# **Supporting information**

## Ultra-fast pyrolysis of ferrocene forming Fe/C heterostructures as

### robust oxygen evolution electrocatalysts

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Catalysts	Iron sources	Carbon sources	Solvents ( during the mixing of reactants)	Mixing process-time (min)	Heating means	Heating time (min)	Post-processing time (min)	Reference
Fe₃C@NG	Fe(NO <sub>3</sub> ) <sub>3</sub>	Urea, glucose	H <sub>2</sub> O	> 60	Programmed heating	260+120	480	1
Fe/Fe₃C@NGL- NCNT	FeCl₃	Terephthalic acid, melamine	DMF	1200	Programmed heating	70+300	1440	2
N-doped Fe- Fe₃C@ graphitic laye	Prussian blue	Prussian blue	#	-	Programmed heating	~75+120	> 600	3
Fe₃C@NCNT/NP C	FeCl <sub>3</sub>	1,4- dicarboxybenzene , melamine	DMF, H <sub>2</sub> O	720	Programmed heating	~80+600	2880	4
Fe-Fe <sub>3</sub> C nanostructures	Ferrocene	Ferrocene, melamine	#	-	Programmed heating	95+180	-	5
Fe₃C@NCNTs- NCNF	tris(acetylace tonate)	Polyacrylonitrile	DMF	720	Programmed heating	800+360	Δ	6
Fe-NxC/CNx	Ferrocene	Melamine, ferrocene	#	-	Programmed heating	95+180	420	7
Fe₃C@Fe/N-G	Ferrocene	Melamine, formaldehyde	Methylbenzene, ethanol	720	Programmed heating	180+60	-	8
Fe <sub>2</sub> O <sub>3</sub> /CNT	FeCl₃	CNTs	H <sub>2</sub> O	1440	Programmed heating	~35+120	Δ	9
CP@FeP	FeCl₃	Carbon fiber paper	H <sub>2</sub> O	1440	Programmed heating	> 60+30	Δ	10
Fe/Fe <sub>2</sub> O <sub>3</sub> @Fe- N-C	FeCl₃	Shrimp shell	H <sub>2</sub> O	360	Programmed heating	60+180	540	11
Fe/C/N	Fe(NO <sub>3</sub> ) <sub>3</sub>	Melamine, formaldehyde	H <sub>2</sub> O	60	Programmed heating	~ 60+90	480	12
Fe@N-C	Ammonium ferric citrate	Dicyandiamide	H <sub>2</sub> O	> 60	Programmed heating	60+120	480	13
Fe/Fe₃C-F@CNT	Ferrocene	Ferrocene, CNTs	#	5	Microwave heating	1.5	Δ	This work
Fe-O-C@CNT (contrast experiment)	Ferrocene	Ferrocene	#	5	Programmed heating	60+180	Δ	This work

#### Table S1. The comparison of preparation processs.

\* #: No solvent; -: represents the data not available in literature;  $\Delta$ : Without Post-process

As shown in Table S1, although some Fe/Fe<sub>3</sub>C materials on graphene and CNTs have been reported before, the preparation processes usually consist of a time-consuming heating method and complex post-treatment. Besides, in order to obtain ideal structure and synergistic effect, solvothermal reactions are used to promote the combination of carbon source and iron source. These treatments not only increase cost, but also go against green production (especially the use of organic solvents). On the contrary, our synthetic strategy without complex process could efficiently decrease reaction time while obtaining novel Fe/C heterostructure. The unique structure greatly improves the conductivity of Fe/Fe<sub>3</sub>C-F@CNT and enhances the OER performance, which is better than the Fe/C catalysts in previous studies and some Ni, Co-based materials in 1 M and 0.1 M KOH (Table S5 and S7). More importantly, the preparation method can be adjusted based on the heating mode in Fig. S1a and S1b as required. So this work can be used to fast prepare a series of materials applied in green energy sources.



**Fig. S1** The schematic of (a) the mixtures of ferrocene and CNTs heated under microwave irradiation, (b) ferrocene, (c) iron (II) oxalate and (d) ferrous carbonate heated by the separated CNTs under microwave irradiation.



Fig. S2 The size distribution of Fe/Fe<sub>3</sub>C nanoparticles in Fe/Fe<sub>3</sub>C-F@CNT.



Fig. S3 The HADDF-STEM images of Fe/Fe<sub>3</sub>C-F@CNT.

