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Supporting Information

Activation free electroless deposition of NiFe over carbon cloth as self-standing flexible electrode towards overall water splitting

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Figure S1. Photographs of the electroless deposited flexible electrode under (a) normal, (b)





electrodes (inset: zoomed part of the particular range of the figures).



@OCC and (b) NiFeP@OCC electrodes synthesized in different batches

Figure S3. SEM images of (a) bare OCC, (b) NiFeS@OCC and (c) NiFeP@OCC electrodes.



Figure S4. Elemental dot mapping images of (a) all elements and separately for (b) Ni, (c) Fe, and (d) S of NiFeS@OCC electrode.





NiFeP@OCC electrode.

Figure S6. Raman spectra of various electrodes (a) OCC, (b) NiFeS@OCC and (c) NiFeP@OCC.



Figure S7. (a) XPS survey spectra and deconvoluted XP spectra of (b) C 1s and (c) O 1s of NiFeS@OCC electrode.



@OCC electrode.

The C 1s spectra can be deconvoluted into three peaks, 284.5, 286.1 and 288.3 eV attributed to C-C, C-O-C, and O-C=O. Also, O 1s spectra can be deconvoluted into two peaks at 532 eV and 533.7 eV signifying the M-O and C-OH bond. The presence of an oxygen-containing group and its interaction with carbon confirms the successful functionalization of carbon cloth.

| Table S1: Atomic percentage of the element | nts obtai | ned from | the XPS a | analysis | |
|--------------------------------------------|-----------|----------|-----------|----------|---|
| Electrode | С | 0 | Ni | Fe | S |

| Electrode | C | 0 | Ni | Fe | S | Р |
|-----------|-------|-------|------|------|------|------|
| NiFeS@OCC | 70.73 | 27.32 | 0.91 | 0.59 | 0.45 | - |
| NiFeP@OCC | 68.92 | 28.48 | 1.17 | 1.40 | - | 0.03 |

The total amount of active material present was obtained by subtracting the amount of carbon and oxygen from the total amount as they were present in the substrate. Thus obtained amount is considered as 100 % and the fraction of individual elements was calculated and stoichiometric ratio was determined.



Figure S9A. Bar diagram representing the optimization of the (a) molar ratio of Ni:Fe (j @ 1.9 V *vs.* RHE) and (b) deposition time in NiFeS@OCC (j @ 1.9 V *vs.* RHE) towards electrocatalytic OER.



Figure S9B. LSV representing the comparison of OER activity in 1M KOH of NiFeS@OCC and NiFeP@OCC synthesized in different batches.



Figure S9C. LSV representing the comparison of OER activity on various electrodes CC, OCC, NiFeS@CC and NiFeS@OCC in 1M KOH.



Figure S9D. LSV of NiFeS@OCC in 1 M KOH (Inset: zoomed part of LSV) at different scan rates.



Figure S9E. Tafel plot for (a) NiFeS@OCC, (b) NiFeP@OCC with their control samples in 1 M KOH, CE: Pt wire; RE: Hg/HgO/1M NaOH.



Figure S10A. Sequential Chronoamperometric measurements and their corresponding absolute current difference *vs.* applied potential curve for NiFeS@OCC (a) & (b) and NiFeP@OCC (c) & (d), the working electrode potential was increased step-wise by 30 mV for every 2 min in 1 M KOH, CE: Pt wire; RE: Hg/HgO/1M NaOH.



Figure S10B. LSV curves of (a) NiFeS@OCC and (b) NiFeP@OCC in 1 M KOH before and after stability tests.



Figure S11A. Elemental dot mapping images of (a) all elements and separately for (b) Ni, (c) Fe, and (d) S of NiFeS@OCC electrode after stability study.



Figure S11B. Elemental dot mapping images of (a) all elements and separately for (b) Ni, (c) Fe, and (d) P of NiFeP@OCC electrode after stability study.



Figure S12A. SEM images of (a) NiFeS@OCC and (b) NiFeP@OCC after stability measurements.



Figure S12B. P-XRD pattern for (a) NiFeS@OCC and (b) NiFeP@OCC after stability measurements.



Figure S13. Chronopotentiometry at various current densities for (a) NiFeP@OCC and (b) NiFeS@OCC in 1 M KOH, CE: Pt wire; RE: Hg/HgO/1M NaOH.



