

## Electronic Supplementary Information

### Self-sorting multimetal-organic gel electrocatalysts for highly efficient oxygen evolution reaction

Yali Xiao,<sup>‡</sup> Qiushi Wang,<sup>‡</sup> Xiying Feng, Jinyi Wu, Peisen Liao, Yexiang Tong\* and Jianyong Zhang\*

*Sun Yat-Sen University, MOE Laboratory of Polymeric Composite and Functional Materials, School of Materials Science and Engineering, School of Chemistry, Guangzhou 510275, China.*

## Experimental section

### Materials and methods

All starting materials and solvents were obtained from commercial sources and used without further purification unless otherwise indicated. SEM was performed with a Quanta 400F instrument and an ultra-high-resolution SU8010 FE-SEM or Quanta 400F-SEM (FEI, working voltage is 20 kV, working current is 10  $\mu$ A) instruments. Prior to the measurements, the wet gel was dispersed in EtOH with the aid of sonication and then deposited on the aluminum foil. TEM investigations were performed with an FEI Tecnai G2 Spirit 120 kV TEM system and the samples were dispersed in EtOH by sonication and then mounted on a carbon-coated copper grid before TEM tests. Powder XRD patterns were collected on a Rigaku SmartLab diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) and perform in the  $2\theta$  range of  $5\sim 70^\circ$  at a scanning rate of  $5^\circ \text{ min}^{-1}$ . X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250 spectrometer operated at 150 W. N<sub>2</sub> adsorption/desorption isotherm at 77 K was carried out using a 3Flex three-station multifunctional gas adsorption instrument (Micromeritics), the sample was vacuum-dried at 80  $^\circ\text{C}$  for 16 h before the test, supplemented with He under normal pressure. FT-IR spectra of bimetallic and multimetallic aerogels were measured with a PerkinElmer Frontier spectrometer scanning from 4000 to 400  $\text{cm}^{-1}$  by KBr troche. The FT-IR spectrum of MG-FeNiCo after stability test was recorded using a Thermo NICOLET-6700 FT-IR spectrometer with ATR accessories in the range of 4000 to 650  $\text{cm}^{-1}$ .

**Preparation of Ni-BTC MOG and Co-BTC MOG.** H<sub>3</sub>BTC (105.1 mg, 0.5 mmol) and TEA (150  $\mu\text{L}$ ) were dissolved in water (2 mL) followed by sonication. The solution was mixed with a solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (174.5 mg, 0.6 mmol) or Co(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (174.6 mg, 0.6 mmol) in EtOH (1 mL). A light green or pink gel was obtained at room temperature within 3 min by stirring violently. After the gel was formed, it was allowed to stand for 24 h. The prepared gels were subjected for solvent exchange with distilled water three times a day to remove the unreacted reactants, and repeated for three days. An aerogel was obtained by freeze-drying for 24 h (Co-BTC MOG, 120.5 mg, 43%; Ni-BTC MOG, 186.4 mg, 67%).

**Preparation of bimetallic and multimetallic aerogels.** A typical procedure for MG-FeNiCo: H<sub>3</sub>BTC (105.1 mg, 0.5 mmol) and TEA (150  $\mu\text{L}$ ) were dissolved in water (2 mL). The solution was mixed with a solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (58.2 mg, 0.2 mmol), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (58.2 mg, 0.2 mmol) and

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (80.8 mg, 0.2 mmol) in EtOH (1.0 mL). A brown gel was obtained at room temperature within 3 min by stirring violently. The solvent in the gel was exchanged with distilled water for three times a day to remove the unreacted reactants, and repeated for three days. The aerogel was obtained by freeze-drying for 24 h (134.6 mg, 45%).

### **Preparation of MG-FeNiCo-xGO aerogels**

Graphene oxide was prepared through a modified Hummers' method.<sup>S1,S2</sup> 1.0 and 2.0 mg mL<sup>-1</sup> of GO aqueous solution were prepared in advance. 0.5 mL, 1 mL, and 2 mL of GO aqueous solution (1.0 mg mL<sup>-1</sup>) were added to obtain MG-FeNiCo-GO with different doping amounts (MG-FeNiCo-0.5GO, MG-FeNiCo-1.0GO, MG-FeNiCo-2.0GO), and 2 mL of GO aqueous solution (2.0 mg mL<sup>-1</sup>) to obtain MG-FeNiCo-4.0GO. A typical procedure for MG-FeNiCo-2.0GO:  $\text{H}_3\text{BTC}$  (105.1 mg, 0.5 mmol) and TEA (0.15 mL, 1.5 mmol) were dissolved in water (2 mL) and the corresponding GO aqueous solution was added. The solution was mixed with a solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (58.2 mg, 0.2 mmol),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (58.2 mg, 0.2 mmol),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (80.1 mg, 0.2 mmol) in EtOH (1.0 mL). A dark brown gel was obtained at room temperature within 3-5 min by stirring violently. The solvent in the gel was exchanged with distilled water three times a day to remove the unreacted reactants, and repeated for three days. The aerogel was obtained by freeze-drying for 24 h (155.8 mg, 51%).

### **Electrochemical measurements**

The electrochemical measurements for HER and OER were performed at room temperature using a typical three-electrode cell controlled by a CHI 660E electrochemical workstation. Graphitic electrode was used as the counter electrode, Ag/AgCl was used as the reference electrode, and nickel foam was the working electrode. The aerogel sample was loaded onto the nickel foam, and the loading was controlled to be  $3.4 \pm 0.3$  mg cm<sup>-2</sup> with a loading area of 1 cm × 1 cm. All samples were tested with a CV cycle of 50 mV s<sup>-1</sup> for 20 cycles (0 – 0.8 V), and then OER was performed. For the OER test, the polarization curves were obtained by sweeping the potential from 0 to 1 V (vs. Ag/AgCl electrode in saturated KCl) at a sweep rate of 5 mV s<sup>-1</sup> in KOH solution (1.0 mol L<sup>-1</sup>). The frequency range of EIS was 0.01-10<sup>5</sup> Hz. All potentials measured with an Ag/AgCl reference electrode were converted to the RHE reference scale by the formula,  $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.197 \text{ V} + 0.059\text{pH}$ . The overpotential ( $\eta$ ) was calculated according to the following formula,  $\eta(\text{V}) = E_{\text{RHE}} - 1.23 \text{ V}$ .

