Electronic supplementary information (ESI)

Oxidised charcoal: an efficient support for NiFe layered double hydroxide to improve electrochemical oxygen evolution[†]

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Experimental

Chemicals:

Activated charcoal, nickel chloride (NiCl₂.6H₂O), iron chloride (FeCl₃), potassium bromide (KBr) and nafion perfluorinated resin solution were purchased from Sigma-Aldrich Pvt. Ltd. Hydrogen peroxide (H₂O₂, 30%), sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃) and potassium hydroxide (KOH) were supplied by Avra Synthesis Pvt. Ltd. Sulphuric acid (H₂SO₄, 98%), nitric acid (HNO₃, 69%), isopropanol and ethanol were obtained from Merck Chemicals Pvt. Ltd. Double distilled water was used in the study.

Synthesis of oxidised charcoal (OC):

A solution of 7.5 ml concentrated HNO₃, H_2SO_4 and H_2O_2 (v/v/v = 2:2:1) was added to 500 mg of activated charcoal in a 50 ml round bottom flask. The mixture was heated at 85 °C for 6 h in continuous stirring. Then it was cooled down to room temperature and separated by filtration. The oxidised charcoal (OC) was washed with water several times to remove the unreacted acids. It was dried in a hot air oven at 50 °C for 3h.

Synthesis of NiFe layered double hydroxide/oxidised charcoal (NiFeLDH/OC):

In this experiment, 1.90 g of NiCl₂.6H₂O and 0.45 g of FeCl₃ were dissolved in 10 ml of double-distilled water. Similarly, 0.70 g of NaOH and 0.60 g of Na₂CO₃ were dissolved in 10 ml of water. After-wards, both the solutions were added drop wise simultaneously to 100 mg of OC dispersed in 20 ml water in stirring condition. The pH of the resultant solution was ~8.5. It was kept on stirring for 24 h. Then, NiFeLDH/OC was filtered, and washed with water and ethanol. Finally, it was dried in hot air oven overnight at 50 °C. For NiFeLDH synthesis, similar experimental procedure was followed without OC.

Characterization:

Fourier-transform infrared spectra (FTIR) of the OC and NiFeLDH/OC were recorded using KBr pellets in Perkin-Elmer 843 spectrometer with a resolution of 4 cm⁻¹ in 4000 – 450 cm⁻¹ range. X-ray diffraction (XRD) analysis of the OC, NiFeLDH and NiFeLDH/OC were collected from Rigaku Smart lab diffractometer using Cu K_a radiation (λ =1.5405 Å) operating 45 kV and 200 mA (9 kW). Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was carried out in Agilent Technologies instrument (Model: 700 series) to estimate the moles of Ni and Fe in NiFeLDH and NiFeLDH/OC. The samples were heat-treated at 500 °C for 3 h and the obtained residue was dissolved in10 vol% HNO₃ to prepare the solution for ICP-OES analysis. For N₂ sorption analysis, the samples were degassed at 120 °C for 4 h and then the adsorption and desorption points were obtained at –196 °C by an Autosorb iQ Station 2. The multipoint Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used to obtain the surface area and the pore size distributions. Transmission electron microscopy (TEM) of the OC and NiFeLDH/OC was carried out using a JEOL JEM2100F microscope equipped with energy dispersive X-ray spectra (EDS) facility. A small amount of the samples was placed on carbon coated Cu mess 200 grids for this purpose. X-ray photoelectron spectra (XPS) of the samples were recorded on a PHI 5000 Versa Probe III with an Al K α X-ray source (hv = 1486.6 eV).

Electrochemical analysis:

The electrochemical experiments were carried out in three electrode configurations using glassy carbon (electrode diameter = 3 mm, area = 0.07 cm^2), Ag/AgCl (in sat. KCl) and pt wire as working, reference and counter electrodes respectively. 1 M KOH solution was used as an electrolyte. For depositing the synthesized materials on glassy carbon electrode a catalyst ink was prepared. Accordingly, 1.2 mg of the sample, 250 µL of distilled water-isopropanol (v/v=3:1) mixture and 12.5 µL of nation perfluorinated resin solution were mixed and dispersed thoroughly by sonication for 5 min. Then the 1 µL of the catalyst ink was deposited on the polished glassy carbon electrode and dried at 50 °C. Prior to the deposition, the electrode was polished by 0.3 micron sized alumina powder and cleaned thoroughly with double distilled water. Finally, three electrodes were connected to an Autolab PGSTAT 302N workstation for electrochemical experiments for the oxygen evolution reaction. Cyclic voltammograms (CVs) were recorded at sweep rate of 2 mV s⁻¹ in a potential range of 0 to 1 V (vs Ag/AgCl reference electrode). The potential of the electrochemical experiments was converted to reversible hydrogen electrode following an equation, E (RHE)= E(Ag/AgCl) + 0.196 + 0.059 pH. The potentials in the manuscript are reported without iR drop correction. Chronopotentiometry (constant current electrolysis experiment) was carried out at 10 mA cm⁻² for 12 h. Electrochemical impedance spectroscopy was obtained from BioLogic instrument with sinsudal amplitude of 5 amp in a frequency range of 10^5 to 10^{-2} Hz at 1.48 V vs RHE. Mass activity, specific activity, turnover frequency (TOF) of the catalysts were calculated following Eqs. 1, 2, and 3, respectively.¹

