Electronic Supplementary Material (ESI) for Energy Advances.

Supporting Information

Strategic Ni-doping improved electrocatalytic H_2 production by Bi_3O_4Br in alkaline water

Manodip Pal,[a] Rathindranath Biswas,[a] Sanmitra Barman*[b] and Arnab Dutta*[a], [c], [d]

[a] Chemistry Department, Indian Institute of Technology Bombay, Powai, Maharashtra 400076

[b] Center for Advanced Materials and Devices (CAMD), BML Munjal University, Haryana-122413

[c] National Center of Excellence, CCU, Indian Institute of Technology Bombay, Powai, Maharashtra 400076

[d] Interdisciplinary Program in Climate Studies, Indian Institute of Technology Bombay, Powai, Maharashtra 400076

*Corresponding author: sanmitra.barman@bmu.edu.in, arnab.dutta@iitb.ac.in

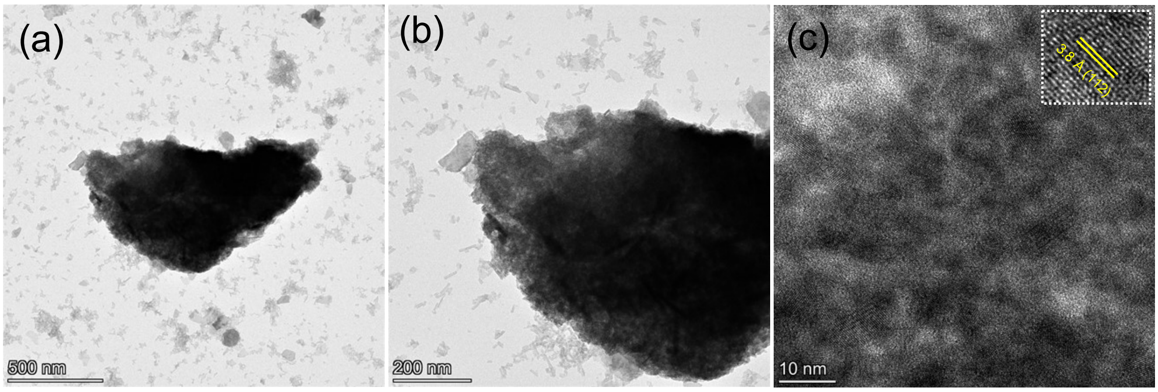
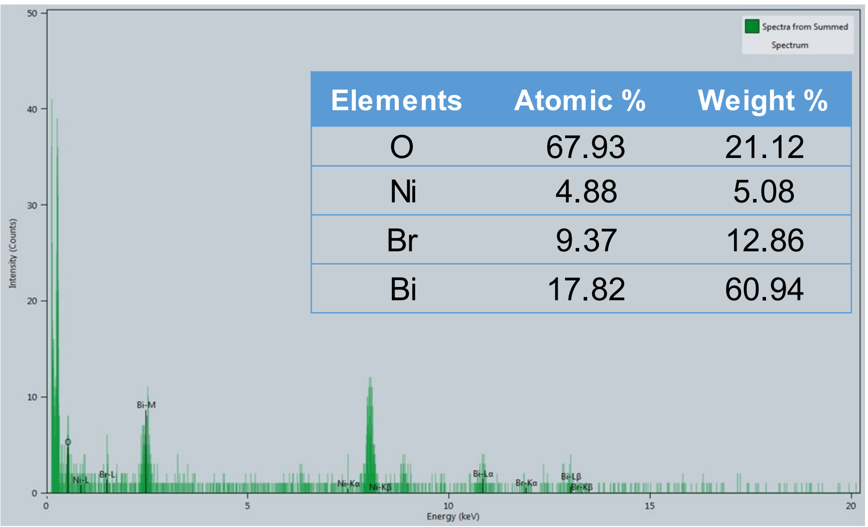


Fig. S1 (a-b) TEM images, and (c) HR-TEM image of of pure Bi_3O_4Br.



Elements	Atomic %	Weight %
O	67.93	21.12
Ni	4.88	5.08
Br	9.37	12.86
Bi	17.82	60.94

Fig. S2 EDS spectra of Ni-doped Bi_3O_3Br.

