

## Supporting Information

### **CoOx electro-catalysts anchored on nitrogen-doped carbon nanotubes for the oxygen evolution reaction**

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## 1. Experimental Section

**1.1. Materials:** Carbon nanotube (CNT) powder, nitric acid (HNO<sub>3</sub>), potassium hydroxide (KOH), polyvinylpyrrolidone (PVP, Mw = 40000) were procured from Sigma-Aldrich. Ethanol (EtOH) was purchased from Thomas Baker. Nitrogen (N<sub>2</sub>) and Ammonia (NH<sub>3</sub>) gas cylinders were purchased from Japanese local vendor. All the chemicals were used as such without any further purification.

**1.2. Preparation of conducting carbon support (fCNT, NCNT):** The cobalt oxide supported CNTs (fCNT, NCNT) was prepared by chemical treatment method. NCNT was prepared by thermal heating of pristine CNT under ammonia environment at 900 °C where, CNT (200 mg) was placed in a tubular furnace quartz tube line was initially heated under N<sub>2</sub> atm. till the temperature was reached to 800 °C with the heating rate of 5 °C min<sup>-1</sup>. Once after maintaining the temperature at 800 °C, a continuous controlled flow of NH<sub>3</sub> gas was maintained at 5 slpm was subjected to the preheated tubular furnace with increased temperature of 900 °C maintaining the constant temperature for 3h. Finally, N-doped CNT sample was recovered after reaching the furnace to room temperature and named as NCNT.

Similarly, for the preparation of functionalized CNT (fCNT), 200 mg of pristine CNT was dispersed well in conc. HNO<sub>3</sub> (400 mL) by stirring followed by sonication for 30 min. The above dispersed CNT solution was subjected to reflux at the temperature of 80 °C for 24h. with continuous stirring. After the completion of oxidation reaction, the oxidized CNT solution was filtered and dried at 60 °C before employing for the preparation of CoOx supported catalysts.

**1.3. Synthesis of CoOx supported catalysts:** A 50 mg of NCNT was dispersed in ethanol:water (3:2) mixture (40 mL) and kept for stirring for 12 h to get a uniform solution. To the above solution PVP (0.16 g) and Co(NO<sub>3</sub>)<sub>2</sub> (1.744 g) was added with continuous stirring followed by the addition of KOH solution to maintain pH of the solution to 13. The well mixed solution was transferred to Teflon lined stainless steel (SS) autoclave (50 mL) and kept in oven at 180 °C for 12 h. During the mixing process of NCNT, PVP and Co(NO<sub>3</sub>)<sub>2</sub>, the Co<sup>2+</sup> ions were supposed to be interacted with the negatively charged doped-N which helps in an effective interaction between the catalytic active sites (CoOx) and conducting support whereas the PVP controls the size of CoOx nanoparticles. The effective interaction between doped-N and Co<sup>2+</sup> ions during the synthesis process prevents the CoOx nanoparticles agglomeration results in uniform distribution during the nucleation and growth of nanoparticles. After the completion of reaction, the resultant solution was filtered and washed well with copious amount of water and ethanol mixture and dried at 60 °C. The resulting catalyst powder was termed as Co@NCNT. Also, for the comparison of the role of carbon support functionalization vs. N-doping in pristine CNT, the catalysts (Co@fCNT, Co@CNT) was prepared under similar conditions as mentioned above by employing respective CNTs instead of NCNT.

**1.4. Characterization techniques:** For the transmission electron microscopy (TEM) analysis, samples were prepared by dispersing 1 mg of powdered catalyst sample in 5 mL isopropyl alcohol (IPA). The dispersed catalyst sample was sonicated for 30 min. to get well separated graphene layers with uniform distribution in the IPA. After getting the well dispersed solution, 5 µl of the solution with catalyst was drop coated on a 200 mesh Cu grid. Finally, after properly drying the catalyst coated copper grid was used for

the TEM analysis. An FEI, TECNAI G2 F20 instrument operated at an accelerated voltage of 200 kV (Cs = 0.6 mm, resolution 1.7 Å) was used for the TEM imaging purposes. A TA-550 instrument was employed for the thermogravimetric analysis (TGA) using oxygen environment with the temperature ramping from room temperature to 900 °C at the rate of 5 °C min<sup>-1</sup>. The powder X-ray diffraction (PXRD) analysis of the prepared powder samples was carried out on a PANalytical instrument using Cu-K<sub>α</sub> radiation ( $\lambda = 1.54 \text{ \AA}$ ) at a scanning rate of 5° min<sup>-1</sup> in 2 $\theta$  range of 10 - 80°. The X-ray photoelectron spectroscopy (XPS) analysis of the samples was carried out by using a commercial XPS apparatus (JPS 9010 TR, JEOL Ltd. X-ray source MgK<sub>α</sub>, 1253.6 Ev, pass energy 20 eV, uncertainty of binding energy: 0.05 eV). The CasaXPS software was used for the XPS data analysis. The Raman spectroscopic analysis was performed by using an HR 800 Raman spectrometer (Jobin Yvon, Horiba, France) equipped with 632 nm red laser (NRS 1500 W).

