Supplementary Information (SI) for Materials Advances.
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"Photo-Assisted Water Splitting over NiCoP/g-C_3N_4 Heterostructure: Understanding the Role of Visible Light in Electrochemical Water Splitting"

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S1. Reagents and Materials

Nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$,98%), cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$,98.5%), 2-methylimidazole ($C_4H_6N_2$), melamine ($C_3H_6N_6$), sodium hypophosphite monohydrate ($NaH_2PO_2·H_2O$), polyvinylidene fluoride (PVDF), Methanol (CH_3OH), N-methyl 2-pyrrolidone (C_5H_9NO) (NMP) and acetone (C_3H_6O) were purchased from Sigma Aldrich. All reagents were used without any treatment, in accordance with standard experimental protocols. Deionised (DI) water from the Milli Q purification system was used for all preparations, and Nickel foam was procured from Global Nanotech.

S2. Material Characterisation

The X-ray diffraction (XRD) analysis of the synthesised samples was performed using an Empyrean 3rd Generation diffractometer from Malvern PANalytical, Netherlands. The measurements were conducted using monochromatic Cu-Kα radiation ($\lambda = 0.154$ nm), scanning over a 2θ range of 5° to 90° at a scan rate of 3°/min. FTIR spectrum was recorded by Spectrum Two FT-IR Spectrometer (PerkinElmer, Singapore) in the spectral range of 500-4000 cm^{-1}. UV-Vis-NIR spectroscopy (Lambda 950) was used to capture diffuse reflectance spectra within the 200-800 nm range. The energy dispersive X-ray (EDAX), elemental mapping, and field emission scanning electron microscopy (FE-SEM) images were taken by Carl Zeiss-Sigma 300 (Germany) and a Jeol, Japan instrument to analyse elemental and surface morphology. Using XPS (PHI Versaprobe III), the material's surface chemical composition and valence state were determined. High-resolution transmission electron microscopy (HR-TEM) was employed to investigate the microstructural features of the samples using a JEOL JEM-2100 Plus microscope.

S3. Electrochemical Measurements

The electrocatalytic performances were examined using a conventional three-electrode configuration with an Autolab PGSTAT204 electrochemical workstation in a 1M KOH aqueous electrolyte (pH=14) at 29°C. The potential concerning Ag/AgCl (saturated KCl) was recorded as the reference electrode, and the Platinum electrode (Pt) was used as the counter electrode, with a diameter of 0.5 mm; the immersed length of the wire during electrochemical measurements was 2 cm, corresponding to an exposed surface area of 0.314 cm^2. The working electrode was prepared by depositing the synthesised material on a nickel foam; the detailed procedure is given in the fabrication section. Utilising a Philips Master Colour CDM-R PAR30L 70 W, Ceramic metal halide (CDM) Lamp light source with a luminous intensity of 13000 cd, the investigation was carried out in illuminated mode. Before recording the electrochemical data of the catalyst, it was activated through Cyclic Voltammetric (CV) scans between its redox peaks at a scan rate of 50 mV s^{-1} till the CV curve showed no differences. All potentials were measured with respect to the reversible hydrogen electrode (RHE) by the equation

$$E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.059 * pH + 0.1976 \qquad \text{(Eq.S1)}$$

Linear Sweep Voltammetry (LSV) was carried out at a scan rate of 5 mV s-1 to evaluate the HER in the potential range of -0.9V to -1.8V vs. RHE and OER in the potential range of 0V to 0.99V vs. RHE in a three-electrode system. Turn Over Frequency (TOF) values of the catalyst were calculated using the following equation,

$$\text{TOF} = \frac{Current\ density \times 6.022 \times 10^{23}}{n \times 96485.3 \times \frac{Area\ under\ oxidaion\ or\ reduction\ peak}{Scan\ rate \times 1.602 \times 10^{-19}}}$$

(Eq.S2)

Where, n =2 for HER and n = 4 for OER

Tafel plots were utilised to assess the reaction kinetics by plotting the potential values against the log(i). The linear region of the Tafel plot is fitted to the Tafel equation, $\eta = b \log j + a$, where overpotential (η), current density(j), Tafel constant (b), and constant value(a) are determined, from which the Tafel slope or constant is determined. Electrochemical Impedance Spectroscopy (EIS) was performed at frequencies ranging from 1 Hz to 0.1 Hz with a 5 mV sinusoidal amplitude, under open-circuit potential (OCP) conditions in a 1 M KOH electrolyte.