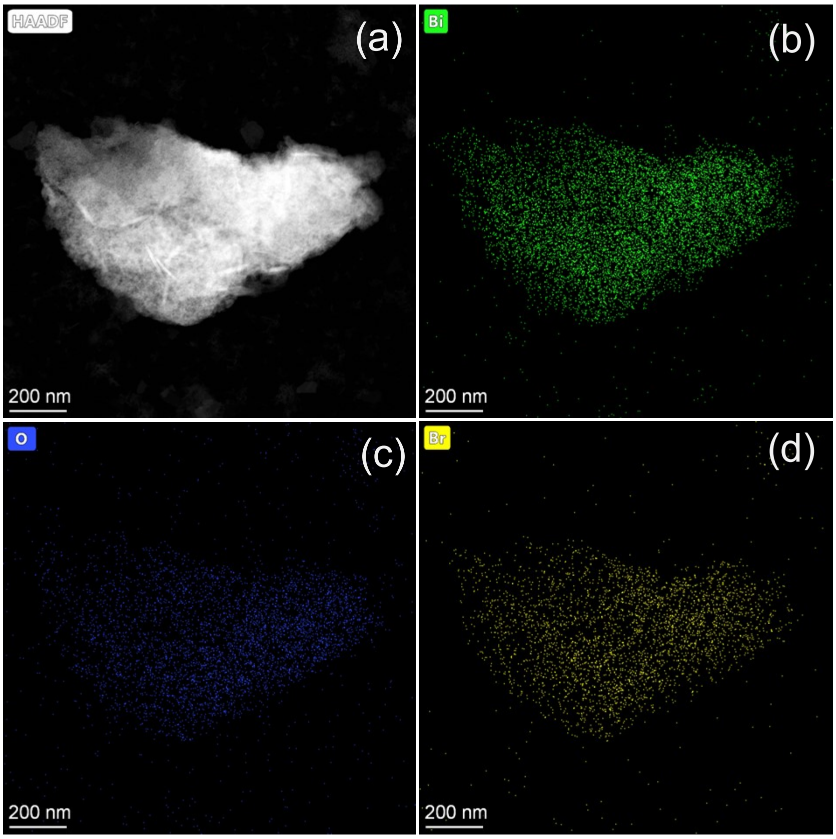


Fig. S3 (a) HAADF image of Bi_3O_4Br for the elemental mapping of (b) Bi, (c) O, (d) Br elements.

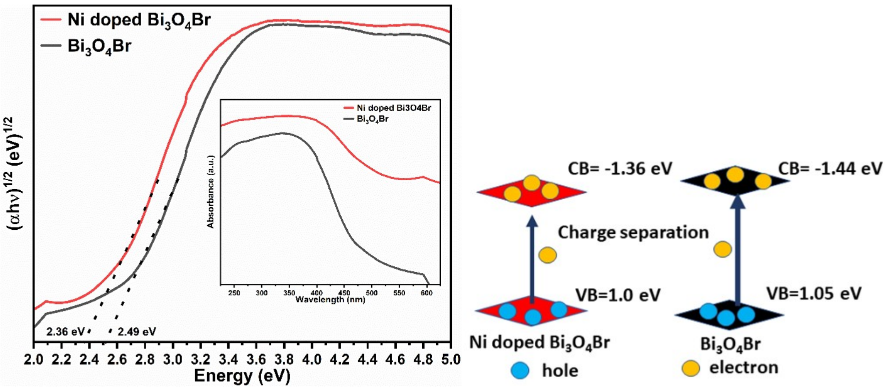


Fig. S4 UV-Vis absorption spectra and bandgap from the Tauc plot for Bi_3O_4Br and Ni-doped Bi_3O_4Br (left) and schematic band structure obtained from the data obtained from the XPS valence spectra and Tauc plot for Bi_3O_4Br and Ni-doped Bi_3O_4Br.

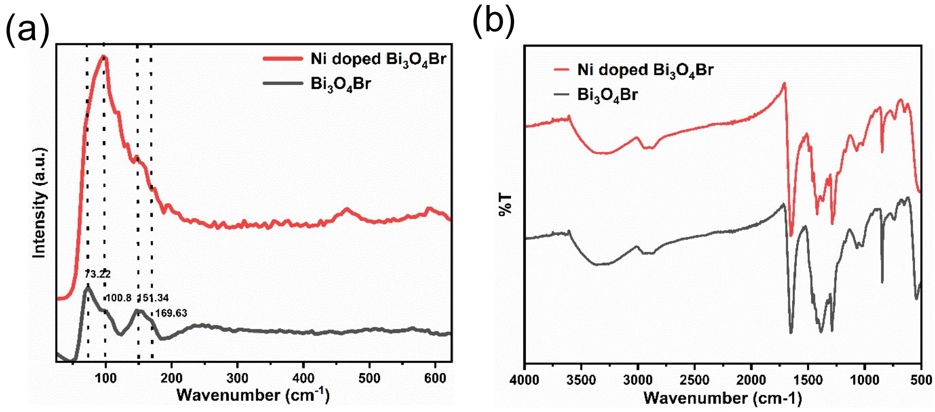


Fig. S5. (a) Raman and (b) FTIR spectra of Bi_3O_4Br and Ni-doped Bi_3O_4Br.

