Supporting Information

MOF Derived Co_3O_4@Co/NCNT Nanocomposite for Electrochemical Hydrogen Evolution, Flexible Zinc-Air Batteries and Overall Water Splitting

Tarandeep Singh,[a] Chayanika Das,[a] Neha Bothra,[b] Nivedita Sikdar,[a] Shubhajit Das,[b] Swapan K. Pati,[b] Tapas Kumar Maji[a]*

[a]Molecular Materials Lab, School of Advanced Materials (SAMat), Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bengaluru, 560064, India.

[b]Advanced Quantum Theory: Molecules to Materials Group, School of Advanced Materials (SAMat), Theoretical Science Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bengaluru, 560064, India.

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1. Physical Measurements

Powder X-ray diffraction of the sample was studied using Bruker D8 discover instrument by varying the 2θ from 10^o to 80^o. Raman spectrum was recorded using Jobin Yvon LabRam HR spectrometer with 632 nm He-Ne laser. Field emission scanning electron microscopy (FESEM) images were taken on Zeiss GeminiSEM 500 by dropcasting the dispersion of **Co_3O_4-@Co/NCNT** (in IPA) on a clean silicon wafer. The silicon wafer was placed under high vacuum with an accelerating voltage of 5kV. Transmission electron microscopy analysis was performed using JEOL JEM-3010 by dropcasting the dispersion onto a carbon coated copper grid and an accelerating voltage of 300 kV. Contact angle measurements were done on a home made setup with a high quality webcam.

2. Computational Details

Spin polarized density functional theory based calculations were performed using the GGA(Generalized gradient approximation) based Perdew−Burke−Ernzerhoff[1] exchange correlation functional as implemented in the Quantum Espresso 5.2.0 package.[2,3] Along with

Rappe-Rabe-Kaxirus-Joannopoulas ultrasoft pseudopotential[4] for valence electrons , the wave function kinetic energy cut-off of 30 Ry was considered. A rectangular supercell of carbon nanotube (CNT) containing 127 atoms of (20 x 20 x 17.2) Å was taken, which is periodic in z-direction only. 1 x 1 x 4 uniform k-point mesh was considered to sample the whole system and 1 x 1 x 12 k-point for the projected density of states (pDOS) calculations. The atoms were allowed to be relaxed fully under the convergence threshold of 10^{-4} eV on total energy and 10^{-3} eV on forces on each atom. The electronic adsorption energies at 0K temperature were obtained through the DFT calculations while the zero point energy correction (ZPE) and entropic effect at finite temperature (300K) were considered from the data of previous reported[5] paper on same class of systems.

3. Electrochemical Measurements

All the electrochemical measurements were done using Autolab PGSTAT-12 Potentiostat/Galvanostat connected with Metrohm RDE-2 rotor. HER experiments were done using rotating disc electrode (RDE) and various voltametery techniques. Glassy carbon rotating disc electrode was polished by rubbing it gently on the polishing cloth along with alumina powder of 0.05 um. This was then rinsed with copious amount of Milli Q water and was sonicated in Milli Q water for approximately 10 sec. The electrode was dried in open air for 1 hour and made ready for the coating. The catalytic ink was prepared by dispersing 1 mg of **Co_3O_4@Co/NCNT** in 98 μL of Milli Q water and 98 μL of isopropanol (IPA) along with 5 μL of Nafion solution (5wt%, Sigma- Aldrich). This was sonicated for an hour to make a uniform dispersion. 4 uL of this dispersion was dropcasted onto the clean glassy carbon electrode and dried in open air for about an hour. All the electrochemical measurements were done in three electrode system using Ag/AgCl (3M KCl) as the reference electrode; **Co_3O_4@Co/NCNT**

coated glassy carbon RDE as the working electrode and Pt coil as the counter electrode. 0.5 M H_2SO_4 was used as the electrolyte and was purged with Ar for 30 minutes to degass the electrolyte. For all the measurements, RDE was rotated at the speed of 1600 RPM to prevent the accumulation of hydrogen gas bubbles evolved onto the electrode surface. All the measurements were carried out at room temperature.

