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Supplementary Information

Synthesis and electrocatalytic mechanism of ultrafine MFe₂O₄ (M: Co, Ni, and Zn) nanocrystallites: M/Fe synergetic effects on electrochemical detection for

Cu(**I**) and hydrogen evolution reaction performances

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1. EXPERIMENTS AND CALCULATIONS

1.1 Material Characterization

The surface morphology was characterized by scanning electron microscopy (SEM) (ZEISS MERLIN Compact, Germany) and transmission electron microscopy (TEM) (FEI, Tecnai G2 F20 S-Twin, America) with selected-area electron diffraction (SAED). The average particle sizes and size distributions were calculated from the diameters of at least 100 particles randomly selected from the TEM micrographs using Nano Measurer 1.2. X-ray diffraction (XRD) (Bruker AXS, D8 Advance, Germany) with Cu K α radiation ($\lambda = 0.154$ nm; 2/min) was used to analyze the phase constitution of the samples. Brunauer-Emmett-Teller (BET) and Barrett Joyner Halenda (BJH) (Micromeritics, ASAP 2020, America) was resorted to measure specific surface area and pore size distribution at 77 K. X-ray photoelectron spectroscopy (XPS) (Thermo, ESCALAB 250XI, America) analyses were conducted on a equipped with a focused monochromatic Al K α X-ray source. The peak energies were calibrated by placing the major C 1s peak at 284.8 eV.

1.2 Electrochemical Measurements

1.2.1 Electrochemical detection of heavy metal ions.

2.0 mg MFO samples were firstly dispersed into the 500 μ L Nafion-ethanol mixed solution (volume ratio is 1:9) and achieve stable suspension by sonicated for 15 min. In addition, 10 μ L suspension was added to the surface of glassy carbon electrode and dried under incandescent lamp to obtain MFO modified electrode.

DPASV was measured with an electrochemical workstation CHI 760E (CHI 760E,

CH Instruments Inc., Shanghai, China). The three-electrode system was composed of ZFO/GCE modified electrode, Ag/AgCl electrode and platinum wire as the working, reference and counter electrodes, respectively. According to the previous work,¹ HMIs was deposited potential (1.2 V) for 120 s at 0.1 M HAc-NaAc buffer solution (pH=5.0) under magnetic stirring. The anodic stripping currents of Cu(II) (reduction of Cu(0) to Cu(II)) were obtained at the potential range of -0.8 to 0.6 V.

1.2.2 Evaluation of the electrocatalytic activity toward HER

To prepare the electrode for HER measurements, some MFO nanoparticles were dispersed in the solution of 500 μ L ethanol and distilled water as well as 30 μ L polytetrafluoroethylene (PTFE) solution. 10 wt% of the stable suspension was then loaded onto the surface of the nickel foam (1×1 cm²). The electrocatalytic activity was measured in a 1 M nitrogen saturated KOH solution using an electrochemical workstation (CHI 760E, CHI Instruments Inc., Shanghai, China) in a standard three electrode system. The three-electrode system was a Ni foam loaded with the MFO samples as a working electrode, a graphite rod as a counter electrode and Ag/AgCl as a reference electrode respectively. All measured potentials are referred to as reversible hydrogen electrodes (RHE) in 1 M KOH by RHE calibration, as shown in the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 1.023V \tag{1}$$

Linear sweep voltammetry (LSV) was carried out at a scan rate of 1.0 mV s⁻¹ for the whole polarization curve.

1.3 Calculations of ECSA:

The ECSA values of the CFO, NFO and ZFO catalysts were estimated according to the method reported elsewhere.^{2, 3} The double layer capacitance (C_{dl}) of catalysts was firstly determined on the basis of the current density versus the scan rate plots in the region of 20-120 mV, in which no significant Faradaic processes were observed. The electrochemical surface area (ECSA) of catalyst was calculated from the Coulombic charge Q for hydrogen desorption based on the equation:

$$ECSA = Cdl \times GSA/CS \tag{S1}$$

Where C_{dl} is the calculated double layer capacitance of the as-prepared samples in 1.0 M KOH (in mF cm⁻²), C_s is the specific capacitance of an atomically smooth surface in 1.0 M KOH ($C_s = 0.06$ mF m⁻²), GSA is the geometric surface area of the glassy carbon electrode (2 cm²).