Bulk electrolysis:

Bulk electrolysis (chrono-amperometry) was performed using four-necked glass vessels, with three of the necks occupied by a coiled Pt electrode as a counter electrode, Ag/AgCl (in 3 M KCl) as a reference electrode, and catalysts drop-casted on carbon paper having an area of 0.25 cm^2 as working electrode. Out of four necks, one left was sealed with a rubber septum and was used for Ar purging and for gas collection over headspace (Via gas-tight syringe VICI made). The headspace gas was collected and, analyzed using (CIC Dhruva) Gas chromatography (GC) instrument equipped with a TCD detector and 5 Å molecular sieve column to separate of the gases with argon as the carrier gas. The GC instrument was calibrated with the available 1%, 2%, and 5% H_2 gases.

Photoelectrochemical measurements:

All the photoelectrochemical studies were performed by using the Metrohm Auto lab potentiostat with a conventional three-electrode system at room temperature. A spiral platinum electrode (Pt) and an Ag/AgCl electrode submerged in 3.0 M KCl were taken as the counter and reference electrodes, respectively. The catalyst ink was then prepared by taking 3.0 mg of catalyst in the solution of 120 µL of HPLC grade IPA, 80 µL of millipore water (18.2 MΩ·cm at 298K), and 30 µL of 5 wt% Nafion. 1.0 M KOH solution (pH 14.0) was utilized as the electrolyte solution. The prepared catalyst ink was deposited on a Fluorine doped tin oxide (FTO) glass (with approximate mass loading of 1.04 mg/cm^2) were directly used as the working electrode. The catalyst was drop casted on an area of 0.5 cm^2 × 0.5 cm^2 FTO. 300W Xe Lamp was used as light source for the photoelectrocatalysis. The LSV measurments was carried out with a scan rate of 10 mV/s and the photocurrent measurments were carried out at an applied potential of -0.73 V (vs. RHE) in 1 M KOH solution for both the Bi_3O_4Br and Ni-doped Bi_3O_4Br catalysts.

Calculation of electrochemically active surface area (ECSA):

Moreover, the electrochemically active surface area (ECSA) proportional to the electrochemical double-layer capacitance (C_{dl}) is estimated from the equation (Eq. (2)):

$$ECSA = C_{dl}/C_s$$

Where C_s is the specific capacitance of flat working electrode and its value is 40 μF cm^{-2} per $cm^2_{ECSA}$for the flat electrode.[1, 2] and C_{dl} is determined from the slope of Δj/2 (where Δj is the difference of J_a and J_c) vs. scan rate. J_a and J_c are anodic and cathodic current densities, respectively.

Mass activity:

Mass activity was calculated using the following equation.

