

1	Modulating Electronic Structure of Porous Nanocubes Derived	
2	from Trimetallic Metal-Organic Frameworks to Boost Oxygen	
3	Evolution Reaction Performance	
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1 Abstract

The preparation of noble metal-free catalysts for water splitting is the key to low cost, 2 3 sustainable hydrogen generation. Herein, through pyrolysis-oxidation process we prepare a series of Co-Fe-Ni trimetallic oxidized carbon nanocubes (Co1-XFeXNi-4 OCNC) with a continuously changeable Co/Fe ratio (X=0, 0.1, 0.2, 0.5, 0.8, 0.9, 1). 5 The Co_{1-x}Fe_xNi-OCNC shows a volcano-type oxygen evolution reaction (OER) 6 activity. And the optimized Co_{0.1}Fe_{0.9}Ni-OCNC achieves low overpotentials of 268 mV 7 at 10 mA cm⁻² with a very low Tafel slope of 48 mV dec⁻¹ in 1 M KOH. At the same 8 9 time, the stability of the Co_{0.1}Fe_{0.9}Ni-OCNC is also outstanding, after 1000th CV cycles, the LSV plot is almost coincident. What's more, the potential remains almost the same 10 value at 10 mA cm⁻² after 12 h in comparison to the initial value. The excellent 11 electrocatalytic properties can be attributed to the synergistic cooperation between each 12 component. Therefore, the Co_{0.1}Fe_{0.9}Ni-OCNC is a promising candidate instead of 13 precious metal-based electrocatalysts for OER. 14

Keywords: Metal-organic frameworks; Trimetallic catalyst; oxygen evolution
 reaction; electrocatalysis

17 Introduction

The demand for a green energy source is growing rapidly with each passing day while the fossil-fuel is decreasing gradually. To address the urgent need for clean renewable energy, electrocatalytic water splitting is considered as an efficient and environmentally friendly way to obtain clean fuel like oxygen and hydrogen. On account of multistep proton-coupled electron transferring, the oxygen evolution reaction (OER) hinder the

realization of efficient water splitting^[1]. To date, Ru- or Ir-based materials are regarded 1 as the benchmark catalysts for OER^[2]. In spite of their outstanding catalytic 2 3 performance, the prohibitive cost, scarce reserve, as well as unsatisfactory stability issues limit these noble metals' practical application. Therefore, extensive efforts have 4 been devoted to synthesizing robust, efficient, and cost-effective OER catalysts over 5 the last few decades, such as metal oxides, hydroxides, chalcogenides, nitrides, 6 phosphides and the carbon-based materials^[3]. However, their performance fell short of 7 what was expected. 8

Non-precious metal-based OER electrocatalysts with high catalytic activity and 9 stability should satisfy the following conditions: (I) The catalysts should contain 10 inherently high OER active elements (such as nickel, iron and cobalt) and their 11 12 composition can be adjusted so that the catalysts' electronic structure can be regulated^[4]. (II) The catalysts should have a high specific surface area so that it can expose more 13 active sites and accelerate mass transfer^[5]. However, it is undoubtedly a big challenge 14 15 to properly design and prepare a catalyst that meets the above criteria. Metal-organic frameworks (MOFs), as a new and unique kind of porous materials, are consisting of 16 metal nodes (clusters) and organic linkers. Benefiting from their porous and easily 17 tunable structures, MOFs have been used in storage, separation, catalysis, sensing, drug 18 delivery and as templates to prepare other porous materials^[6]. And it has been proven 19 that adjusting chemical composition, controlling morphology, and constructing 20 21 composite structure can significantly affect the performance of catalysts. Thus, MOFs is an ideal precursor to construct various transition metal-based materials for the 22

