

Supporting Information

Adjustable Anchoring of Ni/Co Cations by Oxygen-Containing Functional Groups on Functionalized Graphite Paper and Accelerated Mass/Electron Transfer for Overall Water Splitting

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Figure S1. XPS analysis of O 1s spectra: (a) FGP_{0.48}, (b) FGP_{0.35}, (c) FGP_{0.44}, and (d) FGP_{0.41}.

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Figure S5. (a) EIS plots of FGP_{0.48}, FGP_{0.35}, FGP_{0.44}, and FGP_{0.41} at 0.924 V (vs. RHE). Inset: the enlarged EIS plots at the high-frequency region. (b) The resistivity comparison of FGP_{0.48} and FGP_{0.44}.

Figure S6. Photoluminescence (PL) spectra for NCS-NCO/FGP_{0.44}.

Figure S7. CV curve of NCS-NCO/FGP_{0.48} (a), NCS-NCO/FGP_{0.35} (b), NCS-NCO/FGP_{0.44} (c), NCS-NCO/FGP_{0.41} (d), and NCO/FGP_{0.44} (e) under different scan rates.

Figure S8. Raman spectra of NCS-NCO/FGP_{0.48}, NCS-NCO/FGP_{0.35}, NCS-NCO/FGP_{0.44}, and NCS-NCO/FGP_{0.41} with their D and G peaks.

Figure S9. The comparison of C_{dl} from recent report carbon-based bifunctional electrocatalysts and NCS-NCO/FGP_{0.44}.

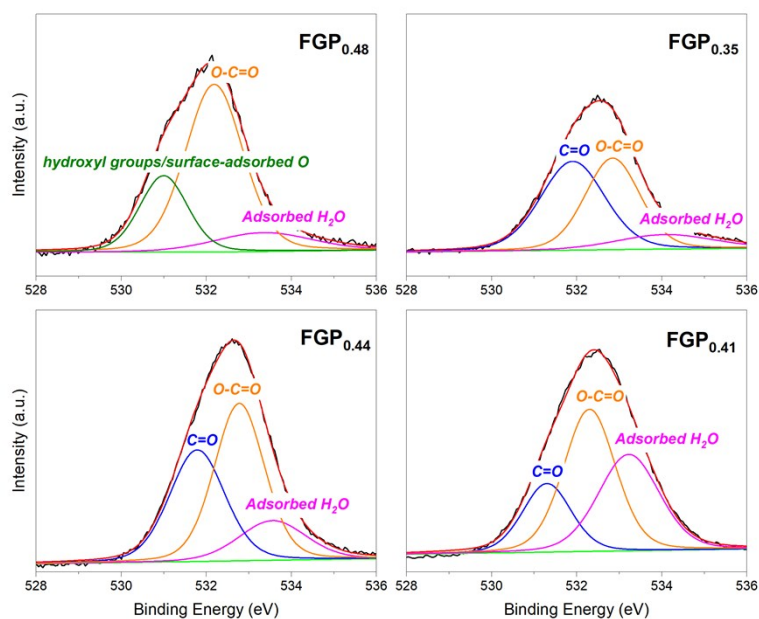


Figure S1. XPS analysis of O 1s spectra: (a) FGP_{0.48}, (b) FGP_{0.35}, (c) FGP_{0.44}, and (d) FGP_{0.41}.

The surface states of O species under different exfoliated times demonstrated in Fig. S1. Firstly, FGP_{0.48} electrode corresponds to three peaks of hydroxyl groups/surface-adsorbed O (531.0 eV), O=C-O groups (532.2 eV), and adsorbed H₂O (533.4 eV), respectively.¹⁻³ After electrochemical exfoliating, FGP_{0.35}, FGP_{0.44}, and FGP_{0.41} electrodes correspond to three peaks of C=O (531.3-531.9 eV), O=C-O groups (532.3-532.8 eV), and adsorbed H₂O (533.2-534.0 eV), respectively.⁴ Obviously, this is consistent with the results of the XPS spectra of C 1s, which further confirms that the functionalized graphite paper electrode successfully introduced the oxygen-containing functional group.