$$Mass\ activity\ (A\ g^{-1}) = \frac{j\ (A\ cm^{-2})}{m\ (g\ cm^{-2})}$$

Where, j = current density, m = mass loading

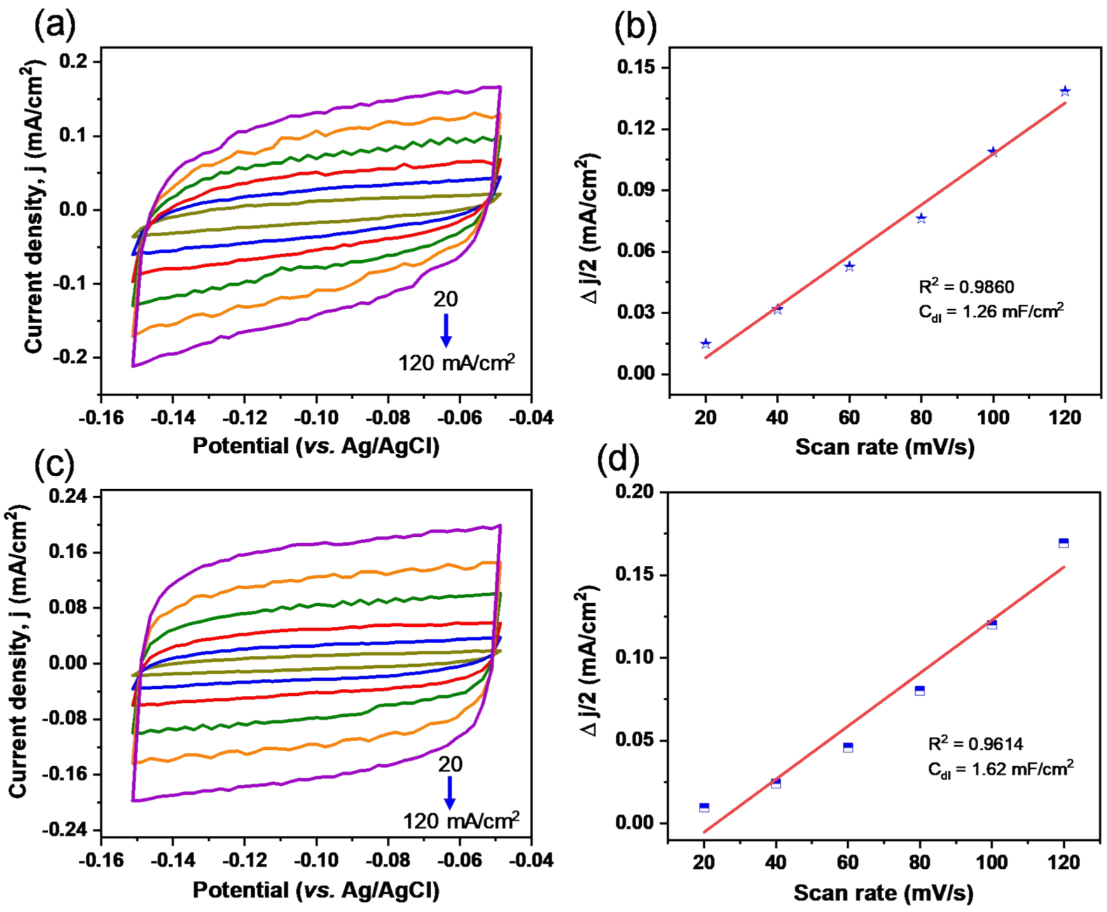


Fig. S6 (a and c) Cyclic voltammetry curves of Bi_3O_4Br and Ni-doped Bi_3O_4Br, respectively. (b and d) corresponding plot of ΔJ/2 *vs.* scan rate at a static potential of -0.1 V (vs. Ag/AgCl) to determine double layer capacitance (C_{dl}).

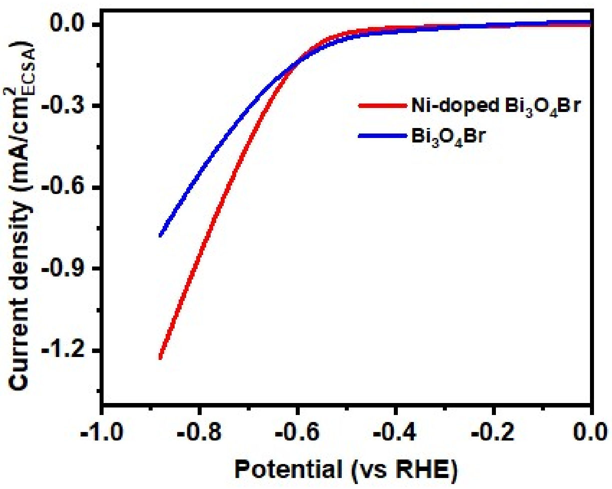


Fig. S7 ECSA normalized LSV polarization curves of Ni-doped Bi_3O_4Br and Bi_3O_4Br catalysts for electrocatalytic HER.

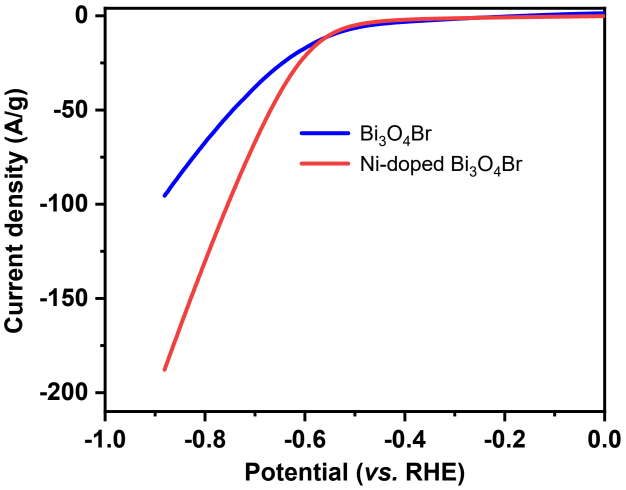


Fig. S8 LSV plots to represent the mass activity (A/g) of Bi_3O_4Br and Ni-doped Bi_3O_4Br catalysts.