1.4 Calculation of turnover frequency (TOF):

The TOF is defined by the rate of hydrogen evolved per active site as described by the following equation⁴

$$TOF(\eta) = \frac{j(\eta)ANA}{nFNC}$$
(S2)

Where $j(\eta)$ is the current density (A cm⁻², geometric area) at an overpotential of η during the linear sweep voltammograms measurement, A is the electrode geometric area (cm²), N_A is the Avogadro's number (6.022×10²³ mol⁻¹), n is the number of electrons required to generate one hydrogen molecule (2 for HER), F is the Faraday constant (96458 C mol⁻¹), N_C is the number of HER active sites, total number of moles of the active metal sites (both M and Fe) of the catalyst that are loaded onto the NF by

assuming that every M and Fe atom is catalytically active in HER(N_C:CFO=2.490×10⁻⁶×N_A, NFO=2.479×10⁻⁶×N_A, NFO=2.419×10⁻⁶×N_A).

1.5 calculation details

All calculations were carried out by spin-polarized density functional theory (DFT) computations using the Vienna *ab initio* simulation package (VASP).⁵ The electron-ion interaction was described by the projector augmented wave (PAW) pseudopotential, and the exchange-correlation energy was treated by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).^{6, 7} The MFe₂O₄ (311) and (220) surfaces (M = Co, Ni and Zn) models were sampled using Brillouin zones with $2 \times 3 \times 1$ grid centered at the gamma (Γ) point for geometry optimization. The cutoff energy of 500 eV was selected for the plane-wave (PW) basis. The van der Waals (vdW) interactions were taken into account by using the DFT-D3 method.^{8,9} The DFT + U method was used to consider the strong electron correlations for M and Fe in MFe_2O_4 . The values of U – J were 3.29 and 3.42 eV for Co and Fe in CoFe₂O₄.¹⁰ The U_{eff} =3.0 eV for Ni and Fe in NiFe₂O₄, and U_{eff} =5.0 eV for Zn and Fe in ZnFe₂O₄ were chosen in this work.^{11, 12} To prevent the interaction between two adjacent periodic images, a 15 Å vacuum lavers were set along the z-axis. During structural optimizations, all atoms were allowed to relax until the residual force and energy were less than 0.05 eV/Å and 10⁻⁴ eV, respectively. The adsorption energies (E_{ads}) of Cu adsorbed on MFe₂O₄ (Cu@MFe₂O₄) was determined by the following the formula:

$$E_{ads} = E_{C_u @MFe_2 O_4} - E_{MFe_2 O_4} - E_{C_u}$$

where ${}^{E_{C_{u}@MFe_{2}O_{4}}}$ is the total energy of the Cu supported on MFe₂O₄ surfaces, and ${}^{E_{MFe_{2}O_{4}}}$ and ${}^{E_{Cu}}$ are the energies of MFe₂O₄ surfaces and single Cu atom, respectively.



Fig. S1 XRD patterns of diffraction angles from 25 to 40 degrees for MFO.



Fig. S2 XPS survey spectra of (a) CFO, (b) NFO, and (c) ZFO; High resolution XPS spectra of (d) Co 2p and (e) Zn 2p for CFO and ZFO, respectively.



Fig. S3 Representative spinel structures of (a, d) $CoFe_2O_4$, (b, e) $NiFe_2O_4$, and (c, f) $ZnFe_2O_4$ in different styles and views.



Fig. S4 SEM images of (a, b) CFO, (c, d) NFO, and (e, f) ZFO.



Fig. S5 Cyclic voltammograms of (a) CFO and (b) ZFO in the solution containing $5.0 \text{ mM} [\text{Fe}(\text{CN})_6]^{3-/4-}$ (1:1) and 0.1 M KCl at different scan rates; (c) and (d) the linear relationship between the anodic peak currents and the square root of the scan rate.