Before electrochemical measurements, the working electrode was immersed in the electrolyte for 30 minutes to ensure sufficient wetting and stabilisation at the electrode-electrolyte interface. The resulting Nyquist plots were fitted using the Randles equivalent circuit model R(C(R(QR)))(CR), comprising solution resistance (R_s), charge transfer resistance (R_{ct}), and constant phase element (CPE). The fitting was performed using Nova 2.1 software. The stability test of the electrode was conducted using chronopotentiometry at a current density of 200 mA cm^{-2} for OER and -200 mA cm^{-2} for HER in a three-electrode system for 24 hours. The electrode's electrochemical active surface area (ECSA) was assessed using CV within the non-faradaic region at varying scan rates of 5, 10, 25, 50, 75, and 100 mV s^{-1}. The ECSA, directly related to the double-layer capacitance (C_{dl}), was calculated by the following equation:

$$\mathrm{ECSA} = C_{dl} / C_S \qquad \text{(Eq.S3)}$$

The standard specific capacitance (C_S) value, corresponding to 0.040 mF/cm^2, is commonly used as a benchmark for an atomically smooth, planar electrode surface in alkaline electrolyte environments [1]. The $2C_{dl}$ value was derived from the slope of the plot of Δj /A cm^{-2} vs. scan rate / mV s^{-1}, where Δj represents the difference between the anodic current density (j_a) and cathodic current density (j_c) [2]. Chronoamperometry (CA) was conducted to measure the current response of the electrode in dark and illuminated conditions. A constant potential of -1.24 V was applied on the cathodic side, and 0.645 V was applied on the anodic side while doing CA. Mott-Schottky (M-S) analysis was performed in a three-electrode configuration to determine the flat-band potential of the catalyst at different frequencies (500, 800, and 1000 Hz). For overall water splitting, the NiCoP/g-C_3N_4 electrocatalysts were used as both anode and cathode in two-electrode configurations and Chronopotentiometry was performed with a current density of 400 mA cm^{-2} using 1M KOH as the electrolyte solution. The faradaic efficiency of the electrodes was calculated using an inverted burette system, recording the volume for every 60s time interval, and the theoretical gas volumes were calculated using Faraday’s law of electrolysis combined with the ideal gas law given as,

$$V_{\mathrm{Theoretical}} = RTQ / Fpz \qquad \text{(Eq.S4)}$$

Here, R is the ideal gas constant, T is the absolute temperature, p is the pressure, F is Faraday’s constant, and z is the number of electrons involved (HER=2, OER=4).

The approximate energy required for the NiCoP/g-C_3N_4 electrode to produce 1kg of H_2 and O_2 under illuminated conditions in 1M KOH was calculated by considering Eq.S3, as referenced in[3,4].

$$Q = \frac{1000g \times N_A \times 2e}{M \times FE}$$

(Eq.S5) Where N_A is Avogadro number (6.022×10^{23} mol^{-1}), e is the charge of an electron (1.602×10^{-19}) and M is the relative molecular mass of hydrogen (2.016 g/mol) or Oxygen (32.0 g/mol). The electrical energy required to generate 1 kg of hydrogen and oxygen was calculated based on the cell voltage (U) at a specific current density and the total charge, as expressed by the following equation:

$$W = QU \tag{Eq.S6}$$

S3.1. Fabrication of the working electrode

The working electrode was prepared by mixing the synthesised catalyst with PVDF in a 9:1 ratio. The mixture was ground in a mortar and pestle with NMP until a thick ink was formed. The resulting ink was then uniformly coated onto a pre-treated nickel foam substrate (1 × 1 cm^2) and dried overnight in a hot air oven at 60°C. Approximately 7-9 mg of the catalyst was uniformly deposited on a 1 cm^2 area of Ni foam.