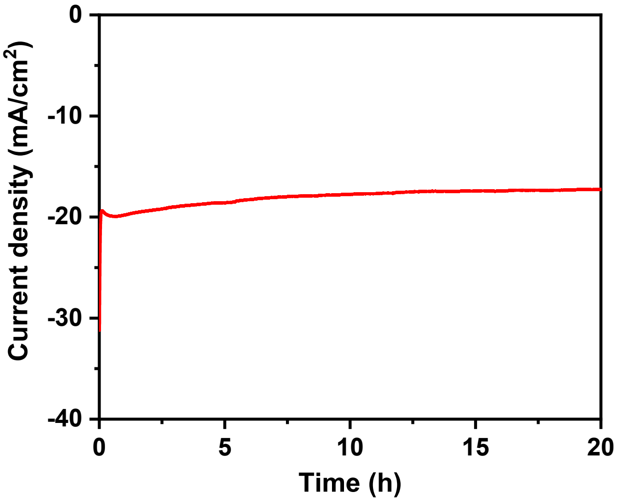


Fig. S9 Chronoamperometry stability test of Bi_3O_4Br at an applied overpotential of 620 mV in an alkaline medium (electrocatalysis)

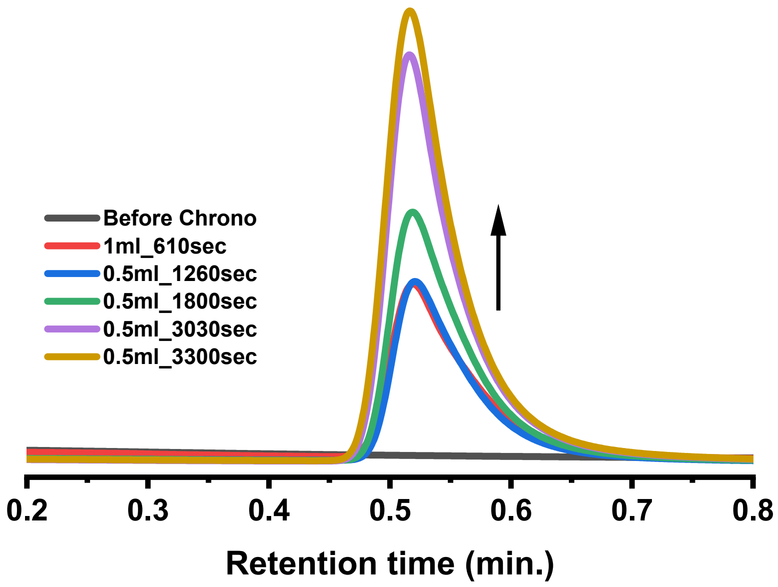


Fig. S10 Volume of hydrogen gas measured during chronoamperometry test by Gas Chromatography for Ni-doped Bi_3O_4Br during electrochemical HER performance.

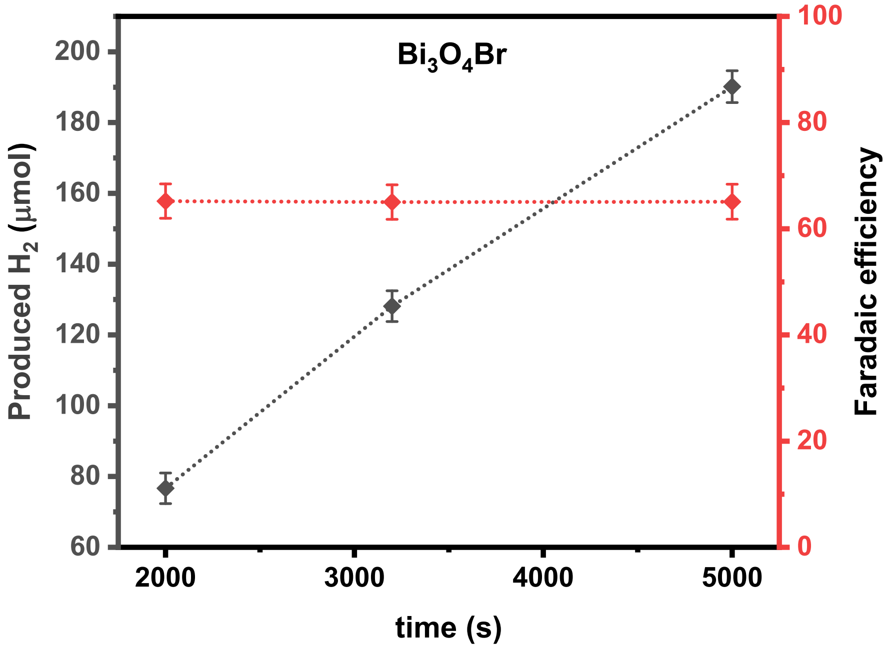


Fig. S11 Time dependent hydrogen gas production (μmol) and faradaic efficiency of Bi_3O_4Br catalyst during electrochemical HER performance.

