

Supporting Information

Green synthesis of fusiform-shaped Fe-PANI as phenomenal dual electrocatalyst for overall water splitting and assessment of its sustainability standards

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1. Experimental Section

1.1. Chemicals

Aniline, propan-2-ol and potassium hydroxide were purchased from SDFCL and FeCl_3 was purchased from HIMEDIA. All chemicals were directly used as received without further purification. Deionized water was used throughout this work.

1.2. Electrocatalytic characterization

The catalytic performances of the electrodes for water oxidation were studied using three-electrode configuration connected to Biologic Electrochemical Workstation SP-200 potentiostat at room temperature. The Fe-PANI on nickel foam (NF) were used as the working electrodes. The Ag/AgCl (sat. KCl) electrode and Pt wire were used as the reference and counter electrodes. The working NF electrode was washed with 1M HCl to remove oxide layer on the nickel surface, then washed with water and acetone and dried. The slurry was prepared by mixing 0.4 mg of catalyst in 1.0 ml solvent mixture of Nafion (5 wt %) and water in v/v ratio of 1/9 for 20 min. in an ultrasonicator. Commercially available catalyst (IrO_2) and (Pt/C) was used. About 1.0 mg/ml of commercial IrO_2 and Pt/C suspension was prepared by following the similar methodology for comparison and bare NF was used directly. The slurry was drop casting on a precleaned NF electrode and the electrode was allowed to dry at 70°C before measurement (catalyst loading 0.4 mg cm^{-2}). The freshly synthesized catalyst and commercial IrO_2 and Pt/C catalysts have been used directly as working electrode without further treatment. All measurements were carried out in 1.0 M KOH (aq). The OER and HER activities of Fe-PANI have been analyzed by polarization curves (LSV), electrochemical impedance spectroscopy (EIS) and chronoamperometry. The activity of the catalyst have been made by linear sweep voltammetry (LSV) on NF electrode (scan rate: 10 mV s^{-1}). The impedance of electrocatalyst

was measured by electrochemical impedance spectroscopy (EIS) over a frequency range of 100 kHz to 10 mHz with sinusoidal perturbation amplitude of 0.5V. Here, the turnover frequency (TOF) rate of evolved molecular O₂ and H₂ per surface active site per second can be calculated. The TOF can be calculated using the equation $TOF = [J \times A / 4 \times F \times m]$ where, J- Current density, A- Area, F- Faraday Constant, m-the number of moles in catalyst. The ECSA can be calculated using the equation (CV: non-faradaic potential window - 0.90-1.10 V) ECSA (C_{dl}/C_s) and roughness factor (RF=ECSA/GSA) [C_{dl} - double layer capacitance (mF); C_s - specific capacitance (0.04 mF cm⁻²); GSA - geometric surface area (0.25 cm²)] [1].

1.3. Physical characterization

Fourier transform infrared (FTIR) spectra of Fe-PANI were recorded on Shimadzu IR Tracer-100. X-ray diffraction (XRD) of Fe-PANI were recorded with Thermo XRD equinox 1000. The morphology of Fe-PANI was determined by using JEOL-JSM-IT 200 scanning electron microscope (SEM) operated at 20 kV. The inductively coupled plasma mass spectroscopy (ICP-OES) was analysed by using Perkin Elmer Optima5300 DV. JOEL, JEM-2100 Plus was used to record transmission electron microscopy (TEM) image of the Fe-PANI and selected area electron diffraction (SAED) pattern also taken from JOEL, JEM-2100 Plus. The elemental composition of Fe-PANI was analyzed by XPS (X-ray photoelectron spectroscopy) with K-ALPHA SURFACE ANALYSIS spectrometer. The surface area and pore size measurements were analyzed by Quantachrome instruments, Autosorb IQ series. Thermal stability was analysed by NETZSCH STA 449F3.

