Conceptual design of three-dimensional CoN/Ni₃N-coupled nanograsses

integrated in N-doped carbon to serve as efficient and robust water

splitting electrocatalysts

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EXPERIMENTAL SECTION

Materials: All reagents were of analytical grade and used without further purification. The glasswares were cleaned with aqua-regia and deionized water was used throughout the experiments.

Structural and surface characterization: X-ray diffraction (XRD) was performed using a The Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). X-ray photoelectron spectroscopy (XPS) was performed in normal mode using a K-alpha (Thermo Scientific Inc. UK) XPS system with monochromatic Al $K\alpha$ X-ray. All XPS spectra were corrected using the C 1s line at 284.6 eV followed by curve fitting and background subtraction. JEOL-7001F field emission scanning electron microscope (FESEM) was used to characterize the morphologies of the catalysts. Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2010 electron microscope. HRTEM and STEM analysis were performed on a JEM-ARM200F Atomic resolution analytical microscope. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted using PerkinElmer Optima 8300.

Electrochemical studies: The electrochemical characterization and catalytic activity of the different as-obtained electrodes were investigated using a three-electrode cell in Ivium-n-Stat multi-channel electrochemical analyzer, using as-fabricated electrodes (1 cm²) as the working electrode, a graphite rod as the counter electrode, and Hg/HgO (in 1.0 M NaOH) as the reference electrode. For evaluating both HER and OER performance of various electrocatalysts, linear sweep voltammetry (LSV) was conducted at a scan rate of 2 mV s⁻¹ in the 1.0 M KOH electrolyte. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 0.01 Hz–10⁴ Hz with 5 mV amplitude at the bias potentials of –0.1 and 1.60 V (vs. RHE) for HER and OER, respectively. Chronopotentiometry curves were recorded at a current density of 10 mA cm⁻². All potentials reported in this paper were normalized with

respect to the reversible hydrogen electrode (RHE) by adding the value of $(0.146 + 0.059 \times pH)$ V. The overall water splitting was performed in a two-electrode cell using NCN/CC electrodes as both the cathode and anode in 1.0 M KOH. The stability of the electrocatalyst in the two-electrode fuel cell system for full water splitting was evaluated using 1.0 M KOH electrolyte at an applied potential of 1.54 V to reach the initial catalytic current density of 10 mA cm⁻².

Preparation of standard electrodes: For the comparison of HER, OER, and overall water splitting with standard materials, Pt/C and RuO₂ were coated on carbon cloth with a mass loading of ~2 mg cm⁻². Specifically, 10.935 mg of Pt/C or 2.55 mg of RuO₂ was dispersed in 1 mL ethanol, and the resulting suspension was coated on carbon cloth (1 cm⁻²) and dried under ambient condition. Then, 50 μ L of 1.0% Nafion solution diluted in ethanol was drop-casted on the coated carbon cloth.

Electrochemical active surface area (ECSA): The active surface area of each catalyst was estimated from their electrochemical capacitances, which was measured using a simple cyclic voltammetry method. The current was measured in a narrow potential window where no Faradic process was observed. Then, the current is only generated for charging the double layer which is expected to show a linear relationship with the active surface area. The plot of the capacitive current density, ΔJ ($J_{anodic} - J_{cathodic}$) against the scan rate resulted in a straight line and the double layer capacitance (C_{dl}) was calculated as half the slope. The C_{dl} value can be further converted into ECSA using the specific capacitance of a standard 1 cm² flat surface which is generally between 20–60 µF cm⁻². Therefore, an average value of 40 µF cm⁻² was used in the calculation.

 $ECSA = C_{dl}$ of catalyst (mF cm⁻²)/0.04 mF cm⁻²

Electrochemical H₂ and O₂ evolution: Electrochemical H₂ and O₂ evolutions were measured using an electrochemical analyzer (CHI660D) in a 100 mL Pyrex reactor. A 1.0 M KOH aqueous solution was used as the electrolyte and P-CoMoS/CC was used as both the anode and cathode at ambient temperature and atmospheric pressure in a two-electrode system with an applied bias voltage of 1.6 V (vs. RHE) and linear sweep voltammograms were recorded at a scan rate of 5 mV s⁻¹. In a typical experiment, the sample was immersed in the KOH electrolyte, which was bubbled with nitrogen for 30 min to ensure almost complete removal of dissolved oxygen. The amount of generated gas was collected by retrieving 50 μ L of the mixed gas from the headspace of the Pyrex reactor using a syringe and then analyzing it by gas chromatography (Agilent technologies 7890A GC system, USA) using a thermal conductivity detector and a 5 Å-molecular-sieve column with Ar as the carrier gas.