The small bright speck on the surface of carbon layer suggests the exsitence of iron-based nano-cluster marked by red arrow.



Fig. S4 The SEM image of multiwalled carbon nanotubes (CNTs).



Fig. S5 The schematic of the formation processes of (a) Fe/Fe<sub>3</sub>C-I@CNT, (b) Fe/Fe<sub>3</sub>C-C@CNT and (c)

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Fe-C-O@CT.
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**Fig. S6.** The TEM images of Fe-C-O@CT.

Different from Fe/Fe<sub>3</sub>C-F@CNT, iron derived from ferrocene can not only react with cyclopentadiene forming Fe/C nanopaticles, but also catalyze the rearrangement of carbon atoms in cyclopentadiene to form CTs.<sup>14, 15</sup> But most of nanopaticles in Fe-C-O@CT are againated and relatively independent with CTs compared with Fe/Fe<sub>3</sub>C-F@CNT.



Fig. S7 The XRD patterns of FeCO<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>-I, Fe<sub>3</sub>O<sub>4</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-F.



Fig. S8 (a) The C 1s and (b) Fe 2p XPS spectra of Fe/Fe<sub>3</sub>C-F@CNT, Fe/Fe<sub>3</sub>C-I@CNT, Fe/Fe<sub>3</sub>C-C@CNT

and Fe-C-O@CT.

samples		Atomic Content, %	
_	С	0	Fe
Fe/Fe <sub>3</sub> C-F@CNT	97.85	1.44	0.71
Fe/Fe <sub>3</sub> C-F@CNT after OER	94.74	4.39	0.87
Fe/Fe <sub>3</sub> C-I@CNT	97.19	1.92	0.89
Fe/Fe <sub>3</sub> C-C@CNT	96.36	2.60	1.04
Fe-C-O@CNT	88.56	7.96	3.48

**Table S2.** The content of C, O and Fe of the catalysts according to the XPS data



Fig. S9 The TG and DTG curves of Fe/Fe<sub>3</sub>C-F@CNT, Fe/Fe<sub>3</sub>C-I@CNT, Fe/Fe<sub>3</sub>C-C@CNT and Fe-C-

#### O@CT.

According to the loss curves, the carbon species in Fe/Fe<sub>3</sub>C-I@CNT, Fe/Fe<sub>3</sub>C-C@CNT and Fe-C-O@CT only have one decomposition temperature, respectively. However, there are two decomposition temperatures in the loss curves of Fe/Fe<sub>3</sub>C-F@CNT. The decomposition temperature from high to low in order is: Fe/Fe<sub>3</sub>C-C@CNT (631 °C), Fe/Fe<sub>3</sub>C-I@CNT (622 °C), Fe/Fe<sub>3</sub>C-F@CNT (566 °C and 506 °C) and Fe-C-O@CT (458 °C). This trend is in common with that of graphitized degree, which further confirms the moderate graphitized degree of Fe/Fe<sub>3</sub>C-F@CNT (Generally, carbon materials with high graphitized degree have high decomposition temperature in the oxygen atmosphere).

	ly of obtained cataly	515.		
Catalysts	Fe/Fe <sub>3</sub> C-F@CNT	Fe/Fe <sub>3</sub> C-I@CNT	Fe/Fe₃C-C@CNT	Fe-C-O@CNT
Resistivity ( $\Omega$ 'cm <sup>-1</sup> )	0.11	0.76	0.64	1.72





**Fig. S10** The N<sub>2</sub> adsorption-desorption isotherm of Fe/Fe<sub>3</sub>C-F@CNT, Fe/Fe<sub>3</sub>C-I@CNT, Fe/Fe<sub>3</sub>C-C@CNT, Fe/

Table S4. The specific surface area of the obtained catalysts.							
Catalysts	Fe/Fe <sub>3</sub> C-C@CNT	Fe/Fe <sub>3</sub> C-I@CNT	Fe/Fe₃C-F@CNT	Fe-C-O@CT	RuO <sub>2</sub>		
,				-			
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	63.02	65.53	70.28	87.17	14.89		



**Fig. S11** (a) The polarization curves based on the geometrical area, (b) overpotential at the current density of 10 and 100 mA cm<sup>-2</sup>, (c) the Tafel plots of the catalytic materials in 1 M KOH.