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1	electrocatalytic OER. Most of the previously reported catalysts derived from MOFs are
2	single-center metal or bimetallic, and it has been proved that bimetallic electrocatalysts
3	can show significantly higher catalytic performance for OER than single-site metal
4	electrocatalysts which can be attributed to the doped metal will incorporate into the
5	lattices of the hybrid and interplay with other metals to modulate their local
6	coordination environment and electronic structures ^[7] . For example, Zhao et al.
7	designed the bimetallic Co _X Fe _{1-X} -MOF-74, which demonstrates remarkable catalytic
8	activity for OER due to the enhanced open metal sites and electron-rich environment in
9	mixed-node MOFs ^[8] . Besides, ultrathin NiCo bimetal-organic framework nanosheets
10	prepared by Zhao et al. exhibited excellent OER performance attributed to the coupling
11	effect between Ni and Co metals. And these coordinatively unsaturated metal atoms act
12	as dominating active centers for the electrocatalytic OER ^[9] . However, the catalytic
13	activity and stability of the bimetallic catalysts are still unsatisfactory. Thus, a ternary
14	Co-Fe-Ni composites has been synthesized to get more remarkable OER performance
15	in an alkaline electrolyte. The enhanced OER performance is attributed to the intensive
16	synergistic effect where the Ni species are served as active sites promoting electrolyte
17	diffusion and proton-coupled electron transfer, while the Fe and Co components play a
18	role in tuning the intrinsic properties of catalysts ^[10] . Taking advantage of the promising
19	electrocatalytic properties of Ni and Co based oxides' synergistic interactions in
20	combination with Fe, Kazakova et al. designed the trimetallic catalysts $Fe_xNi_xCo_1$.
21	_{2x} /MWCNT which exhibited higher electrocatalytic activity compared to the bimetallic
22	Fe-Co, Fe-Ni and Co-Ni systems ^[11] . And Sayeed et al. created a catalytically active

FeCoNiO_xH_y amorphous material. The trimetallic catalyst is more active than any single or bimetallic oxide combination towards OER as a result of the synergetic effect among the three components^[12]. Despite some progress has been approached, discovery of novel trimetallic catalysts toward OER with stable operation and low overpotentials in alkaline media are still requisite.

Herein, we report the fabrication of a series of Co_{1-x}Fe_xNi-oxidized carbon 6 nanocubes (Co1-xFexNi-OCNC) derived from MOFs, in which the molar ratios of Fe 7 and Co can be precisely tuned. The Co_{0.1}Fe_{0.9}Ni-OCNC catalyst exhibits extraordinary 8 9 performance for the OER under alkaline condition which needs a low overpotential of just 268 mV to achieve a current density of 10 mA cm⁻² and has a small Tafel slope of 10 48 mV dec⁻¹. Moreover, the stability of the Co_{0.1}Fe_{0.9}Ni-OCNC is also outstanding, after 11 12 1000th CV cycles, the LSV plot is almost coincident. And as indicated by the chronopotentiometry (CP) measurements, the potential almost unchanged after 12 h in 13 comparison to the initial value. The strategy in this work may give a new alternative for 14 15 precious-metal-free catalysts for alkaline OER and reveals the three metals synergistic 16 effect towards performance enhancement.

17 **Results and Discussion**

The strategy to synthesize $Co_{1-x}Fe_xNi$ -oxidized carbon nanocubes ($Co_{1-x}Fe_xNi$ -OCNC, X and 1-X represent the molar ratio of the Fe and Co) is based on the previously reported article and is schematically shown in **Scheme 1**^[13]. Firstly, $Co_{1-x}Fe_xNi$ nanocubes ($Co_{1-x}Fe_xNi$ -NC) are synthesized through tuning different molar ratios on the basis of the molar ratio of cobalt to iron by a coprecipitation method. The PXRD

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patterns of Co_{1-x}Fe_xNi-NC with different molar ratios of Co/Fe have similar diffraction 1 peaks (Figure S1 in the Supporting Information), which confirmed the successful 2 3 creation of these trimetallic MOFs. And then they were used as precursors. The Co₁xFexNi-OCNC was obtained by two step thermal treatment of the precursors. In general, 4 the prepared Co_{1-x}Fe_xNi-NC was calcinated in a nitrogen atmosphere at 800 °C for 2 5 hours to obtain Co_{1-x}Fe_xNi-carbon nanocubes (Co_{1-x}Fe_xNi-CNC). After acid treatment, 6 the Co_{1-x}Fe_xNi-CNC was transformed into Co_{1-x}Fe_xNi-OCNC via a low-temperature 7 oxidation reaction under a O₂ atmosphere at 350 °C for 4 hours (more synthetic details 8 9 can be found in the ESI).



Scheme 1. Schematic illustration of the preparation of Co_{1-X}Fe_XNi-OCNC.

