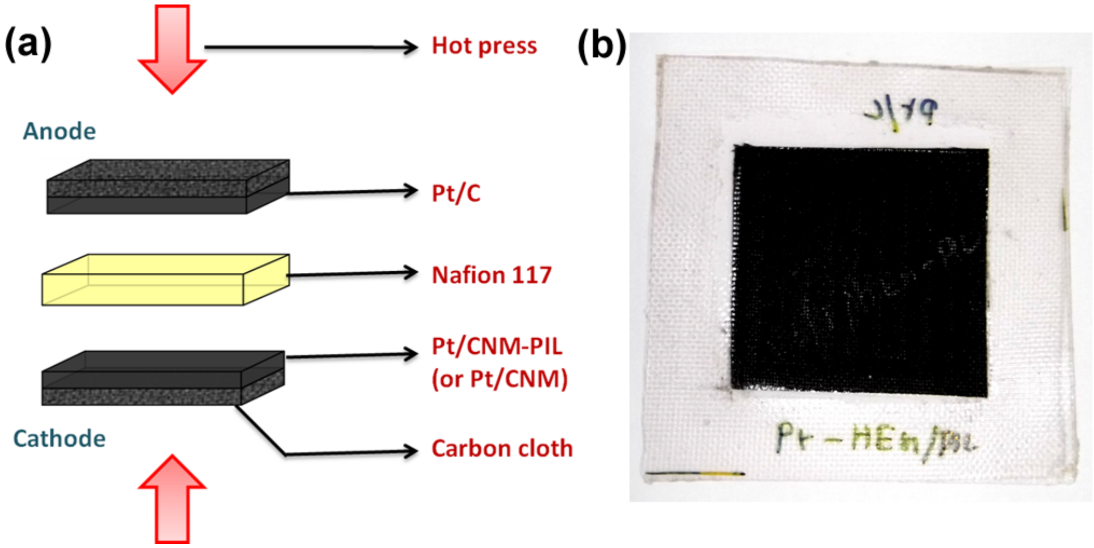

Fig S1. (a) Schematic diagram of membrane electrode assembly (MEA) fabrication and (b) Photograph of MEA (with Pt/HEG-PIL cathode catalyst).

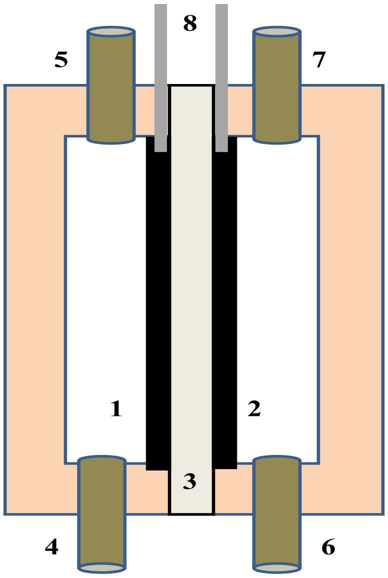

Fig S2. Schematic diagram of the electrochemical cell. Parts: 1. Cathode, 2. Anode, 3. Nafion electrolyte, 4. cathode reservoir inlet, 5. cathode reservoir outlet, 6. anode reservoir inlet, 7. anode reservoir outlet, 8. Current collectors.

The channels with 3 mm width and 5 mm depth were carved on 10 mm thick graphite plates by rotor milling machine, which are used as anode and cathode reservoirs. The graphite plates function as current collectors as well. Both ends of the channels are connected to SS tubes (3 mm outer diameter) using a water resistant glue, to function as reservoir inlet and outlet. Silicon sealant coated PTFE gaskets were used at both sides of the MEA in order to prevent leakage. This assembly was further equipped with anode and cathode reservoirs to the respective sides. The electrical connections were given by stainless steel plates, which were in contact with graphite reservoirs. Further this complete setup was tightly packed between two thick SS plates (Fig. S2) and dried over night at room temperature. The photograph of polymer electrolyte membrane CO_2 conversion cell is shown in Fig. S3.