S4. RESULTS AND DISCUSSION

The electrochemical impedance spectra were fitted to the equivalent circuit model of R(C(R(QR)))(CR), the various circuit parameters are solution resistance (R_S), double-layer capacitance (C_{dl}), charge-transfer resistance (R_{ct}), polarisation resistance (R_p), effective interfacial capacitance (C_{eff}), space-charge capacitance (C_{SC}), and space-charge resistance (R_{SC}). Here, R_S represents the electrolyte and contact resistance, C_{dl} corresponds to the double-layer capacitance formed at the catalyst and electrolyte interface, and R_{ct} indicates the charge transfer resistance across that interface. R_P and C_{eff} are related to ion diffusion and charge storage within the porous electrode structure, whereas C_{SC} and R_{SC} describe the capacitance and resistance associated with the semiconductor space-charge region, respectively

Sample	**R_s (Ω)**	**C_{dl} (mF)**	**R_{ct} (Ω)**	**R_P (Ω)**	**C_{eff} (F)**	**C_{SC} (F)**	**R_{SC} (Ω)**
Dark	0.915	9×10^{-10}	0.602	0.602	0.542	900f	1.64m
Light	1.000	45.7	0.373	0.373	1.100	8.33m	47.2m

Table S1. *Various circuit parameters and values of NiCoP /g-C_3N_4 in dark and light conditions fitted to the R(C(R(QR)))(CR) circuit.*