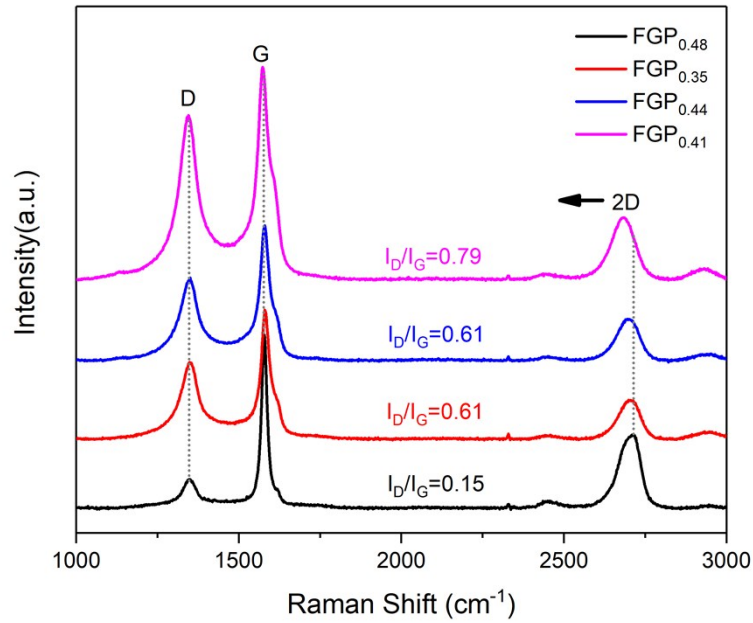


Figure S2. Raman spectra of FGP_{0.48}, FGP_{0.35}, FGP_{0.44}, and FGP_{0.41} in the wavenumber region from 1000 to 3000 cm⁻¹.

To analyze the graphitization degree and defect degree of the graphite catalysts, the vibrational peaks of D-band, G-band, and 2D-band at ~1350, ~1580, and ~2670 cm⁻¹ were measured. The D-band corresponds to the vibration of sp³-hybridized carbon atoms in disordered and defective regions, while G-band belongs to the E_{2g} vibration mode of sp² carbon atom. Thus, using the I_D/I_G ratio can qualitatively evaluate the graphitization sequence and defects of carbonaceous materials. The 2D waveband is a two-phonon resonance mode, and its strength reflects the stacking degree of graphene.⁵