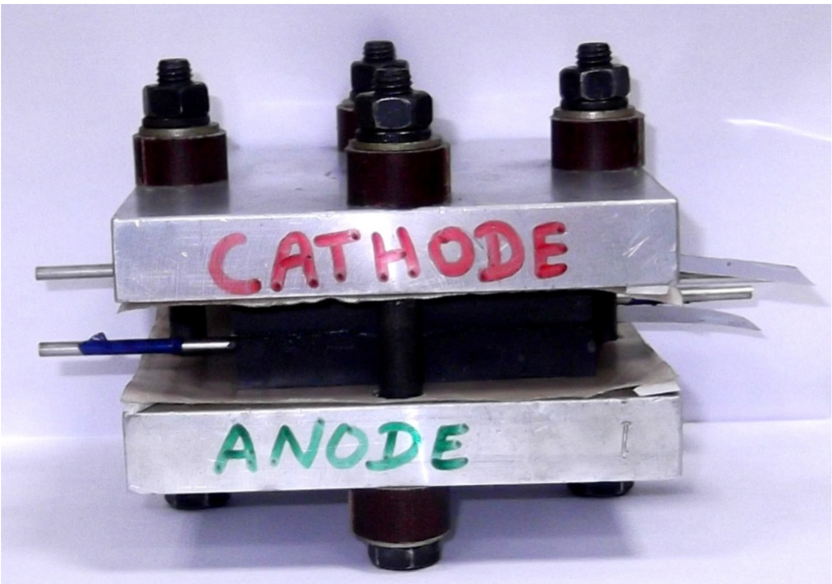

Fig S3. Photograph of polymer electrolyte membrane CO_2 conversion cell.

Since the volume of cathode and anode reservoirs are tiny (less than 5 cm^3) external tanks were connected to the respective reservoirs as shown in Fig. S4. Cathode reservoir and external tanks are connected through a peristaltic pump, which continuously circulates the catholyte. This arrangement continuously removes the products and feeds fresh reactants to the electrode. All these parts are connected by chemically inert flexible silicone tubes. Cathode reservoir, external tank and tubing arrangements are tightly sealed. The cathode external tank is equipped with septum-syringe needle arrangement to sample the cathode reservoir solution. The advantage of external tank and catholyte circulation arrangement are better realized in continuous flow mode. Photograph of the complete experimental setup is presented in Fig. S4.