**Fig. S12** (a) The polarization curves, (b) the Tafel plots, (c) the EIS at 1.52 V vs. RHE and (d) the stability of Fe<sub>3</sub>O<sub>4</sub>-I, Fe<sub>3</sub>O<sub>4</sub>-C and Fe<sub>2</sub>O<sub>3</sub>-F in 1 M KOH.



**Fig. S13** (a) The cyclic voltammetry curves from -0.28 V to 0.92 V *vs*. RHE with a scan rate of 50 mV s<sup>-1</sup>, (b) the oxidation peaks, (c) reduction peaks of Fe/Fe<sub>3</sub>C-F@CNT, Fe/Fe<sub>3</sub>C-I@CNT, Fe/Fe<sub>3</sub>C-C@CNT, Fe-C-O@CT and Fe<sub>2</sub>O<sub>3</sub>-F in 1 M KOH. (d) the cyclic voltammetry curve of Fe<sub>2</sub>O<sub>3</sub>-F from -0.28 V to 0.92 V *vs*. RHE with a scan rate of 50 mV s<sup>-1</sup> in 1 M KOH.

During the preparation process, ferrocene is not only carbon resource but also iron resource, therefore the iron-based compounds will exist on the surface of carbon layer. As shown in Fig.S13, there are a pair of iron redox peaks in the cyclic voltammetry curve of Fe/Fe<sub>3</sub>C-F@CNT. This result confirms the existence of

exposed iron-based compounds on the surface of carbon layer, which is consistent with Fig. S3 and these iron-based nano-clusters on the surface of carbon layer are efficient catalytic sites for OER.

The iron compounds in Fe/Fe<sub>3</sub>C-F@CNT, Fe/Fe<sub>3</sub>C-I@CNT, Fe/Fe<sub>3</sub>C-C@CNT, Fe-C-O@CT and Fe<sub>2</sub>O<sub>3</sub>-F show different oxidation-reduction potentials (Fe(II)/Fe(III)).<sup>16</sup> The peak potential differences ( $\Delta E=E_{\text{oxidation peak}}$ -  $E_{\text{reduction peak}}$ ) of these catalysts from high to low in order is: Fe<sub>2</sub>O<sub>3</sub>-F ( $\Delta E= 0.371 \text{ V}$ ), Fe-C-O@C ( $\Delta E= 0.338 \text{ V}$ ), Fe/Fe<sub>3</sub>C-I@CNT ( $\Delta E= 0.321 \text{ V}$ ), Fe/Fe<sub>3</sub>C-C@CNT ( $\Delta E= 0.307 \text{ V}$ ) and Fe/Fe<sub>3</sub>C-F@CNT ( $\Delta E= 0.280 \text{ V}$ ), which is similar with the order of resistivity in Table S3. These differences indicate that the interaction between carbon materials and iron compounds change the electrochemical activity of iron compounds in these catalysts. Generally, the lower  $\Delta E$  suggests a better reversibility of the redox reaction resulting from good electrical conductivity of electrode materials.<sup>17, 18</sup> The combination of iron compounds and CNTs greatly improve the electrical conductivity according to the massive reduction of  $\Delta E$ . Besides, the novel Fe/C heterostructure makes Fe/Fe<sub>3</sub>C-F@CNT obtain the lowest  $\Delta E$  and the best electrical conductivity compared with other three Fe/C materials in this work.



**Fig. S14** (a) The cyclic voltammetry curves from -0.28 V to 0.92 V vs. RHE with a scan rate of 50 mV s<sup>-1</sup> of Fe/Fe<sub>3</sub>C-F@CNT, the acid etched Fe/Fe<sub>3</sub>C-F@CNT (1 M HCl, 80  $^{\circ}$ C, 2 h) and the acid etched Fe/Fe<sub>3</sub>C-F@CNT after OER (from 0.92 V to 1.72 V vs. RHE, 100 cycles), (b) the polarization curves of Fe/Fe<sub>3</sub>C-F@CNT and the acid etched Fe/Fe<sub>3</sub>C-F@CNT.

As shown in Fig. S14, the redox peak current becomes small after acid corosion, which suggests that some exposed iron-based compounds on the surface of carbon are dissolved. The catalytic activity of the acid etched Fe/Fe<sub>3</sub>C-F@CNT in Fig. S14b decreases due to the the decrease of catalytic sites. The degree of decay of catalytic activity is lower than that of catalytic sites. This is due to that the remaining iron-based compounds have stronger interaction with carbon and these remaining catalytic sites are around the edge or defect, therefore they could show higher catalytic performance. But the catalytic sites decrease largely, so the total catalytic activity decreases.