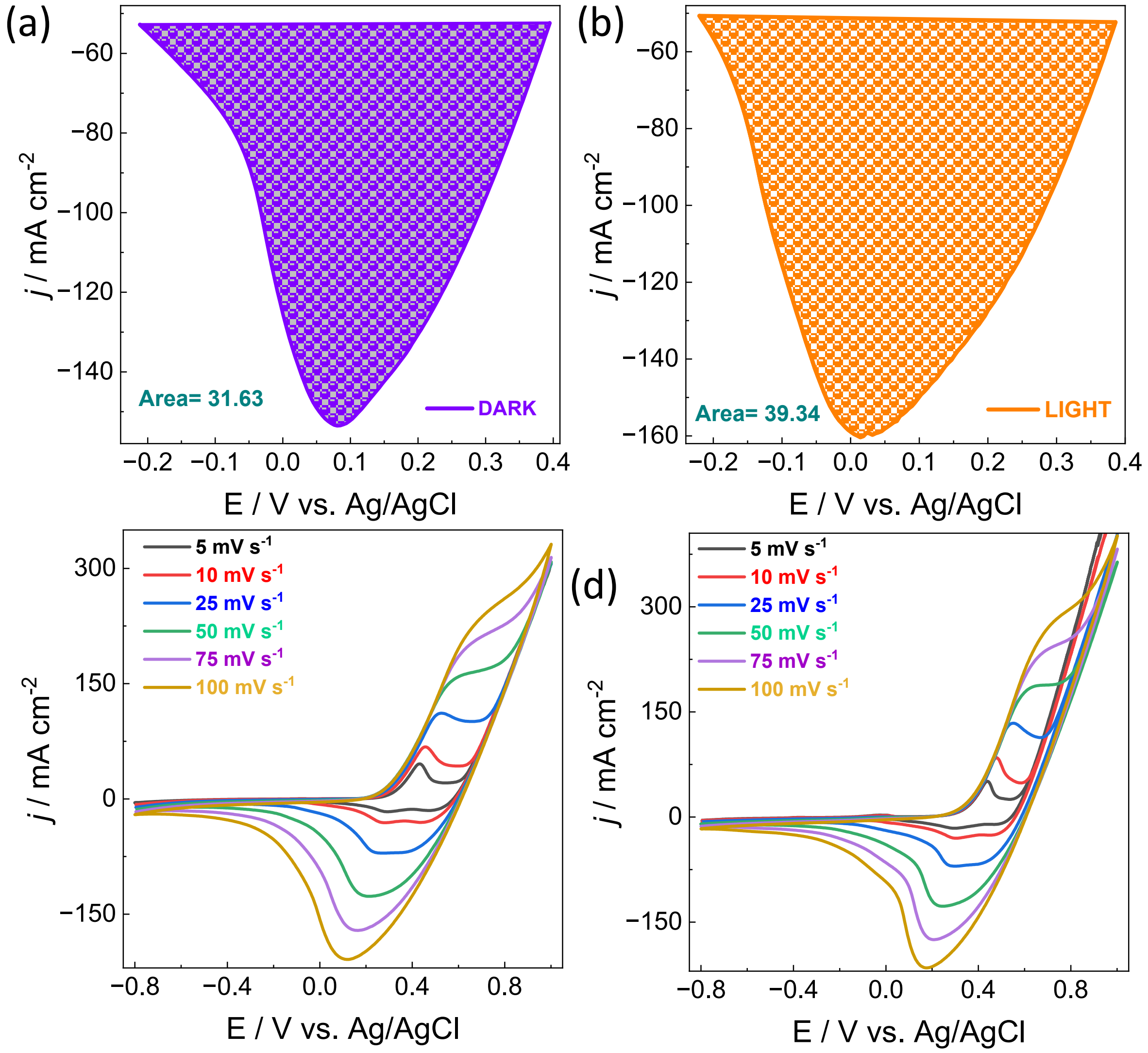

Figure S1. *(a) Reduction peak area analysis of NiCoP/g-C_3N_4 in dark condition, (b) Reduction peak area analysis of NiCoP/g-C_3N_4 in illuminated condition, (c)Scan rate study of NiCoP/g-C_3N_4 under dark conditions, (d) Scan rate study of NiCoP/g-C_3N_4 under illuminated conditions.*