3.1 Zn-Air Battery Tests

All the zinc-air battery tests were carried out in two electrode configuration in a home made setup. The dispersion was made by sonicating 3 mg of the catalyst in 500 µL of IPA with 25 µL of Nafion (5%, Sigma Aldrich). The dispersion was coated onto the carbon cloth GDL having an effective area of 1.13 cm^2 such that the effective loading was equivalent to 1 mg/cm^2. Zinc foil was used as the anode and **Co_3O_4@Co/NCNT** coated carbon cloth as the gas diffusion layer and the cathode. For the rechargeable battery, 6 M KOH and 0.2 M zinc acetate was used as the electrolyte.

3.2 Wearable Zn-Air Battery

Wearable Zn-Air battery was fabricated by using carbon fiber cloth as flexible electrodes along with polyvinyl alcohol-polyethylene oxide (PVA-PEO) gel electrolyte as well as a separator. For the anode, electrochemical deposition of zinc was carried out in two electrode configuration by using carbon fiber cloth as the working electrode and high purity Zn foil as both counter and reference electrode. 1 M of $ZnSO_4.7H_2O$ and 1 M of KCl in Milli Q water was used as the electrolyte. Electrochemical deposition of zinc was performed by passing the current equivalent to -10 mA/cm^2 for 90 min. For the fabrication of cathode, above prepared dispersion of **Co_3O_4@Co/NCNT** was coated onto carbon fiber cloth such that the amount of loading is

equivalent to 1 mg/cm^2. PVA-PEO gel electrolyte was prepared by adding 1g of polyvinyl alcohol(PVA) and 0.1 g of polyethylene oxide(PEO) to 10 mL of water under stirring for 15 min followed by heating at 95 ^oC along with stirring. After a clear solution was obtained 1 mL of 18 M KOH was added to the hot solution and stirring was continued for another 30 min. The hot transparent solution was then poured into a petridish and was cooled down to -3 ^oC for 1 hour followed by 1 hour cooling at 0 ^oC. Then this was brought to room temperature. For the fabrication of wearable battery, PVA-PEO gel was sandwiched between the anode and the cathode.

4. Experimental Section

4.1 Materials

All the desired chemicals and solvents were purchased from Sigma-Aldrich and were used without any further purification. $ZnSO_4.7H_2O$ and KCl used for electrodeposition were purchased from SD Fine Chemicals and Merck & Co. respectively. Carbon cloth DURA-GDL-CC-400LP was used as a gas diffusion layer and was purchased from Sainergy Fuel Cell Pvt. Ltd.

4.2 Synthesis of Co_3O_4@Co/NCNT and characterization

Core-shell **Co_3O_4@Co/NCNT** was synthesized according to the known procedure.[6] In brief, MOF $\{[Co(bpe)_2(N(CN)_2)].(N(CN)_2).5(H_2O)\}_n$ was synthesized by making a solution of $Co(NO_3)_2.6H_2O$ (291.03 mg) and $Na(N(CN)_2)$ (106.8 mg) in 15 mL of distilled water. Another solution of 1,2-bis(4-pyridyl)ethane (bpe) (220 mg) was mixed in 5 mL of ethanol. Then, bpe solution was added to the aqueous dicyanamide and $Co(NO_3)_2.6H_2O$ solution and stirred for 20 min. The pink precipitates formed were filtered and washed with copious amount of water ethanol mixture. The obtained MOF (800 mg) was carbonized in alumina boat under H_2/Ar (5%

H_2 in 95 % Ar) flow. Temperature was raised to 800 ^oC at the rate of 5 ^oC min^{-1} and the temperature was maintained for 4 hours. The sample was cooled to room temperature. For the formation of Co_3O_4 shell, the carbonized sample was calcined in air at 250 ^oC (rate of heating is 5 ^oC min^{-1}) for 2 hours.