Fig. S15 The SEM images of (a, b) Fe<sub>3</sub>O<sub>4</sub>-I, (c, d) Fe<sub>3</sub>O<sub>4</sub>-C and (e, f) Fe<sub>2</sub>O<sub>3</sub>-F.

The particles in  $Fe_3O_4$ -I,  $Fe_3O_4$ -C and  $Fe_2O_3$ -F is larger than that in  $Fe/Fe_3C$ -I@CNT,  $Fe/Fe_3C$ -C@CNT and  $Fe/Fe_3C$ -F@CNT, indicating CNTs play a important role in the dispersion of iron resource.



**Fig. S16** (a) The XRD patterns, (b) the polarization curves of Fe/Fe<sub>3</sub>C-F@CNT with different mass ratio of CNT and ferrocene in precursors.



Fig. S17 (a) The XRD patterns, (b) the polarization curves of Fe/Fe<sub>3</sub>C-F@CNT with different microwave

time.

Catalysts	Tafel slope (mV dec ⁻¹)	Overpotential (mV) @ 10 mA cm <sup>-2</sup>	References
FeO <sub>x</sub>	93	558	19
CoFe <sub>2</sub> O <sub>4</sub>	31	314	20
FeOOH nanoparticles	-	~330	21
FeOOH@NF	60	307	22
Fe <sub>2</sub> O <sub>3</sub> /CNT	61	370	9
Fe-m <mark>Co</mark> <sub>3</sub> O <sub>4</sub> /GC	60	380	23
NiCo LDH	40	367	24
Zn <sub>x</sub> Co <sub>3-x</sub> O <sub>4</sub>	51	320	25
np- ( <mark>Co<sub>0.52</sub>Fe0.48)</mark> 2P	30	270	26
Amorphous Ni-Co binary oxide	39	325	27
CP@FeP	64	350	10
Fe/Fe <sub>3</sub> C-F@CNT	36	322	This work
Fe/Fe₃C- F@CNT@Fe	49	286	This work
Fe/Fe <sub>3</sub> C-I@CNT	41	331	This work
Fe/Fe₃C-C@CNT	51	328	This work
Fe-C-O@CT	59	401	This work

Table S5. The comparison of OER catalytic activity in 1 M KOH



Fig. S18 The simplified randles equivalent circuit for the test of the electrochemical impedance

spectroscopy.

Table 50. The R <sub>ct</sub> values of the obtained catalysts in TWI ROTI.								
Catalysts	Fe/Fe₃C-F@CNT	Fe/Fe₃C-I@CNT	Fe/Fe₃C-C@CNT	Fe-C-O@CNT				
R <sub>ct</sub> (Ω)	30.98	65.22	54.37	164.26				

Table S6.	The R <sub>ct</sub>	values	of the	obtained	cataly	sts in	1M KOH.
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Fig. S19 The schematic of electronic transmission channel during the OER process for Fe/Fe<sub>3</sub>C-F@CNT.



**Fig. S20** (a) The polarization curves, (b) the Tafel plots of the Fe/Fe<sub>3</sub>C-F@CNT@Fe and Fe foam in 1M KOH, (c) the voltage curves at the current density of 10, 50, 100, 200, 300, 400 and 500 mA cm<sup>-2</sup>, (d) the long time stability test of the Fe/Fe<sub>3</sub>C-F@CNT@Fe at the current density of 100 mA cm<sup>-2</sup>.

In order to decrease the influence of the consumption of OH<sup>-</sup> on catalytic activity, we change the electrolyte every 72 hours during the long time stability test of Fe/Fe<sub>3</sub>C-F@CNT@Fe. At the beginning, the overpotential continues to rise, which is due to that the catalytic materials are peeled off from foamed iron and active sites are lost. But the magnitude of the increased voltage is small ( $\leq 20 \text{ mV}$  after 72 h), and the overpotential remains relatively stable in the subsequent stability test. The long time stability test ( $\geq 320 \text{ h}$ ) fully confirms the superior stability of Fe/Fe<sub>3</sub>C-F@CNT@Fe for OER.



**Fig. S21** (a) the polarization curves, (b) the overpotential at the current density of  $10\text{mA cm}^{-2}$ , (c) the Tafel plots and (d) the EIS at 1.55 V *vs*. RHE of the catalytic materials in 0.1 M KOH.