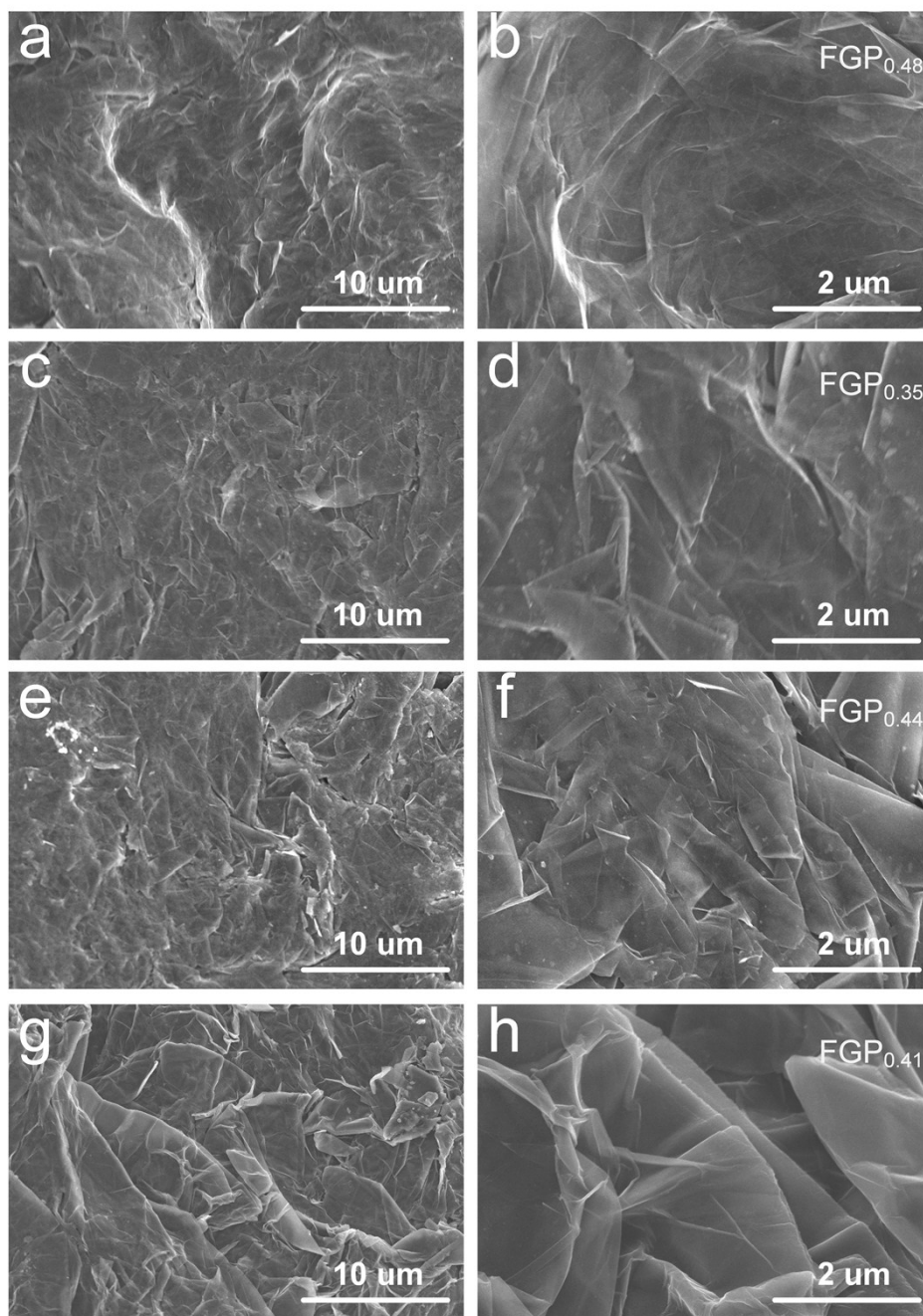


Figure S3. FE-SEM images of FGP_{0.48} (a and b), FGP_{0.35} (c and d), FGP_{0.44} (e and f), and FGP_{0.41} (g and h).

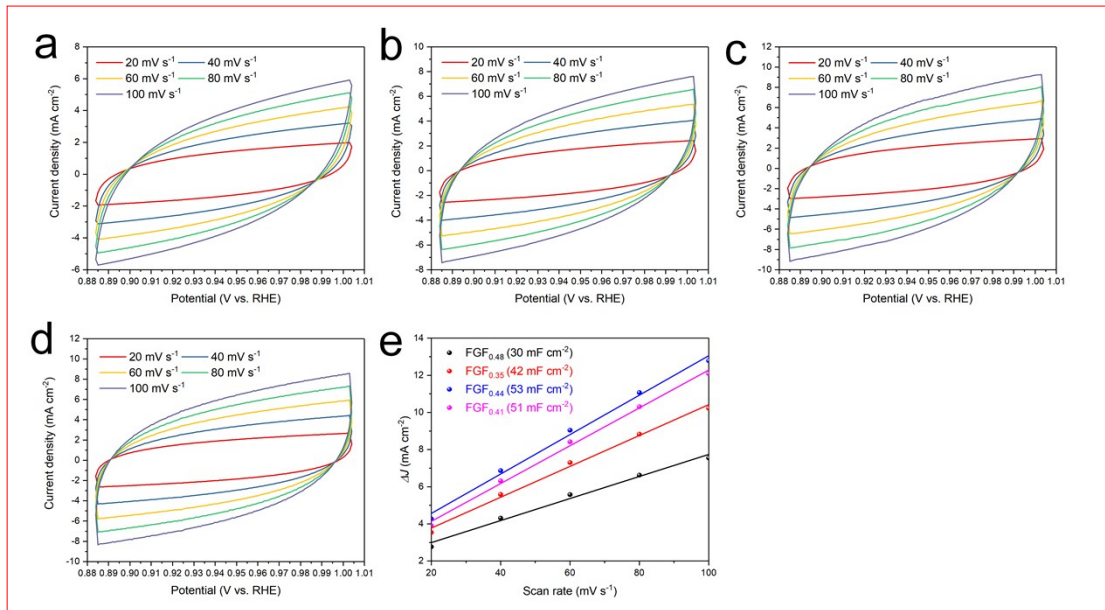


Figure S4. CV curve of (a) FGP_{0.48}, (b) FGP_{0.35}, (c) FGP_{0.44}, and (d) FGP_{0.41} under different scan rates at a voltage range of 0.884 V-1.004 V (vs. RHE). (e) Plots of current density difference (Δj) at 0.944 V (vs. RHE) against different scan rates for calculation of C_{dl} .

The C_{dl} of the FGP electrodes were calculated from the results of the CV scan, and the ECSA values were calculated (Figure S4a-e). The calculated C_{dl} of the FGP electrodes are: 30, 42, 53, 51 mF cm⁻², and their corresponding ECSA are: 750, 1050, 1325, 1275 cm².