The morphology and detailed structural information of the as-synthesized samples 12 are characterized by scanning electron microscopy (SEM) and transmission electron 13 microscopy (TEM). The SEM image in Figure 1a reveals that the obtained 14 $Co_{0.1}Fe_{0.9}Ni$ -NC are unified cubic crystals. As shown in Figure 1b, the surface of 15 $Co_{0.1}Fe_{0.9}Ni$ -CNC becomes a little rough with some nanoparticles. Notably, after the 16 oxidation, Co_{0.1}Fe_{0.9}Ni-OCNC inherits the same cubic structure and possesses rougher 17 18 surfaces as indicated in Figure 1 c. That means much more nanoparticles are generated. 19 Of special note, it can be seen clearly from Figure 1d that there are some carbon 20 nanotubes are formed, due to the transition metals such as Fe, Co and Ni being prone to form carbon nanotubes^[14]. And the nanoparticles are embedded at the terminals of 21

1 the nanotubes, as indicated by the darker areas in Figure 1d. It turns out that there are 2 about 17 carbon layers which surround the metal nanoparticles (Figure 1e). Such 3 structure would promote the effective electron transfer and enhance the stability of the catalyst during the electrocatalysis process. Furthermore, the high-resolution TEM 4 (HRTEM) images (Figure 1f) display that the interplanar spacings of 0.20 nm and 0.24 5 nm correspond to the (111) crystal plane of Ni₃Fe and the (311) crystal plane of Co₃O₄, 6 respectively. The elemental mapping images for Co_{0.1}Fe_{0.9}Ni-OCNC demonstrated that 7 8 O, Fe, Co and Ni elements are homogeneously distributed in the nanocube, as shown 9 in Figure 1 g-k).



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11 Figure 1. a-c) SEM images of Co_{0.1}Fe_{0.9}Ni-NC, Co_{0.1}Fe_{0.9}Ni-CNC, Co_{0.1}Fe_{0.9}Ni-OCNC; d-f) TEM

12 images of Co_{0.1}Fe_{0.9}Ni-OCNC; g-k) The elemental mapping images of Co_{0.1}Fe_{0.9}Ni-OCNC.

13 Meanwhile, the variation of microstructural features was investigated by powder X-

14 ray diffraction (PXRD). Seen from the Figure S2 (see in the Supporting Information),

1	the Co _{1-x} Fe _x Ni-OCNC display a poor crystallinity. And three major phases can be
2	identified: a Co ₃ O ₄ phase (JCPDS no. 74-1656), a NiO phase (JCPDS no. 71-1179) and
3	a well-crystallized Ni_3Fe alloy phase (JCPDS no. 88-1715). It is noted that as the iron
4	content increases, the peak of Ni_3Fe alloy shifts to the left and the peak of Co_3O_4 decays.
5	Besides, we used N ₂ adsorption-desorption isotherms to measure the specific surface
6	area of the obtained samples (Figure S3 in the Supporting Information). The specific
7	surface area and the diameter of the pore size of $Co_{1-X}Fe_XNi$ -OCNC are listed in Table
8	S1 . The specific surface area of the Co _{1-x} Fe _x Ni-OCNC can be as high as 300.31 m ² g ⁻
9	¹ and the isotherm curves of the samples are all categorized as type IV, hence implying
10	the existence of large numbers of mesopores in the samples. Such large specific surface
11	area and unique mesoporous structure are prone to facilitate reactant diffusion, the
12	intimate contact between reactant as well as accessible active sites.
13	In order to further determine the valence states of the chemical elements in the
14	catalyst, X-ray photoelectron spectroscopy (XPS) measurements was carried out. The

15 presence of Fe, Co, Ni, C, N, O elements were confirmed in CoNi-OCNC, Co_{0.5}Fe_{0.5}Ni-OCNC, Co_{0.2}Fe_{0.8}Ni-OCNC, Co_{0.1}Fe_{0.9}Ni-OCNC, FeNi-OCNC (Figure S4a) in the 16 17 Supporting Information) and the quantitative analyses of Co_{1-X}Fe_XNi-OCNC was listed 18 in Table S3. As shown in Figure 2a, three major peaks in the O 1s spectra for Co_1 -19 xFexNi-OCNC (x=0, 0.5, 0.8, 0.9 and 1) can be observed and there was no evident difference in the O 1s spectra of the samples, suggesting that the nature of the oxygen 20 21 species on the sample surface wasn't influenced by the Co:Fe:Ni ratio. The peak at around 530 eV and 529.7 eV corresponds to oxygen vacancies and typical metal-22