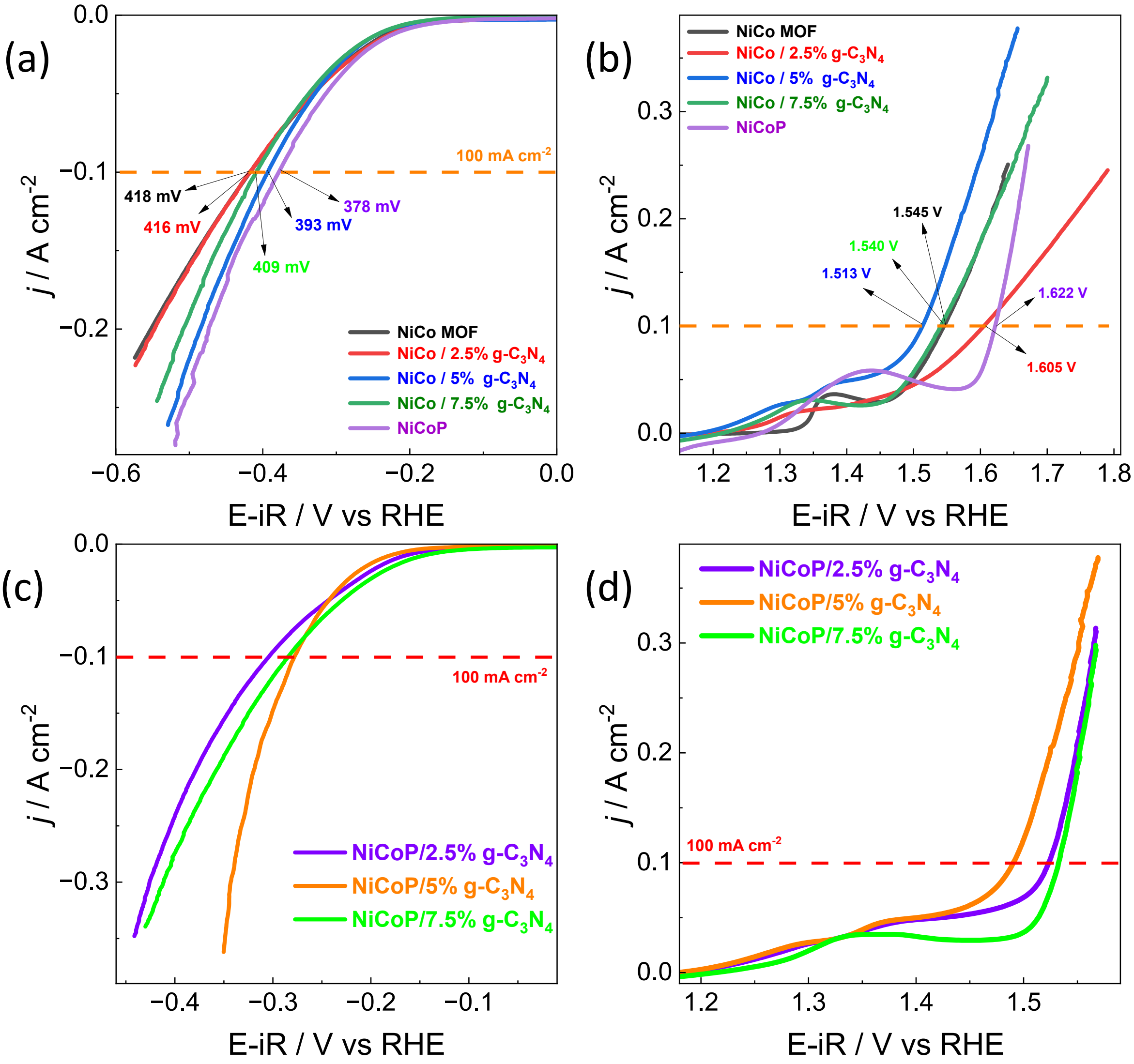

Figure S2.: *(a) iR corrected LSV curves for HER of NiCo-MOF, NiCo/2.5%g-C_3N_4, NiCo/5%g-C_3N_4, NiCo/7.5%g-C_3N_4, and NiCoP, (b)iR corrected LSV curves for OER of NiCo-MOF, NiCo/2.5%g-C_3N_4, NiCo/5%g-C_3N_4, NiCo/7.5%g-C_3N_4, and NiCo, (c) iR corrected LSV curves for HER of NiCoP/2.5%g-C_3N_4, NiCoP/5%g-C_3N_4, NiCoP/7.5%g-C_3N_4, (d) iR corrected LSV curves for OER of NiCoP/2.5%g-C_3N_4, NiCoP/5%g-C_3N_4, NiCoP/7.5%g-C_3N_4.*

