Supplementary Information (SI) for Sustainable Energy & Fuels.
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Supporting information

Cobalt Phthalocyanine-Ketjen Black Hybrid Electrocatalyst for Efficient and Stable Alkaline Water Splitting

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Materials

Benzylideneacetophenone, benzaldehyde, Benzene-1,2-diamine ($C_6H_8N_2$), 2,2-diphenylacetic acid ($C_{14}H_{12}O_2$), ammonium chloride, ammonium molybdate, anhydrous potassium carbonate, and HCl were purchase from Sigma Aldrich south korea. 5% Nafion solution, N, N'-dicyclohexylcarbodiimide, 2,3,4,6,7,8,9,10-Octahydropyrimido[1,2-a] azepine (DBU), 2-pentanol, 8- hydroxyquinoline, Oxolane, sodium sulfide, N, N'-dimethylformamide, methanol, ethanol was purchased from Merck, South korea. Electrodes were obtained from fuel cell store, south korea. 2, 10, 16, 24- tetrakis {4-((2-benzhydrylamino) phenyl) amino)-2-isocyanobenzonitrile} cobalt phthalocyanine (CoTBPc)were synthesized according to the literature [JEAC-hydrazine]. Methanol (CH_3OH), ethanol (C_2H_5OH), acetone (CH_3COCH_3), n-hexane (C_6H_{14}), tetrabutyl ammonium perchlorate (TBAP: $C_{16}H_{36}ClNO_4$) were purchased from Sigma-Aldrich and used as received.

Methods

The melting point of the sample was ascertained using a Sisco instrument (model no. 70818209). Elemental composition analysis of the synthesized materials was conducted with a Vario ELIII CHNS elemental analyzer. The electronic absorption spectrum of the sample was recorded using an Ocean Optics spectrometer equipped with a flame (FLAME-S-UV-VIS-ES, serial no. FLS04808) over the wavelength range of 300–800 nm. Fourier-transform infrared (FT-IR) spectroscopy was carried out on a Spectrum Two FT-IR spectrometer (PerkinElmer) with a resolution of 1 cm^{-1}, employing the KBr pellet method. The thermal stability of the phthalocyanine was evaluated using a STA 6000 Simultaneous Thermal Analyzer (PerkinElmer) within the temperature range of 20–1000 °C at a heating rate of 10 °C/min under an air flow of 30 mL/min. X-ray diffraction (XRD) analysis was carried out using a Bruker D8 Advance diffractometer. Scanning Electron Microscopy (SEM) images and Energy Dispersive X-ray Spectroscopy (EDX) data were acquired from a JSM-IT500LA (JEOL), X-ray Photoelectron Spectroscopy (XPS) analysis was performed on a SPECS MXPS system.

All electrochemical measurements were conducted using a Corrtest potentiostat electrochemical workstation CS350M with a conventional three-electrode setup. The Glassy carbon electrode (GCE) served as the working substrate, with Hg/HgO (3M KCl) as the reference electrode and a platinum wir as the counter electrode. The Nernst equation was employed to convert all measured potential values from the Hg/HgO electrode to RHE values, using equation 1S.

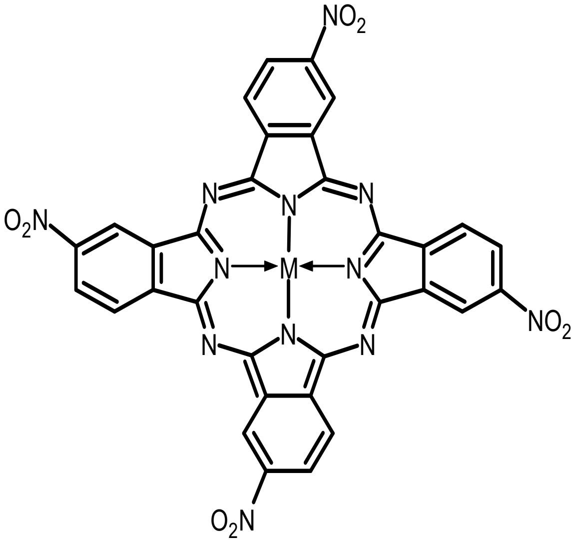
Modification of the electrode

The electrochemical measurements of modified electrodes were performed using Corrtest potentiostat electrochemical workstation CS350M. Electrochemical performance of CoTBPc, NiNPc, FeNPc and CoTBPc+KB was studied employing cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronopotentiometry, and electrochemical impedance in an electrochemical workstation with a typical two-electrode configuration.[1] A standard two-electrode configuration was set up to carry out all the electrochemical esperiments using Corrtest potentiostat electrochemical workstation CS350M. A glassy carbon electrode (GCE) was utilized as the working electrode, while a mercury/mercury oxide (Hg/HgO, 3M KCl) electrode served as the reference electrode, and a platinum wire functioned as the counter electrode. The Nernst equation was used to convert all recorded potential values from the Hg/HgO electrode to RHE values, as described by equation 1S.[2]

$$E_{RHE} = E_{Hg/HgO} + 0.098 + 0.059pH \text{ ---------------- Eqn.............. 1}$$

