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### **Supplementary Information**

# Improved alkaline water electrolysis system for Green Energy: Sulfonamide Antibiotics-assisted anodic oxidation integrated with hydrogen generation

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#### Synthesis of Fe<sub>2</sub>O<sub>3</sub>@NF and NiFe<sub>2</sub>O<sub>4</sub>@NF

#### Synthesis of Fe<sub>2</sub>O<sub>3</sub>@NF

The synthesis process of  $Fe_2O_3$  is the same as  $Fe_2O_3/NiFe_2O_4@NF$  except that  $Ni(NO_3)_2 \cdot 6H_2O$  was not added during the hydrothermal process, and we named the prepared sample  $Fe_2O_3@NF$ .

#### Synthesis of NiFe<sub>2</sub>O<sub>4</sub>@NF

The precursor nanosheet array was first prepared with 0.75 mmol Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 1.5 mmol FeCl<sub>2</sub>·4H<sub>2</sub>O while other parameters were kept constant as that of Fe<sub>2</sub>O<sub>3</sub>/NiFe<sub>2</sub>O<sub>4</sub>@NF.

#### Operation Details of H<sub>2</sub>O<sub>2</sub> and K<sub>2</sub>FeO<sub>4</sub> detection

#### H<sub>2</sub>O<sub>2</sub> detection method

In acidic solutions,  $H_2O_2$  is titrated directly with  $K_2MnO_4$  solution using  $Mn^{2+}$  as catalyst. oxidized quantitatively by potassium permanganate. The endpoint is indicated by the color change of the excess  $K_2MnO_4$  solution to pink. The amount of  $H_2O_2$  is determined according to the consumption of the standard solution of potassium permanganate.

#### K<sub>2</sub>FeO<sub>4</sub> detection method

ABTS is a substrate of catalase, and the redox potential of ABTS/ABTS<sup>++</sup> is 0.68 V<sup>1</sup>. It is very easy to transfer electrons and generate the stable green radical ABTS<sup>++</sup>, which has a specific absorption at 415 nm. The specific experimental steps were as follows: firstly, 5 mL of phosphate buffer solution (pH = 2.1, 0.2 M) was added to a 25 mL colorimetric tube, then 1 mL of ABTS solution was added to it, and finally, the K<sub>2</sub>FeO<sub>4</sub> solution to be measured was added, and the mixture was capacitated to 25 mL and then shaken, as the reaction was rapid, it was fully mixed and ready for measurement. A portion of the solution was measured at 415 nm using a suitable quartz cuvette (1 or 5 cm), and a blank correction was performed.

#### **Calculation Details**

All the spin-polarized density functional theory (DFT) calculations were carried out using the Vienna ab initio Simulation Package (VASP)<sup>2</sup>. The generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) functional was employed for the DFT exchange-correlation energy. The projector augmented wave (PAW) method was used to describe the electron-ion interaction. The number of plane wave was determined by an energy cutoff of 500 eV. The Brillouin zone was sampled by a  $3 \times 5 \times 1$  and  $2 \times 2 \times 1$  k-points grid for the structure optimizations for Fe<sub>2</sub>O<sub>3</sub> and NiFe<sub>2</sub>O<sub>4</sub>, respectively. The convergence tolerances

were set to  $5.0 \times 10^{-6}$  eV per atom for energy, and  $0.03 \text{ eV }\text{Å}^{-1}$  for maximum force. According to the Gaussian scheme, we use the electron smearing of  $\sigma = 0.1$  eV. The Fe<sub>2</sub>O<sub>3</sub> was modeled by a periodic three-layer Fe<sub>2</sub>O<sub>3</sub>(110) slab repeated in 2 × 1 surface unit cell. The NiFe<sub>2</sub>O<sub>4</sub> was modeled by a periodic one-layer NiFe<sub>2</sub>O<sub>4</sub>(111) slab repeated in  $\sqrt{3} \times \sqrt{3}$  surface unit cell. The vacuum zone was 15 Å in the z direction to separate the slabs.

Quantum chemistry calculations were performed with a Gaussian 09 software package. The SMX was optimized under the B3LYP-D3/6-31 + G(d,p) method. The effect of solvents on all of the calculations was modeled using the implicit polarizable continuum model (PCM)<sup>3</sup>. The Multiwfn 3.8(dev) code41 performs the Orbital-Weighted Dual Descriptor (OWDD)<sup>4</sup>. The isosurface maps and structure were visualized by Gaussview 05 package and visual molecular dynamics (VMD)<sup>5</sup>.