Formation mechanism:

In the designed synthesis protocol PANI is directly grown on CC. Then Ni-Co precursor is synthesized over PANI/CC via simple hydrothermal route. At last the Ni-Co precursor on PANI/CC is pyrolyzed under Ar atmosphere at 700 °C. As per previous literature reports nitrogen-enriched moiety like urea,^{S1} polypyrrole,^{S2} release nitrogenous gases, such as NH₃ in time of pyrolysis. As expected in our case, PANI is acting as N-source, which will provide NH₃ gas at high temperature pyrolysis which promotes the formation of nickel-cobalt nitride. Previously, Ho *et al.*^{S3} reported degradation mechanism of polyaniline nanofibre. Using TGA technique they demonstrate that, around 200-400 °C the slight weight loss occurred due to breakage of inter-chain crosslinking and followed by dramatic weight loss around 400-600 °C due to release of ammonia gas which remove the N- and H-atoms away and leads to the

carbonization process. They also confirmed this process by FTIR spectra where after 600 °C the C-N stretching band disappeared.

Therefore, in our synthetic protocol also followed the same pathway where the released ammonia gas from PANI in time of pyrolysis, leads to formation of NCN/CC by reacting with Ni-Co precursor.



Fig. S1 FESEM images of CN/CC (a, b) and Ni-Co-PANI/CC (c, d) at low and high magnifications.



Fig. S2 (a, b) XRD patterns and (c, d) FESEM images of CoN and NiN/CC, respectively.



Fig. S3 Half differences in current density $(J_a - J_c)$ at 0.22 V vs. RHE plotted against the scan rate fitted to a linear regression.



Fig. S4 Comparative iR-corrected (a) OER and (b) HER performance of NCN and NCO/CC in 1.0 M KOH and (c, d) the corresponding Nyquist plots.



Fig. S5 (a, b) FESEM images of NCN-500 and NCN-900, respectively. Comparative iR-corrected LSV and EIS plots of NCN-500, NCN-700, and NCN-900/CC for (c, e) OER and (d, f) HER in 1.0 M KOH.



Fig. S6 (a, b) FESEM images of NCN-2 and NCN-1/CC, respectively. (c) Oxygen evolution polarization curves and (d) hydrogen evolution polarization curves of the electrocatalysts with different Ni and Co molar ratios at a scan rate of 2 mV s⁻¹ in 1.0 M KOH solution.



Fig. S7 (a) HER and (b) OER performance of NCN/CC in 0.5 M H_2SO_4 medium. (c) Comparative LSV curves of NCN, and Pt-C-RuO2/CC for full water splitting and (d) corresponding chronoamperometric investigation for 24 h at a constant 10 mA cm⁻² current density in acidic electrolyte.



Fig. S8 FESEM, TEM, and HRTEM images of NCN/CC after (a, c, and d) HER and (b, e and f) OER, respectively.



Fig. S9 Comparative XPS analyses of NCN/CC for (a) Co 2p, (b) Ni 2p, (c) N 1s, and (d) O 1s before and after catalysis.



Fig. S10 (a, b) XRD patterns and (c, d) FESEM images of PANI and NCN-powder samples, respectively.



Fig. S11 (a) HER and (b) OER performance of NCN-powder in 1.0 M KOH medium. (c) Comparative LSV curves of NCN-powder, NCN, and Pt-C-RuO2/CC for full water splitting and (d) corresponding chronoamperometric investigation for 24 h at a constant 10 mA cm⁻² current density in 1.0 M KOH medium.