Aerogels were loaded onto nickel foam (NF) in the following steps. 1) Nickel foam was cleaned with distilled water using ultrasonic for 20 min, then with anhydrous ethanol for 20 min, and then dried in vacuum at 60 °C. 2) 36 mg of aerogel sample and 4 mg of polyvinylidene fluoride (sample:PVDF = 9:1) were put in 0.5 mL of *N*-Methyl pyrrolidone (NMP) with stirring at 800 r min<sup>-1</sup> for more than 3 h. 3) The clean foaming nickel-metal mesh was cut into 3 cm × 3 cm blocks. The catalyst ink was loaded on 1 cm × 3 cm area, then dried in vacuum at 60 °C for 24 h. 4) The loading amount of aerogel samples was precisely controlled by weighing the mass before and after the sample loading.

Turnover frequency (TOF) was evaluated by the following equations<sup>S3</sup>

$$\text{TOF} = J \times A / (4F \times n) \quad (1)$$

$$n = m_{\text{loading}} \times r_{\text{FeNiCo}} / M_w \quad (2)$$

Here,  $J$  is obtained at 90 % iR-corrected overpotential = 300 mV,  $R$  is the series resistance obtained from the fitting of EIS,  $A$  is the geometric area of nickel foam (1 cm<sup>2</sup>),  $F$  is the Faraday constant (96485 C mol<sup>-1</sup>),  $n$  is the number of cobalt, nickel, and iron atoms on the electrode, calculated via equation (2).

According to equation (2),  $m_{\text{loading}}$  is the loading mass,  $r_{\text{FeCoNi}}$  is the molar ratio of FeCoNi in multimetallic aerogels,  $M_w$  is the molecular weight of multimetallic aerogels. All the metal sites were assumed to be actively involved in the electrochemical reaction.

**Table S1** Gelation tests of metal-organic systems with 1,3,5-benzenetricarboxylic acid (H<sub>3</sub>BTC).

Entry	System	Results	Time
1	Ni:BTC = 0.5:1	S	/
2	Ni:BTC = 1:1	G	3-5 min
3	Ni:BTC = 1.2:1	G	3-5 min
4	Ni:BTC = 1.5:1	S	/
5	Co:BTC = 0.5:1	G	3-5 min
6	Co:BTC = 1:1	G	3-5 min
7	Co:BTC = 1.2:1	G	3-5 min
8	Co:BTC = 1.5:1	P	/

S, solution; G, gel; P, precipitate.

**Table S2** Gelation ability of bimetallic and multimetallic gels.

Entry	the ratio of metal ions	Result	Time/min
1	MG-NiCo <sub>0.5</sub>	pink gel	3-5 min
2	MG-NiCo <sub>2</sub>	pink gel	30 min
3	MG-NiCo	pink gel	~5 min
4	MG-FeCo	brown gel	~5 min
5	MG-FeNi	brown gel	~5 min
6	MG-FeNiCo	brownish red gel	~5 min
4	MG-Fe <sub>1</sub> Ni <sub>2</sub> Co <sub>3</sub>	brownish red gel	~5 min
5	MG-Fe <sub>1</sub> Ni <sub>3</sub> Co <sub>8</sub>	brownish red gel	~5 min
6	MG-FeNiCo-0.5 GO	brown red	~5 min
7	MG-FeNiCo-1.0 GO	brown red	~5 min
8	MG-FeNiCo-2.0 GO	brown red	~15 min
9	MG-FeNiCo-4.0 GO	brown red	~20 min

**Table S3** OER performance of bimetallic and multimetallic aerogels.

Sample	$R_{ct}/\Omega$	$E$ (50 mA cm <sup>-2</sup> )	$E$ (100 mA cm <sup>-2</sup> )	Tafel slope (mV dec <sup>-1</sup> )
MG-FeNi	1.01	413	548	86
MG-FeCo	0.57	312	342	66
MG-NiCo	3.51	432	550	108
MG-FeNiCo	0.44	272	298	49
MG- Fe <sub>1</sub> Ni <sub>2</sub> Co <sub>3</sub>	0.88	319	347	74
MG- Fe <sub>1</sub> Ni <sub>3</sub> Co <sub>8</sub>	0.55	312	337	68
MG-FeNiCo-0.5GO	0.56	285	292	49
MG-FeNiCo-1.0GO	0.36	280	307	44
MG-FeNiCo-2.0GO	0.28	263	288	36
MG-FeNiCo 4.0GO	0.58	300	324	74
FeBTC+NiBTC+CoBTC	1.46	313	383	96
RuO <sub>2</sub>	0.76	330	380	76

**Table S4** Comparison of OER activity for recently reported various electrocatalysts (Overpotentials are mostly derived from the potentials at 10 mA cm<sup>-2</sup> unless otherwise stated).