4.2.1 PXRD

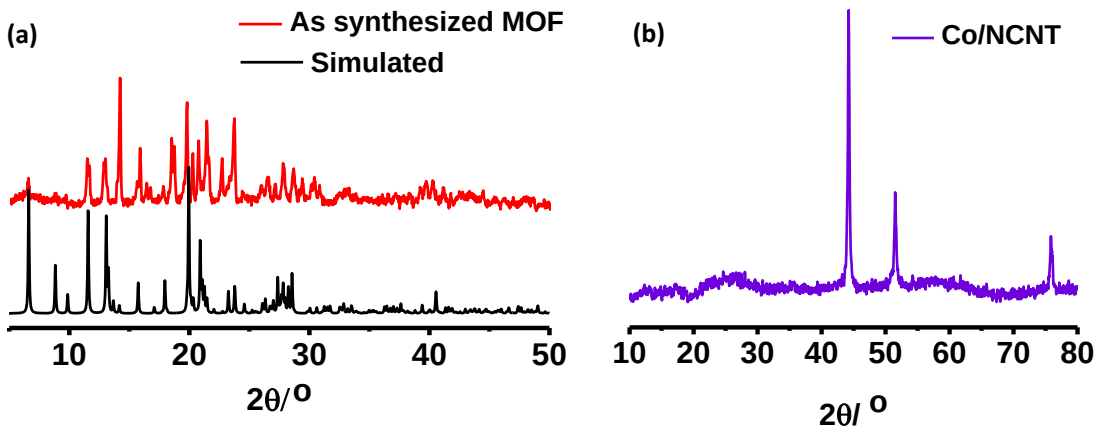

Fig. S1 (a) PXRD of $\{[Co(bpe)_2(N(CN)_2)].(N(CN)_2).(5H_2O)\}_n$ [**CoMOF-1**]; (b) PXRD of **Co/NCNT**.

4.2.2 TEM

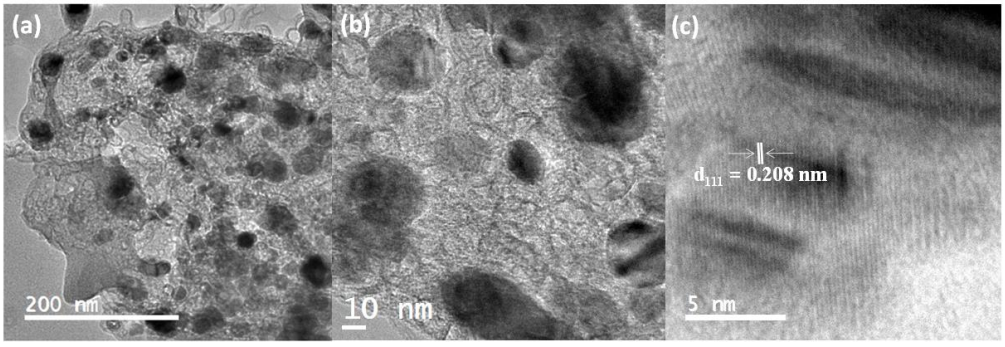

Fig. S2 (a) TEM images of **Co/NCNT**; (b) Enlarged image showing the core Co in NCNT (c) HRTEM image of Co in **Co/NCNT** showing lattice spacing of Co.

5. Electrochemical and Computational Results

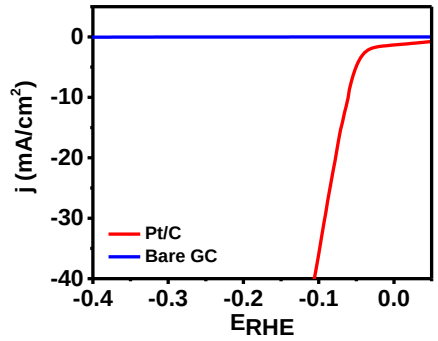

Fig. S3(a) LSV of Pt/C and Bare GC.

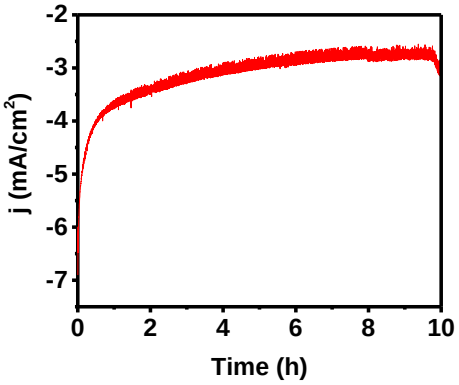

Fig. S3(b) Figure showing the chronoamperometrey curve for HER.