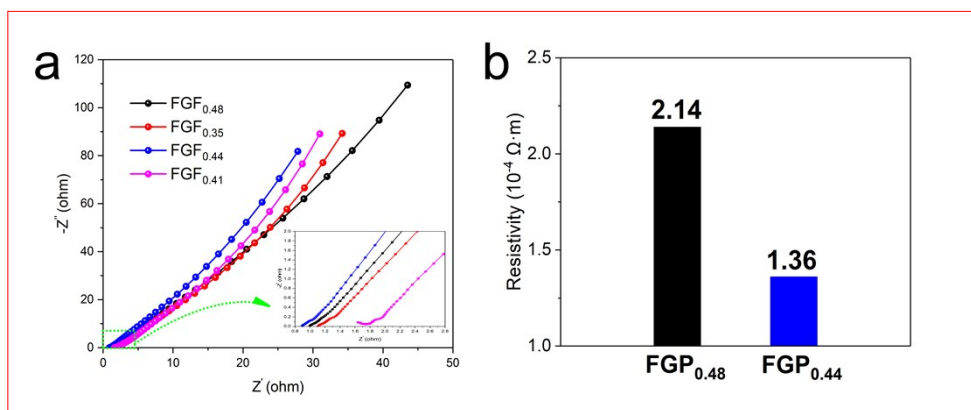


Figure S5. (a) EIS plots of FGP_{0.48}, FGP_{0.35}, FGP_{0.44}, and FGP_{0.41} at 0.924 V (vs. RHE). Inset: the enlarged EIS plots at the high-frequency region. (b) The resistivity comparison of FGP_{0.48} and FGP_{0.44}.

The EIS of FGP electrodes were measured to characterize their conductivity and Fig. S5a shows their Nyquist plots. Obviously, FGP_{0.44} has the largest slope and the smallest X-axis intercept (the inset of Fig. S5a), showing its optimal electron transport process and conductivity.⁶ The total impedance values of FGP_{0.48}, FGP_{0.35}, FGP_{0.44}, and FGP_{0.41} after fitting are: 1.189, 1.092, 0.943, and 2.439 Ω , respectively. The larger impedance value of FGP_{0.41} may be due to the large number of functional groups adsorbed on the exfoliated graphene surface during the electrochemical process, which results in a larger contact resistance between the electrolyte and the graphene so that it shows an increased resistance value. Besides, the resistivities of the FGP_{0.48} and FGP_{0.44} electrodes were detected by a four-point probe measurement (Fig. S5b). The results show that the resistivity of the FGP after exfoliating decreased from 2.14×10^{-4} to 1.36×10^{-4} $\Omega \cdot m$, showing the increased electrical conductivity of the functionalized graphene.

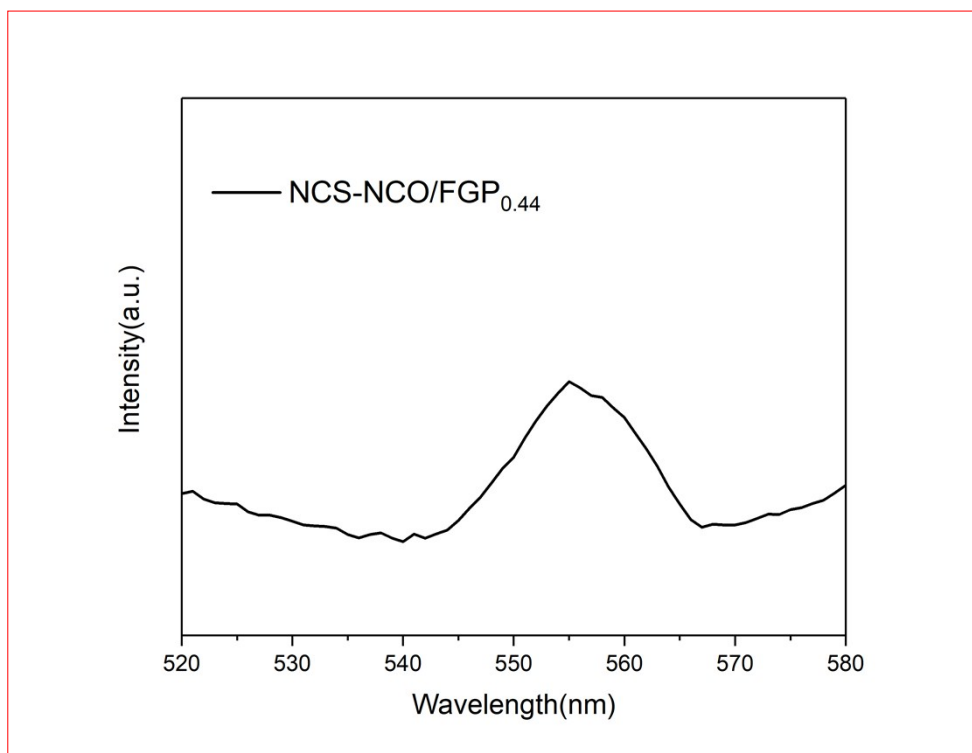


Figure S6. Photoluminescence (PL) spectra for NCS-NCO/FGP_{0.44}.