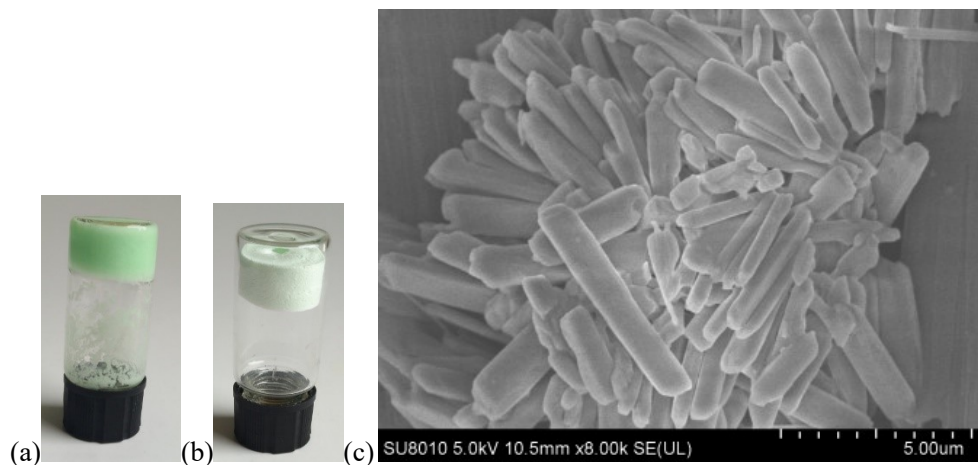
Classification	Material	Overpotential /mV	Tafel slope /mV dec <sup>-1</sup>	Electrolyte	Conductive substrate	Ref
MOF	FeNi <sub>3</sub> bimetal	236	49	1.0 M KOH	NF	S4
Amorphous MOF	αMOF-NC	249	39.5	1.0 M KOH	GCE	S5
MOF	FeNiCo@NC	245	32	1.0 M KOH	NF	S6
Coordination polymers	Fe <sub>1</sub> Ni <sub>2</sub> (BDC-NH <sub>2</sub> )	228	30.3	1.0 M KOH	NF	S7
Oxides	CoFeZr	264@20 mA cm <sup>-2</sup>	54.2	1.0 M KOH	NF	S8
Hydroxides	Co <sub>5</sub> Mo <sub>1</sub> P/NiF e-LDH	225@50 mA cm <sup>-2</sup>	55	1.0 M KOH	NF	S9
Hydroxides	Ni <sub>5</sub> Co <sub>3</sub> Mo-OH	280@50 mA cm <sup>-2</sup>	56	1.0 M KOH	NF	S10
Gel derived oxide	CoFeNi-O-1	244	55.4	1.0 M KOH	GCE	S11
Aerogel	(Co <sub>1-x</sub> Ni <sub>x</sub> )S <sub>2</sub> /N-graphene	330	47	1.0 M KOH	RDE	S12
Aerogel	Ni <sub>3</sub> FeN/r-GO	270	54	1.0 M KOH	NF	S13
Aerogel	(Ni,Co)Se <sub>2</sub> /G A	250	70	1.0 M KOH	NF	S14
Aerogel	Ni/MnO/rGO	370	67	0.1 M KOH	RDE	S15
Metallogels	Co-Mac-1	320	54	1.0 M KOH	GCE	S16
xerogel	CoGel1 xerogel	321	55	1.0 M KOH	GCE	S17
Aerogel	MG-FeNiCo	248@20 mA cm <sup>-2</sup>	49	1.0 M KOH	NF	This work
Aerogel	MG-FeNiCo-2.0GO	263@50 mA cm <sup>-2</sup>	36	1.0 M KOH	NF	This work

NF referred to nickel foam, GCE referred to glassy carbon electrode, RDE referred to rotating disk electrode.

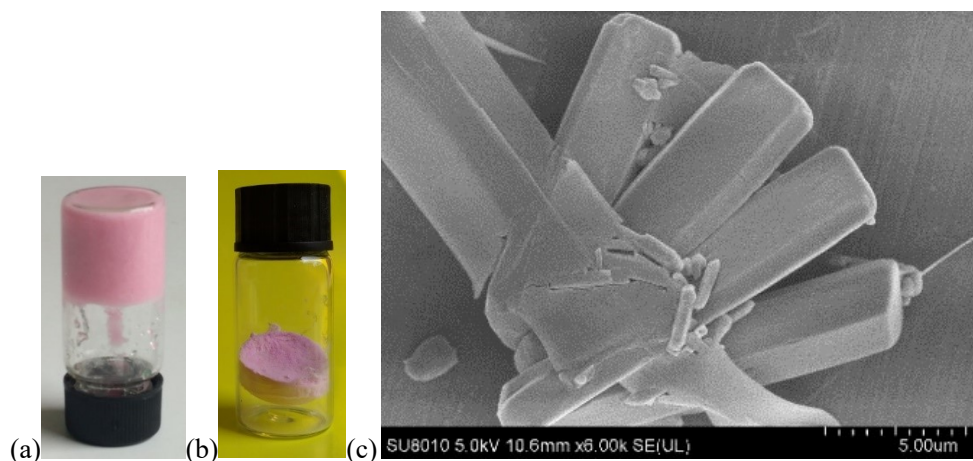
## References

- S1 W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**,1339–1339.
- S2 Y. X. Xu, H. Bai, G. W. Lu, C. Li, G. Q. Shi, *J. Am. Chem. Soc.*, 2008, **130**, 5856–5857.
- S3 B. Zhang, X. Zheng, O. Voznyy, R. Comin, M. Bajdich, M. Garcia-Melchor, L. Han, J. Xu, M. Liu, L. Zheng, F. P. Garcia de Arquer, C. T. Dinh, F. Fan, M. Yuan, E. Yassitepe, N. Chen, T. Regier, P. Liu, Y. Li, P. De Luna, A. Janmohamed, H. L. Xin, H. Yang, A. Vojvodic and E. H. Sargent, *Science*, 2016, **352**, 333-337.
- S4 F. Zheng, Z. Zhang, D. Xiang, P. Li, C. Du, Z. Zhuang, X. Li and W. Chen, *J. Colloid Interf. Sci.*, 2019, **555**, 541-547.

