Supporting Information

Fe_xNi_y/CeO_2 Loaded on N-doped Nanocarbon as an Advanced Bifunctional Electrocatalyst for the Overall Water Splitting

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Chemicals

Melamine Monomer ($C_3H_6N_6$) was purchased from TCI (Shanghai) Development Co. Ltd. $Fe(NO_3)_3 \cdot 9H_2O$ (MW: 404) and $Ce(NO_3)_3 \cdot 6H_2O$ (MW: 434.22) were obtained from MACKLIN Co., Ltd. $Ni(NO_3)_2 \cdot 6H_2O$ (MW: 290.79), Nafion (5 wt%), commercial Pt/C (20 wt%) catalyst and commerical IrO_2 catalyst were ordered at Sigma – Aldrich Co. Ltd. All of the reagents were purchased and directly used without further purification.

Synthesis Method

Synthesis of $Fe_xNi_y/CeO_2/NC$ catalyst: In a typical synthesis procedure, 1.0 g of $C_3H_6N_6$ was added into 40 mL of deionized water under vigorously stirring to form a homogeneous solution. Then, 0.1 g of $Fe(NO_3)_3 \cdot 9H_2O$, 0.1 g of $Ce(NO_3)_3 \cdot 6H_2O$ and 0.1 g of $Ni(NO_3)_2 \cdot 6H_2O$ were successively added to the above solution and continuously stirred for 12 h at room temperature. Afterward, the emulsion-like solution was heated to 70 °C to remove the most solvent and then further dried in vacuum at 80 °C for 2 h. After that, the obtained black power was annealed at 700 °C for 2 h under an Ar atmosphere with a gas flow rate of 150 mL min^{-1}. When cooled to room temperature at Ar atmosphere, the obtained products were collected and directly used for electrochemical tests.

Synthesis of Fe-Ni/NC, Fe-Ce/NC, Ni-Ce/NC catalysts: The synthetic methods of Fe-Ni/NC, Fe-Ce/NC, and Ni-Ce/NC catalysts are similar with that of $Fe_xNi_y/CeO_2/NC$ catalyst, except without the addition of $Ce(NO_3)_3 \cdot 6H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ into the reaction systems.

Electrochemical Measurements

The electrocatalytic hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) performances of the prepared catalysts were tested in a 1.0 M KOH

electrolyte using a traditional three-electrode system, using a graphite rod and a reversible hydrogen electrode as the counter electrode and the reference electrode, respectively. The working electrode was prepared by loading 5 μL of the catalyst ink on a glass carbon (GC, 3 mm) electrode. The catalyst ink was obtained by dispersing 3.0 mg of catalyst powers and 60 μL of Nafion (5 wt%) in 0.3 mL of ultra-pure water and 0.15 mL of ethanol by ultrasonic for 15 min. The polarization curves were measured at a scan rate of 5 mV s^{-1}. All the data are originally obtained without iR compensation. The electrocatalytic stability of the catalysts was investigated by the chronoamperometry method at a constant potential of -0.24 V (vs. RHE) for HER and 1.47 V (vs RHE) for OER. The electrochemically active surface area (ECSA) of the $Fe_xNi_y/CeO_2/NC$ is systematically evaluated by the electrochemical double-layer capacitance (C_{dl}) using CVs with varied scan rates in the potential range of 0.1 V – 0.2 V (vs RHE).

Overall water splitting. The overall water splitting performance of the $Fe_xNi_y/CeO_2/NC$ catalyst was evaluated in a self-assembled two-electrode setup with the catalyst as both the anode and cathode. The Ni foam (1 × 1 cm) with loading 0.2 mg of catalyst as the working electrode. The polarization curves were recorded at a scan rate of 5 mV s^{-1}. The applied voltage was fixed at 0.8 V - 2.0 V. The durability test was investigated by the chronoamperometry method at a constant voltage of 1.70 V for 24 h.