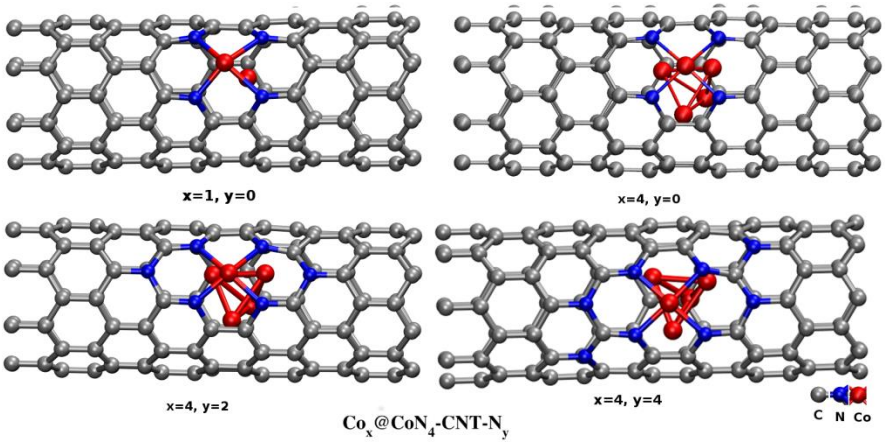

Fig. S3(c) Systems considered: $Co@CoN_4$-CNT, $Co_4@CoN_4$-CNT, $Co_4@CoN_4$-CNT-N_2, $Co_4@CoN_4$-CNT-N_4.

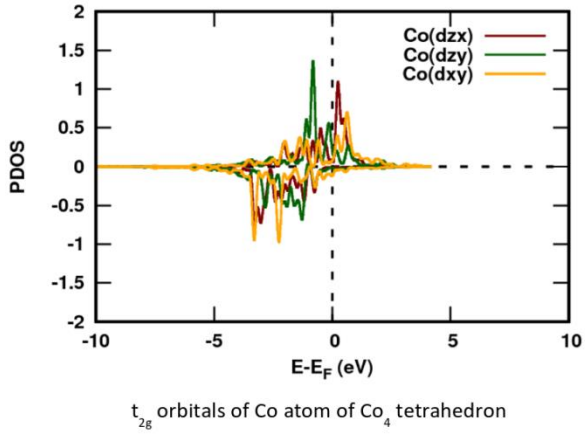

Fig. S4 The pDOS plot of Co atom of Co_4 tetrahedral cluster.

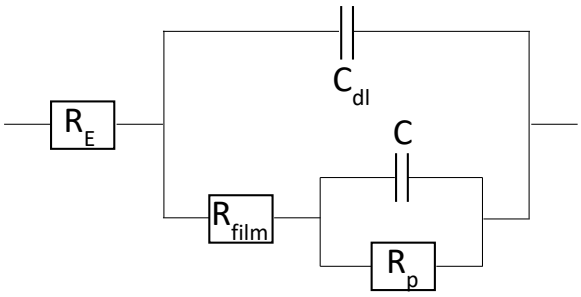

Fig. S5 Equivalent Circuit diagram as obtained from EIS.

6. Contact angle measurement

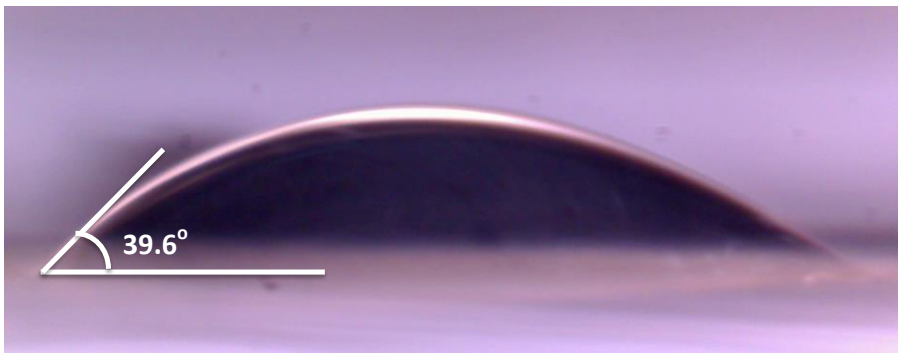

Fig. S6: Contact angle of water droplet on **Co_3O_4@Co/NCNT** surface.