Catalysts	Tafel slope (mV dec <sup>-1</sup> )	Overpotential (mV) @ 10 mA cm <sup>-2</sup>	References
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> NA/CC	52	420	28
$Mn_3O_4/CoSe_2$	49	450	29
FeOOH nanoparticles	78.6	390	21
$Fe/Fe_2O_3@Fe-N-C$	77.5	540	11
Fe <sub>2</sub> O <sub>3</sub> /CNT	131	490	9
FeO <sub>x</sub>	-	450	30
Fe/C/N	-	360	12
Fe@N-C	-	480	13
NiCo/PFC	106	400	31
Co-N/C-800	61	370	32
Fe/Fe <sub>3</sub> C-F@CNT	46	356	This work
Fe/Fe <sub>3</sub> C-I@CNT	51	390	This work
Fe/Fe₃C-C@CNT	57	404	This work
Fe-C-O@CT	59	474	This work

**Table S7.** The comparison of OER catalytic activity in 0.1 M KOH.



**Fig. S22** The double-layer capacitance measurements of Fe/Fe<sub>3</sub>C-F@CNT, Fe/Fe<sub>3</sub>C-I@CNT, Fe/Fe<sub>3</sub>C-C@CNT, Fe-C-O@CNT, Fe<sub>3</sub>O<sub>4</sub>-I, Fe<sub>3</sub>O<sub>4</sub>-C, Fe<sub>2</sub>O<sub>3</sub>-F and RuO<sub>2</sub>; (a-h) cyclic voltammograms of the catalysts at a series of scan rates of 5, 10, 20, 50 and 100 mV s<sup>-1</sup> from -0.2 to -0.1 V vs. Ag/AgCl in CH<sub>3</sub>CN with 0.15 M KPF<sub>6</sub>; (i) linear fitting of the oxidation currents of the catalysts at -0.12 V vs. Ag/AgCl versus scan rates.

Electrical double-layer capacitance measurements were used to determine electrochemical active surface area of the catalysts. The electrochemical double layer capacitance measurements are performed in aprotic organic electrolyte (CH<sub>3</sub>CN containing 0.15 M KPF<sub>6</sub>) in order to get rid of the extra current that arise from  $H^+/OH^-$  adsorption in protic solvents.<sup>33</sup> According to Fig. S22i, the electrical double-layer capacitance could be obtained. Then the electrochemical active surface area could be obtained based on the specific capacitance value of a smooth standard with a real surface area of 1 cm<sup>-2</sup>. 16 uF cm<sup>-2</sup> is considered as the value of specific capacitance for a smooth standard with a real surface area of 1 cm<sup>-2</sup> based on previous studies.

The electrochemical active surface area could be obtained via the following equation:

$$A_{ECSA} = \frac{\text{The electrical double-layer capacitor}}{16}$$

For example:

Fe/Fe<sub>3</sub>C-F@CNT: 
$$A_{ECSA} = \frac{858.98}{16} = 53.69 \text{ cm}^2_{ECSA}$$

Catalysts	Fe/Fe₃C- F@CNT	Fe/Fe₃C- I@CNT	Fe/Fe₃C- C@CNT	Fe-C- O@CT	Fe <sub>3</sub> O <sub>4</sub> -I	Fe <sub>3</sub> O <sub>4</sub> -C	Fe <sub>2</sub> O <sub>3</sub> -F	RuO <sub>2</sub>
Specific Capacitance (uF cm <sup>-2</sup> )	858.98	819.76	800.55	1089.68	53.56	60.91	72.38	170.22
ECSA (cm <sup>2</sup> <sub>ECSA</sub> )	53.69	51.24	50.03	68.10	3.35	3.81	4.52	10.64



Fig. S23 The polarization curves and Tafel plots normalized to ECSA of these catalysts.

<b>Table S9.</b> The content of iron according to the ICP-AES.							
Catalysts	Fe/Fe <sub>3</sub> C-F@CNT	Fe/Fe <sub>3</sub> C-I@CNT	Fe/Fe <sub>3</sub> C-C@CNT	Fe-C-O@CNT			
-							
wt %	10.16	11.51	15.93	36.53			

The low iron content in Fe/Fe<sub>3</sub>C-F@CNT is due to the combination of CNTs and ferrocene, which is not only an iron source but also an important carbon source (the carbon content about 64%). Fe-C-O@CNT without the introduction of additional CNTs possesses the highest iron content.