Fig. S6 (b) CV curves of (a) Bare GCE, (c) CFO/GCE (e) NFO/GCE and (g) ZFO/GCE at different scan rates (10-100 mV s⁻¹) with 0.1M HAc-NaAc buffer solution containing 5.00 mM Cu(II) and (b) Bare GCE, (d) CFO/GCE, (f) NFO/GCE and (h)



ZFO/GCE linear fitting diagram of oxidation peak current and the square root of scanning rate.

Fig. S7 Typical DPASV curves of (a) 0.01-0.05 μ M, (c) 0.1-1.0 μ M and (e)1.0-10.0 μ M Cu(II) with NFO/GCE; (b, d and e) The illustration shows the linear relationship between the peak current and the Cu(II) concentration.



Fig. S8 DPASV response of (a) bare GCE, (c) CFO/GCE, (e) ZFO/GCE for the individual analysis of Cu(II) at pH=5.0 HAc-NaAc (0.1 M) buffer solution; (b, d and e) The illustration shows the linear relationship between the peak current and the Cu(II) concentration.



Fig. S9 (a) Fifteen repetitive measurements of DPASV response for 1.0μ M Cu(II) on CFO/GCE in 0.1 M HAc-NaAc solution; (b) Fifteen repetitive measurements of DPASV response for 1.0μ M Cu(II) on ZFO/GCE in 0.1 M HAc-NaAc solution; (c) The reproducibility DPASV responses of seven different CFO/GCE for 1.0μ M Cu(II) in 0.1 M HAc-NaAc solution; (d) The reproducibility DPASV responses of seven different ZFO/GCE for 1.0μ M Cu(II) in 0.1 M HAc-NaAc solution.

Material	Fe-O	Со-О	Ni-O	Zn-O
CFO	1.861 Å	1.875 Å		
NFO	1.893 Å		1.853 Å	
ZFO	1.849 Å			1.865 Å

Table. S1 MFO bond length data

Material	Fe ²⁺ /Fe ³⁺	Ni ²⁺ /Ni ³⁺	Co ²⁺ /Co ³⁺	OI (%)	O Ⅱ (%)
CFO	0.783		0.95	81.79	18.21
NFO	1.120	1.16		67.01	32.99
ZFO	0.692			82.48	17.52

Table. S2 Relative atomic ratio of Fe^{2+}/Fe^{3+} , Ni^{2+}/Ni^{3+} , Co^{2+}/Co^{3+} and relative percentage of O component.

Electrodes	Method	Detection Sensitivity		References
		limit (nM)	(µA µM ⁻¹)	
Ca ²⁺ MOF	SWASV	25.0	12.8	13
rGO/SMOF/PEI	DPASV	229	1.196	14
IAP30/RTIL	SWASV	6	13.4	15
Au–COF	DPASV	0.9	4.38	16
GC/Cys/Au/FcHT	DPASV	13	0.95	17
ZIF-67/EG	SWASV	2.23	6.91	18
AgNPs	DPASV	0.48	1.3	19
N@MOG-C	SWASV	2.2	11.00	20
Pd/PAC	DPASV	4.29	4.110	21
NiCo ₂ O ₄	SWASV	2.6	12.35	22
Fe ₃ O ₄	SWASV	120	0.6	23
AuNPs/GC	SWASV	32.0	8.72	24
NiFe ₂ O ₄	DPASV	1.14	18.3	This work

Table. S3 Comparison of NFO/GCE and other modified electrodes for the determination of Cu(II).

Interfering ions	Concentration	CFO	NFO	ZFO
	(µM)	(%)	(%)	(%)
Mn(I)	10	2.84	2.91	2.01
Al(III)	10	-1.49	-1.99	-1.91
Na(I)	10	6.21	-2.34	3.85
Cr(III)	10	2.68	2.29	-2.29
K(I)	10	4.03	1.03	3.01
Ca(II)	10	-2.87	-1.28	1.28
Mg(II)	10	-1.75	-1.91	1.93

Table. S4 Interferences of other metal ions on the peak currents of Cu(II).