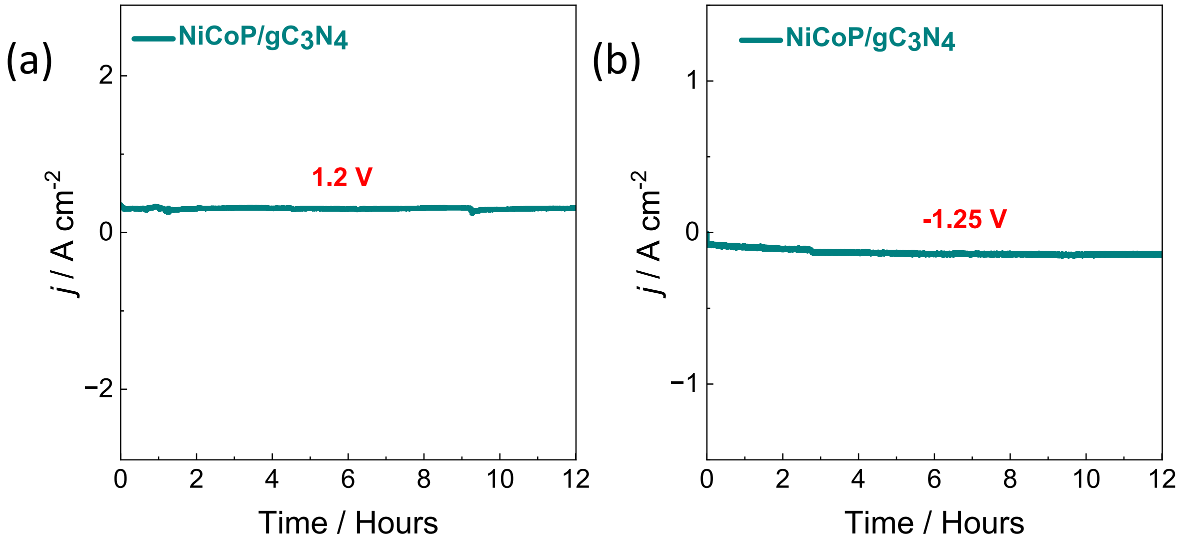

Figure S3. *Chronoamperometry test for NiCoP/g-C_3N_4 under illuminated conditions for 12 hours.*