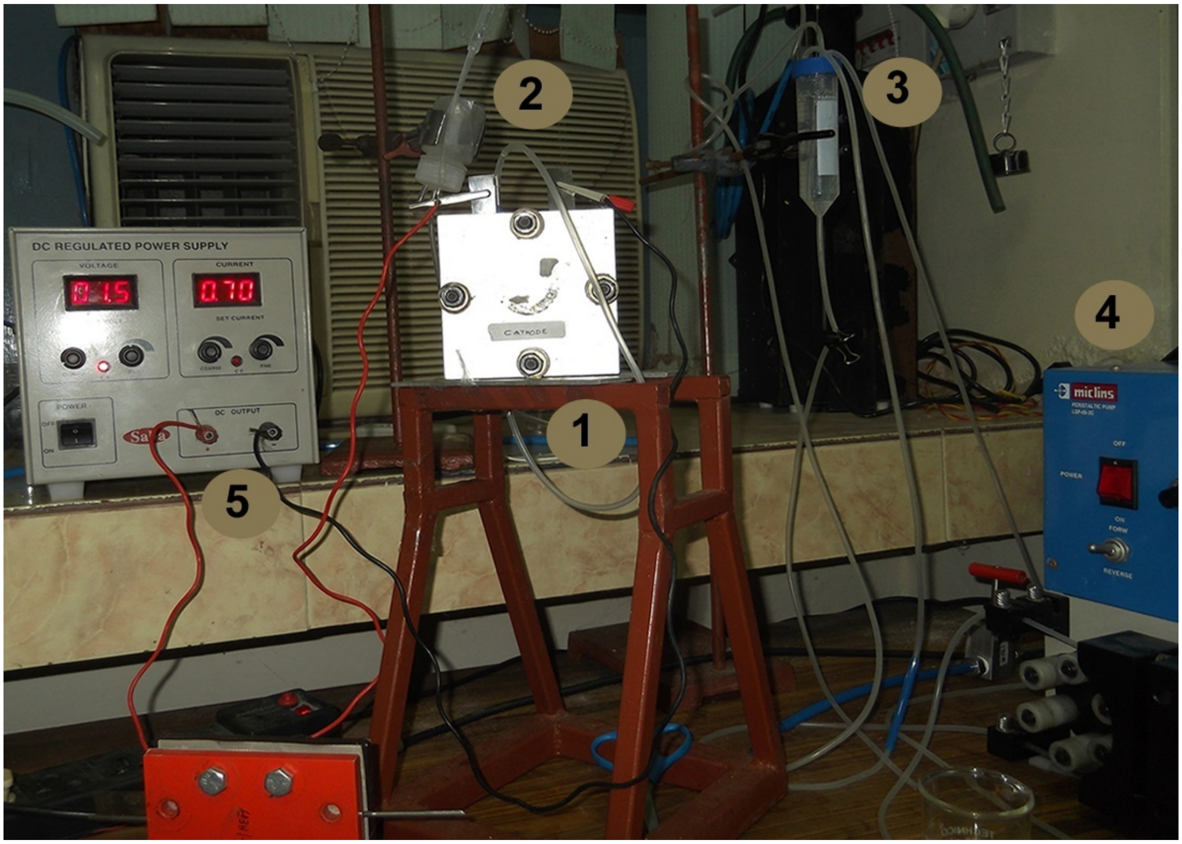

Fig S4. Photograph of complete experimental setup of PEM cell based CO_2 conversion. (1) PEM conversion cell, (2) Anode reservoir tank, (3) Cathode reservoir tank, (4) Peristaltic pump and (5) Power supply.

ESI 2: XRD pattern of HEG-PIL

It was expected to have a weak peak around 15 – 20 degree 2 theta value from possible tacticity, since PIL is a polymer. But, no significant signal has been observed. In general, bulk materials of long chains of polymers with small side chains show tacticity. In the present case, PIL forms a thin layer or small islands on the surface of graphene. In addition, the side chain of polymer (methylimidazolium) is very big in comparison with the polymeric part (vinyl).

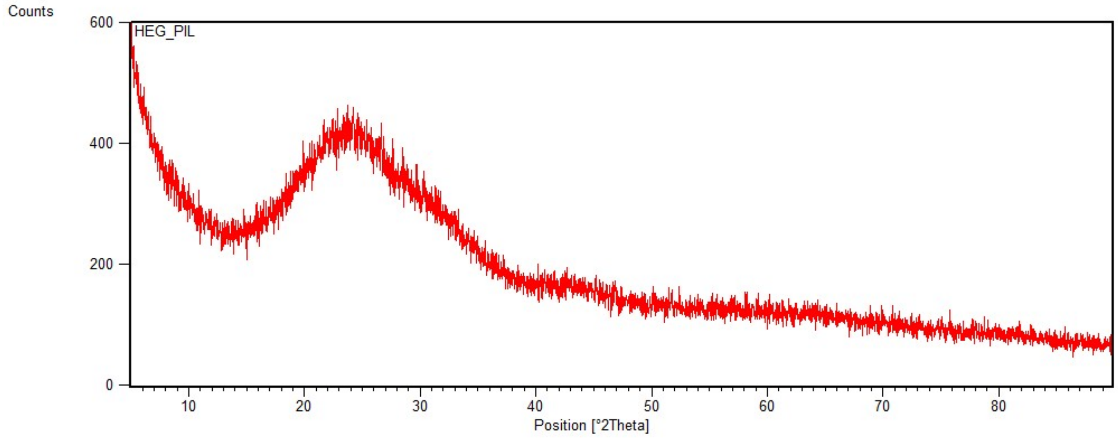

Fig. S5: XRD pattern of HEG-PIL

ESI 3: Calibration of spectrophotometer

The cathode reservoir samples were analyzed by UV-Vis spectrophotometer, which shows a peak with maxima at 230-240 nm and matches well with commercial formic acid (Fig. S5).[1] Hence, spectrophotometer was calibrated using commercial formic acid, in order to quantify the formic acid formation efficiency, by serial dilution method using the peak maxima at 230-240 nm. Here, CO_2 saturated DI water was used as reference.