	Spiked	Found	Recovery	RSD (n=3)
	(µM)	(µM)	(%)	(%)
Sample 1	0.3	0.277	91.6	3.2
Sample 2	0.4	0.423	105.8	2.8
Sample 3	0.5	0.475	95.0	3.1

Table. S5 Determination of Cu(II) in real water samples.

Electrocatalysts	$E_j=10A \text{ cm}^{-2}$ (mV)	Tafel slope (mV dec ⁻¹)	Electrolyte	Substrate	References
Fe-Ni@NC-CNTs	202	113.7	1 M KOH	GCE	25
S-NiFe ₂ O ₄	138	63.1	1 M KOH	Nickel foam	26
(NiFeO _x (OH)y@MoS ₂ /rGO	170	80	1 М КОН	Nickel foam	27
FeCo ₂ O ₄ @FeCo ₂ S ₄ @PPy	98.2	65.1	1 М КОН	Nickel foam	28
Fe _{1.0} Co _{1.1} Ni _{1.4} -NC	175	60.0	1 М КОН	Nickel foam	29
C-(Fe-Ni)P@PC/(NiCo)P	142	98.0	1 М КОН	carbon cloth	30
(Ni, Fe)S ₂ @MoS ₂	130	101.2	1 М КОН	carbon cloth	31
Ni ₃ S ₂ /MnO ₂	102	83.5	1 М КОН	Nickel foam	32
NiFe ₂ O ₄	93	55.4	1 М КОН	Nickel foam	This work

Table. S6 Comparison of the HER performance of NFO with other reported NiFebased electrocatalysts tested under similar conditions.

Electrocatalysts	C _{dl} , mF cm ⁻²	ECSA, cm ²	n _{ECSA}	TOF (s ⁻¹) at η=200 mV
CFO	6.60	220.00	1.05	0.07
NFO	9.20	306.67	1.46	0.21
ZFO	6.30	210.00	1.00	0.025

Table. S7 The C_{dls} , ECSAs, Δn_{ECSA} and TOF values of the prepared electrodes for HER electrolysis.

References

H. H. Fu, L. Chen, Y. L. Shi, W. W. Kong, X. Zhang, J. Hou, H. L. Li, G. Wang,
 F. Yu and X. H. Guo, Electrochim. Acta, 2019, 320, 9.

2. W. Y. He, X. J. Zheng, J. F. Peng, H. Dong, J. W. Wang and W. Zhao, Chem. Eng. J., 2020, 396, 7.

3. J. B. Zhu, S. Li, M. L. Xiao, X. Zhao, G. R. Li, Z. Y. Bai, M. Li, Y. F. Hu, R. F.

Feng, W. W. Liu, R. Gao, D. Su, A. P. Yu and Z. W. Chen, Nano Energy, 2020, 77, 11.
4. H. L. Fei, J. C. Dong, M. J. Arellano-Jimenez, G. L. Ye, N. D. Kim, E. L. G.
Samuel, Z. W. Peng, Z. Zhu, F. Qin, J. M. Bao, M. J. Yacaman, P. M. Ajayan, D. L.

Chen and J. M. Tour, Nature Communications, 2015, 6, 8.

5. G. Kresse and J. Furthmüller, Physical review B, 1996, 54, 11169.

6. J. P. Perdew, K. Burke and M. Ernzerhof, Physical review letters, 1996, 77, 3865.

7. L. Li, B. Li, Q. Guo and B. Li, Journal of physical chemistry, 2019.

8. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, The Journal of chemical physics, 2010, 132, 154104.

9. L. Li, X. Wang, H. Guo, G. Yao, H. Yu, Z. Tian, B. Li and L. Chen, Small Methods, 2019, 1900337.

10. Y. Hou, X. Yan, Y. Huang, S. Zheng, S. Hou and Y. Ouyang, Journal of Magnetism and Magnetic Materials, 2020, 495, 165862.