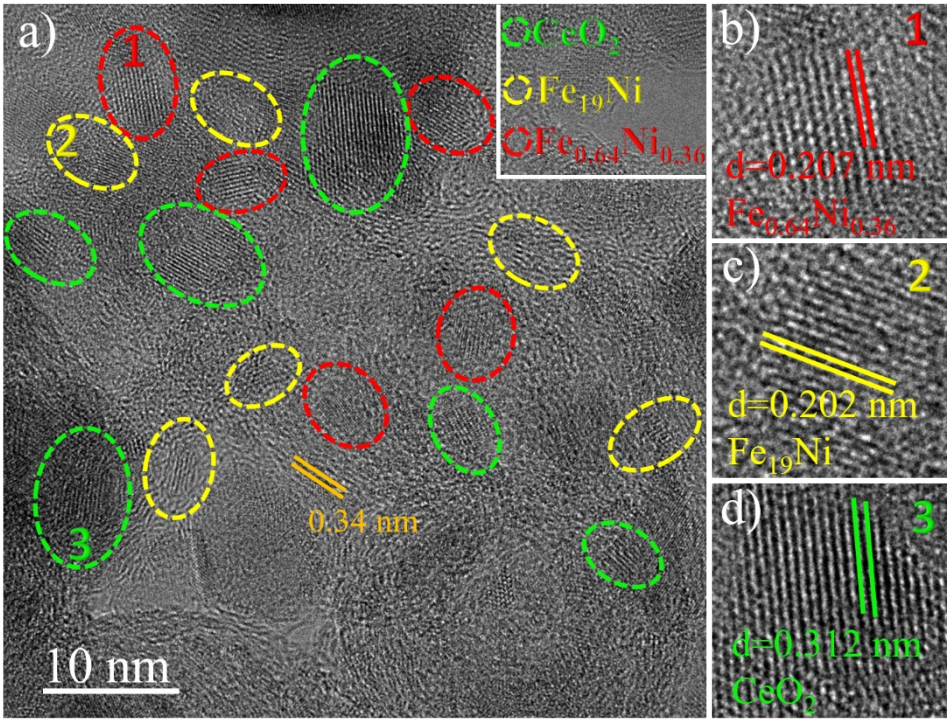
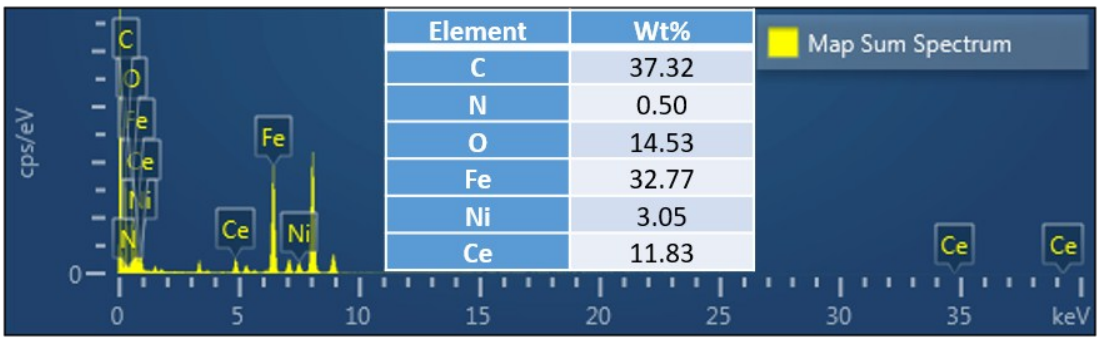


Fig. S1 The distribution of CeO_2, $Fe_{19}Ni$, and $Fe_{0.64}Ni_{0.36}$ nanoparticles on the carbon substrate.



Element	Wt%
C	37.32
N	0.50
O	14.53
Fe	32.77
Ni	3.05
Ce	11.83

Fig. S2 The EDS spectrum of the prepared $Fe_xNi_y/CeO_2/NC$.