**1.5. Working electrode preparation and electrochemical characterization:** For the electrochemical analysis, the working electrode was prepared by coating the known amount of catalyst slurry maintaining the loading of catalysts on the polished glassy carbon electrode. To make the catalysts slurry, 5mg of the catalyst powder was dispersed in 1 mL of Isopropyl alcohol (IPA): water (H<sub>2</sub>O) mixture (3:2) with the addition of 40  $\mu\text{L}$  of Nafion<sup>®</sup> solution (5%). The resulting mixture was ultrasonicated for 30 min. for making the homogeneous solution. Before coating the catalysts, the glassy carbon electrode (GCE) was polished with 0.05 and 0.30  $\mu\text{m}$  alumina slurries and washed properly with water and ethanol. To the polished GCE, 20  $\mu\text{L}$  of the prepared catalysts slurry was coated and dried at room temperature (the active catalyst loading was maintained to  $\sim 0.5 \text{ mg cm}^{-2}$ ). For the electrochemical investigation of the electrochemical properties of catalysts, a Metrohm Autolab Potentiostat-Galvanostat (PGSTAT302N) was used. A conventional 3-electrode test cell with reference electrode (RHE), counter electrode (platinum wire) and working electrode (catalyst coated GCE) was employed for the cyclic voltammetry (CV), linear sweep voltammetry (LSV). The obtained current was normalized with the electrode geometrical area to get the current density.

**1.6. Hg/HgO reference electrode calibration and conversion to RHE:** The Hg/HgO electrode calibration was performed in the similar way as reported previously (Singh et. al. DOI: 10.1002/admi.201600532) in which 3-electrode system with Hg/HgO as the reference electrode, a platinum as the working electrode and a graphite rod as the counter electrode was used. Hydrogen saturated 1M KOH solution was used as the electrolyte for the electrochemical reaction. With the mentioned set-up LSV was recorded at a scan rate of 0.5 mV/s. The observed zero current potential (0.918 V during the LSV measurement was taken as the thermodynamic potential for the hydrogen electrode reactions. Hence, the Hg/HgO electrode potential was converted to RHE by using the below equation.

$$E \text{ (RHE)} = E \text{ (Hg/HgO)} + 0.918 \text{ V}$$

## 2. Experimental Results:

### 2.1. C 1s and O 1s XPS spectra

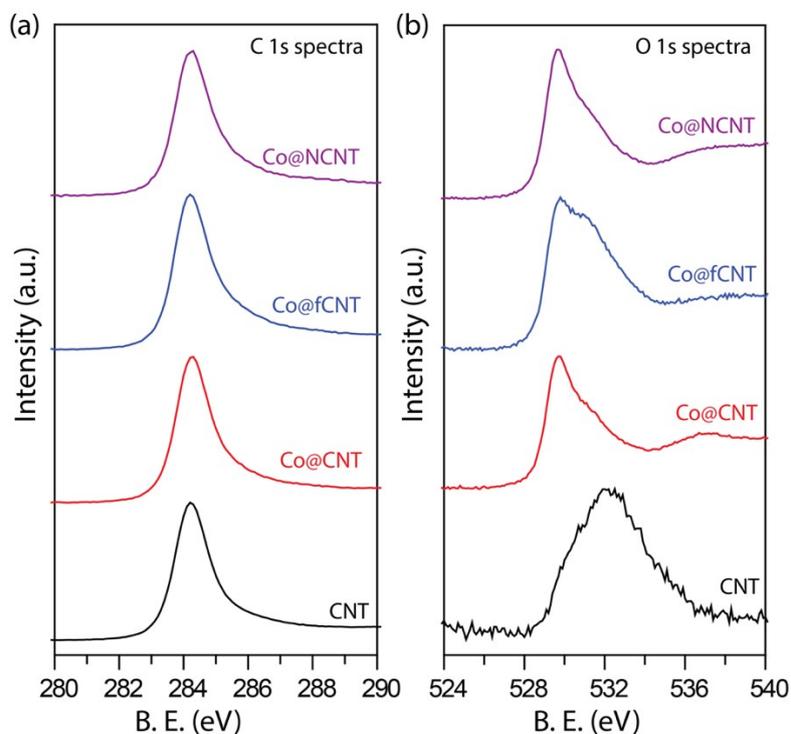
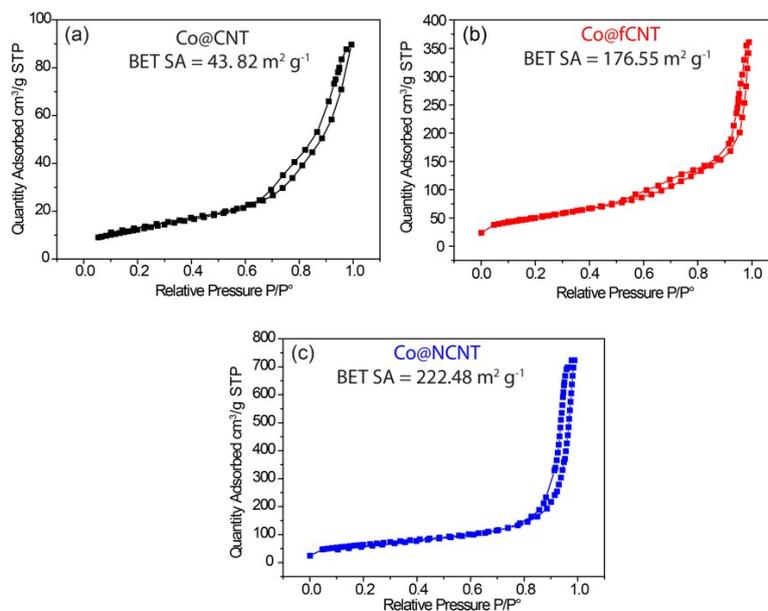