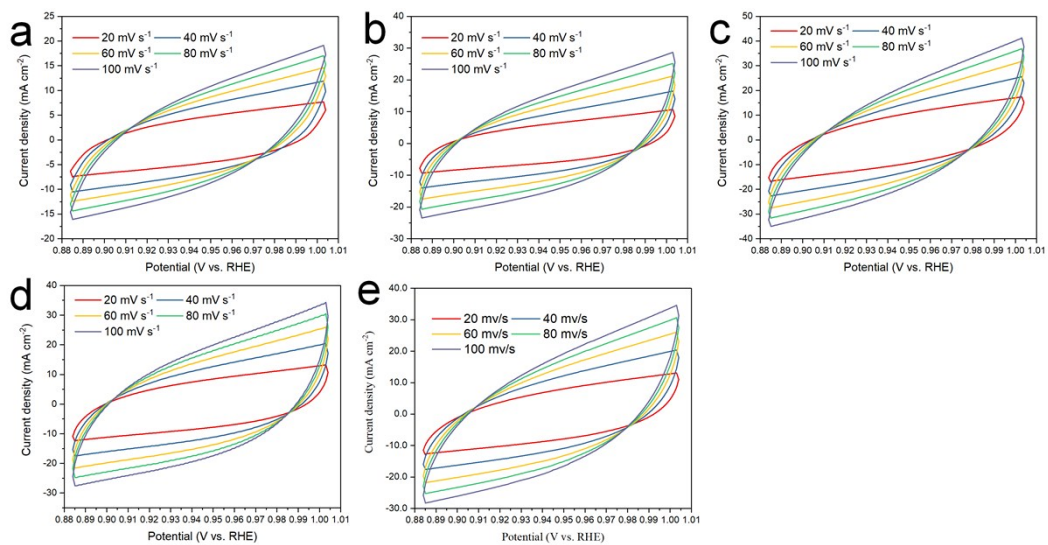


Figure S7. CV curve of NCS-NCO/FGP_{0.48} (a), NCS-NCO/FGP_{0.35} (b), NCS-NCO/FGP_{0.44} (c), NCS-NCO/FGP_{0.41} (d), and NCO/FGP_{0.44} (e) under different scan rates.

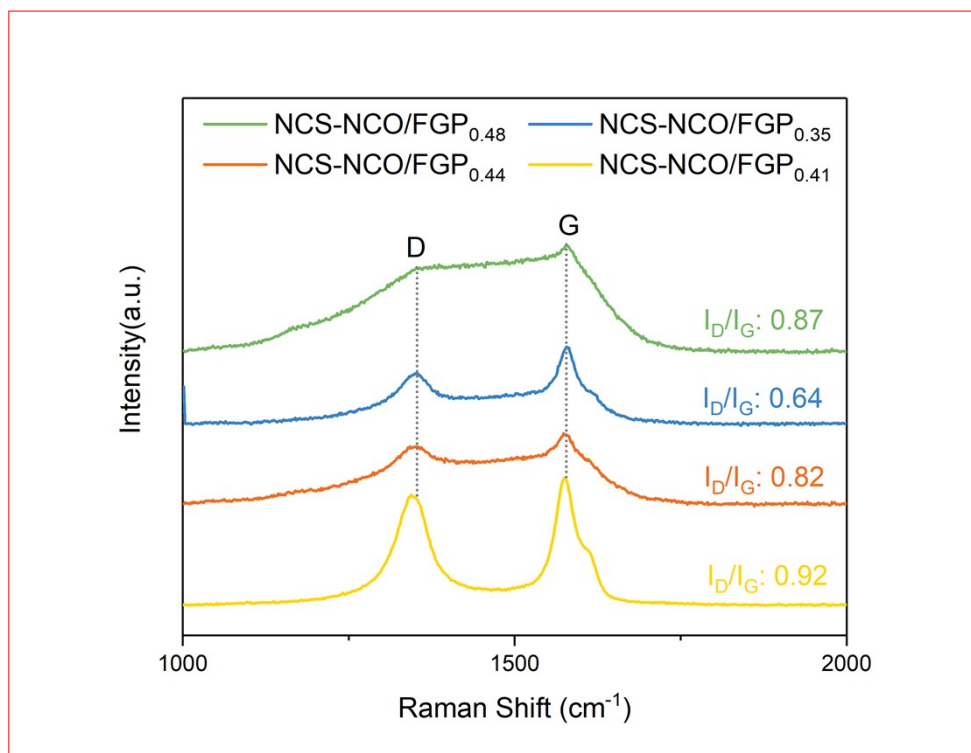


Figure S8. Raman spectra of NCS-NCO/FGP_{0.48}, NCS-NCO/FGP_{0.35}, NCS-NCO/FGP_{0.44}, and NCS-NCO/FGP_{0.41} with their D and G peaks.