#### **Electrochemical Measurements Details**

All Cyclic voltammetry (CV) was measured at a scan rate of 10 mV s<sup>-1</sup>, while the scan rate for linearsweep voltammetry (LSV) and Tafel was 5 mV s<sup>-1</sup>. The Tafel slope is derived from the Tafel equation,  $\eta = b$ log I + a, where  $\eta$ , I, and b represent overpotential, current density, and Tafel slope, respectively. Electrochemical impedance spectroscopy (EIS) of the electrodes were measured at frequency ranges from 100 kHz to 0.01 Hz. To estimate the electrochemical active surface area (ECSA), C<sub>dl</sub> was measured by repeated CV at a series of scan rates between 20 mV s<sup>-1</sup> and 80 mV s<sup>-1</sup> within the range of open circuit potential (OCP)  $\pm 0.03$  V, ECSA = C<sub>dl</sub> / 0.04.

#### **The Detailed Acquisition Method**

Fable. S1	Gradient elution program	of mobile phase	(mobile phase	A:0.1% formic	acid solution;	mobile
		phase B:N	lethanol).			

Time <i>t</i> /min	Flow rate v/mL min <sup>-1</sup>	Mobile phase A/%	Mobile phase B/%
0	0.1	90	10
5	0.1	90	20
10	0.1	70	40
15	0.1	60	30
20	0.1	60	10
30	0.1	90	10

$$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_{3}$$

(S1)

$$Ni^{2+} + 2OH^{-} \rightarrow Ni(OH)_{2}$$
(S2)

$$Fe(OH)_3 \rightarrow \beta - FeOOH + H_2O$$
 (S3)

$$2\beta - FeOOH + Ni(OH)_2 \rightarrow NiFe_2O_4 + H_2O$$
 (S4)

$$4Fe^{3+} + 3O_2 \rightarrow 2Fe_2O_3 \tag{S5}$$



Fig. S1 (a-b) SEM, (c) EDS, (d) XRD of Fe<sub>2</sub>O<sub>3</sub>@NF. (e-f) SEM, (g) EDS, (g) XRD of NiFe<sub>2</sub>O<sub>4</sub>@NF.



Fig. S2 (a) XRD, (b-c) SEM, (d) EDS, (e) XPS of the precursor before annealing.

atom percent (%)			
Ni	Fe	0	
34.3	14.9	50.8	
34.3	20.0	45.7	
38.3	15.2	46.5	
55.2	16.0	28.8	
-	-	-	
	Ni 34.3 34.3 38.3 55.2	atom percent (%)       Ni     Fe       34.3     14.9       34.3     20.0       38.3     15.2       55.2     16.0	

Table. S2a EDS results of atom ratio of Ni, Fe and O in different annealing temperature.

Table. S2b ICP results of atom ratio of Ni and Fe in different annealing temperatures.

Temperature (°C)	Concentration	n (mg L <sup>-1</sup> )
	Ni	Fe
300	511.997	787.658
350	505.211	801.476
400	508.247	813.244
450	611.654	705.275
500	-	-

Table. S3. The Analysis of XRD results at different annealing temperature.

Temperature (°C)	2θ (°)	FWHM	$d_{hkl}$ (nm)
300	35.647	0.387	2.517
350	35.690	0.366	2.514
400	35.792	0.406	2.507
450	35.719	0.236	2.515
500	35.701	0.236	2.512

300 350 400 450 500 M-OH 49.26 63.69 54.95 49.50 78.13 **Oxygen Vacancies** 30.54 26.73 20.38 25.27 13.28 Chemisorbed Oxygen 20.20 15.92 19.78 23.76 8.59

Table. S4 The ratio of M-OH, oxygen vacancies, and chemisorbed oxygen in different annealing

temperatures.



Fig. S3 The XRD spectra of bare NF and  $Fe_2O_3/NiFe_2O_4$ -500.





Fig. S4 The potential of electrode in different annealing temperature.

Fig. S5 EDLC measurements of electrodes at different annealing temperature.

Table. S5. The resistance of electrodes at different annealing temperature of OER.

	300°C	350°C	400°C	450°C	500°C	
$\operatorname{Rs}(\Omega)$	1.678	1.622	1.618	1.912	1.888	
$\mathrm{Rp}\left(\Omega\right)$	1.896	1.554	0.78948	2.885	3.473	



Fig. S6 The comparison of OER activities of previously reported NiFe-based electrocatalysts in alkaline environment, Reference:<sup>6-17</sup>

$$H_2O + M + e^- \rightarrow MH_{ads} + OH^-$$
 (S6)

Heyrovsky step

$$H_2O + MH_{ads} + e^- \rightarrow M + OH^- + H_2$$
(S7)

Tafel step

$$2MH_{ads} \rightarrow 2M + H_2$$
 (S8)

$$j_{specific} = \frac{j}{R_f}$$
(S9)

$$R_f = \frac{C_{dl}}{0.06} \tag{S10}$$

Table. S6. The resistance of electrodes at different annealing temperature of HER

	300°C	350°C	400°C	450°C	500°C
Rs $(\Omega)$	1.56	1.783	1.973	2.021	2.254
$\mathrm{Rp}\left(\Omega\right)$	0.70284	1.106	1.818	3.027	2.184



Fig. S7 The normalized OER LSV curves of electrodes annealed at different temperatures.