The obtained absorption spectra were fitted to Gaussian function after baseline correction. The fitted spectra are given in Fig. S6 for future use of readers. The solution obeys Beer-Lambert law up to 64 mM. But, above 100 mM (measured at 128 mM) it deviated largely from the law. This can be attributed to the effect of subexcitation electrons of water molecules. As per literature, subexcitation electrons of water significantly influences at the molar concentrations of order of 100 mM.[2] The curve (Fig. S7) was obtained by straight line fit to calibration data, which shows R^2 value 0.993 and molar absorptivity (ε) of 1.22 L mol^{-1} cm^{-1} and is in good agreement with literature.[2]

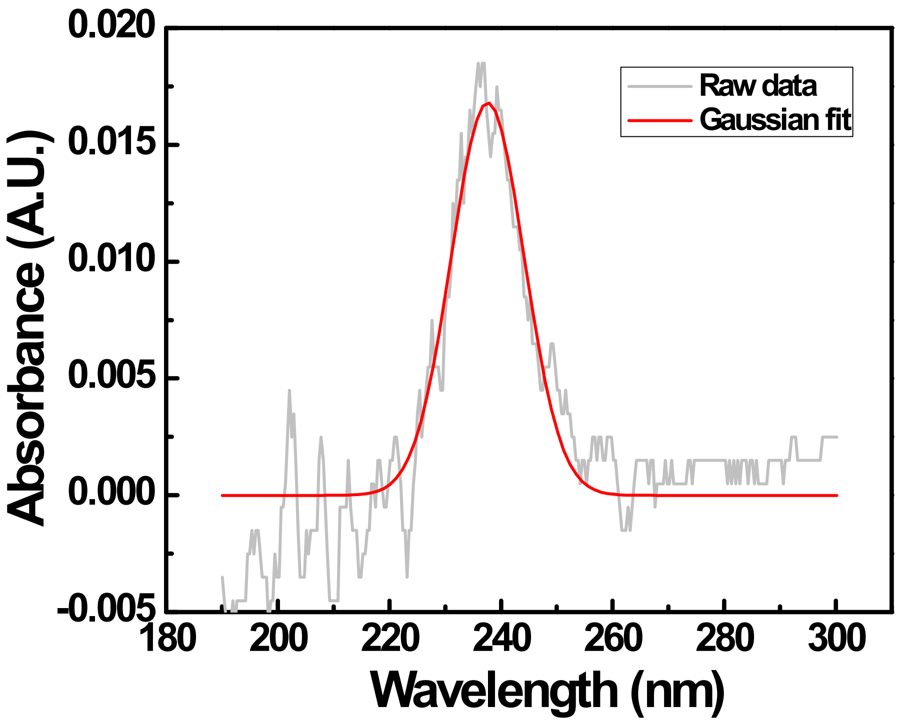

Fig S6. Typical optical absorption spectra of cathode reservoir solution (Recorded with Pt/HEG cathode in DF mode after 150 min reaction)