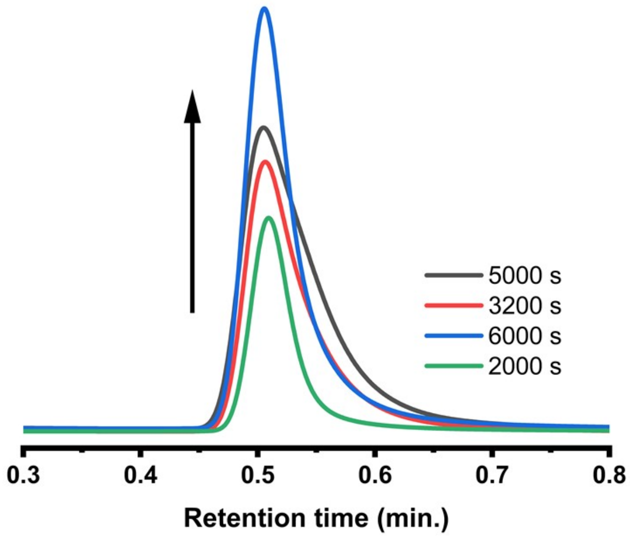


Fig. S12 Volume of hydrogen gas measured during chronoamperometry test by Gas Chromatography for Bi_3O_4Br during electrochemical HER performance.

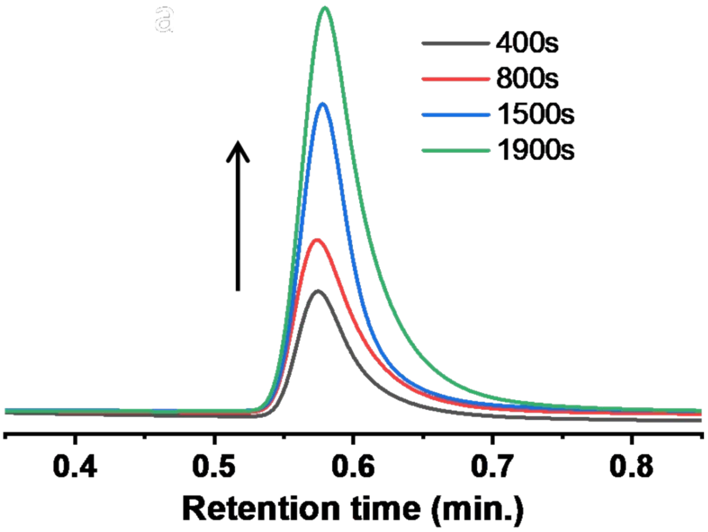


Fig. S13 Volume of hydrogen gas measured during chronoamperometry test by Gas Chromatography for Ni-doped Bi_3O_4Br during photoelectrochemical HER performance.

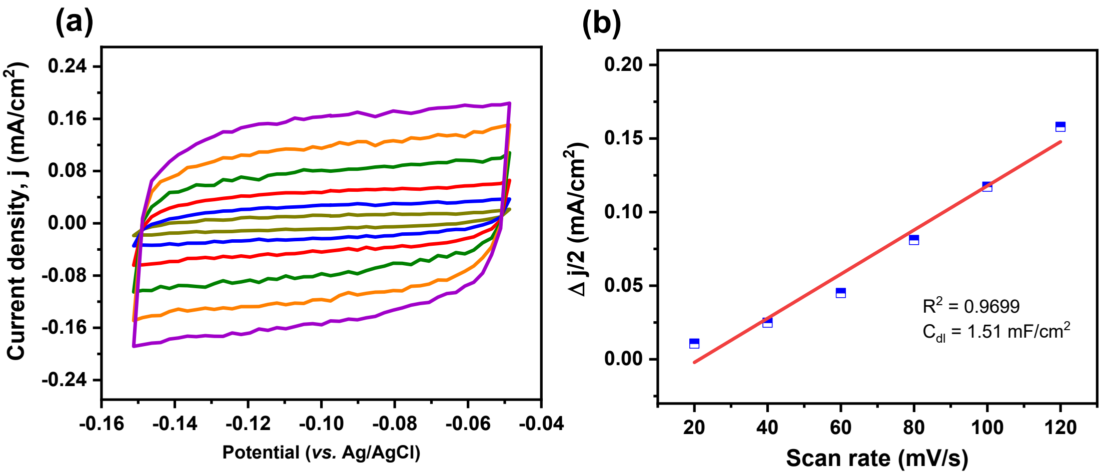


Fig. S14 Post catalysis: (a and c) Cyclic voltammetry curves of Bi_3O_4Br and Ni-doped Bi_3O_4Br, respectively. (b and d) corresponding plot of ΔJ/2 *vs.* scan rate at a static potential of -0.1 V (vs. Ag/AgCl) to determine double layer capacitance (C_{dl}).