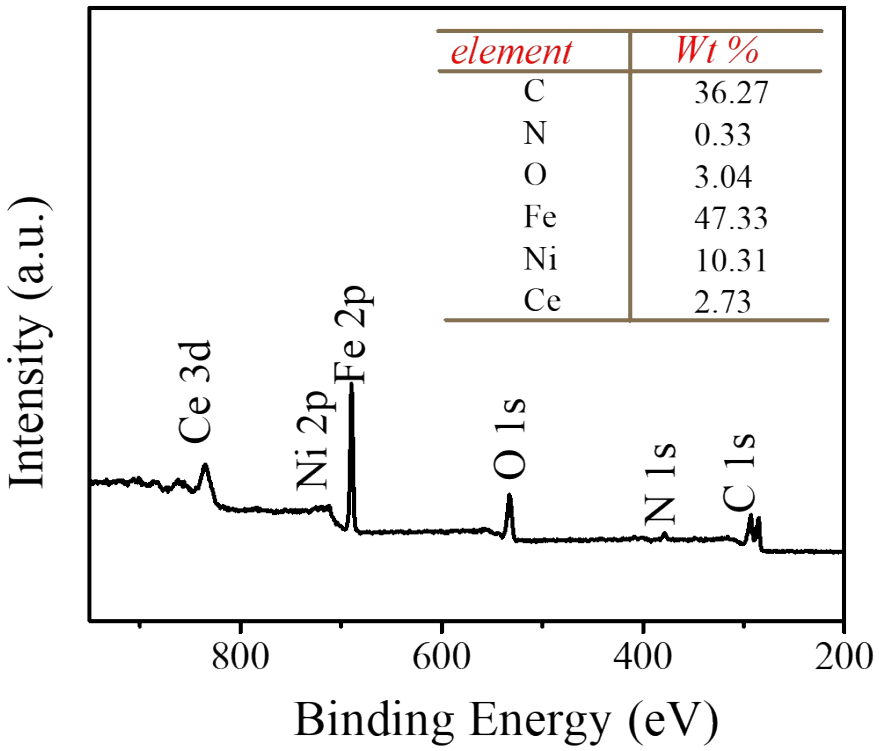


Fig. S3 The XPS survey spectrum of the $Fe_xNi_y/CeO_2/NC$ catalysts.

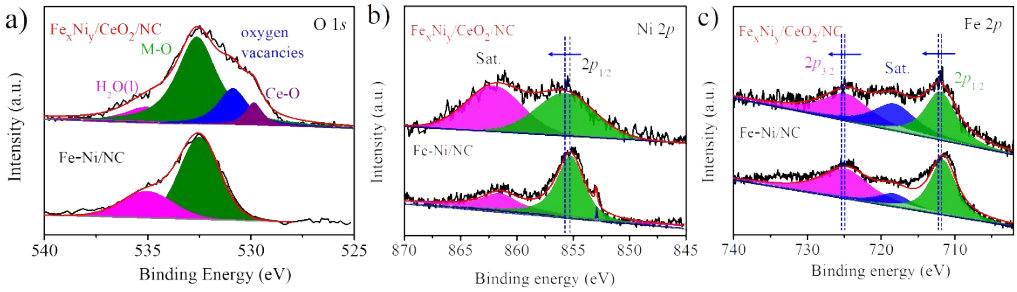


Fig. S4 The comparison of the binding energies of O 1*s*, Fe 2*p* and Ni 2*p* in $Fe_xNi_y/CeO_2/NC$ and Fe-Ni/NC: a) O 1s, b) Ni 2p, c) Fe 2p.

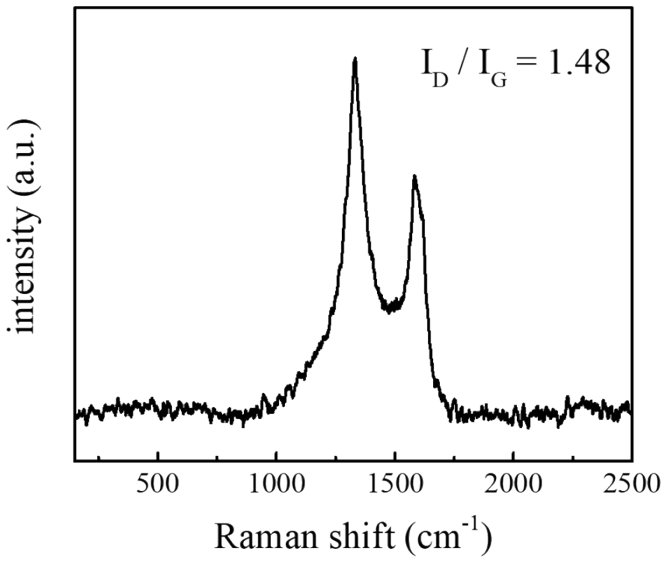


Fig. S5 Raman spectrum of $Fe_xNi_y/CeO_2/NC$.