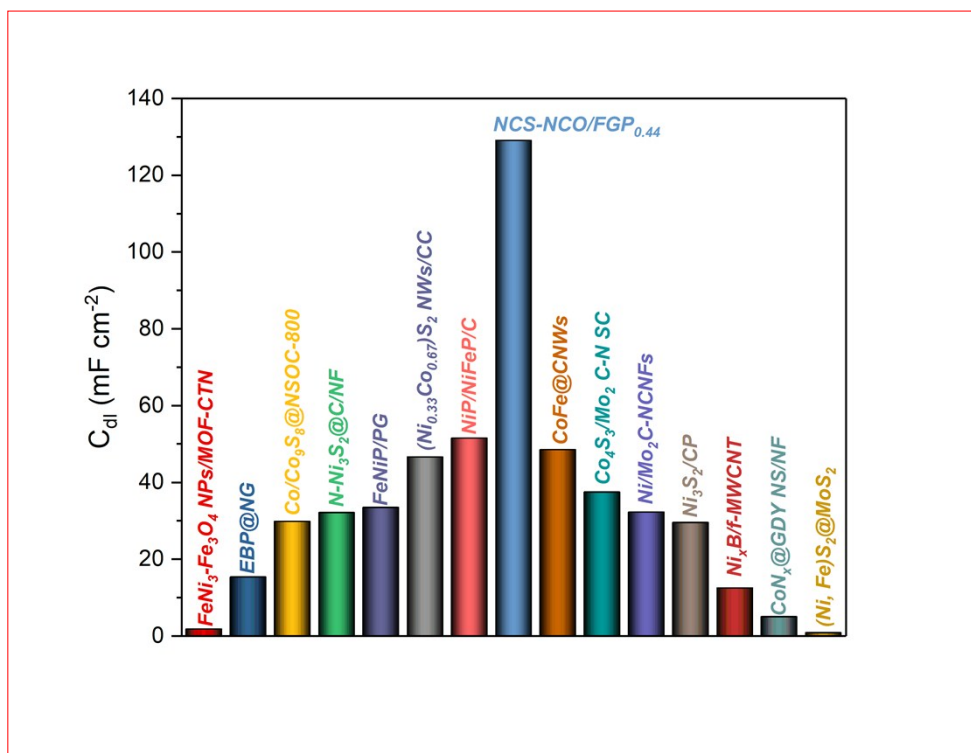


Figure S9. The comparison of C_{dl} from recent report carbon-based bifunctional electrocatalysts and NCS-NCO/FGP_{0.44}.

The C_{dl} of these carbon-based bifunctional electrocatalysts were performed in a 1M KOH solution. Its calculations are all derived from the CV curves without Faradaic progress. ⁷⁻²⁰

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Table S2. The atomic content of anchored Ni and Co cations for NCS-NCO/FGP_{0.48}, NCS-NCO/FGP_{0.35}, NCS-NCO/FGP_{0.44}, NCS-NCO/FGP_{0.41}, which was calculated by ICP-OES.

Table S3. EIS data fitting results of NCS-NCO/FGP_{0.48}, NCS-NCO/FGP_{0.35}, NCS-NCO/FGP_{0.44}, NCS-NCO/FGP_{0.41}, and NCO/FGP_{0.44} electrodes for OER, respectively.

Table S4. Comparison of the electrochemical performances of NCS-NCO/FGP_{0.44} electrode for OER with recently reported catalysts in 1.0 M KOH.

Table S5. EIS data fitting results of NCS-NCO/FGP_{0.48}, NCS-NCO/FGP_{0.35}, NCS-NCO/FGP_{0.44}, NCS-NCO/FGP_{0.41}, and NCO/FGP_{0.44} electrodes for HER.

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Table S9. Parameter settings of NCS-NCO/FGP_{0.44} electrode during microwave hydrothermal synthesis.

Table S1. The percentage areas of oxygen-containing functional groups in FGP_{0.48}, FGP_{0.35}, FGP_{0.44}, and FGP_{0.41}, which calculated by fitting the corresponding XPS peaks, respectively.