Synthesis of Cobalt (II) tetra nitro phthalocyanine (Co (II)NPc).[3,4]

Cobalt (II) tetra nitro phthalocyanine (Co (II)NPc) was prepared by making slight modifications to the procedure outlined for synthesizing metal phthalocyanines. A mixture of 0.5 g (0.0038508 mol) of Co (II)Cl2, 2.66 g (0.0153641 mol) 1,2-benzenedicarbonitrile, and 2-pentanol solvent (20 mL) with 4 drops of 2,3,4,6,7,8,9,10-Octahydropyrimido[1,2-a] azepine (DBU) was reflux for 28 hours by continuous stirring, maintaining a constant temperature of 135–138 °C.[5] The greenish-blue product was cooled and filtered off and was washed thoroughly with methanol,2 acetone and hexane. A yield of 96% Co (II)NPc was achieved and its theoretical molecular weight is 751.46 g mol^{-1}. The theoretical chemical composition ($C_{32}H_{12}N_{12}O_8Co$) is 51.78% C, 1.99% H, 23.03% N, 16.24% O, 6.96% Co.

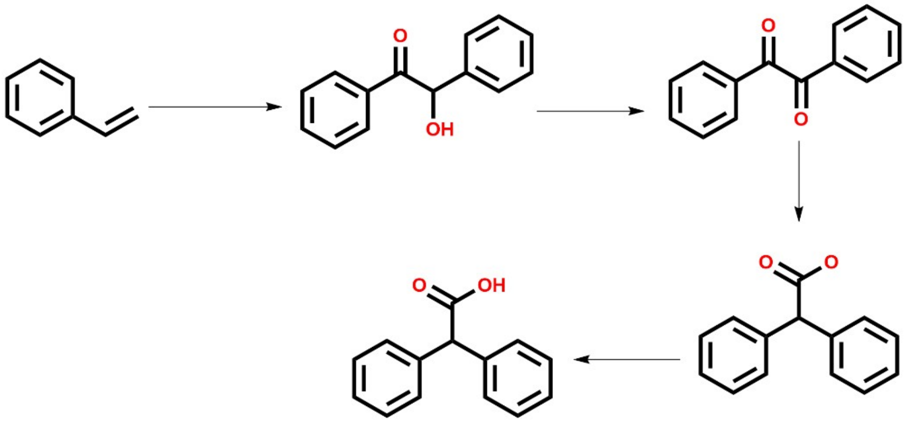


M=Co, Ni, Fe……etc.,

Scheme. SI1. General synthetic route for CoNPc.

***Synthesis of 2,2-diphenylacetic acid*[6]**

Begin with 1 g (0.009423 mole) of benzylideneacetophenone (chalcone) and mix it with 1.96 g (0.0094 mol) of benzaldehyde in ethanol as the solvent. Add a catalytic amount of NaOH (0.1 mol, 4.0 g) and stir the reaction mixture at room temperature for 12–24 hours to allow aldol condensation to occur, forming the β-hydroxy ketone intermediate. Upon completion, acidify the reaction mixture to neutralize the base and isolate the crude product by filtration. Dry and purify the chalcone by recrystallization. Next, subject the chalcone to oxidative cleavage using 1.48 g (0.009365 mol) of potassium permanganate in aqueous acidic medium (e.g., H_2SO_4) under cooling. After reaction completion, filter off the manganese dioxide and extract the diketone product using dichloromethane. Dry and concentrate the organic layer. Finally, heat the diketone under reflux with a catalytic amount of acid (e.g., HCl) to induce intramolecular cyclization, forming the hydroxy-substituted dihydroisobenzofuran. Recrystallize the final product from ethanol.[7] The overall mole ratio is 1:1:1 (benzylideneacetophenone: benzaldehyde: oxidant), with catalytic amounts of base and acid.



Scheme. SI2. General synthetic route for 2,2-diphenylacetic acid.