Figure S1. As-repared Fe-PANI electrocatalyst



Figure S2. TEM – Histogram plot of Fe-PANI

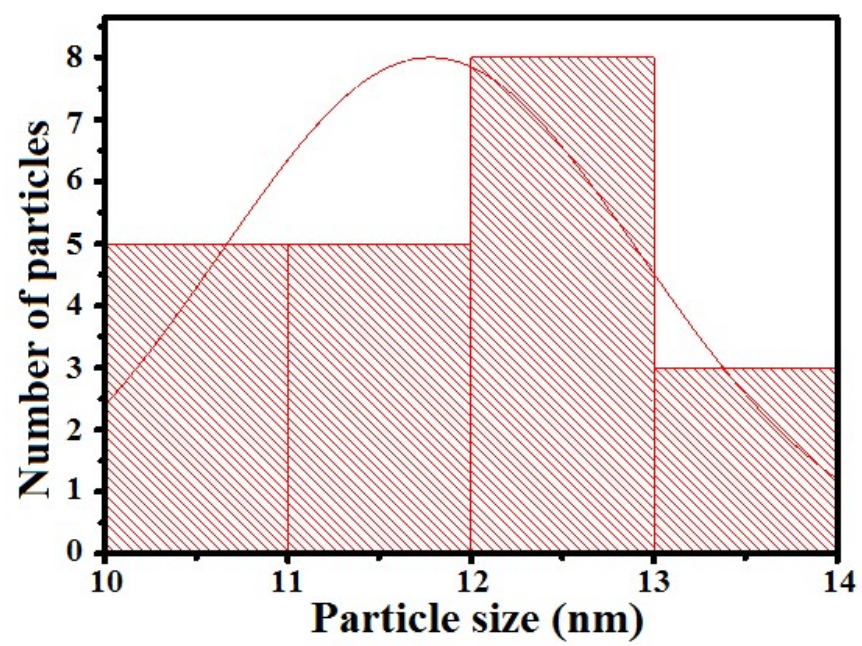


Figure S3. XPS-Survey spectra of Fe-PANI

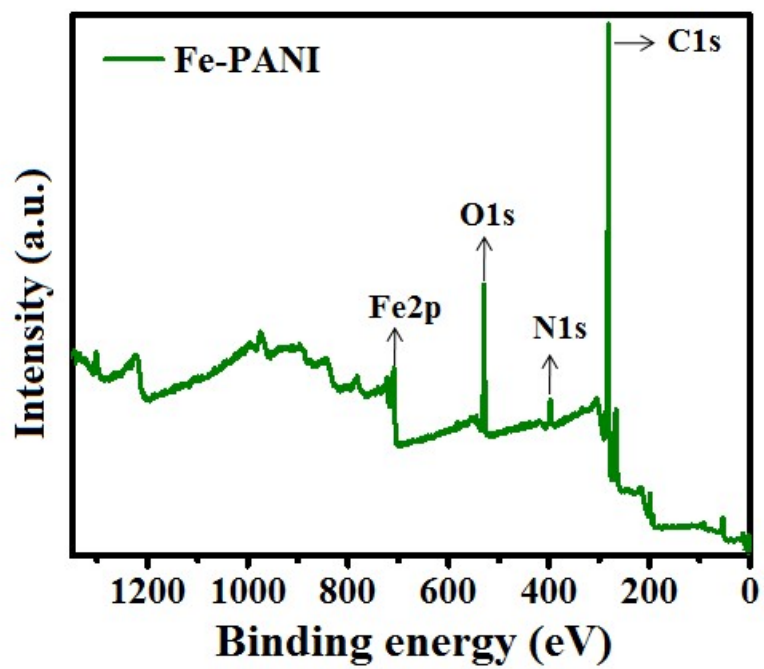


Figure S4. Post-OER FE-SEM elemental mapping of Fe-PANI