ICP-AES analysis:

2 mg of sample were dissolved in 10 mL of Aqua regia. Then it was heated at 80°C under stirring condition. When the solution was left around 2 mL, composite sample was completely digested. Then Volume was increased up to 10 mL through dilution using Milli-Q millipore water. **After then, 1 mL of this solution was taken and further diluted up to 10 mL as a final stock solution for ICP-AES analysis**, where a series of external standards was used for calibration over the relevant concentration range.

So now 0.2 mg of sample is present in 10 mL solution.

According to ICP data, amount of Ni = 0.374 ppm (mg/Lit. of solution) that is 0.374 mg of Ni in 1 Lit solution.

So, the amount of Ni in 10 mL solution containing 0.2 mg sample = $\frac{0.374}{1000} \times 10$ mg = 0.00374 mg in 10 mL.

So, weight % of Ni = $\frac{0.00374}{0.2} \times 100\%$ = 1.87 %

After post catalytic ICP-AES analysis, the concentration of Ni was found to be 0.352 ppm where the amount of sample was 0.2 mg in a total of 10 mL solution.

So, the amount of Ni in 10 mL solution containing 0.2 mg sample = = $\frac{0.352}{1000} \times 10$ mg = 0.00352 in 10 mL.

So, weight % of Ni = $\frac{0.00352}{0.2} \times 100\%$ = 1.76 %

Hence, % of Ni retained post-electrolysis = $100 - \left[\frac{(1.87 - 1.76)}{1.87} \times 100\right] = 94.12\ \%$

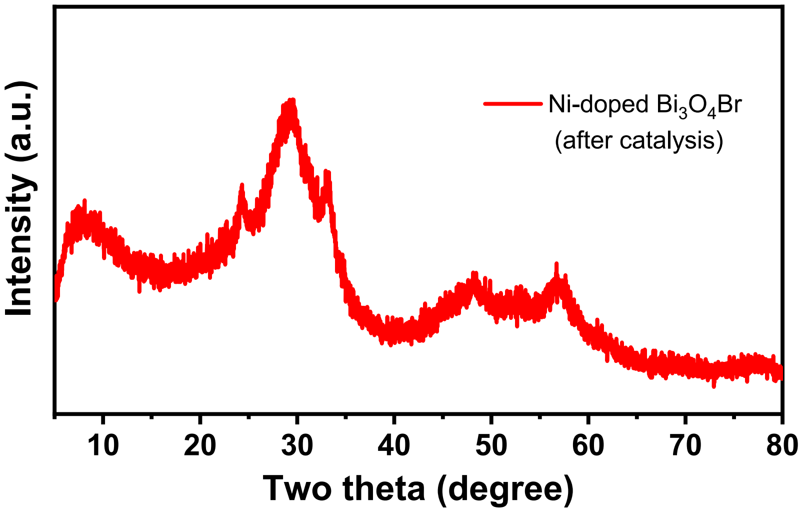
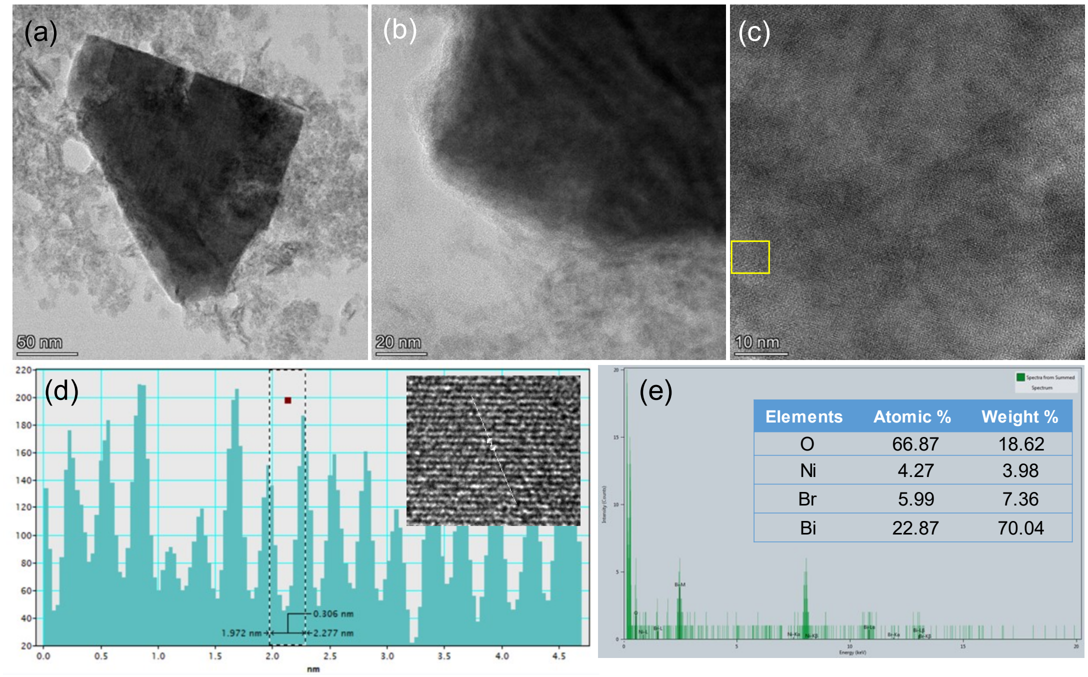