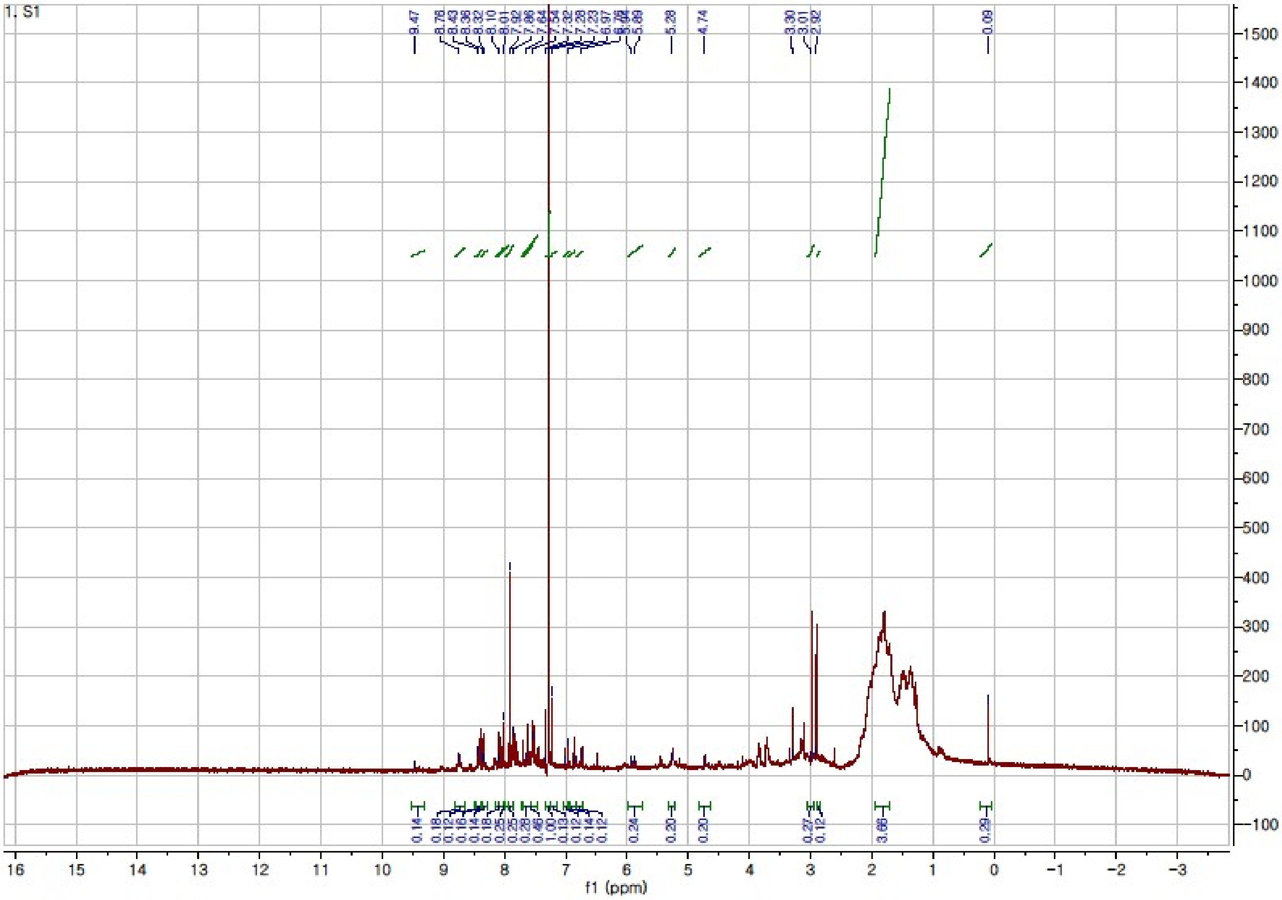


Figure SI1(a). H¹ NMR analysis Compound 3.

