Encapsulation of Multiple Enzymes in Metal-Organic Framework with Enhanced Electro-enzymatic Reduction of CO_2 to Methanol

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Table S1. Kinetic parameters of enzymes for different reaction[1]

Enzyme	**Reaction**	***Km* (mM)**	**V_{max} (mM min^{-1})**
Formate dehydrogenase	CO_2 → HCOOH	30-50	0.002
	HCOOH → CO_2	3.3	0.02
Formaldehyde dehydrogenase	HCOOH → HCHO	NA	NA
	HCHO → HCOOH	0.06	0.01
Alcohol dehydrogenase	HCHO → CH_3OH	17.5	0.3
	CH_3OH → HCHO	275	0.5×10^{-3}

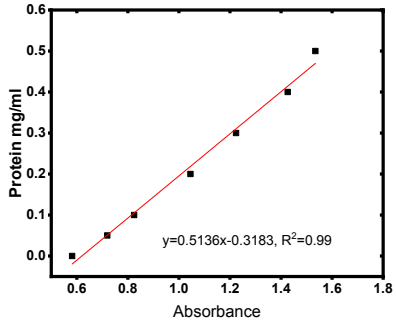

Figure S1. Standard calibration curve of protein in Tris-HCl buffer using Bradford assay method.

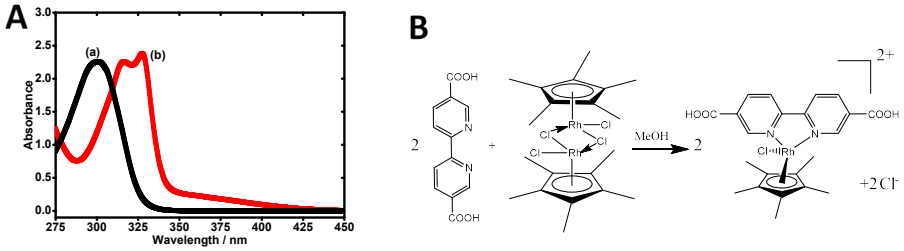

Figure S2. (A) UV-vis absorption spectra of (a) 2,2'-bipyridyl-5,5'-dicarboxylic acid and (b) complexation of carboxylic pyridine with $(RhCp^*Cl_2)_2$. (B) Corresponding illustration of the complexation process

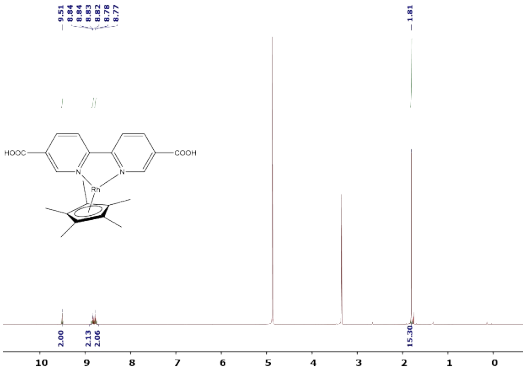

Figure S3. NMR of Rh complex Cp*Rh(2,2'-bipyridyl-5,5'-dicarboxylic acid)Cl_2 compound. ^{1}H NMR (600 MHz, methanol-d_4): δ= 9.51(s, 2H), 8.87-8.81(m, 2H), 8.78 (d,J=8.4 Hz, 2H), 1.81(s, 15H).

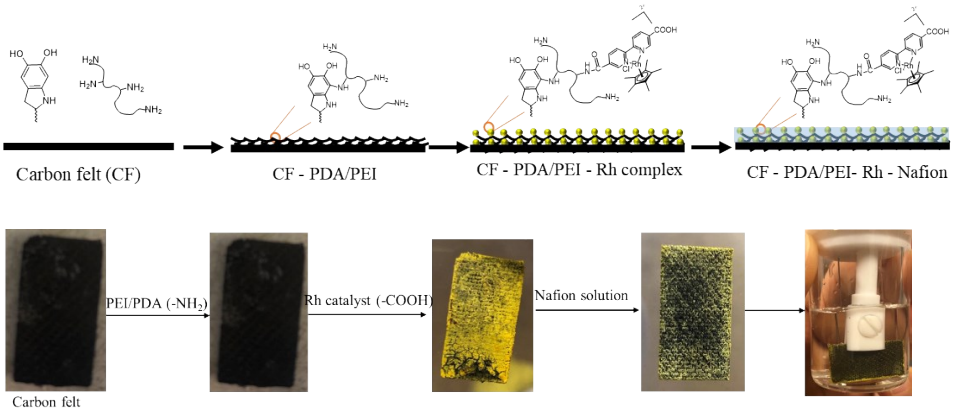

Figure S4 The fabrication process of the Rh complex-grafted electrode.

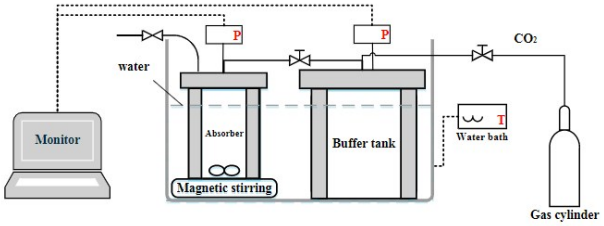

Figure S5. Schematic diagram of the CO_2 solubility apparatus[2]

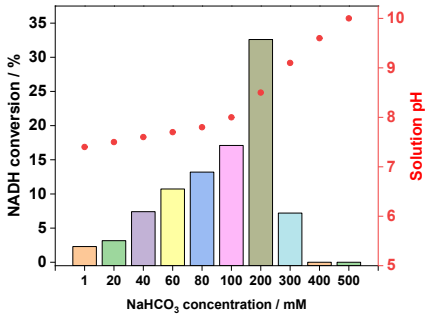

Figure S6. effect of $NaHCO_3$ concentration on NADH conversion.

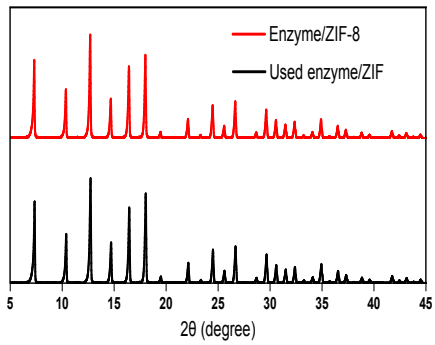

Figure S7. XRD patterns of enzymes/ZIF-8 composite and used enzymes/ZIF-8 composite in Tirs-HCl buffer.

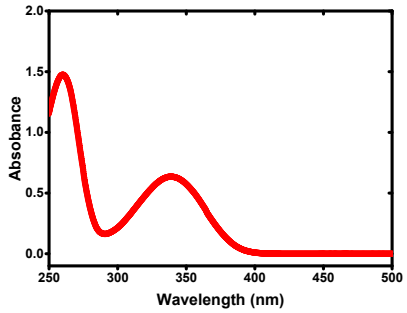

Figure S8. UV spectrum during reduction of NAD^+ to NADH.

1. J. Luo, A. S. Meyer, R. V. Mateiu and M. Pinelo, *New Biotechnology*, 2015, **32**, 319-327.

2. C. Y. Ma, S. Sarmad, J. P. Mikkola and X. Y. Ji, *Proceedings of the 9th International Conference on Applied Energy*, 2017, **142**, 3320-3325.