Massactivity =
$$\frac{j}{m}$$
 (1)

Specific activity =
$$\frac{j}{10S_{BET} * m}$$
 (2)

$$\mathrm{T}OF = \frac{j}{4Fn} S_{geo} \qquad (3)$$

The terms *j*, *m*, S_{BET} are used to represent the current density (mA cm⁻²) at overpotential of 350 mV, deposited mass density (mg cm⁻²) and BET surface area (m² g⁻¹) of the catalyst, respectively. S_{geo}, F and n are the geometric area of the electrode (0.07 cm²), Faraday's constant and numbers of moles of the metal atoms present in the deposited catalyst.



Fig. S1 FTIR spectra of (a) activated charcoal and (b) OC; the peak assignments are mentioned with (st) and (bn) to indicate stretching and bending, respectively.



Fig. S2 FTIR spectra of (a) OC and (b) NiFeLDH/OC.



Fig. S3 XRD of the activated charcoal in 10-70 $^{\circ}2\theta$.



Fig. S4 (a,b) Low, (c) high resolution TEM images and (d) EDS spectra of NiFeLDH/OC, Cu signal appeared from the TEM grid used in the study.

	Test Results	*		
			In ppm	
SN	Name of the sample	Iron	Nickel	
1	Blank	0.1698	0.0012	
2	LDH	29.5938	84.7225	
3	LDH/OCC	26.5431	78.4106	

Fig. S5 ICP-OES analysis of Ni and Fe in NiFeLDH and NiFeLDH/OC.



Fig. S6 (a, b) Low resolution TEM image and EDS of OC, respectively. Carbon coated Cu grid was used in the study. The appearance of EDS signal near 8 eV is due to Cu, appeared from the carbon coated Cu grid in the TEM analysis.



Fig. S7 N₂ adsorption - desorption isotherm and the pore size distribution (inset) of OC.



Fig. S8 N₂ adsorption - desorption analysis of activated charcoal; inset shows the pore size distribution.



Fig. S9 N_2 adsorption-desorption isotherm of (a) NiFeLDH and (b) NiFeLDH/OC; the surface area and pore size distribution for each case are provided in the inset of the figures.



Fig. S10 Electrolysis of OC at 1.8 V vs RHE for 4 h. The increased current density at the initial stage and decline in the later part to the values of starting points suggest further oxidation of OC. This indicates that the appearance of small peak for OC at 1.8 V vs. RHE in Fig. 5a is due to the carbon oxidation. Hence, the possibility of OER kinetics in this case is ruled out.

 $\label{eq:stables} \textbf{Table S1} \text{ Overpotential, mass activity, specific activity and TOF of the catalysts.}$

Sample	NiFeLDH	NiFeLDH/OC
Overpotential @ 10 mA cm ⁻² (mV)	357	240
Mass activity (A g ⁻¹)	141.2	528
Specific activity (mA cm ⁻²)	0.32	0.88
$TOF(s^{-1})$	0.25	1.05



Fig. S11 CVs of NiFeLDH/OC in OER, where OC was synthesized using (a) HNO_3 and (b) HNO_3 and H_2O_2 , respectively. The disturbance in CV plots is due to O_2 bubbles produced during OER. We found lowest overpotential (240 mV) in case of NiFeLDH/OC catalyst, where OC was synthesized using our reported oxidizing agent i.e. HNO_3 , H_2O_2 , and H_2SO_4 in the manuscript.

Elucidation of enhanced catalytic activity of NiFeLDH/OC

It is established that oxygen evolution reaction (OER) in alkaline conditions proceeds through multistep mentioned in the equations (1) to (5).² In first step , an adsorption of OH⁻ (produced in alkaline conditions) on the catalytically active 'M' metal sites takes place to evolve M-OH species. Further, a reaction of OH⁻ with the metal adsorbed OH (M–OH) releases proton and electron to form M-O (equation 2). The next step includes the formation of M-OOH in a process where M-O combines with the OH⁻. The reaction is slowest in the mechanism and thus acknowledged to be the rate determining step of the OER. The release of proton from M-OOH in presence of OH⁻ produces MO_2^- (equation 4). Following discharge of electron and desorption of O_2 from MO_2^- produce O_2 gas (equation 5).