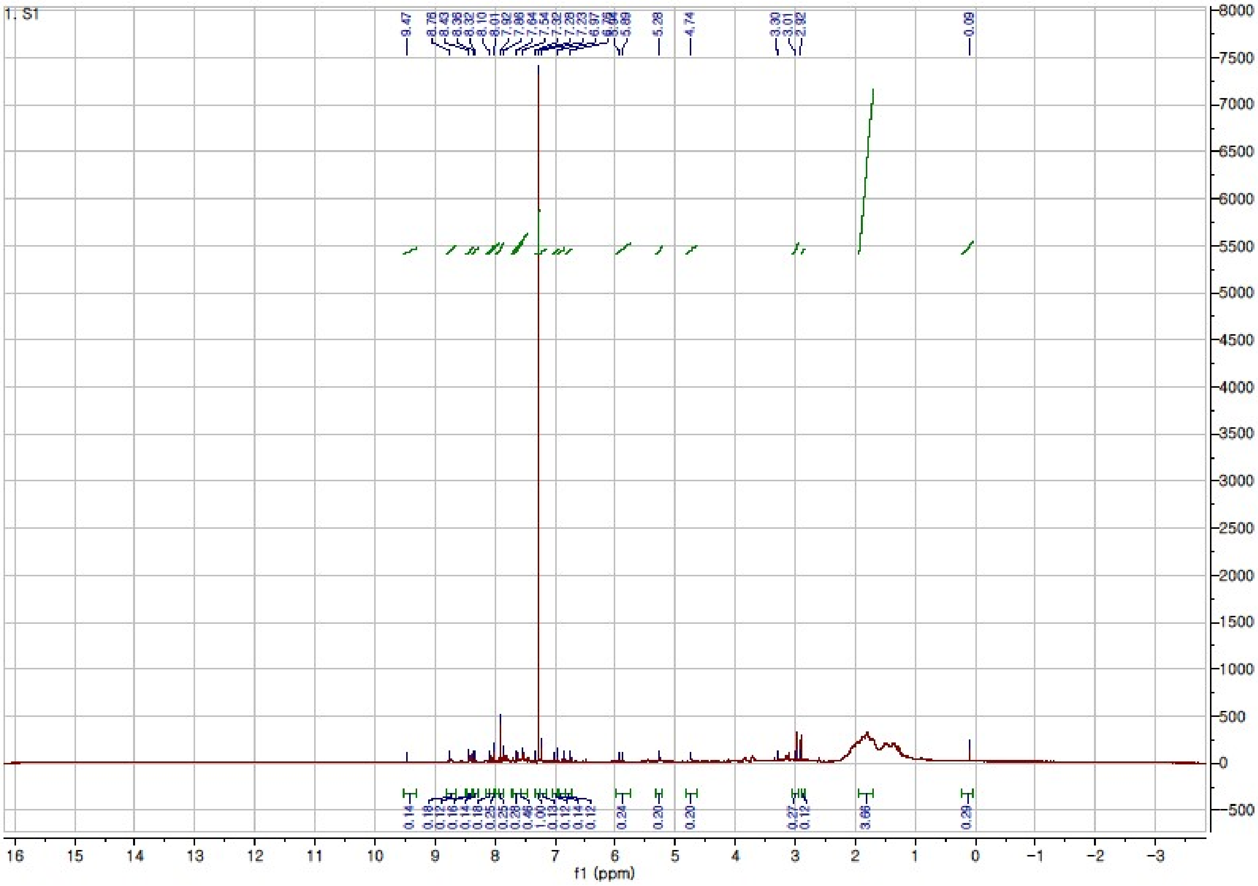


Figure SI1(b). H^1 NMR analysis Compound 3.

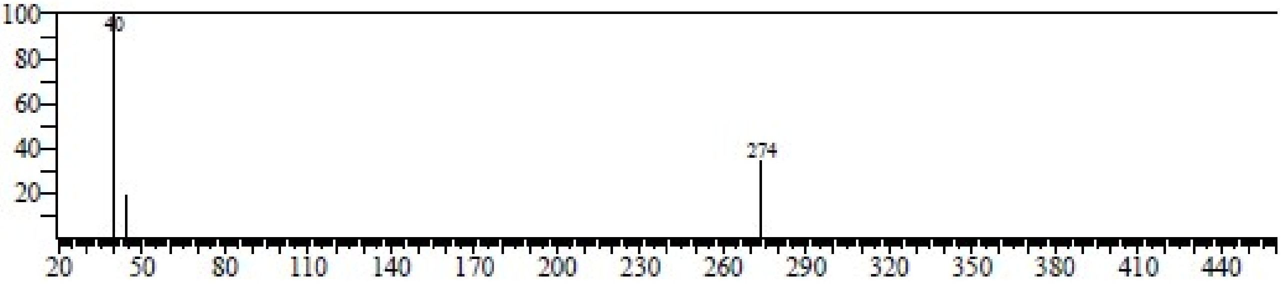


Figure SI1(c). Mass analysis Compound 3.