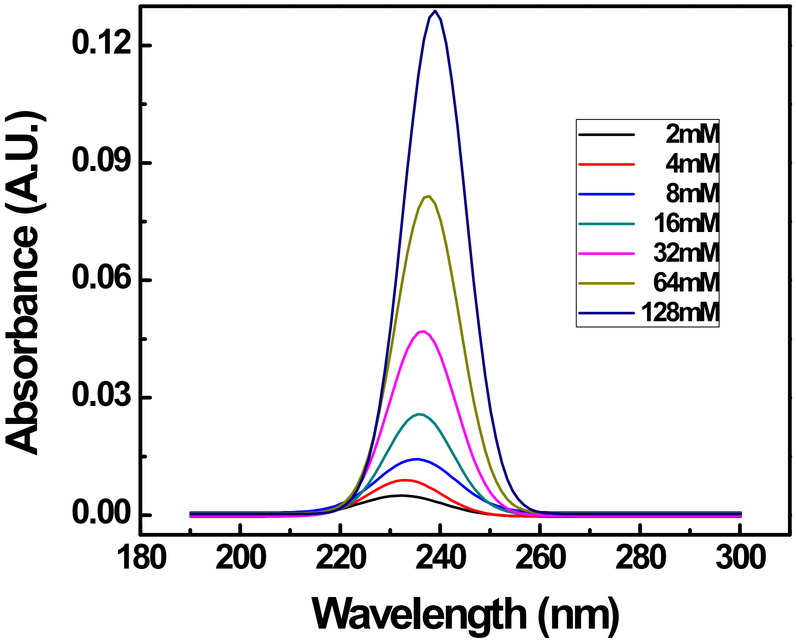

Fig S7. UV-Vis absorption spectra of formic acid with various concentrations in water.

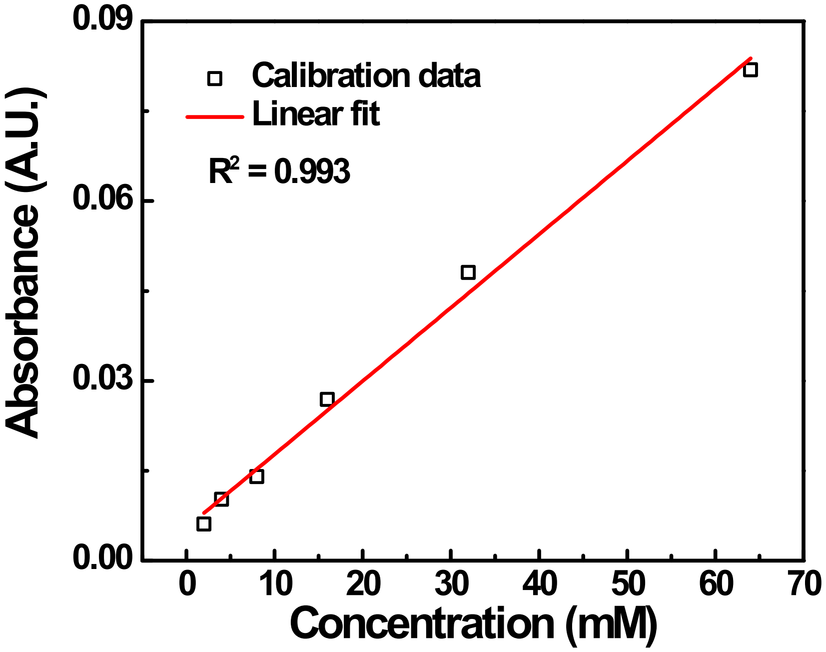

Fig S8. Formic acid optical absorbance vs. concentration calibration curve.

ESI 4: Formic acid formation rate (FFR) determination

The Pt/HEG and Pt/HEG-PIL cathode catalyst based cells were tested in both DF and CF modes. The cathode reservoir solution was samples at certain time interval and analyzed with spectrophotometer. A set of absorption spectra of these solutions were presented in Figs. S8, S9, S10 and S11. A gradual improvement in peak intensity was observed with time in all cases.