 $M + OH^{-} \rightarrow M - OH + e \tag{1}$

 $M-OH+OH^{-} \rightarrow M-O+H_{2}O+e$ (2)

 $M-O+OH^{-} \rightarrow M-OOH + e$ (3)

 $M-OOH + OH^{-} \rightarrow MOO^{-} + H_2O$ (4)

$$MOO^{-} \rightarrow M + O_2 + e \tag{5}$$

The contribution of electronic structure of metal centre is important in these steps to control the OER kinetics because M involves in the adsorption and desorption processes that are dependent on the charge density of the metal surfaces. It is acknowledged that electropositive metal centre is required to enhance the adsorption of OH on 'M' metal site and that facilitate the formation of MOOH. Alternatively, high positive charge at the metal centre hinders the O_2 desorption process required at the final stage of the OER and thus slows down the O_2 gas production. So, the increased electrons density of 3d orbital in metal site from support could make strong metal-support interaction and mitigate the O_2 evolution by lowering M-O₂ bond strength;³⁻⁸ this is in consistent with the mechanism proposed by Zhang et al. and other groups.³⁻⁶ In the context of our work, the electronic enrichment of Ni and Fe sites by the OC support is expected to enhance the O_2 desorption process. The increased electronic contribution of 3d orbital in metals by the electron delocalization impact of OC makes the strong metal carbon coordination and weakens the metal-oxygen bonds (MOO⁻) in the final step of OER. Hence, NiFeLDH/OC in our case eases O_2 desorption and attains superior catalytic activity.

Sl No	Catalyst	Catalyst loading (mg cm ⁻²)	η @10 mA cm ⁻²	Tafel slope (mV dec ⁻¹)	Stability	Ref.
1	NiFeLDH/OC	0.06	240	75	12 h	Our work
2	Graphdiyne supported NiFeLDH	1.00	260	95	6 h	<i>ACS Appl. Mater. Interfaces</i> , 2019, 11 , 2662
3	NiFeLDH	0.07	270	53.4	-	Angew. Chem. Int. Ed., 2019, 58 , 736
4	FeNi-LDH/Ti ₃ C ₂ - Mxene	0.20	298	42	12 h	Nano Energy, 2018, 44 , 181
5	N doped NiFe LDH/N-rGO	0.36	258	63	9.5 h	Appl. Catal. B, 2017, 205, 551
6	NiFe LDH-CNT	0.28	420	45	~0.9 h	<i>Chem. Commun.</i> , 2016, 52 , 1439
7	NiFe-LDH/GMC	0.14	320	57	2 h	ChemSusChem., 2016, 9, 1835
8	NiFe LDHs/N doped graphene	0.25	337	45	~3.3 h	Adv. Mater., 2015, 27, 4516
9	NiFe LDH/nanocarbon	0.25	350	54	~2.8 h	<i>J. Mater. Chem. A</i> , 2015, 3 , 24540
10	O-NiCoFeLDH	1.00	340	93	10 h	<i>Adv. Energy Mater.</i> , 2015, 5 1500245
11	Exfoliated NiFeLDH	0.07	300	40	12 h	Nat. Commun., 2014, 5, 4477
12	NiFe LDH/CNT	0.20	407	31	1 h	J. Am. Chem. Soc., 2013, 135 , 8452
Other	Electrocatalysts					
1	Co/Co ₃ O ₄ @NC	-	260	88	8 h	small, 2020, 16, 1907029
2	K(MgMnFeCoNi)F ₃	0.70	369	61	10 h	J. Am. Chem. Soc., 2020, 142 , 4550
3	Co-Mo-N/Au	7.25	237	46	25 h	Adv. Mater., 2020, 32 , 1907214
4	α-MnS	1.30	292	91	10 h	<i>J. Mater. Chem. A</i> , 2020, 8 , 3901
5	Mn-doped Co ₃ O ₄ nanoflakes	0.65	263	60	16 h	ACS Sustainable Chem. Eng., 2019, 7, 9690
6	CeOx/NiCo ₂ S ₄ /CC	4.00	270	126	20 h	<i>ACS Appl. Mater. Interfaces</i> , 2019, 11 , 39841
7	CoFe ₂ O4	0.36	275	42	10 h	J. Mater. Chem. A, 2019, 7, 7328

 $\label{eq:solution} \begin{array}{l} \textbf{Table S2} \mbox{ Catalyst loading, overpotential (η), Tafel slope, and stability of the metal oxide/hydroxide catalysts studied recently for OER in alkaline condition \end{array}$

8	Co–MoOx	0.28	340	49	2.8 h	J. Mater. Chem. A, 2019, 7,
						1005
9	Co ₃ Fe ₁ N/graphene	0.20	266	32	16 h	J. Mater. Chem. A, 2019, 7, 12489
10	NCoM-Cb-Ar	0.14	340	76	12 h	Angew. Chem., 2019, 131 , 8418

Post catalysis characterization of NiFeLDH/OC

For post catalysis characterization, an electrolysis experiment using NiFeLDH/OC was carried out at 10 mA cm⁻² current density for 5 h and XPS was recorded with the obtained material. The XPS result is presented in Fig. S12 for Ni and Fe components. It shows two peaks at 854.6 and 859.8 eV, respectively which can be indexed as Ni²⁻⁸ $2p^{3/2}$ and its satellite peak, respectively. A Fe³⁻⁸ $2p^{3/2}$ XPS peak was obtained at 709.9 eV with a broad Ni LMM auger peak at 711 – 716 eV in Fig. S12b.⁹ It shows only the presence of electron rich metal components, which precludes the metal surface oxidation in OER.



Fig. S12 High resolution XPS of (a) Ni2p and (b) Fe2p of NiFeLDH/OC.

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