Figure S14. Photographs of electroless deposited carbon cloth electrodes showing high flexibility with various bending angles.



Figure S15. Linear sweep voltammogram of NiFeS@OCC at various bending angles.



Figure S16. Bar diagram showing the overpotential required by the various catalyst to reach current density 10 mA cm⁻² in 1 M KOH, CE: Pt wire; RE: Hg/HgO/1M NaOH.



Comparison of Tafel slope benchmark RuO₂ catalyst.



Figure S18. Tafel plot for (a) NiFeS@OCC and (b) NiFeP@OCC with their control samples in 1 M KOH, CE: Pt wire; RE: Hg/HgO/1M NaOH, (c) Comparison of overpotential of catalysts with state of art towards HER.

| Catalyst | Electrolyte | OER | | HER | | Stability | Reference |
|------------------------|-------------|---------------|----------------|---------------|----------------|-----------|-----------|
| | | Overpotential | Tafel slope | Overpotential | Tafel slope | - | |
| NiFeS@OCC | 1M KOH | 220 | 75 | 233 | 62 | 48 hrs. | This work |
| NiFeP@OCC | 1M KOH | 270 | 76 | 300 | 76 | 48 hrs. | This work |
| NiFe@OCC | 1М КОН | 281 | 64 | 256 | 85 | 17 hrs. | 1 |
| CoMoO ₄ -CC | 1М КОН | 290 | 94 | - | - | 10 hrs. | 2 |
| NiMoO ₄ -CC | 1М КОН | 353 | 116 | - | - | 10 hrs. | 2 |
| IrO ₂ -CC | 1М КОН | 354 | 72 | - | - | 10 hrs. | 2 |
| CoP/CC | 1М КОН | 282 | 62 | 95 | 60 | 72 hrs. | 3 |

 Table S2: Comparison of NiFeS@OCC and NiFeP@OCC activity with other similar

 electrocatalysts reported in the literature.

Electrochemical impedance measurements: The role of resistance in catalyst behavior was studied for the NiFe composite in 1 M KOH electrolyte (pH 14) containing 5 mM K₄[Fe (CN)₆] using electrochemical impedance spectroscopy by applying 1.284 V vs. RHE, DC potential over an AC perturbation of 10 mV with logarithmic frequency step over a single sine wave. The resulting Nyquist plot exhibited a semicircular behavior towards high frequency and a stout tail towards low frequency. The solution resistance (R_s) was obtained from the semicircle intersection at the real high-frequency axis, and the polarization resistance (R_p) at the low frequency near the electrode-electrolyte interface. The charge transfer resistance (R_{ct}) was calculated from the difference in R_p and R_s .



Figure S19. Nyquist plot for (a) NiFeS@OCC and (b) NiFeP@OCC catalyst and their controls in 5 mM K₄[Fe(CN)₆] at pH 14.

| S.N. | Electrode | <i>Rs</i> (Ω) | $Rp(\Omega)$ | $R_{ct}(\Omega)$ |
|------|-----------|---------------|--------------|------------------|
| 1 | NiFeS@OCC | 2.12 | 2.69 | 0.57 |
| 2 | FeS@OCC | 2.61 | 6.66 | 4.05 |
| 3 | NiS@OCC | 2.23 | 5.98 | 3.75 |
| 4 | NiFeP@OCC | 5.78 | 6.73 | 0.95 |
| 5 | FeP@OCC | 6.45 | 9.73 | 3.28 |
| 6 | NiP@OCC | 5.88 | 8.86 | 2.98 |

Table S3: Electrochemical Impedance analysis extracted from Figure S19.

Electrochemical surface area (ECSA):⁴

To investigate the actual number of exposed sites of the catalyst during the electrochemical reaction, the electrochemicaly active surface area of NiFeS@OCC and NiFeP@OCC was determined by calculating the double-layer pseudo-capacitance (C_{dl}). Initially, cyclic voltammetry was performed in the non-faradic potential region 1.134 V and 1.434 V *vs*. RHE with different scan rates (10 to 320 mV s⁻¹). The double-layer pseudo capacitance was determined as the slope

of both anodically and cathodically averaged current density versus the scan rate. Thus, the obtained C_{dl} was divided by the specific capacitance of the flat standard surface (20-60 μ F cm⁻²)⁵ to obtain the (ECSA), here we considered it to be 40 μ F cm⁻².