7. Zinc-air battery

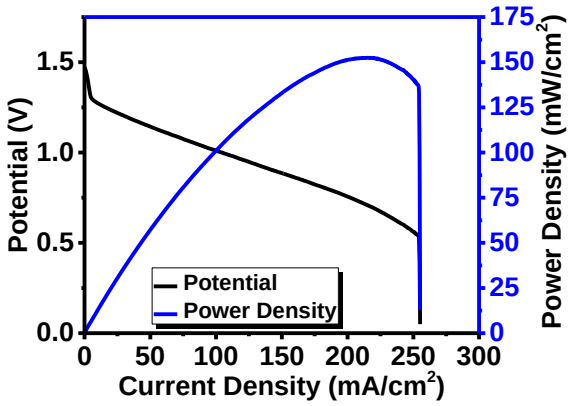

Fig. S7 Power Density curve of Pt/C.

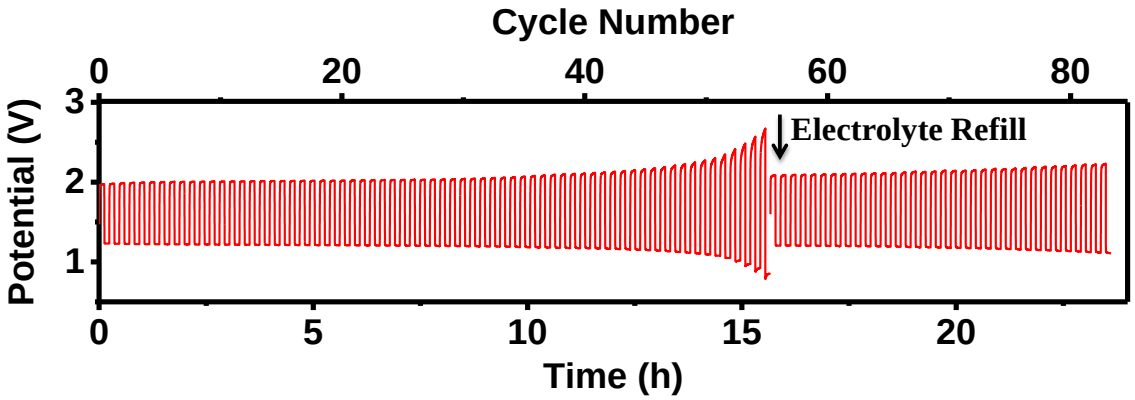

Fig. S8 Galvanostatic charge-discharge at 5mA/cm^2.

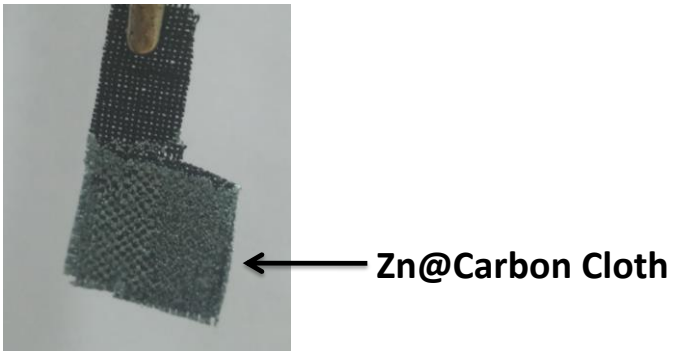

Fig. S9 Optical image showing the electrochemically deposited Zinc on the carbon cloth.