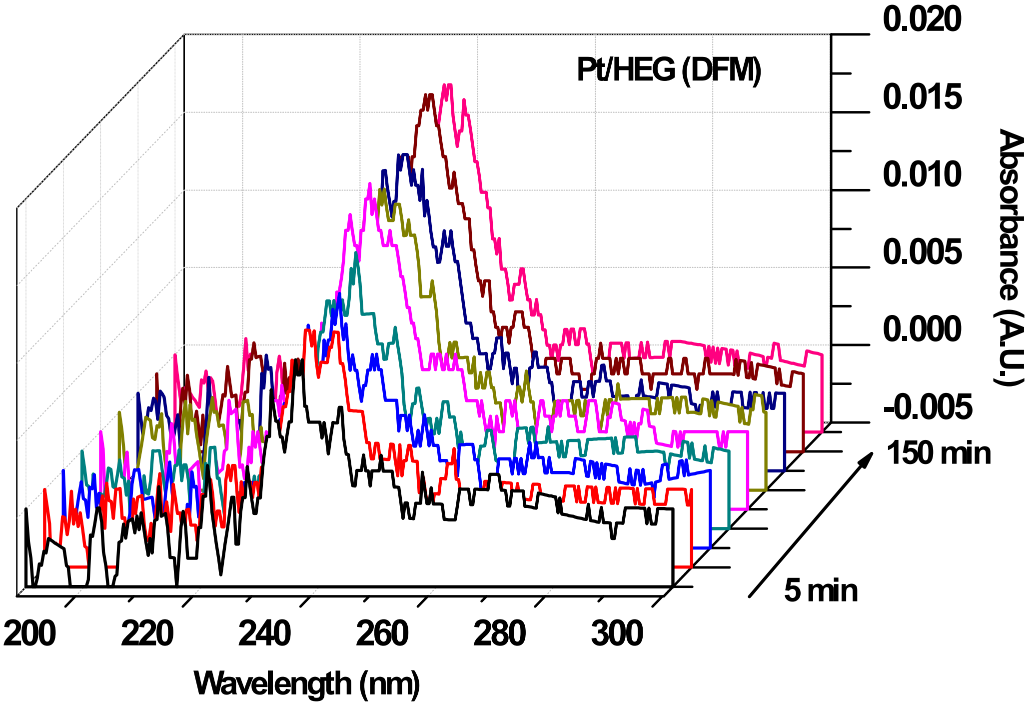

Fig S9. UV-Vis analysis data of cathode reservoir solution in DF mode with Pt/HEG cathode.

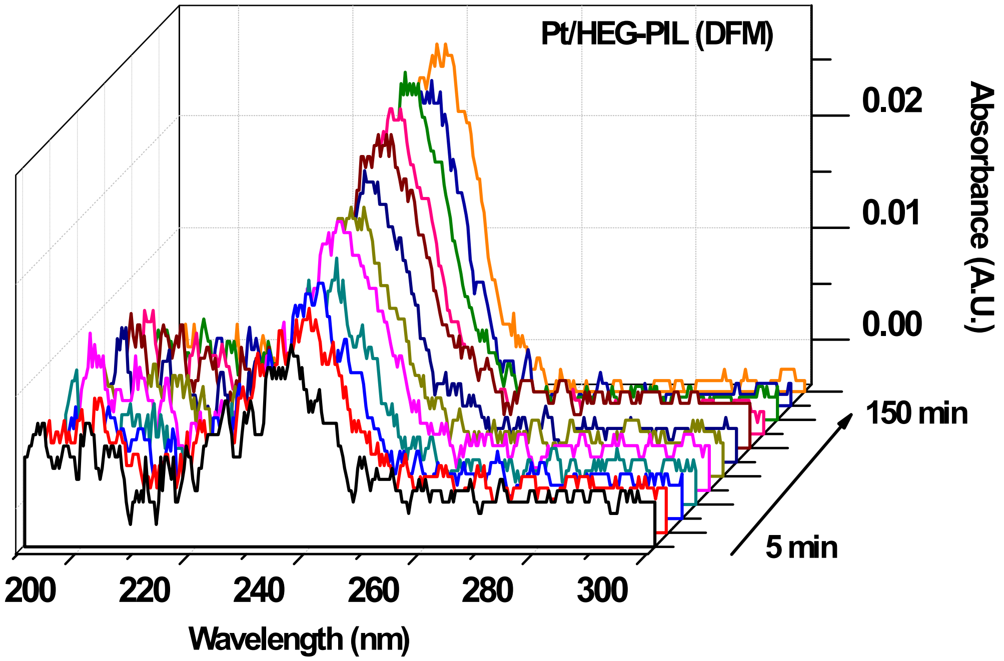

Fig S10. UV-Vis analysis data of cathode reservoir solution in DF mode with Pt/HEG-PIL cathode.