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1	oxygen bond respectively, indicating there also existed a small amount of cobalt oxide
2	and nickel oxide in all samples ^[15] . Notably, the oxygen vacancy in Co _{1-x} Fe _x Ni-OCNC
3	(x=0, 0.5, 0.8, 0.9 and 1) is dominant for oxygen species which plays a significant role
4	in improving the conductivity and accelerating the kinetics of oxidation reactions, and
5	accordingly will enhance electrocatalytic performance of for OER ^[16] . And the binding
6	energy at 531.5 eV and 532.4 eV can be due to the coordinated action of oxygen on
7	their surface unsaturated ^[17] . Moreover, as shown in Figure 2b, the Ni 2p region for
8	Co _{1-X} Fe _X Ni-OCNC (X=0, 0.5, 0.8, 0.9 and 1) shows two typical peaks around 855 eV
9	and 873 eV corresponding into Ni $2p_{3/2}$ and Ni $2p_{1/2},$ respectively, along with the
10	satellite peaks at 861 and 879 eV. By deconvolution, Ni $2p_{3/2}$ spectrum shows two peaks
11	that correspond to Ni ²⁺ oxidation state and metallic state, respectively ^[18] . Interestingly,
12	compared with bimetallic catalysts, the Ni $2p_{3/2}$ in trimetallic catalysts are all shifted to
13	a higher binding energy which should be originate from the coordination environment
14	of the active center's modification. The Ni $2p_{3/2}$ in $Co_{0.1}Fe_{0.9}Ni$ -OCNC located at the
15	highest binding energy, proving at this ratio it has the greatest impact on the electronic
16	structure of Ni (Figure 2c). As shown in Figure S6a the Co 2p spectrum of Co _{1-x} Fe _x Ni-
17	OCNC (x=0, 0.5, 0.8, 0.9 and 1) all display two major peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$
18	at around 780.6 and 796.7 eV, respectively, and two shakeup satellite peaks (787.0 and
19	802.7 eV). For the high-resolution XPS spectra of Fe 2p (Figure S6b in the Supporting
20	Information), all the samples show two main peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ at 723.8 eV
21	and 716.35 eV. It worth noting that compared with CoNi-OCNC and FeNi-OCNC, the
22	peak intensity of Co 2p or Fe 2p in trimetallic catalysts all weakened. And the

incorporation of Fe led to a positive shift in the binding energy of Co 2p_{3/2} and Co 2p_{1/2}, with respect to their counterpart of CoNi-OCNC, indicating that intercalating another metal indeed caused significant electronic modulation. And it verified the work previously reported by Boettcher et al, further demonstrating that the strong electronic coupling effect between Fe and Ni/Co^[19]. We are sure that the synergy effect of the mixed metals and modulating the electronic environment of the active metal sites would improve the catalytic OER.



with CoNi-OCNC (346 mV at η_{10}), FeNi-OCNC (278 mV at η_{10}), Co_{0.2}Fe_{0.8}Ni-OCNC 1 (293 mV at η_{10}), Co_{0.5}Fe_{0.5}Ni-OCNC (306 mV at η_{10}), Co_{0.8}Fe_{0.2}Ni-OCNC (312 mV at 2 3 η_{10}) and Co_{0.9}Fe_{0.1}Ni-OCNC (333 mV at η_{10}) (see Table S2 in the Supporting Information), indicating the excellent OER performance of $Co_{0.1}Fe_{0.9}Ni$ -OCNC. 4 What's more, the Tafel slope is one direct measure to evaluate the effect of the rate-5 limiting step on the electrocatalytic reaction process. The Tafel slope for the 6 $Co_{0.1}Fe_{0.9}Ni$ -OCNC is 48 mV dec⁻¹, which is significantly the lowest compared with 7 other catalysts' Tafel plot, highlighting the faster reaction kinetics for the Co_{0.1}Fe_{0.9}Ni-8 9 OCNC. (Figure 3b and Table S2 in the Supporting Information). Apparently, compared 10 with Co_XFe_{1-X}Ni-CNC, the electrochemical performance of the Co_XFe_{1-X}Ni-OCNC was enhanced demonstrating that the oxidation process improves OER activity and the 11 12 capability of charge transfer. Such OER catalytic activity of Co_{0.1}Fe_{0.9}Ni-OCNC is also superior to majority of other earth-abundant transition-metal oxide OER 13 electrocatalysts as well as Fe, Co or Ni-based electrocatalysts that previously reported. 14 15 The detailed comparisons are shown in Table S2. The electrochemical impedance 16 spectroscopy (EIS) was measured to gain further insight into the OER kinetics over these electrocatalysts (see Figure S8b in the Supporting Information). It can be seen 17 18 clearly that the Co_{0.1}Fe_{0.9}Ni-OCNC presents a much lower charge transfer resistance 19 which indicates the most efficient charge transport during OER processes. The result shed light to the previous reported that mixed metal-oxide effects as well as 20 21 incorporating of a third metal are available to yield high performance OER catalysts. 22 Besides, the catalysts can be endowed with the best OER activity by adjusting the ratio

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1 between the metal species^[20].</sup>