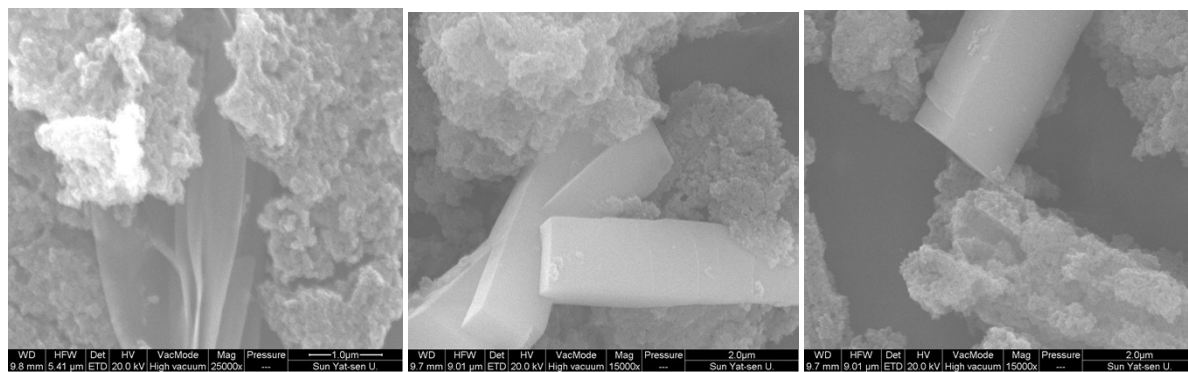
- S5 C. Liu, J. Wang, J. Wan, Y. Cheng, R. Huang, C. Zhang, W. Hu, G. Wei and C. Yu, *Angew. Chem. Int. Ed.*, 2020, **59**, 3630-3637.
- S6 S. Ren, X. Duan, F. Ge, M. Zhang and H. Zheng, *J. Power Sources*, 2020, **480**, 228866.
- S7 J. Ma, X. Bai, W. He, S. Wang, L. Li, H. Chen, T. Wang, X. Zhang, Y. Li, L. Zhang, J. Chen, F. Meng and Y. Fu, *Chem. Commun.*, 2019, **55**, 12567-12570.
- S8 L. Huang, D. Chen, G. Luo, Y. R. Lu, C. Chen, Y. Zou, C. L. Dong, Y. Li and S. Wang, *Adv. Mater.*, 2019, **31**, 1901439.
- S9 W. Mai, Q. Cui, Z. Zhang, K. Zhang, G. Li, L. Tian and W. Hu, *ACS Appl. Energy Mater.*, 2020, **3**, 8075-8085.
- S10 S. Hao, L. Chen, C. Yu, B. Yang, Z. Li, Y. Hou, L. Lei and X. Zhang, *ACS Energy Lett.*, 2019, **4**, 952-959.
- S11 Z. Cao, Z. Jiang, Y. Li, C. Huang and Y. Li, *ChemSusChem*, 2019, **12**, 2480-2486.
- S12 H. Han, K. M. Kim, H. Choi, G. Ali, K. Y. Chung, Y.-R. Hong, J. Choi, J. Kwon, S. W. Lee, J. W. Lee, J. H. Ryu, T. Song and S. Mhin, *ACS Catal.*, 2018, **8**, 4091-4102.
- S13 Y. Gu, S. Chen, J. Ren, Y. A. Jia, C. Chen, S. Komarneni, D. Yang and X. Yao, *ACS Nano*, 2018, **12**, 245-253.
- S14 X. Xu, H. Liang, F. Ming, Z. Qi, Y. Xie and Z. Wang, *ACS Catal.*, 2017, **7**, 6394-6399.
- S15 G. Fu, X. Yan, Y. Chen, L. Xu, D. Sun, J. M. Lee, Y. Tang, *Adv. Mater.*, 2018, **30**, 1704609.
- S16 Q. Liu, Q. Wang, J. Wang, Z. Li, J. Liu, X. Sun, J. Li, Y. Lei, L. Dai and P. Wang, *Adv. Funct. Mater.*, 2020, **30**, 2000593.
- S17 E. Saha, K. Karthick, S. Kundu and J. Mitra, *ACS Sustain. Chem. Eng.*, 2019, **7**, 16094-16102.



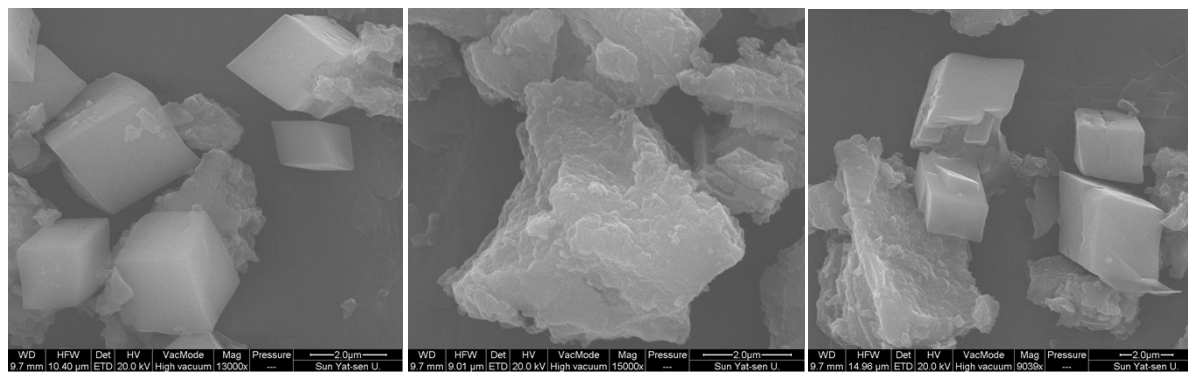
**Fig. S1** Photographs of Ni-BTC MOG, (a) wet gel, (b) after freeze-drying, and (c) SEM images of Ni-BTC MOG aerogel.