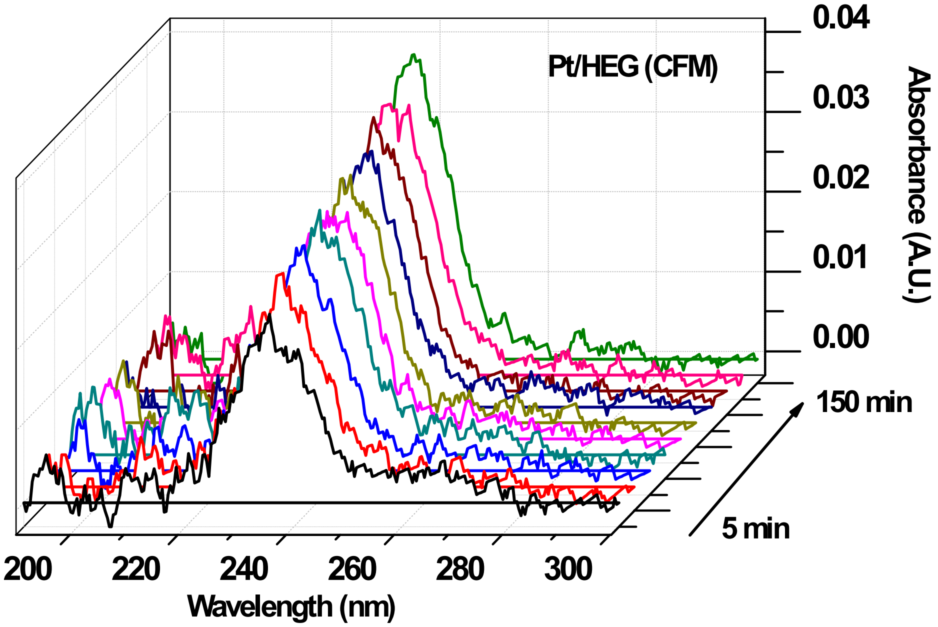

Fig S11. UV-Vis analysis data of cathode reservoir solution in CF mode with Pt/HEG cathode.

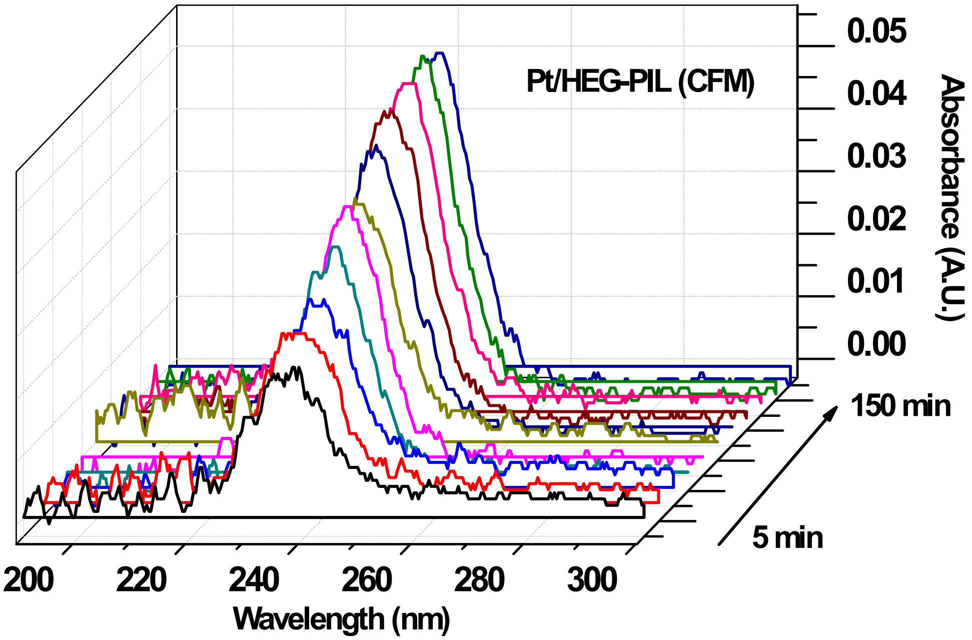

Fig S12. UV-Vis analysis data of cathode reservoir solution in CF mode with Pt/HEG-PIL cathode.

ESI 11: References

1. S. R. Narayanan, B. Haines, J. Soler and T. I. Valdez, *J. Electrochem. Soc.*, 2011, **158**, A167-A173.
2. E. J. Hart, *J. Am. Chem. Soc.*, 1959, **81**, 6085-6086.