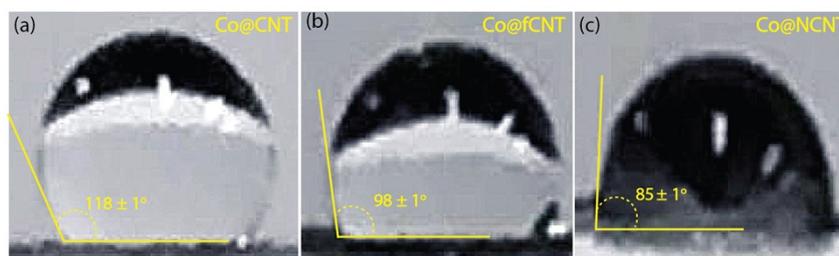
Fig. S1: Comparative XPS spectra (a) C 1s and (b) O 1s for CNT, Co@CNT, Co@fCNT and Co@NCNT.

### 2.2. Contact angle analysis of the catalyst samples



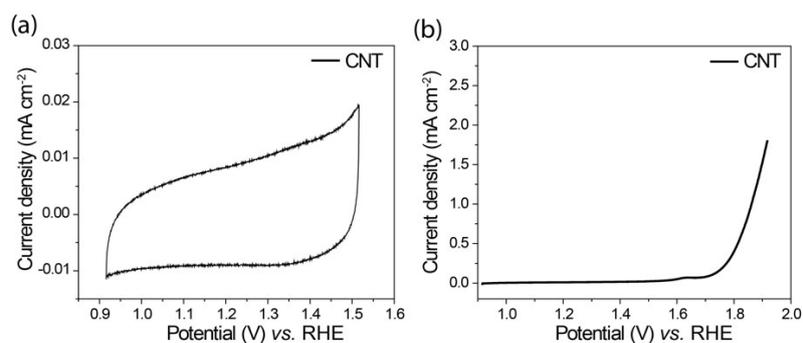
**Fig. S2.** BET surface area analysis of the (a) Co@CNT, (b) Co@fCNT and (c) Co@NCNT showing the estimated surface area of 43.82, 176.55 and 222.48 m<sup>2</sup> g<sup>-1</sup> respectively.