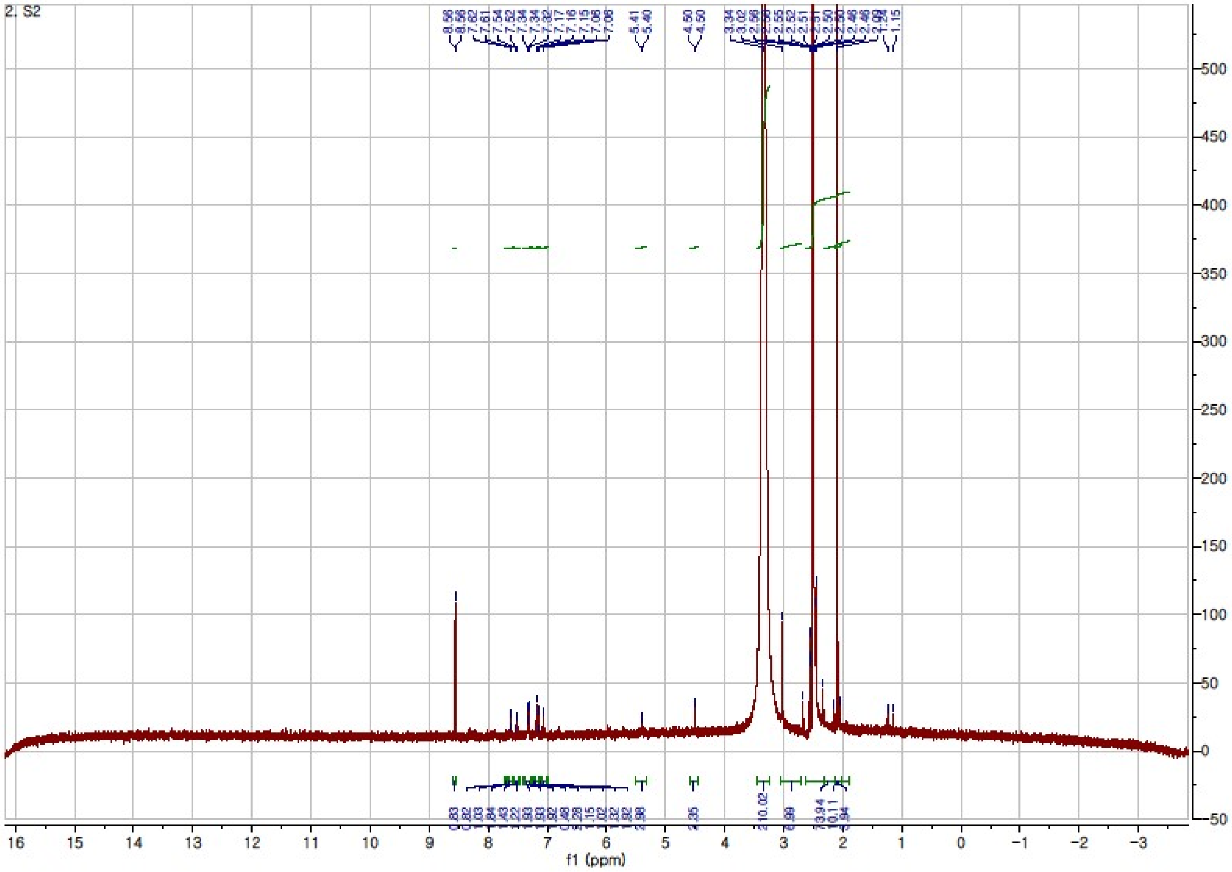


Figure SI2. H^1 NMR analysis Compound 5.

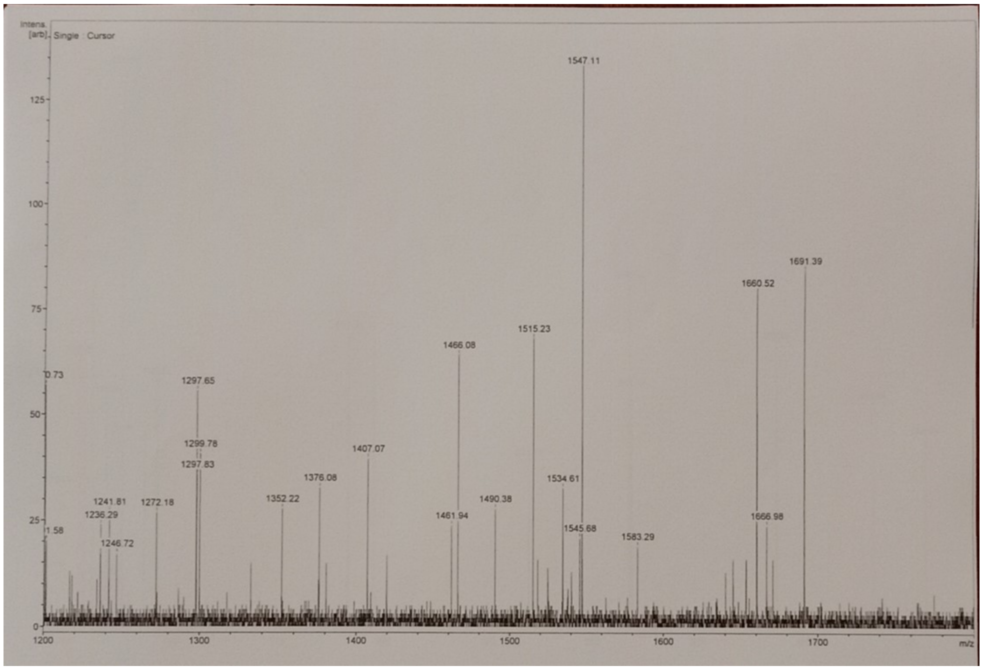


Figure SI3. Mass analysis Compound 6.