**Fig. S2** Photographs of Co-BTC MOG, (a) wet gel, (b) after freeze-drying, and (c) SEM images of Co-BTC MOG aerogel.

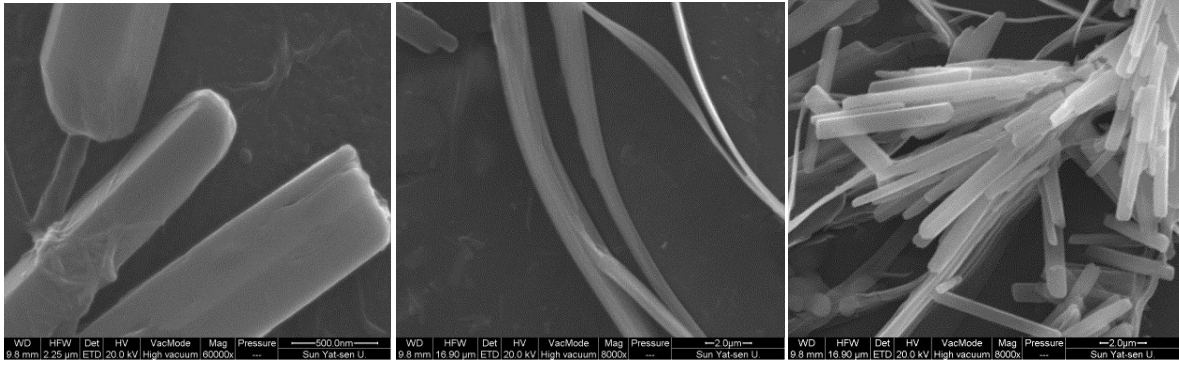


**Fig. S3** SEM images of MG-FeNi aerogel.

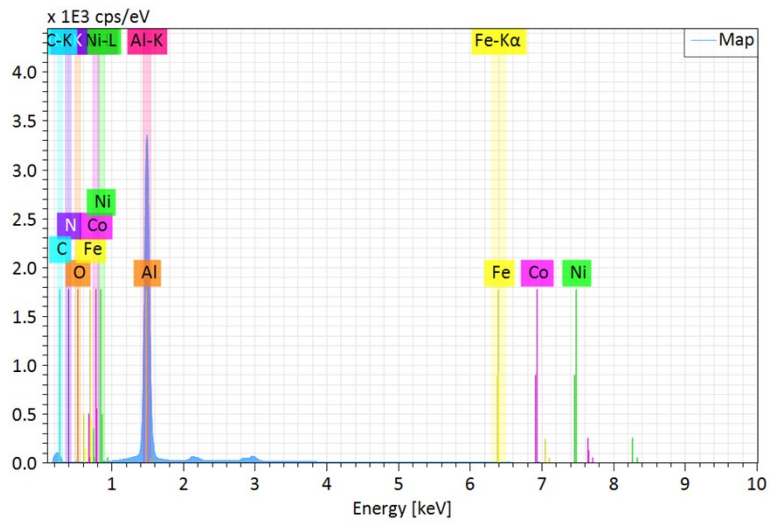


**Fig. S4** SEM images of MG-FeCo aerogel.

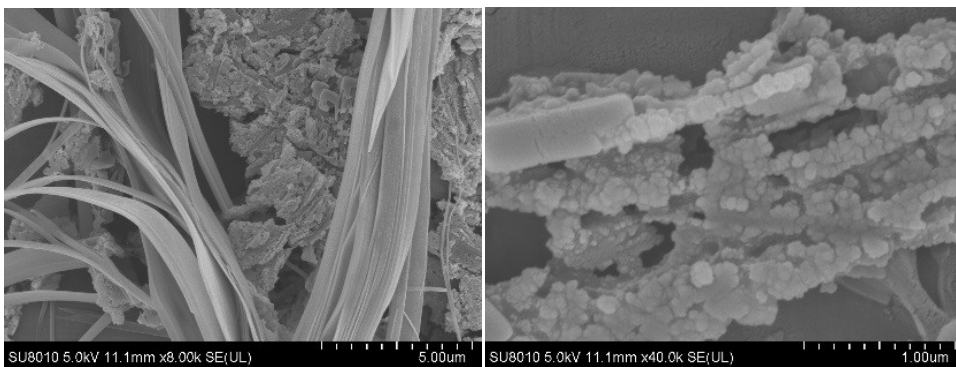




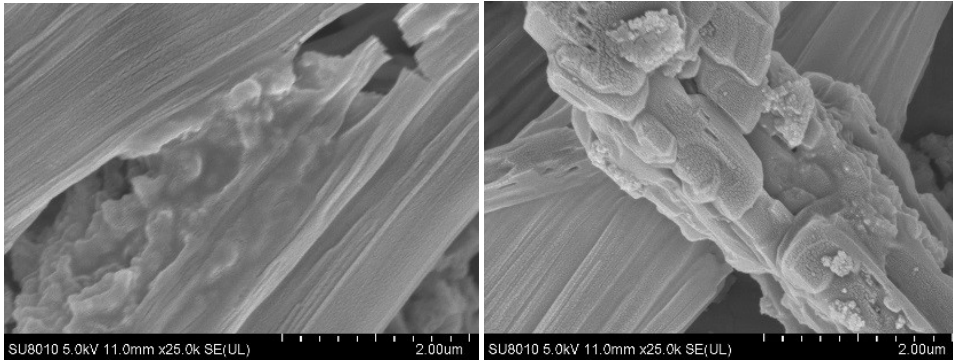
**Fig. S5** SEM images of MG-NiCo aerogel.