### 2.3. Contact angle analysis of the catalyst samples



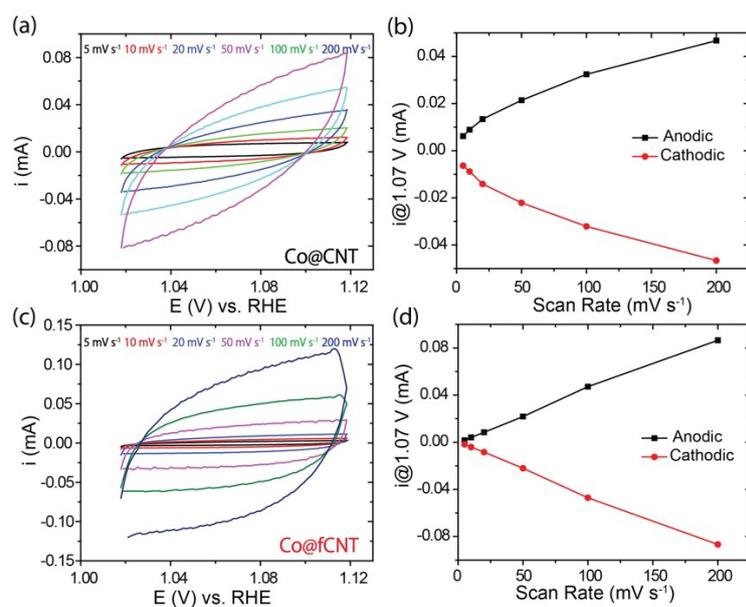
**Fig. S3:** Contact angle measurement of the catalytic sample showing the contact angle of 118°, 98°, and 85° for the Co@CNT, Co@fCNT and Co@NCNT samples respectively.

### 2.4. CV and LSV analysis of pristine CNT



**Fig S4:** Electrocatalytic performance of pristine CNT; (a) CV analysis of the CNT showing capacitive behaviour with low current density; (b) LSV analysis of the CNT with low current density even cannot achieve the practical current density of 10 mA cm<sup>-2</sup>.

### 2.5. ECSA measurement



**Fig. S5:** Electrochemical surface area estimation for Co@CNT and Co@fCNT catalysts.

**Table S1:** The catalysts with their OER performance.

S.N.	Catalyst	$\eta@10 \text{ mA cm}^{-2}$ (mV)	Tafel slope ( $\text{mV dec}^{-1}$ )	ECSA ( $\text{cm}^2$ )
1.	CNT	-----	-----	-----
2.	Co@CNT	480	155.32	7.50
3.	Co@fCNT	360	93.44	16.30
4.	Co@NCNT	310	74.67	45.79

**Table S2:** Comparison of the electrocatalyst's OER performance with reported literature.

S.N.	Catalyst	Electrolyte	$\eta@10 \text{ mA cm}^{-2}$ (mV)	Tafel slope ( $\text{mV dec}^{-1}$ )	Reference
1.	Fe-Co <sub>3</sub> O <sub>4</sub>	1.0 M KOH	280	55	<i>Inorg. Chem. Front.</i> , <b>2020</b> , <i>7</i> , 3327-3339
2.	Co/N-doped C HN	0.1 M KOH	285	88.6	<i>Sustainable Energy Fuels</i> , <b>2020</b> , <i>4</i> , 3370-3377
3.	Co <sub>3</sub> O <sub>4</sub> /NrmGO	0.1 M KOH	310	67	<i>Nature Mater</i> <b>2011</b> , <i>10</i> , 780-786
4.	Co@NCNT	1.0 M KOH	310	74.67	This Work
5.	Co/PNG	1.0 M KOH	335	63	<i>ACS Sustainable Chem. Eng.</i> <b>2020</b> , <i>8</i> , 11947-11955
6.	N-CG-CoO	1.0 M KOH	340	71	<i>Energy Environ. Sci.</i> , <b>2014</b> , <i>7</i> , 609-616
7.	Co@NGC-NSs	0.1 M KOH	360	86	<i>ACS Appl. Energy Mater.</i> <b>2020</b> , <i>3</i> , 7813-7824
8.	N-GC/Co@CoO/rGO	1.0 M KOH	360	-----	<i>RSC Adv.</i> , <b>2019</b> , <i>9</i> , 16534-16540
9.	NC-CoO/C	1.0 M NaOH	362	45.2	<i>ChemCatChem</i> <b>2017</b> , <i>9</i> , 1503
10.	Co/PCNF	1.0 M KOH	365	110.2	<i>ChemPhysChem</i> <b>2017</b> , <i>18</i> , 223
11.	PB-Co/Co-N-PHCS	1.0 M KOH	370	92	<i>ACS Sustainable Chem. Eng.</i> <b>2020</b> , <i>8</i> , 8318-8326
12.	Co/N-C-800	0.1 M KOH	371	61.4	<i>Nanoscale</i> , <b>2014</b> , <i>6</i> , 15080-15089
13.	Co(Ox) <sub>50</sub> @PNC	1.0 M KOH	387	75.3	<i>Chem. Commun.</i> , <b>2016</b> , <i>52</i> , 11947-11950
14.	Co <sub>3</sub> O <sub>4</sub> /mMWCNT	0.1 M KOH	390	65	<i>J. Mater. Chem. A</i> , <b>2013</b> , <i>1</i> , 12053-12059
15.	Co@N-CNT/rGO-0.1	0.1 M KOH	480	251	<i>Energy Fuels</i> <b>2020</b> , <i>34</i> , 8931-8938