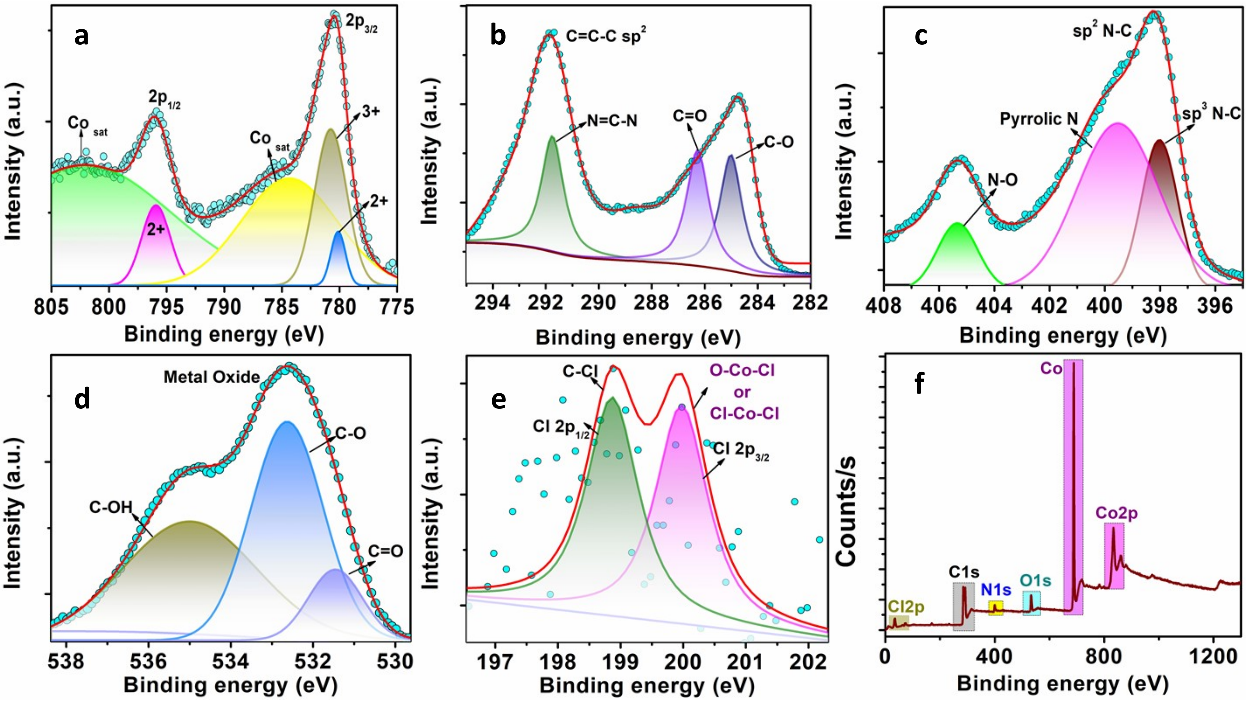


Figure SI4. XPS profiles Before stability of CoAPc+KB nanocomposite on glass substrate: **f)** survey scan, **a)** Co2p, **b)** C1s, **c)** N1s, **d)** O1s and **e)** Cl1s profiles and f) Survey scan of CoTBPc+KB.