Electrode s	C-C	oxygen-containing functional groups				Area 1 ^a	Area 2 ^b	Percentage ^c
		C-OH	C-O	C=O	O-C=O			
FGP _{0.48}	61502.34	32044.11	14845.46	-	10156.81	118548.72	57046.38	0.48
FGP _{0.35}	78944.59	9268.97	16531.68	4790.32	11381.39	120916.94	41972.35	0.35
FGP _{0.44}	65612.39	11239.78	22391.02	9781.33	8191.45	117215.97	51603.58	0.44
FGP _{0.41}	127433.30	27318.62	25924.30	20520.75	14584.25	215781.22	88347.92	0.41

^a The areas of all peaks in C 1s.

^b The areas of the peaks of oxygen-containing functional groups.

^c The percentage areas of oxygen-containing functional groups.

Table S2. The atomic content of anchored Ni and Co cations for NCS-NCO/FGP_{0.48}, NCS-NCO/FGP_{0.35}, NCS-NCO/FGP_{0.44}, and NCS-NCO/FGP_{0.41}, which were counted by ICP-OES.

Electrodes	The atomic content of metal cations anchored ($\mu\text{mol cm}^{-2}$)		
	Ni	Co	Sum ^a
NCS-NCO/FGP _{0.48}	4.29	10.53	14.82
NCS-NCO/FGP _{0.35}	4.17	15.49	19.66
NCS-NCO/FGP _{0.44}	4.36	13.37	17.73
NCS-NCO/FGP _{0.41}	5.06	14.51	19.57

^a The sum atomic content of anchored metal cations.

Table S3. EIS data fitting results of NCS-NCO/FGP_{0.48}, NCS-NCO/FGP_{0.35}, NCS-NCO/FGP_{0.44}, NCS-NCO/FGP_{0.41}, and NCO/FGP_{0.44} electrodes for OER, respectively.

Electrode	R _s (Ω)	R _{dl} (Ω)	R _{ct} (Ω)	R _{tot} (Ω)
NCS-NCO/FGP _{0.48}	1.129	1.326	4.253	6.708
NCS-NCO/FGP _{0.35}	1.307	1.238	4.068	6.613
NCS-NCO/FGP_{0.44}	1.095	1.277	3.215	5.587
NCS-NCO/FGP _{0.41}	1.389	1.658	4.057	7.104
NCO/FGP _{0.44}	1.389	0.641	4.909	6.939

Table S4. Comparison of the electrochemical performances of NCS-NCO/FGP_{0.44} electrode for OER with recently reported catalysts in 1.0 M KOH.

Electrode	Substrate	j (mA cm ⁻²)	η (mV vs RHE)	Ref.
NCS-NCO/FGP _{0.48}	FGP _{0.48}	10	246	This work
NCS-NCO/FGP _{0.35}	FGP _{0.35}	10	291	
NCS-NCO/FGP_{0.44}	FGP_{0.44}	10	117	
NCS-NCO/FGP _{0.41}	FGP _{0.41}	10	199	
NCO/FGP _{0.44}	FGP _{0.44}	10	304	
RuO ₂ /FGP _{0.44}	FGP _{0.44}	10	320	
CoS ₂ -C@MoS ₂	-	10	391	21
Ni ₃ S ₂	-	10	295	17
Ni ₃ S ₂	NF	10	296	22
CoMoS ₄ /Ni ₃ S ₂	NF	10	200	23
CoS _x Se _{2(1-x)}	CC	10	285	24
CoN _x @GDY	GDY ^a -modified NF	10	260	19
MoS ₂ /NiCoS heterostructure	-	10	290	25
(Ni, Fe) S ₂ @MoS ₂ heterostructures	CFP ^b	10	270	20
Pt-αFe ₂ O ₃	NF	50	304	26
Ru/Cu ₂₊₁ O	CuF ^c	10	210	27

^a Graphdiyne.

^b Carbon fiber paper.

^c Cu foam

Table S5. EIS data fitting results of NCS-NCO/FGP_{0.48}, NCS-NCO/FGP_{0.35}, NCS-NCO/FGP_{0.44}, NCS-NCO/FGP_{0.41}, and NCO/FGP_{0.44} electrodes for HER.