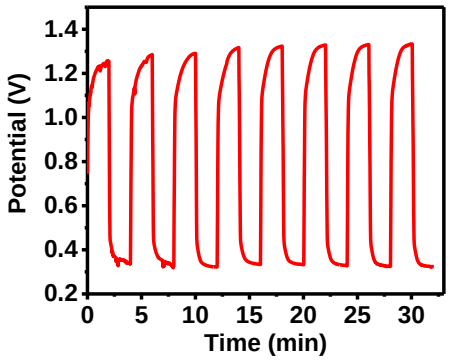

Fig. S10 Charge Discharge curves after making holes in the battery.

Table S1: Comparison of HER results of **Co_3O_4@Co/NCNT** with the the MOF derived electrocatalysts reported in literature.

Electrocatalyst	Overpotential (@10mA/cm^2) (mV)	Tafel Slope (mV/dec)	Exchange Current Density	Experimental Condition	Ref.
Py-ZIF	260	84	-	0.5 M H_2SO_4	*ChemSusChem* **2018**, 11, 3473
mC-Mo-850	173	55	0.0514 mA/cm^2	1 M KOH	*Adv. Funct. Mater*. **2019**, 29, 1807419
Co@NCNT/rGO	87	52	0.96mA/cm^2	0.5 M H_2SO_4	*Adv. Mater*. **2018**, 30, 1802011
Co/N-Carbon	103	-	-	1 M KOH	*ACS Sustainable Chem. Eng*. **2017**, 5, 7, 5646
MoS_2/NCNH-800-50	185	57	-	0.5 M H_2SO_4	*ACS Sustainable Chem. Eng*. **2017**, 5, 11, 10240
HCUST-100	234	80	0.011 mA/cm^2	0.5 M H_2SO_4	*Chem. Commun*., **2018**,54, 1964
Co_9S_8/NC@MoS_2	117	68.8	0.73 mV/cm^2	0.5 M H_2SO_4	*ACS Appl. Mater. Interfaces* **2017**, 9, 34, 28394
MOF derived Ni NPs	61	71	-	1 M KOH	*J. Mater. Chem. A*, **2015**,3, 16435
Core-shell Co_3O_4@Co/NCNT	171	121	1.035 mA/cm^2	0.5 M H_2SO_4	This Work

Table S2: Comparison of ORR, OER and Zn-air battery results with the reported literature results.

Catalyst	ORR onset (V)	OER at 10 mA/cm^2	Loading for battery (mg/cm^2)	OCP (V)	Peak Power Density (mW/cm^2)	Specific Capacity (mAh/g)	Anode in fZAB	Ref.
Co-N,B-CSs	0.89	1.66	0.5	1.43	100.4	-	Zn Foil	*ACS Nano* **2018**, 12, 1894
Co-N-CNTs	0.97	1.69	1	-	101	-	Zn Foil	*Adv. Funct. Mater.* **2018**, 28, 1705048
$NiCo_2O_4$@NiMn LDH core–shell array	-	1.48	2	1.4	160.8	675@20 mA/cm^2 722@ 5mA/cm^2	Zn Foil	*J. Mater. Chem. A*, **2018**,6, 10243
N-doped-CNT	0.925	1.49	-	1.47	190	623.4	Zn Foil	*Nano Energy* **2017**, 37, 98
$NiCo_2O_4$@N-OCNT	0.93	1.5	0.58	1.4	50	-	Zn Wire (Wire shaped battery)	*Small* **2018**, 14, 1803409
Atomic layer thin Co_3O_4	-	-	-	-	-	-	Zn deposited on cotton yarn	*Small* **2018**, 14, 1702987
CoNi-MOF/rGO	0.88	1.54	0.6	1.37	97	711	NA	*ACS Appl. Mater. Interfaces* **2019**, 11, 17, 15662
S,N-co-doped bamboo carbons (SNBC-12)	0.85 ($E_{1/2}$)	-	4	1.5	156	-	NA	*ACS Catal.* **2019**, 9, 3389
Co_3O_4@Co/NCNT	0.9	1.61	1	~1.4	135	891		**This Work**

8. References

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