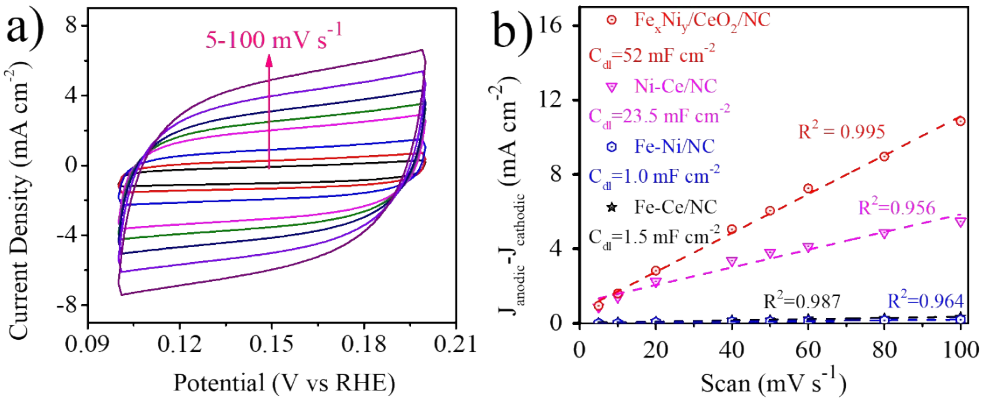


Fig. S6 a) Cyclic voltammograms recorded for a $Fe_xNi_y/CeO_2/NC$ electrode in the approximate region of 0.1-0.2 V vs. RHE at various scan rates for the purpose of determining the double layer capacitance. b) Plot showing the extraction of the double-layer capacitance (C_{dl}) of $Fe_xNi_y/CeO_2/NC$, Fe-Ni/NC, Fe-Ce/NC, Ni-Ce/NC.

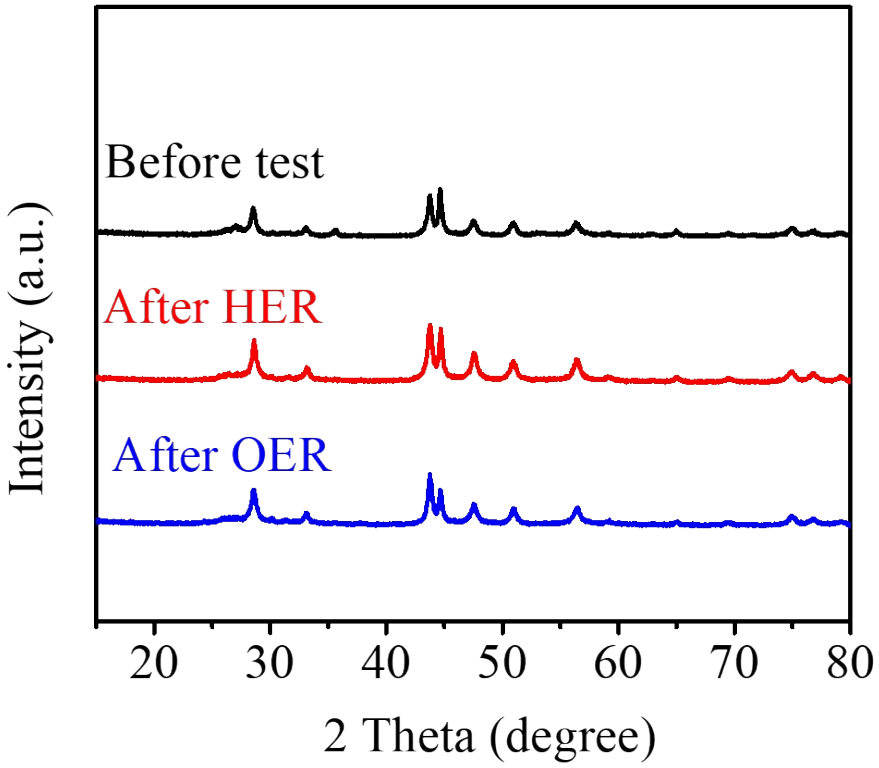


Fig. S7 The XRD patterns of the $Fe_xNi_y/CeO_2/NC$ catalysts before and after HER and OER testing.