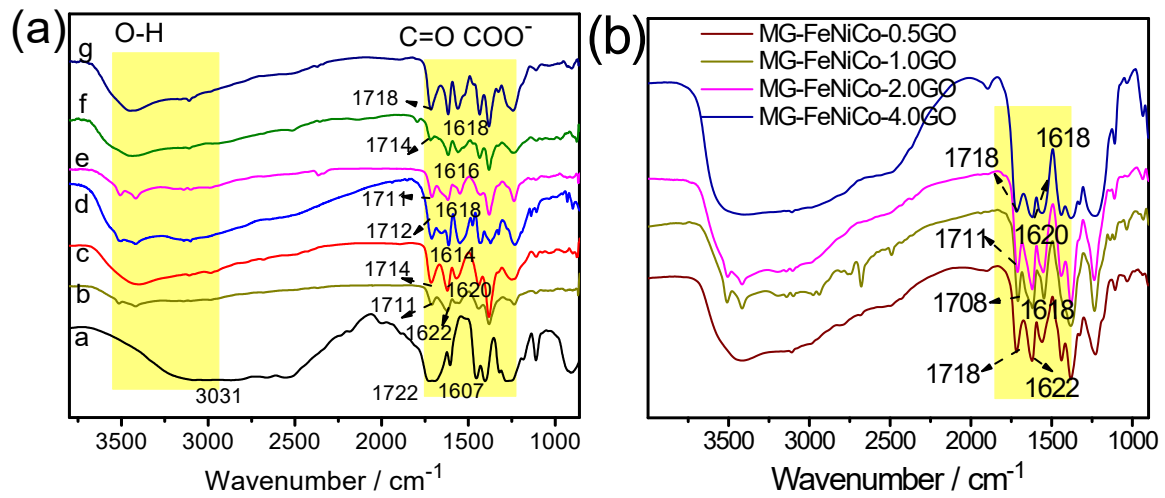
**Fig. S6** EDX spectrum of MG-FeNiCo aerogel (Quantitative value/atom%: N 44.22%, Al 42.10%, C 5.96%, O 5.57%, Fe 1.71%, Co 0.26%, Ni 0.20%).



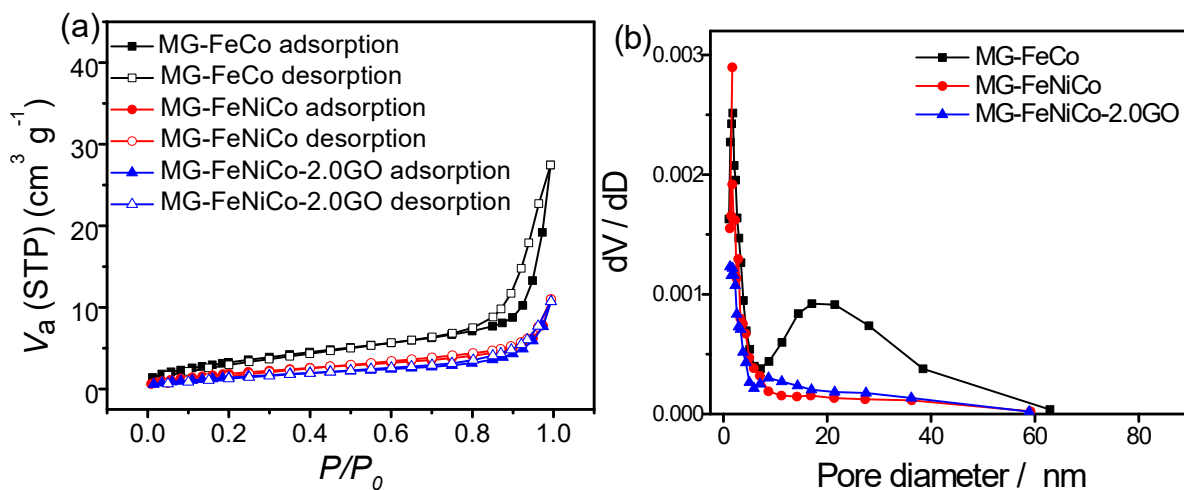
**Fig. S7** SEM images of MG-Fe<sub>1</sub>Ni<sub>2</sub>Co<sub>3</sub> aerogel.



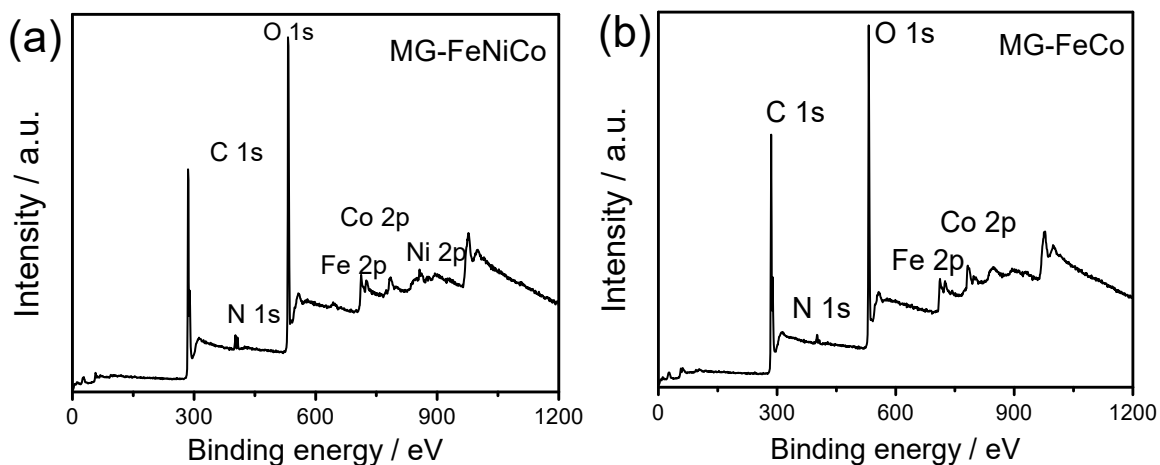
**Fig. S8** SEM images of MG-  $\text{Fe}_1\text{Ni}_3\text{Co}_8$  aerogel.