Electrode	R _s (Ω)	R _{dl1} (Ω)	R _{dl2} (Ω)	R _{ct} (Ω)	R _{tot} (Ω)
NCS-NCO/FGP _{0.48}	1.027	0.556	1.390	5.100	8.073
NCS-NCO/FGP _{0.35}	1.413	0.324	1.046	4.400	7.183
NCS-NCO/FGP_{0.44}	1.075	0.204	0.757	3.335	5.371
NCS-NCO/FGP _{0.41}	0.883	0.374	1.293	4.330	6.880
NCO/FGP _{0.44}	1.469	0.341	1.289	4.882	7.981

Table S6. Comparison of the electrochemical performances of NCS-NCO/FGP_{0.44} electrode for HER with recently reported catalysts in 1.0 M KOH.

Catalyst	Substrate	j (mA cm ⁻²)	η (mV vs. RHE)	Ref.
NCS-NCO/FGP _{0.48}	FGP _{0.48}	10	-219	This work
NCS-NCO/FGP _{0.35}	FGP _{0.35}	10	-172	
NCS-NCO/FGP_{0.44}	FGP_{0.44}	10	-145	
NCS-NCO/FGP _{0.41}	FGP _{0.41}	10	-199	
NCO/FGP _{0.44}	FGP _{0.44}	10	-235	
Pt/C/FGP _{0.44}	FGP _{0.44}	10	-30	
CoS ₂ -C@MoS ₂	-	10	-173	21
Ni ₃ S ₂	-	10	-112	17
Ni ₃ S ₂	NF	10	-189	22
CoMoS ₄ /Ni ₃ S ₂	NF	10	-76	23
CoS _x Se _{2(1-x)}	CC	10	-225	24
CoN _x @GDY	GDY-modified NF	10	-70	19
MoS ₂ /NiCoS heterostructure	-	10	189	25
(Ni, Fe) S ₂ @MoS ₂ heterostructures	CFP	10	-130	20
Pt-αFe ₂ O ₃	NF	10	-90	26
Ru/Cu ₂₊₁ O	CuF	10	-32	27

Table S7. Catalyst loading of NCS-NCO/FGP_{0.48}, NCS-NCO/FGP_{0.35}, NCS-NCO/FGP_{0.44}, NCS-NCO/FGP_{0.41}, and NCO/FGP_{0.44} electrodes.

Electrode	Mass of catalyst (mg cm ²)		Catalyst loading (mg cm ²)
	m ₀ ^a	m ₁ ^b	Δm^c
NCS-NCO/FGP _{0.48}	148.6	134.1	14.5
NCS-NCO/FGP _{0.35}	128.5	113.1	15.4
NCS-NCO/FGP _{0.44}	139.3	122.6	16.7
NCS-NCO/FGP _{0.41}	136.5	119.9	16.6
NCO/FGP _{0.44}	129.3	119.1	10.2

^a The mass of the catalysts before acid treatment

^b The mass of the catalysts after acid treatment

^c Catalyst loading: $\Delta m = m_0 - m_1$

Table S8. Comparison of the electrochemical performances of NCS-NCO/FGP_{0.44} electrode for overall water splitting with recently reported catalysts in 1.0 M KOH.

Catalyst	Substrate	j (mA cm ⁻²)	η (mV vs RHE)	Ref.
NCS-NCO/FGP _{0.48}	FGP _{0.48}	10	1.580	
NCS-NCO/FGP _{0.35}	FGP _{0.35}	10	1.544	This work
NCS-NCO/FGP_{0.44}	FGP_{0.44}	10	1.481	
NCS-NCO/FGP _{0.41}	FGP _{0.41}	10	1.596	
NCO/FGP _{0.44}	FGP _{0.44}	10	1.636	
RuO ₂ /FGP _{0.44} Pt/C/FGP _{0.44}	FGP _{0.44}	10	1.583	
Ni ₃ S ₂	-	10	1.63	17
Ni ₃ S ₂	NF	10	~1.55	22
CoMoS ₄ /Ni ₃ S ₂	NF	10	1.568	23
CoS _x Se _{2(1-x)}	CC	10	1.74	24
CoN _x @GDY	GDY-modified NF	10	1.48	19
MoS ₂ /NiCoS heterostructure	NF	10	1.50	25
(Ni, Fe) S ₂ @MoS ₂ heterostructures	CFP	10	1.56	20
Pt-αFe ₂ O ₃	NF	10	1.51	26
Ru/Cu ₂₊₁ O	CuF	10	1.53	27

Table S9. Parameter settings of NCS-NCO/FGP_{0.44} electrode during microwave hydrothermal synthesis.

Experimental stage	Temperature (°C)	Operating time (min)	Power (W)
1	30	0	600
2	120	10	600
3	120	5	600
4	160	10	600
5	160	5	600
6	200	12	600
7	200	45	600

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