11. P. V. Kumar, M. P. Short, S. Yip, B. Yildiz and J. C. Grossman, The Journal of Physical Chemistry C, 2013, 117, 5678-5683.

12. J. M. Quintero, K. S. Rodríguez, C. R. Torres and L. Errico, Journal of Alloys

and Compounds, 2019, 775, 1117-1128.

A. D. Pournara, A. Margariti, G. D. Tarlas, A. Kourtelaris, V. Petkov, C. Kokkinos, A. Economou, G. S. Papaefstathiou and M. J. Manos, J. Mater. Chem. A, 2019, 7, 15432-15443.

Z. Z. Xu, Z. J. Liu, M. Xiao, L. L. Jiang and C. Q. Yi, Chem. Eng. J., 2020, 394,
 9.

S. Q. Xiong, J. C. Xu, F. Z. Xie, X. H. Hu, G. H. Gong, Z. Y. Wu and L. M.
 Yao, Chem. Eng. J., 2017, 316, 383-392.

16. W. Xiong, L. Zhou and S. T. Liu, Chem. Eng. J., 2016, 284, 650-656.

H. Gu, Q. Hou, Y. Liu, Y. J. Cai, Y. Q. Guo, H. Y. Xiang and S. Chen, Biosens.
 Bioelectron., 2019, 135, 111-119.

L. F. Ma, X. Y. Zhang, M. Ikram, M. Ullah, H. Y. Wu and K. Y. Shi, Chem.
 Eng. J., 2020, 395, 12.

19. L. Cui, J. Wu, J. Li, Y. Q. Ge and H. X. Ju, Biosens. Bioelectron., 2014, 55, 272-277.

20. L. Cui, J. Wu and H. X. Ju, ACS Appl. Mater. Interfaces, 2014, 6, 16210-16216.

21. P. Veerakumar, V. Veeramani, S. M. Chen, R. Madhu and S. B. Liu, ACS Appl Mater Interfaces, 2016, 8, 1319-1326.

22. X. Y. Yu, X. Z. Yao, T. Luo, Y. Jia, J. H. Liu and X. J. Huang, ACS Appl Mater Interfaces, 2014, 6, 3689-3695.

23. X. Z. Yao, Z. Guo, Q. H. Yuan, Z. G. Liu, J. H. Liu and X. J. Huang, ACS Appl.

Mater. Interfaces, 2014, 6, 12203-12213.

24. X. X. Xu, G. T. Duan, Y. Li, G. Q. Liu, J. J. Wang, H. W. Zhang, Z. F. Dai and W. P. Cai, ACS Appl. Mater. Interfaces, 2014, 6, 65-71.

25. X. J. Zhao, P. Pachfule, S. Li, J. R. J. Simke, J. Schmidt and A. Thomas, Angew. Chem.-Int. Edit., 2018, 57, 8921-8926.

J. L. Liu, D. D. Zhu, T. Ling, A. Vasileff and S. Z. Qiao, Nano Energy, 2017,
 40, 264-273.

F. Zhou, X. Zhang, R. J. Sa, S. Zhang, Z. H. Wen and R. H. Wang, Chem. Eng.
 J., 2020, 397, 8.

28. D. P. Zhao, M. Z. Dai, Y. Zhao, H. Q. Liu, Y. Liu and X. Wu, Nano Energy, 2020, 72, 8.

29. M. Khalid, A. M. B. Honorato, G. Tremiliosi and H. Varela, J. Mater. Chem. A, 2020, 8, 9021-9031.

30. C. N. Lv, L. Zhang, X. H. Huang, Y. X. Zhu, X. Zhang, J. S. Hu and S. Y. Lu, Nano Energy, 2019, 65, 9.

Y. K. Liu, S. Jiang, S. J. Li, L. Zhou, Z. H. Li, J. M. Li and M. F. Shao, Appl.
 Catal. B-Environ., 2019, 247, 107-114.

32. Y. Xiong, L. L. Xu, C. D. Jin and Q. F. Sun, Appl. Catal. B-Environ., 2019, 254, 329-338.