Materials	Ni (Wt%)	Co (Wt%)
NCN/CC	7.9	14.2
NCN-1/CC	10.2	10.7
NCN-2/CC	13.6	7.5
Post-HER NCN/CC	7.6	13.8
Post-OER NCN/CC	6.9	12.6

Table S1: ICP-OES results of various materials

Materials	0	DER	I	IER	Full water	References
	η ₁₀ (mV)	Tafel slope (mV dec ⁻¹)	η ₁₀ (mV)	Tafel slope (mV dec ⁻¹)	splitting/J ₁₀ (V)	
NiFe ₃ N/NF	202	40	75	98	1.62	40
Co _{0.85} Se/NiFe- LDH/EG	270ª	57	260	160	1.67	56
NiCo ₂ S ₄ /CC	280 ^b	89	263°	141	1.68	57
NiFe/NiCo ₂ O ₄ /NF	240 ^d	38.8	105	88	1.67	58
Ni ₅ P ₄ / Ni foil	290	40	150	53	1.7	59
CP/CTs/Co-S	306	72	190	131	1.74	60
NiCoP/Ti	310	52	-	-	1.64	61
Co ₁ Mn ₁ CH/NF	294 ^f	-	180	-	1.68	62
NiCo ₂ O ₄ /NF	290	53	110	49.7	1.65	63
NiMoP ₂ /CC	330 ^g	90.6	199 ^h	112	1.67	64
Fe ₂ Ni ₂ N/NF	200e	34	180	101	1.65	65
NCN/CC	257	63	72	69	1.56	This work

Table S2: Comparison of the electrocatalytic performances of the recently reported

 bifunctional electrocatalysts in alkaline medium

 η_{10} =Overpotential at 10 mA cm⁻² current density; J_{10} = Potential at 10 mA cm⁻² current density.

^a η₁₅₀; ^b η₂₀; ^c η₅₀; ^d η_{onset}; ^e η_{onset}; ^f η₃₀; ^g η₁₀₀; ^h η₁₀₀

Table S3: Summary of electrochemical parameters for the HER and OER

Materials	η (mV)		Tafel slope (mV dec ⁻¹)		ECSA	Mass loading (mg cm ⁻²)	R _{ct} (ohm)	
	OER	HER	OER	HER			OER	HER
	(η ₁₀)	(η ₁₀)						
CN/CC	490	215	161	169	186.5	2.4	28.96	8.97
NiN/CC	390	150	120	138	277.5	2.5	18.74	5.71
CoN/CC	280	130	84	120	512.0	2.3	6.48	4.53
NCN/CC	247	68	63	69	726.7	2.1	1.5	2.03
Pt-C	-	48	-	51	-	1.9	-	1.22
RuO ₂	252	-	71	-	-	2.0	3.44	-

Table S4: Comparison of the electrocatalytic performances of the recently reported Ni and Co

 based electrocatalysts

Catalysts	Electrolyte	Overpotential (mV)		Full water	References	
		HER	OER	at 10 mA cm ⁻²)		
Ni@graphene	1.0 M KOH	$\eta_{10} = 240$	$\eta_{10} = 370$	NA	S4	
Ni/N/C	1.0 M KOH	$\eta_{10} = 190$	$\eta_{10} = 390$	NA	S 5	
Ni@C	0.5 M H ₂ SO ₄	$\eta_{10} = 34$	NA	NA	S 6	
MOF-derived Ni NPs	1.0 M KOH	$\eta_{10} = 61$	NA	NA	S7	
commercial Ni wires	1.0 M KOH	$\eta_{20} = 430$	NA	NA	S 8	
Ni nanopowders	1.0 M KOH	$\eta_{20} = 270$	NA	NA	89	
Ni NPs @ MWCNTs	1.0 M KOH	$\eta_{20} = 220$	NA	NA	S10	
Ni@NC	1.0 M KOH	$\eta_{10} = 205$	$\eta_{10} = 280$	1.60	S11	
Co-NRCNTs	0.5 M H ₂ SO ₄	$\eta_{10} = 260$	NA	NA	S12	
	1.0 M KOH	$\eta_{10} = 370$	-			
Co@NG	0.5 M H ₂ SO ₄	$\eta_{10} = 183$	NA	NA	S13	
	1.0 M KOH	$\eta_{10} = 220$	-			
Co@NC/NG	0.5 M H ₂ SO ₄	$\eta_{10} = 49$	NA	NA	S14	
PNC/Co	1.0 M KOH	$\eta_{10} = 298$	$\eta_{10} = 270$	1.64	S15	
NCN/CC	0.5 M H ₂ SO ₄	$\eta_{10}=35$	$\eta_{10} = 300$	1.59	This work	
	1.0 M KOH	$\eta_{10} = 68$	$\eta_{10} = 247$	1.56		

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