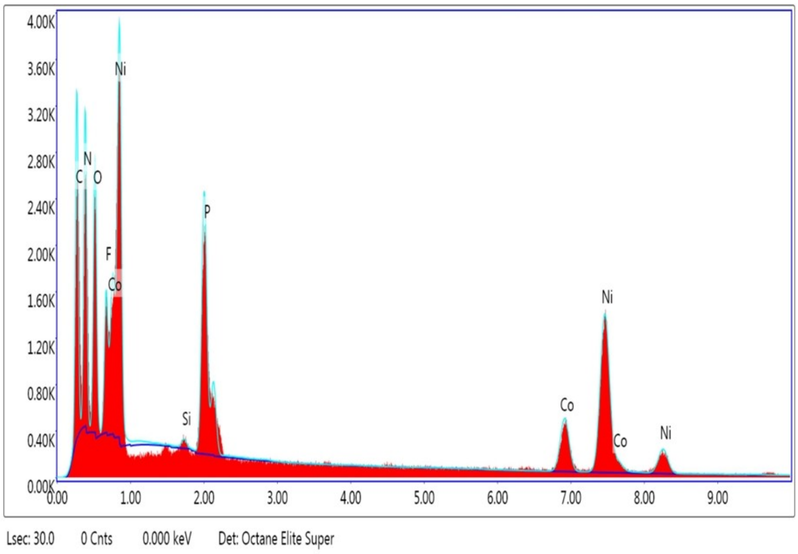

Figure S4. *EDS of NiCoP/g-C_3N_4.*

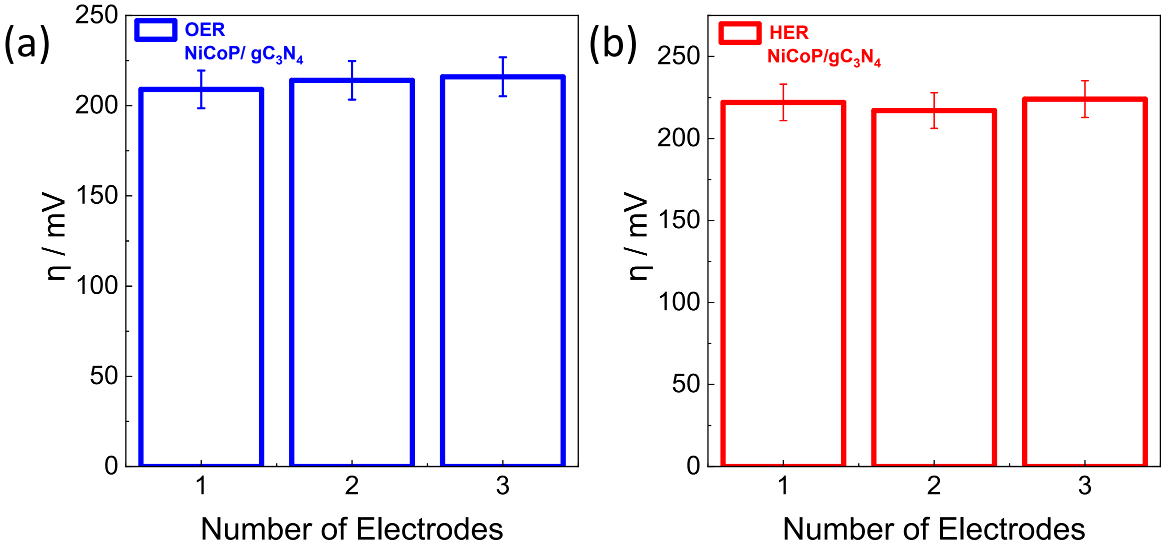

Figure S5. *Reproducibility assessment of NiCoP/gC_3N_4 using three independently prepared electrodes: (a)OER Overpotential bar graphs, (b)HER Overpotential bar graphs.*

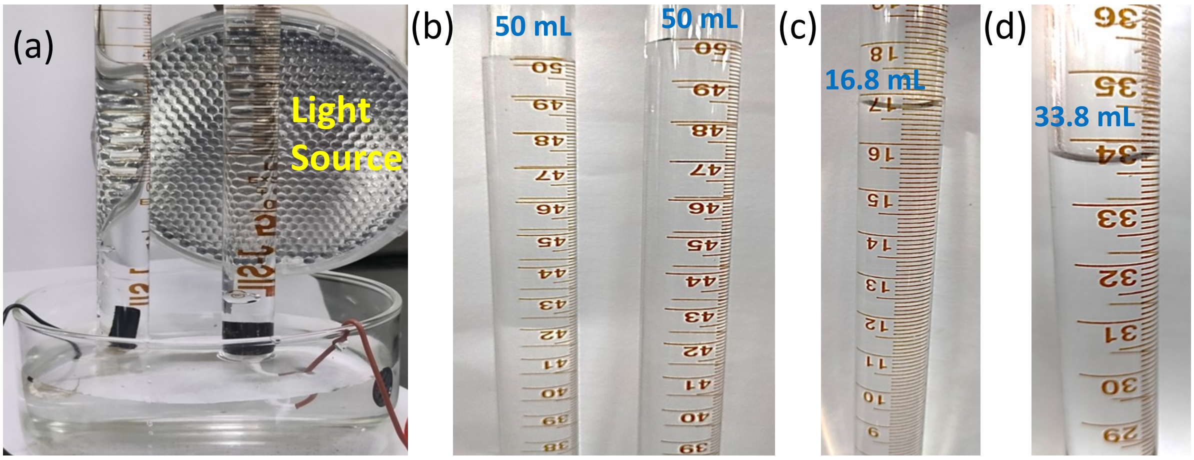

Figure S6. *(a)A digital photograph of the inverted burette apparatus with light source used to measure the H_2 and O_2 released, (b)Volume of KOH before conducting chrono potentiometry, (c)Volume of KOH at cathode side after 720s of chrono potentiometry test under illuminated condition, and (d) Volume of KOH at anode side after 720s of chrono potentiometry test under illuminated condition.*