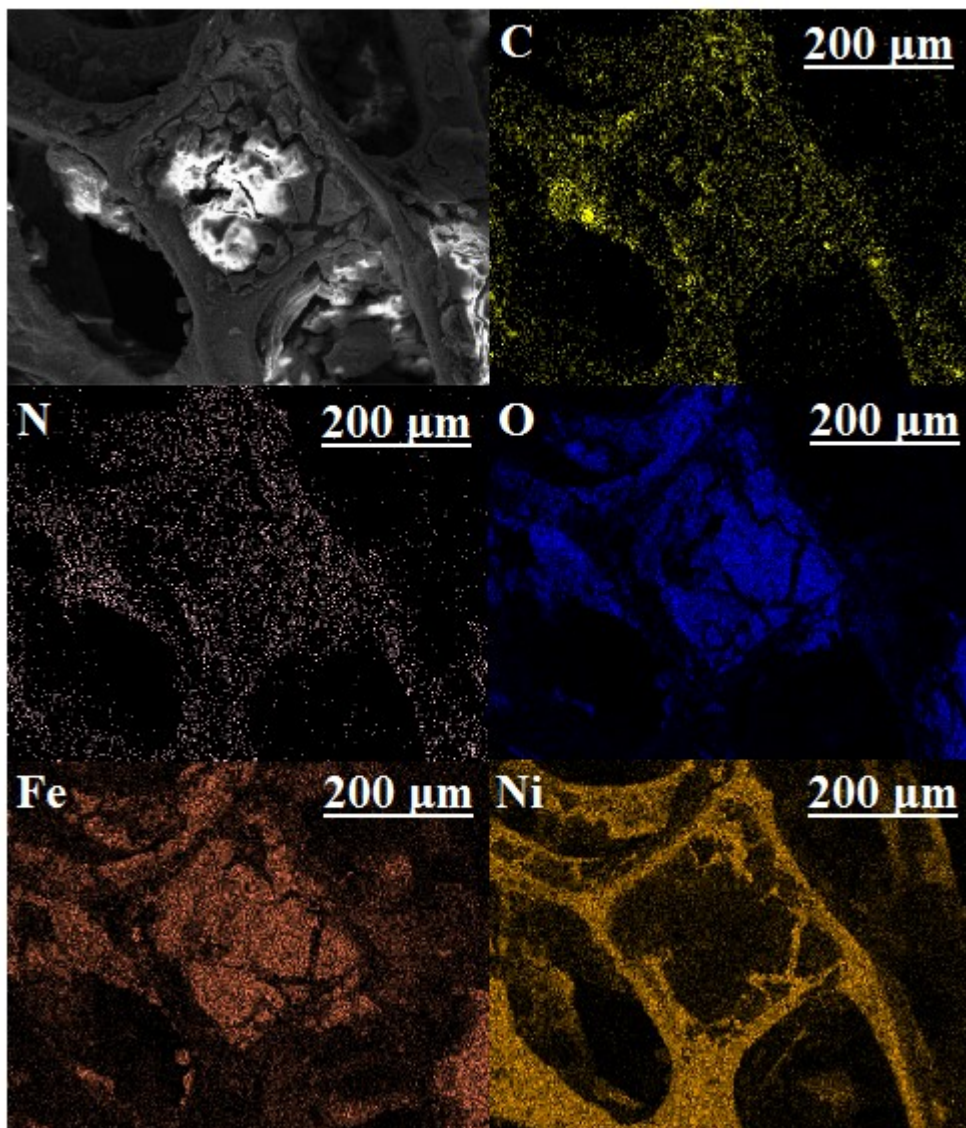


Figure S5. Post-HER FE-SEM elemental mapping of Fe-PANI

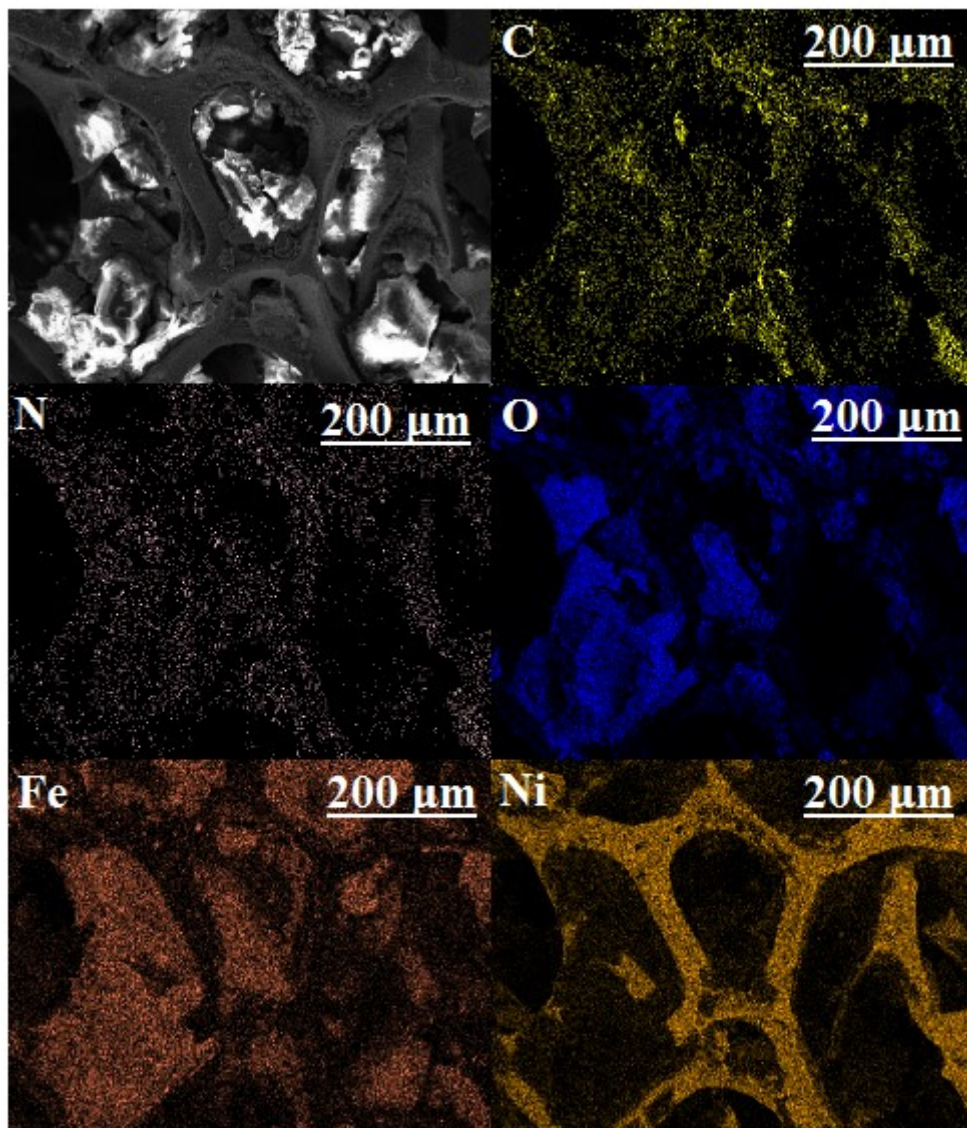


Table S1: Elemental composition of Fe-PANI measured by ICP-OES.

Elecatrocatalyst	Element symbol and wavelength (nm)	Weight of sample in gms / Volume in ml	Dilution Factor	Concn.in ppm $\mu\text{g/ml}$ (or) mg/litre
Fe-PANI	Fe 238.204	0.0202g/50ml	1	54.30 mg/L

Table S2: ECSA and roughness factor for electrocatalysts.

Catalysts	ECSA (m²/g)	Roughness factor (r_f)
Fe-PANI	7.4	29.8
NF	3.3	13.5

SI-1. Calculation of hydrogen generation.