Fig. S8 EIS of electrodes at different annealing temperatures in 1 M KOH solution of HER.







Fig. S10 (a) CV, (b) LSV, and (c) Tafel results of Fe<sub>2</sub>O<sub>3</sub>/NF, NiFe<sub>2</sub>O<sub>4</sub>/NF, and Fe<sub>2</sub>O<sub>3</sub>-NiFe<sub>2</sub>O<sub>4</sub>-400.



Fig. S11 LSV of bare NF, the overpotential at the current density of 10 mA cm<sup>-2</sup> on NF,  $Fe_2O_3@NF$ ,  $NiFe_2O_4@NF$ , and  $Fe_2O_3-NiFe_2O_4-400@NF$ .

Experimental Condition	Concentrat	C/C.		
Experimental Condition	initial time	After 4 h	$C/C_{\theta}$	
10 mL/s O <sub>2</sub>	50	50	100%	
10 mL/s O <sub>2</sub> + 10 mM K <sub>2</sub> Fe <sub>2</sub> O <sub>4</sub>	50	32.394	64.79%+2.25%	

Table. S7. The remova	l rate of O <sub>2</sub>	and K <sub>2</sub> FeO <sub>4</sub>
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Fig. S12 The concentration of  $H_2O_2$  at different current densities.



Fig. S13 The final concentration of Fe (VI) at different current densities.



Fig. S14 Effect of scavengers on SMX removal.



Fig. S15 (a) The electronic structures of  $Fe_2O_3$ -Ni $Fe_2O_4$ , (b) top view, and (c) side view.



Fig. S16 The electronic structures of (a)  $NiFe_2O_4$ , and (b)  $Fe_2O_3$ .



Fig. S17 The Fukui Function distribution of every atom in SMX.

Compound	Structure	Formula	Rt (min)	Experimental mass [M+H] <sup>+</sup>	Calculated mass [M+H] <sup>+</sup>	Error (mg L <sup>-</sup> <sup>1</sup> )
SMX	N N N N N N N N N N N N N N N N N N N	$C_{10}H_{11}N_3O_3S$	8.156	253.278	253.0462	0.9160 38
TP1		$C_{10}H_8N_3O_5S$	8.283	284.6186	284.03	2.0723 16
TP2		$C_{10}H_9N_3O_6S$	16.012	299.0179	299.04	-0.0739
TP3	H <sub>3</sub> N H S NO <sub>2</sub>	$\mathrm{C_7H_8N_3O_4S}$	16.892	246.8204	246.04	3.1718 42
TP4	O NH	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> S	11.846	156.3436	156.01	2.1383 24
TP5		$\mathrm{C_{10}H_8N_3O_5S}$	8.283	156.9480	157.0	- 0.3312 1
TP6	N N N N N N N N N N N N N N N N N N N	$C_{10}H_{12}N_{3}O_{4}S$	10.699	269.8347	270.05	- 0.7972 6
TP7		$C_{10}H_{10}N_{3}O_{5}S$	10.012	267.1466	267.03	0.4366 55
TP8	HS O NO <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> NO <sub>5</sub> S	25.349	203.0207	203.04	- 0.0950 6
TP9	O NH2	$C_4H_7N_2O$	11.438	98.9495	98.05	9.1738 91
TP10	NO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	13.651	123.9012	124.04	- 1.1189 9

# Table S8. UPLC-QTOF-MS spectrometry analysis of SMX and intermediates

TP11		$C_{20}H_{13}N_6O_6S2$	18.338	504.7651	504.09	1.3392 45
TP12		$C_{20}H_{14}N_6O_7S2$	7.767	519.5766	520.08	- 0.9679 3
TP13	OH NH <sub>2</sub>	C <sub>4</sub> H <sub>12</sub> NO	21.709	88.9590	89.08	- 1.3583 3

Table S9 The concentration of Ni and Fe in the solution after 54-h reaction

Element	Ni	Fe
concentration (mg L <sup>-1</sup> )	0.007	0.037

Table S10. The atom ratio of NiFe-400 after 54-h reaction

Temperatrue _	atom percent (%)		
	Ni	Fe	0
400°C	31.6	18.1	50.3



Fig. S18 (a-b) SEM, (c) EDS of  $Fe_2O_3$ -Ni $Fe_2O_4$ -400 after 54 h reaction.

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