**Fig. S24** (a) The polarization curves normalized to ECSA and (b) the mole quantity of iron in Fe/Fe<sub>3</sub>C-F@CNT, Fe<sub>3</sub>O<sub>4</sub>-I, Fe<sub>3</sub>O<sub>4</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-F.

The introduction of CNTs significantly improves the intrinsic activity of active sites in Fe/Fe<sub>3</sub>C-F@CNT compared with the Fe-only materials (Fe<sub>3</sub>O<sub>4</sub>-I, Fe<sub>3</sub>O<sub>4</sub>-C, and Fe<sub>2</sub>O<sub>3</sub>-F).



Fig. S25 (a) The XRD pattern, (b) TG and DTG curves,(c) and (d) SEM images of Fe/Fe<sub>3</sub>C@AB.



**Fig. S26** (a) The polarization curves, (b) the overpotential at the current densities of 10 and 100 mA cm<sup>-2</sup>, (c) the Tafel plots, (d) the stability of Fe/Fe<sub>3</sub>C@AB and RuO<sub>2</sub>.

Although RuO<sub>2</sub> has a low overpotential to reach the current density of 10 mA cm<sup>-2</sup>, the Tafel slope of Fe/Fe<sub>3</sub>C@AB is smaller than that of RuO<sub>2</sub>, and the current density of Fe/Fe<sub>3</sub>C@AB rapidly rise above that of RuO<sub>2</sub> in the potential over 1.69 V vs. RHE. In industrial production, the current density is larger than 150 mA cm<sup>-2</sup>. The overpotential of Fe/Fe<sub>3</sub>C@AB is lower than RuO<sub>2</sub> under large current density (>150 mA cm<sup>-2</sup>), and the advantage of Fe/Fe<sub>3</sub>C@AB becomes large with the increase of current density. More importanly, the stability of Fe/Fe<sub>3</sub>C@AB is markedly better than RuO<sub>2</sub>. Therefore, the ideal practicability of Fe/Fe<sub>3</sub>C@AB suggests the preparation method in our work is in favor of promoting the development of cheaper and greener OER catalysts.



**Fig. S27** (a) The SEM image of Fe/Fe<sub>3</sub>C-F@CNT after OER; (b) C 1s, (c) Fe 2p XPS spectra of Fe/Fe<sub>3</sub>C-F@CNT before and after OER.



**Fig. S28** (a)The TEM image and (b) the Cs-corrected STEM image of Fe/Fe<sub>3</sub>C-F@CNT after OER, (c) the corresponding carbon elemental mapping, (d) iron elemental mapping, (e) oxygen elemental mapping and (f) the combined elemental mapping of C, Fe, and O.

As shown in Fig. S28, the Fe/Fe<sub>3</sub>C-F@CNT after OER almost maintains the initial morphology. There is overlap between the crystal lattice of Fe/Fe<sub>3</sub>C and carbon layer, so the crystal lattice at the junction of the carbon layer and Fe/Fe<sub>3</sub>C nanoparticle is special. Besides, if the carbon layer is unbroken, the carbon coated Fe/Fe<sub>3</sub>C nanoparticle isn't oxidized during OER process. The nether Fe/Fe<sub>3</sub>C nanoparticle in Fig. S28a has an unbroken carbon layer, therefore the Fe/Fe<sub>3</sub>C nanoparticle remains unchanged. But the carbon layer of the other Fe/Fe<sub>3</sub>C nanoparticle in Fig. S28a is destroyed and the Fe/Fe<sub>3</sub>C nanoparticle is oxidized partially during the OER process. The crystal lattice assigned to Fe/Fe<sub>3</sub>C is only observed in the inside of nanoparticle. As shown in Fig. S28b, the carbon layer of this nanoparticle is destroyed. The corresponding EDS maps (Fig. S28 c-f) of the elements (C, Fe and O) of Fe/Fe<sub>3</sub>C-F@CNT after OER further confirmed the oxidation of Fe/Fe<sub>3</sub>C nanoparticle, which is consistent with the result of XPS spectra of the Fe/Fe<sub>3</sub>C-F@CNT after OER. Besides, the redox peak current becomes large after OER process in Fig. S14a, indicating the increase of exposed iron-based compounds.



Fig. S29 The faladaic efficiency of the Fe/Fe<sub>3</sub>C-F@CNT at the current density of 20 mA cm<sup>-2</sup>.

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