Based on the displaced amount of water due to the hydrogen bubbles the amount of hydrogen generated was calculated using the below relationships.

$$\text{Amount of hydrogen generated in 1 h} = \text{amount of water displaced in liters} \quad (1)$$

$$\left. \begin{array}{l} \text{Amount of hydrogen generated} \\ \text{in moles for 1 h} \end{array} \right\} \frac{\text{Amount of water displaced (liters)}}{22.4 \text{ liters}} \quad (2)$$

We also calculated the hydrogen generation rate from the electrical charge passed through the electrode using the equation given below.

$$\text{Current obtained} \times \text{Time duration for} = \text{Coulomb} \quad (3)$$

$$\frac{\text{Coulomb} \times F}{96485C} = \text{No. of moles of } e^- \text{ for H}_2 \text{ generation} \quad (4)$$

$$\left. \frac{\text{No. of moles of electron for H}_2 \text{ generation} \times 1 \text{ mole of H}_2 \text{ gas}}{\text{mole of electron}} \right\} = \text{Moles of hydrogen 2 generated} \quad (5)$$

SI-2. Environmental impact assessment

Equation S1

$$\text{Mass Intensity} = \frac{\text{Mass of all reactents used excluding water}}{\text{Mass of product}} \text{kg/kg product}$$

Equation S2

$$\text{Water Intensity (Wp)} = \frac{\text{Mass of all water used}}{\text{Mass of product}} \text{kg/kg product}$$

Equation S3

$$\text{Reaction Mass Efficiency (RME)} = \frac{\text{Mass of product}}{\text{Mass of all reactents}} \times 100\%$$

Equation S4

$$\text{Energy Intensity} = \frac{\text{Amount of non renewable energy used}}{\text{Mass of product}} \text{kW.h/kg}$$

Equation S5

$$E \text{ factor} = \frac{[\text{kg}(\text{raw material}) - \text{kg}(\text{desired product})]}{[\text{kg}(\text{total product including water})]}$$

Table S3. Comparison of HER, OER and overall water splitting performance of Fe-PANI with recently reported non-noble bifunctional electrocatalysts

Electrolyte : 1 M KOH

Bifunctional Electrocatalysts	OER $\eta_{j=10}$ (mV)	HER $\eta_{j=10}$ (mV)	Overall water splitting $E_{j=10}$ (V)	Reference
Fe-PANI	261	155	1.64	This Work
3D-CNTA	360	185	1.68	[2]
Ni-Fe-P nanocubes	271	182	1.67	[3]
NiFe-NCs	271	197	1.67	[4]
Co₄Mo₂@NC	330	218	1.74	[5]
Ni/Mo₂C-PC	368	179	1.66	[6]
Co NPs/NSC	337	336	1.88	[7]
Co₂P/Mo₂C	368	182	1.74	[8]
Co₁Mn₁CH/NF	296	180	1.68	[9]
Ni₂P/MoO₂@MoS₂	280	159	1.72	[10]
Co₂B/CoSe₂	320	300	1.73	[11]
Co-ZnO/CF	360	275	2.06	[12]
MnMoO₄/PANI	410	155	1.65	[13]

MoS₂-NiS₂/NGF	370	172	1.64	[14]
Ni-Fe-P	271	182	1.68	[15]
1D-CoS	280	159	1.75	[16]
Co (OH)₂@NCNTs	270	170	1.72	[17]
NiMoP₂/CC	330	199	1.67	[18]
Co₁Mn₁CH/NF	294	180	1.68	[19]
CP/CTs/Co-S	306	190	1.74	[20]
NiCo₂S₄/CC	280	263	1.68	[21]
Co_{0.85}Se/NiFe-LDH/EG	270	260	1.67	[22]
Ni₃S₂/NF	280	223	1.76	[23]
Ni(OH)₂/NF	350	298	1.82	[24]
CTs/Co-S	301	190	1.74	[25]

Table S4. Comparison of solar to hydrogen efficiency of Fe-PANI with recently reported electrocatalyst.

Electrocatalysts	STH Efficiency (mmol h⁻¹ cm⁻²)	Reference
Fe-PANI	4.57	This Work
Co@SPANI-800	3.91	[26]
Co ₄ Ni ₁ @PANI	4.03	[27]
RCFC-10	4.51	[1]
Co@PANI-600	4.01	[28]

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