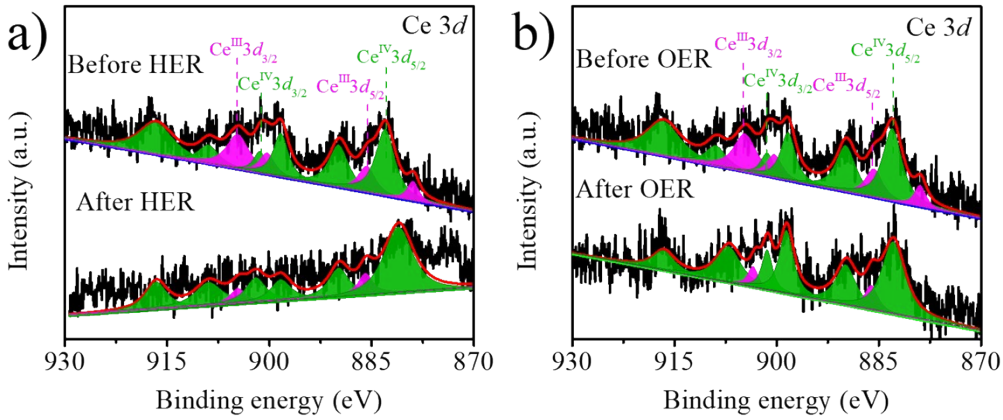


Fig. S8 High resolution XPS spectra of the as-synthesized Fe_xNi_y/CeO_2/NC composite. a) Ce 3*d* before and after OER testing. b) Ce 3*d* before and after HER testing.

Table S1 The change of the relative contents of Ce^{3+} and Ce^{4+} in the hybrid catalyst before and after HER/OER testing.

Condition	Percentage of Ce^{3+}	Percentage of Ce^{4+}
Before test	28.3%	71.7%
After HER	10.26%	89.74%
After OER	9.4%	90.6%