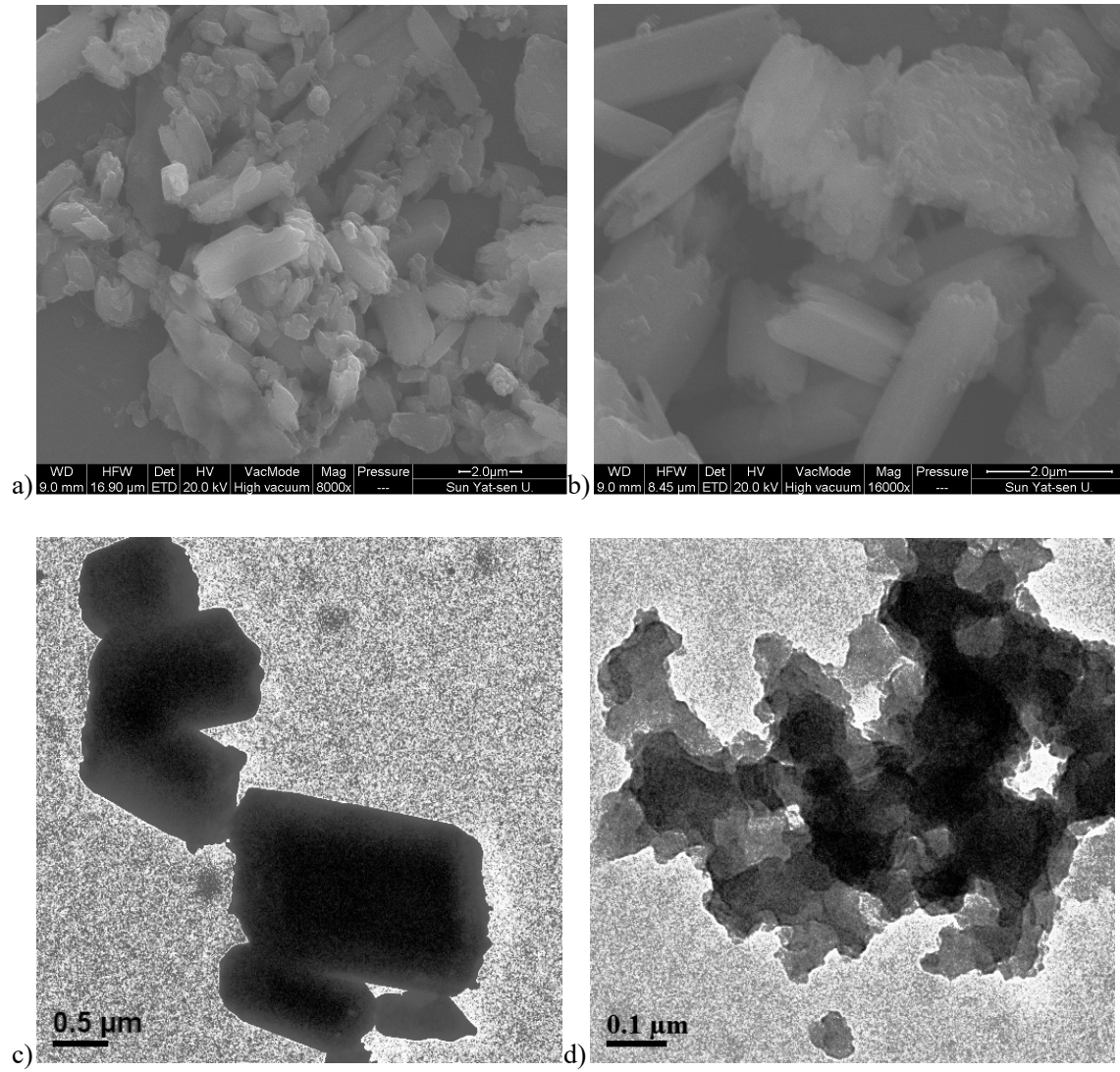
**Fig. S9** FT-IR spectra of (a) bimetallic and multimetallic aerogels (a. 1,3,5-benzenetricarboxylic acid, b. MG-FeCo, c. MG-FeNi, d. MG-NiCo, e. MG-FeNiCo, f. MG- $\text{Fe}_1\text{Ni}_2\text{Co}_3$ , g. MG- $\text{Fe}_1\text{Ni}_3\text{Co}_8$ ), and (b) MG-FeNiCo- $x$ GO aerogels.



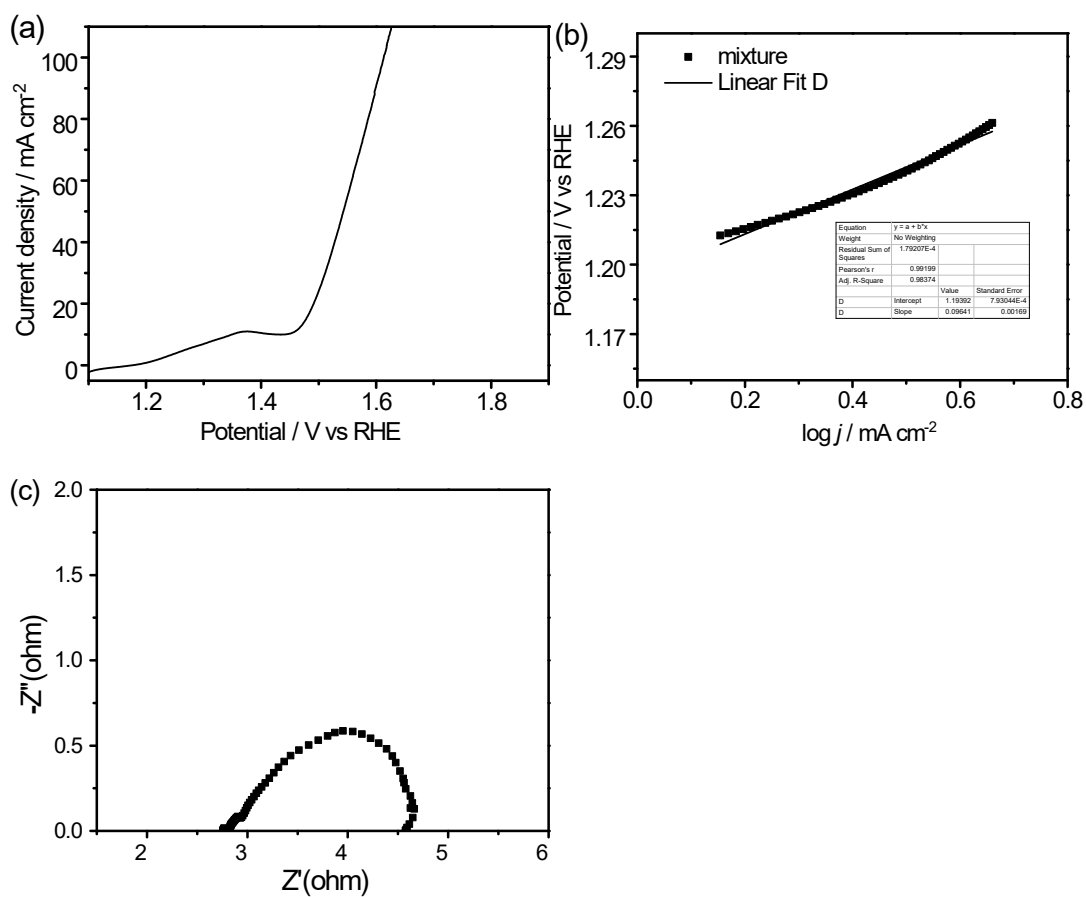
**Fig. S10** (a)  $\text{N}_2$  adsorption (closed symbols) /desorption (open symbols) isotherms at 77 K, and (b) pore size distribution of MG-FeCo, MG-FeNiCo and MG-FeNiCo-2.0GO aerogels.