Fig. S15 Powder XRD pattern for the Ni-doped Bi$_3$O$_4$Br after electrocatalysis.



Elements	Atomic %	Weight %
O	66.87	18.62
Ni	4.27	3.98
Br	5.99	7.36
Bi	22.87	70.04

Fig. S16 Post electrocatalytic TEM analysis: (a-b) TEM images of Ni-doped Bi_3O_4Br, (c) HR-TEM image, (d) line-scanning intensity profile of the inserted inverse FFT of live FFT of the selected area in Fig. c. (g) EDS spectrum and corresponding aromic % and weight % (FFT = Fast Fourier Transition).

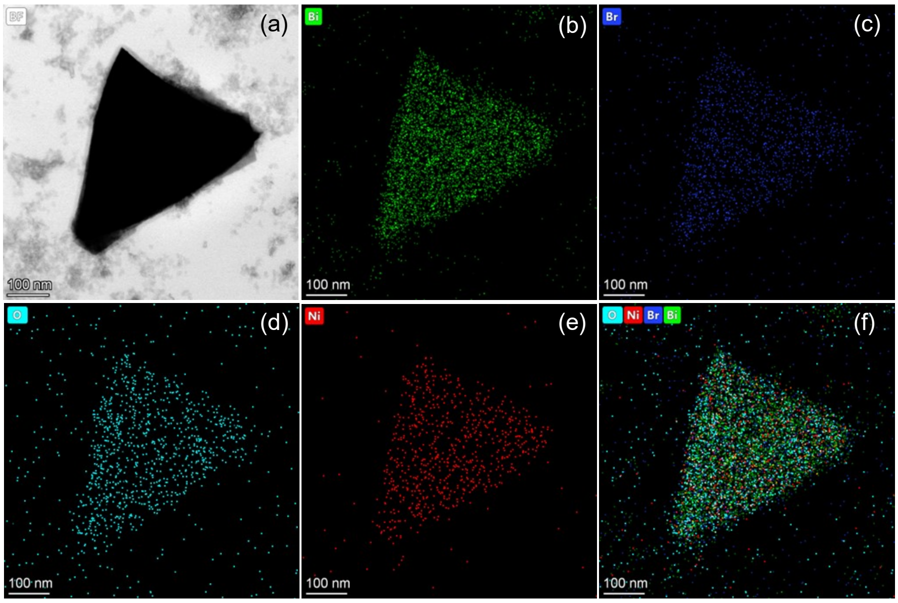


Fig. S17 (a) Bright Field (BF) image of Ni-doped Bi_3O_4Br for the elemental mapping of (b) Bi, (c) Br, (d) O, (e) Ni, and (f) mixed elements of Bi, O, Br, and Ni after electrochemical HER stability test.

References

1. S. Shit, S. Chhetri, W. Jang, N. C. Murmu, H. Koo, P. Samanta and T. Kuila, *ACS Appl. Mater. Interfaces*, 2018, **10**, 27712-27722.
2. Y. Li, F.-M. Li, X.-Y. Meng, S.-N. Li, J.-H. Zeng and Y. Chen, *ACS Catal.*, 2018, **8**, 1913-1920.