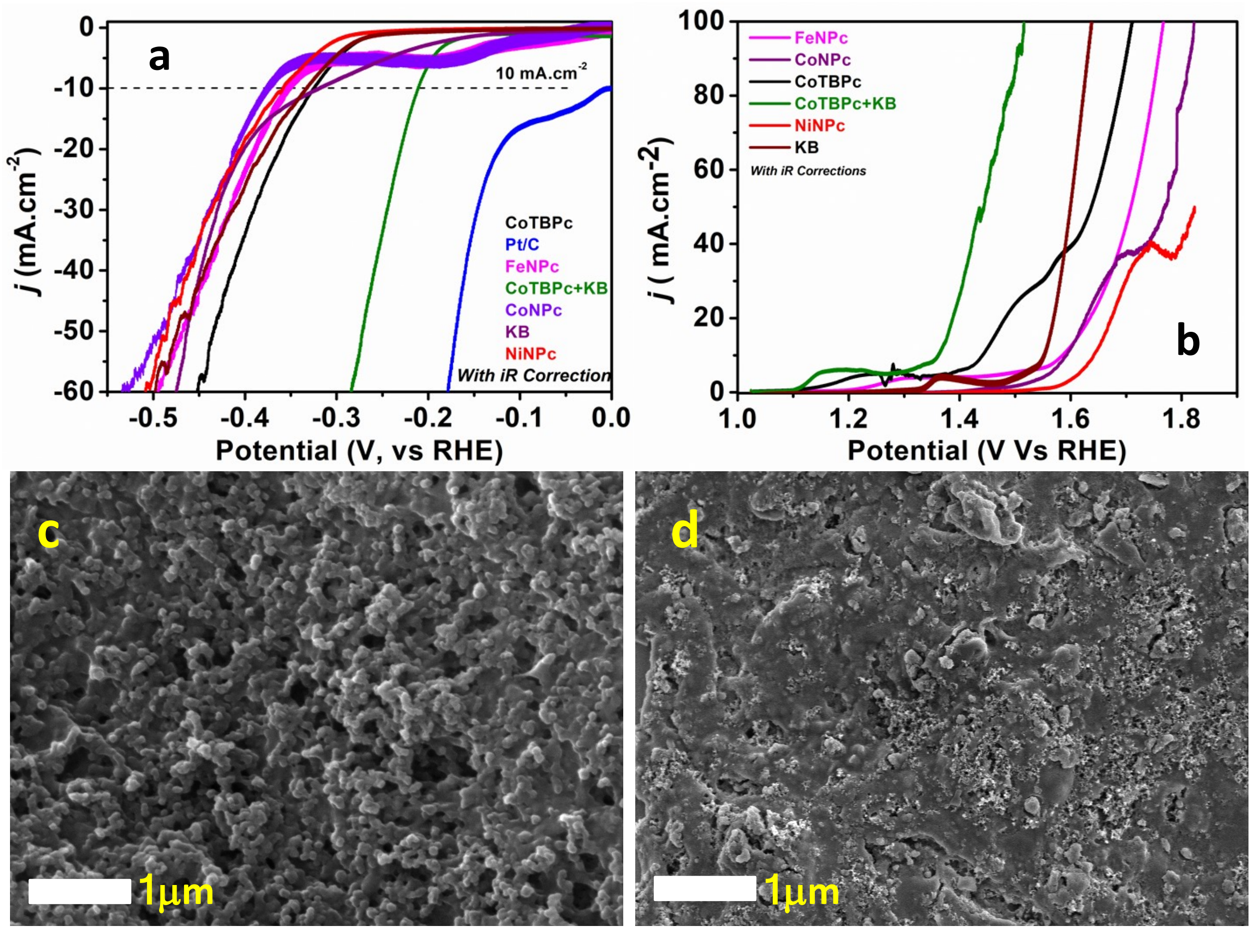


Figure SI5. a) LSV iR corrected polarization curves for a) HER for CoNPc, FeNPc, NiNPc, KB, CoTBPc, Pt/C and hybrid composite of CoTBPc+KB b) OER CoNPc, FeNPc, NiNPc, KB, CoTBPc and hybrid composite of CoTBPc+KB in a 1.0 M KOH electrolyte at scan rate of 5 mV s^{-2}. SEM Images of c) Before Stability and d) After Stability.