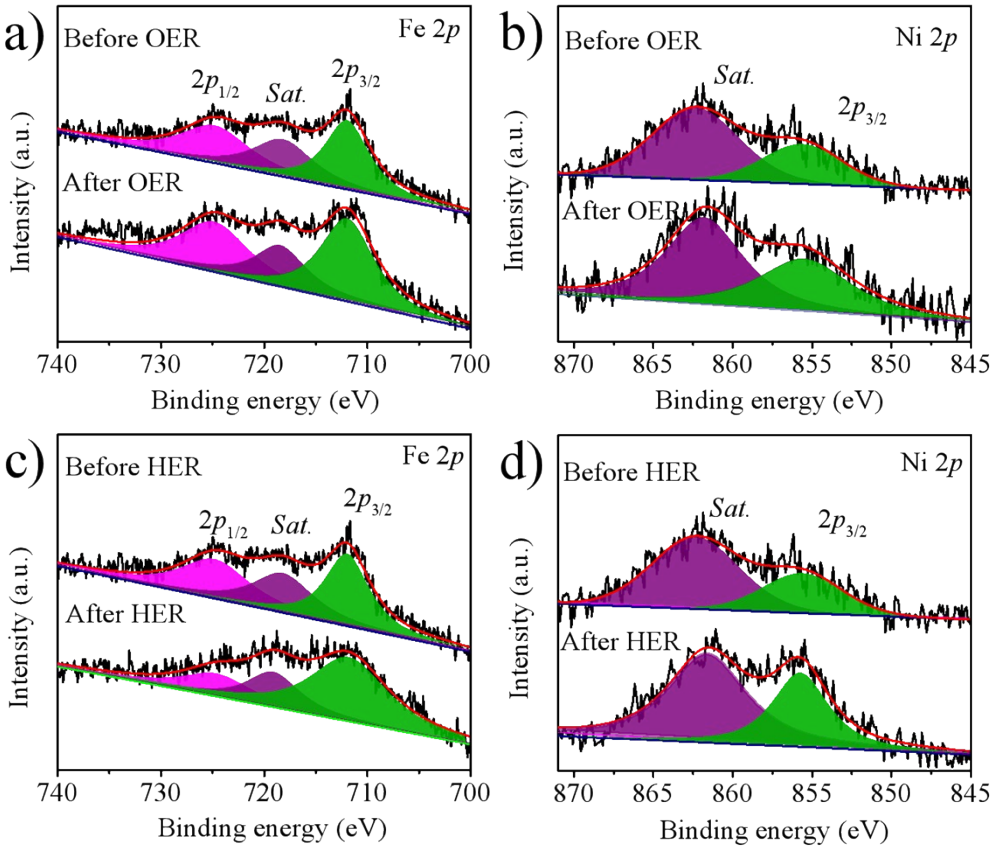


Fig. S9 XPS spectra of the as-synthesized $Fe_xNi_y/CeO_2/NC$ composite. a) Fe 2*p*, and b) Ni 2*p* before and after OER testing. c) Fe 2*p* and d) Ni 2*p* before and after HER testing.

Table S2 Comparison of catalytic properties of $Fe_xNi_y/CeO_2/NC$ and reported catalyst HER in alkaline electrolyte

Catalysts	Catalyst loading ($mg\ cm^{-2}$)	Overpotentia@j (mV@10 mA cm^{-}	Electrolyte	Ref.
FeNi&CeO_2/C	0.41	240	1.0 M KOH	This work
NiFe LDH-NS@DG10	0.28	300	1.0 M KOH	[1]
EG/$Co_{0.85}$Se/NiFe-LDH	4.00	~260	1.0 M KOH	[2]
Ni_3FeN-NPs	0.35	158	1.0 M KOH	[3]
NiCoP/rGO	0.15	209	1.0 M KOH	[4]
Ni_3S_2/NF	N/A	223	1.0 M KOH	[5]
FeP NAs/CC	N/A	218	1.0 M KOH	[6]
NCNT/MnO-$(MnFe)_2O_3$	0.14	212	1.0 M KOH	[7]

Table S3 Comparison of catalytic properties of Fe_xNi_y/CeO_2/NC and reported catalyst OER in alkaline electrolyte

Catalysts	Catalyst loading	Overpotentia@j (mV@10 mA cm^{-2})	Electrolyte	Ref.
FeNi&CeO_2/C	0.41	240	1.0 M KOH	This work
NiFe LDH-NS@DG10	0.28	210	1.0 M KOH	[1]
FeCoNi-2	0.32	325	1.0 M KOH	[8]
Porous Ni-P	N/A	~312	1.0 M KOH	[9]
NiFe LDH/NGF	0.25	340	0.1 M KOH	[10]
$NiCo_2O_4$	0.28	380	1.0 M KOH	[11]
Ni_3FeN/r-GO	0.50	279	1.0 M KOH	[12]
$NiCo_2O_4$hollow microcuboids	1.00	290	1.0 M NaOH	[13]
NiFe LDH/r-GO	0.25	210	1.0 M KOH	[14]
NiFe-SW film	N/A	240	1.0 M KOH	[15]
NiFe-MoO_xNS	0.20	276	1.0 M KOH	[16]

Table S4 Comparison of catalytic performance of $Fe_xNi_y/CeO_2/NC$ for two-electrode water splitting to reported catalysts

Catalysts	Catalyst loading	Voltage@j (V@10 mA cm^{-}	Catalyst support	Ref.
FeNi&CeO_2/C	0.20	1.70	NF	This work
Ni_3S_2/NF	N/A	1.76@13	NF	[5]
NCNT/MnO-$(MnFe)_2O_3$	0.21	1.71	NF	[7]
$Ni_{0.33}Co_{0.67}S_2$NWs	0.30	1.72	TF	[17]
NiFe LDH	N/A	1.70	NF	[18]
Ni_5P_4	3.5	1.70	NF	[19]
Co_1Mn_1CH	5.6	1.68	NF	[20]
Fe-Co CF	1.2 or 2.0	1.68	CFP	[21]
NiFe/$NiCo_2O_4$	N/A	1.67	NF	[22]
Fe-CoP/Ti	N/A	1.60	TF	[23]
NiCoP/Ni foam	5.0	1.77	NF	[24]

NF: Ni foam; CFP: carbon fiber paper; TF: Ti foil

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