To understand the reason for the difference between OER activities, firstly, we used 2 3 the CV to measure the electrochemically active surface area (ECSA) of different catalysts in 1 M KOH. ECSA that indicates the real number of active sites is commonly 4 used to assess the intrinsic OER activities of catalysts^[21]. As shown in Figure S9 (in 5 the Supporting Information), the ECSAs of trimetallic catalysts are larger than that of 6 bimetallic catalysts, indicating that introducing a third metal can increase the ECSAs 7 of the catalysts. Then, we normalized the polarization curves of all the samples to BET 8 9 surface area (Figure S10 in the Supporting Information) which presents a consistent trend with the previous polarization curve that the $Co_{0.1}Fe_{0.9}Ni$ -OCNC exhibited the 10 best OER activity. And we believe that the large specific surface area and rich 11 12 mesoporous structure are able to expose more active sites and facilitate rapid diffusion of reactants and products, resulting in better catalytic performance. 13

14 The stability of the catalyst is rather important that affects its practical application. 15 The LSV plot of Co_{0.1}Fe_{0.9}Ni-OCNC after 1000th CV cycles was recorded to measure the cycling durability, which almost coincides with the initial one (Figure 3c). 16 Meanwhile, the SEM image (Figure S11, Supporting Information) of Co_{0.1}Fe_{0.9}Ni-17 OCNC after 2000th CV cycles showed that its morphology remained almost unchanged. 18 19 And in order to evaluate the composition of Co_{0.1}Fe_{0.9}Ni-OCNC after 2000th CV cycles, X-ray photoelectron spectroscopy (XPS; Figures S12, Supporting Information) was 20 conducted. It can be seen clearly that after OER measurement, both of the Fe³⁺ and 21 metallic Ni species disappear indicating that Fe³⁺ species is reduced to Fe²⁺ while 22

metallic Ni species is oxidized to Ni²⁺ species during the OER electrochemical process.
Notably, the peak intensity of Co 2p decreased after OER measurement. Therefore, the
cobalt-based oxides serve as active sites in Co_{0.1}Fe_{0.9}Ni-OCNC and endow its
outstanding OER performance.

5 Furthermore, we use chronopotentiometry to investigate the long-term stability of the $Co_{0.1}Fe_{0.9}Ni$ -OCNC. When working at a constant current density of 10 mA cm², the 6 Co_{0.1}Fe_{0.9}Ni-OCNC resents no obvious increase in overpotential over the 12 h operation 7 (Figure S13), indicating the high durability of the Co_{0.1}Fe_{0.9}Ni-OCNC. In general, the 8 9 conditions of commercial electrolysis cells are more demanding therefore the durability 10 of the Co_{0.1}Fe_{0.9}Ni-OCNC in 6 M KOH was tested. And the overpotential shows only slight increase after 10 h (as shown in Figure S14 in the Supporting Information), 11 12 indicating its extraordinary stability. This excellent stability is mainly attributed to the proper protection of the relatively thick graphite layers. 13





5 Conclusion

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In summary, high-performance and stable OER catalysts derived from MOFs are 6 obtained by a controllable carbonation-oxidation strategy. The Co_{0.1}Fe_{0.9}Ni-OCNC 7 8 needs the lowest overpotential of just 268 mV to achieve a current density of 10 mA cm⁻² with a small Tafel slope of 48 mV dec⁻¹ indicating that the synergy effect of the 9 10 mixed metals can efficiently influence the OER activity. In addition, the Co_{0.1}Fe_{0.9}Ni-OCNC also has excellent durability, and there is almost invariable even after 12 hours 11 12 of electrocatalytic oxygen evolution reaction at a current density of 10 mA cm⁻². Moreover, we anticipate that our work will stimulate the extensive preparation and 13

1	application of complex transition metal-based materials for manufacturing renewable
2	energy.
3	Supporting Information
4	Supporting Information is available from the Wiley Online Library or from the author.
5	
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Through pyrolysis-oxidation process a series of Co-Fe-Ni trimetallic oxidized carbon nanocubes (Co_{1-x}Fe_xNi-OCNC) with a continuously changeable Co/Fe ratio were prepared. The synergistic cooperation between trimetallic components endow the Co-Fe-Ni trimetallic oxidized carbon nanocubes electrocatalysts with excellent OER activity and outstanding durability. The result will stimulate the extensive preparation and application of complex transition metal-based materials for manufacturing renewable energy.

- 10 Keyword: Electrocatalysis
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Modulating Electronic Structure of Porous Nanocubes Derived from Trimetallic Metal Organic Frameworks to Boost Oxygen Evolution Reaction Performance

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