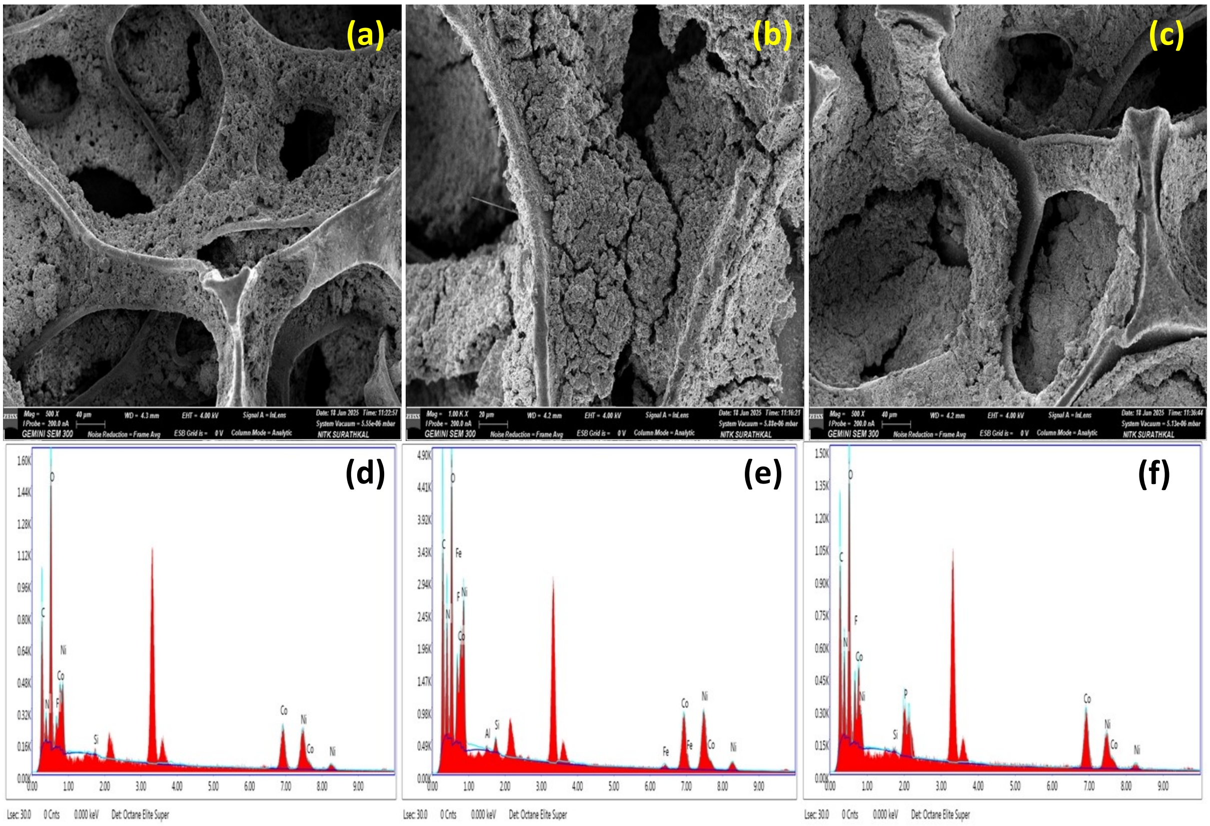

Fig. S7. *FE-SEM images and EDS spectra of NiCoP/g-C_3N_4 on Nickel foam before and after 24 h stability testing: Fig. (a,d) Fresh electrode, Fig.(b,e) anode after chronopotentiometry test, and Fig.(c,f) cathode after chronopotentiometry test.*

Reference:

1 L. Yu, Q. Zhu, S. Song, B. McElhenny, D. Wang, C. Wu, Z. Qin, J. Bao, Y. Yu, S. Chen and Z. Ren, *Nat Commun*, 2019, **10**, 5106.
2 M. You, L. Gui, X. Ma, Z. Wang, Y. Xu, J. Zhang, J. Sun, B. He and L. Zhao, *Applied Catalysis B: Environmental*, 2021, **298**, 120562.
3 H. Wu, Z. Wang, Z. Li, Y. Ma, F. Ding, F. Li, H. Bian, Q. Zhai, Y. Ren, Y. Shi, Y. Yang, Y. Deng, S. Tang and X. Meng, *Advanced Energy Materials*, 2023, **13**, 2300837.
4 X. Lin, S. Cao, X. Chen, H. Chen, Z. Wang, H. Liu, H. Xu, S. Liu, S. Wei and X. Lu, *Adv Funct Materials*, 2022, **32**, 2202072.