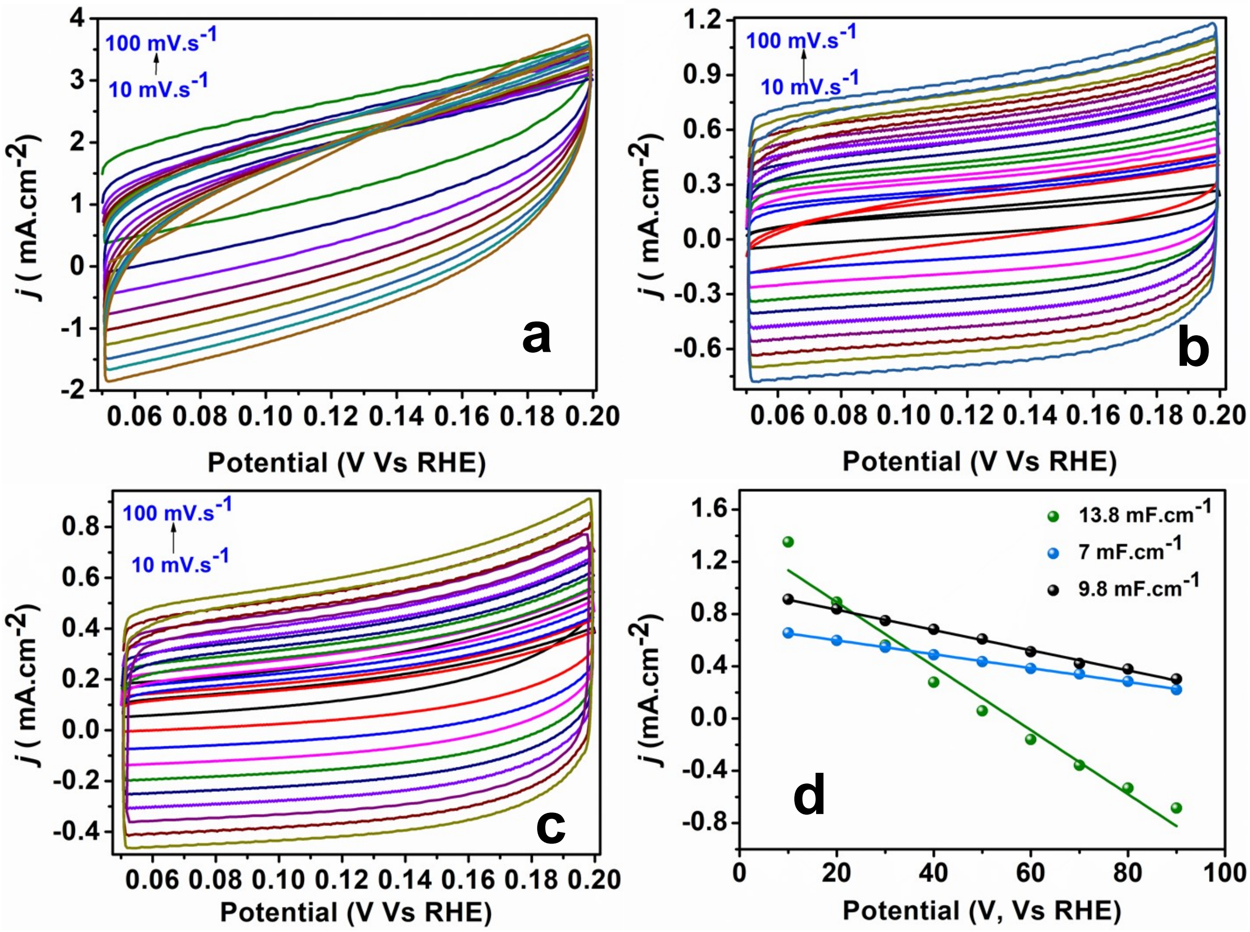


Figure SI6. Double layer capacitance of a) CoTBPc+KB/GCE, b) CoTBPc/GCE, c) Bare GCE and d) Corresponding linear plots of current density versus scan rate for the calculation of C_{dl} values.

Table S1: Comparison of HER and OER activities of CoTBPc+KB/GC (4mg:1mg) catalyst in basic media with catalysts reported in the literature.

Material	Overpotential (η) [mV]	Tafel (mV dec^{-1})	Electrolyte	Ref
CoLBr$_2$(HER)/CC NiLBr$_2$(OER)/CC	η_{10} =-256 η_{10} =376	155 86	1M KOH	8
Complexes 10/CC Complexes 10/RRDE	η_{10} =-375 η_{10} =-336	144 112	1M KOH 0.5 M H_2SO_4	9
ZIF-9-Fe3-Pyrol (OER)	η_{10} =320	99	0.1M KOH	10
ZIF-9(III)/Co LDH-15	η_{10} =297	81	1M KOH	11
Co–P/NC/CC (carbon cloth, ZIF-67/CC, and Co/NC/CC)	η_{10} =-171 η_{10} =360	52(HER) 62(OER)	1M KOH	12
MoS2/CoB–Se/CC	η_{10} =272 η_{10} =270	119 (HER) 86 (OER)	1M KOH	13
CoP@ZIF-8/pNF	η_{10} =77(HER) η_{10} =226(OER)	55.3 77.7	1MKOH	14
ZIF-67	η_{10} =72(HER) 329(OER)	65 107	1M KOH	15
b-ZIF-67/Mxene	η_{10} =0.170 (HER) 1.47 (OER)	69 74	0.5 M H_2SO_4 0.1M KOH	16
ZIF-67	η_{10} =1.49(OER)	62.1	1M KOH	17
Co–Fe-MOF	η_{10} =310 (OER)	53	1M KOH	18
ZIF–9+BCN+rGO/CC	η_{10} =-222 η_{10} =374	39 73	1M KOH	19
CoPc@rGO-MOF	η_{10} =98	56	1M KOH	20
1-Fe@CNT(HER) 1-Co@CNT(OER)	η_{10} =445(HER)	-	1M KOH	21
FCG-6/Ni-foam hybrid	η_{100}=313 (OER) η_{100}=263 (HER)	51.1 111.5	1M KOH	22
CoTBPc-KB	**η_{100}=313 (OER)** **η_{10}=229 (HER)**	**289** **42**	**1M KOH**	**This work**

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