Figure S20A. Cyclic voltammograms of (a) NiFeS@OCC (b) NiFeP@OCC in non-faradic potential region at various scan rates (b) &(d) are corresponding average current density *vs.* scan rate plot for ECSA determination in 1M KOH. CE: Pt wire; RE: Hg/HgO/1 M NaOH.



Figure S20B. Cyclic voltammograms of (a) NiS@OCC, (c) NiP@OCC (e) FeS@OCC and (g) FeP@OCC in non-faradic potential region at various scan rates (b), (d), (f) and (h) are corresponding average current density versus scan rate plot for ECSA determination in 1 M KOH.

| S.No. | Electrocatalyst | C _{dl} * (μF) | ECSA (cm ²) |
|-------|-----------------|------------------------|-------------------------|
| 1 | NiFeS@OCC | 262 | 6.55 |
| 2 | NiFeP@OCC | 193 | 4.82 |
| 3 | NiS@OCC | 144 | 3.6 |
| 4 | NiP@OCC | 140 | 3.5 |
| 5 | FeS@OCC | 130 | 3.25 |
| 6 | FeP@OCC | 136 | 3.4 |

Table S4: Electrochemical surface area (ECSA) determination from Figure S20.



Figure S21. LSVs of the full cell study with two electrodes set up before and after chronoamperometric stability for (a) NiFeS@OCC and (b) NiFeP@OCC electrodes respectively.



Figure S22. LSVs of NiFeS@OCC and NiFeP@OCC showing bifunctional activity towards OER and HER in the alkaline electrolyte (1.0 M KOH).



Figure S23. Photograph of setup during estimation of O₂ and H₂ evolved via eudiometric method.

Quantification of evolved gases:6,7

The hydrogen and oxygen evolution were estimated quantitatively by measuring the H_2 and O_2 content using eudiometry method. The experiment was performed with a three-electrode system in a homemade set up where electrochemical cell was constructed by keeping the working electrode inside the inverted burette filled with the electrolyte 1 M KOH (pH 14). The NiFe deposited carbon cloth operated as a working electrode along with a Pt wire counter electrode referenced against Ag/AgCl/3M KCl. Then the chronoamperometric experiment was performed at an overpotential of 400 mV for OER and 300 mV for HER for 1.5 hrs respectively. Thereafter, resulted gas volume was noted and the amount of H_2 and O_2 evolved was determined by using ideal gas approximation.

The turnover number (TON) was estimated by diving the amount of gas evolved (mmol) with the amount of NiFeS and NiFeP catalyst loaded over carbon cloth

| а | omp r | of od n u | c ut o | <i>n</i> . | t | 0 | f | | m | т | |
|----------------------|-------|-----------|--------|------------|---|---|-----|---|---|-----|---|
| $TON = \overline{a}$ | m | ⊕ n | ио | n . | t | 0 | o f | f | т | c m | а |

Here, the no. of moles of active materials was estimated from the mass percentage of individual atoms which were calculated from XPS data. Whereas, the TON per unit time *i.e.*, turnover frequency (TOF) was determined as;

$$TOF = \frac{TON}{time}$$

 Table S5: Calculated turn over frequencies.

| S.No. | Composite | TOF for OER at 400 mV overpotential | TOF for HER at 300 mV overpotential |
|-------|-----------|-------------------------------------|-------------------------------------|
| | - | (\$-1) | (s ⁻¹) |

| 1. | NiFeP@OCC | 0.018 | 0.013 |
|----|-----------|-------|-------|
| 2. | NiFeS@OCC | 0.019 | 0.020 |

The overall water splitting studies were carried out in a two compartment H-cell separated by the Nafion N117 membrane. Where NiFe deposited carbon cloth electrodes were used as both anode and cathode for water splitting in two electrode cell setups in 1 M KOH respectively. The chronopotentiometric study was performed to study the water electrolysis. In order to quantify the amount of hydrogen and oxygen evolved during overall water splitting the study was performed by keeping the electrodes inside the inverted burette filled with electrolyte and the amount of gas evolved was measured as shown in Fig. S23. By applying ideal gas approximation, the amount of gas evolved during water electrolysis was calculated.

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