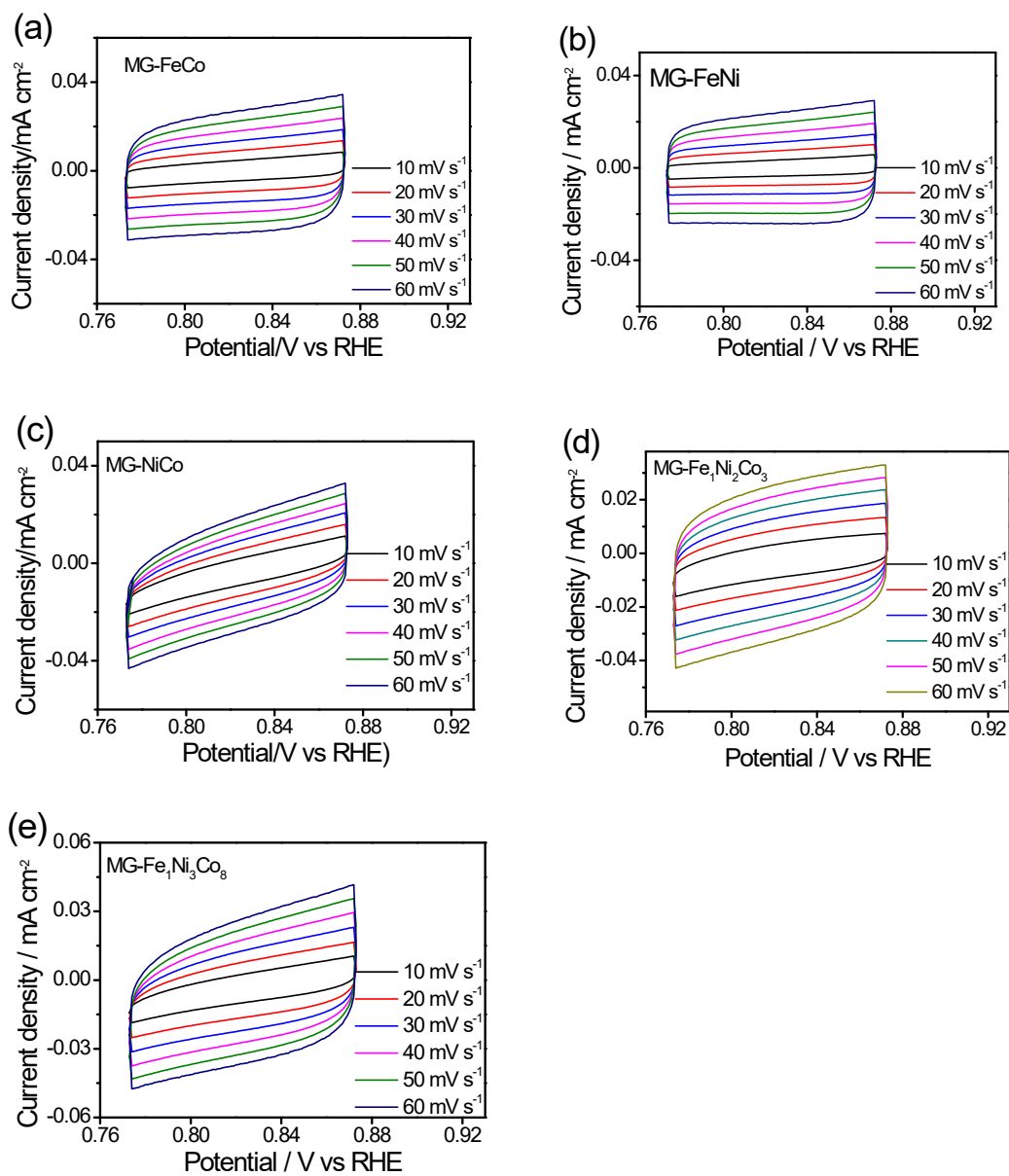
**Fig. S11** XPS survey spectra of (a) MG-FeNiCo and (b) MG-FeCo.



**Fig. S12** (a,b) SEM and (c,d) TEM images of mechanically mixed Fe-BTC MOG, Co-BTC MOG and Ni-BTC MOG.

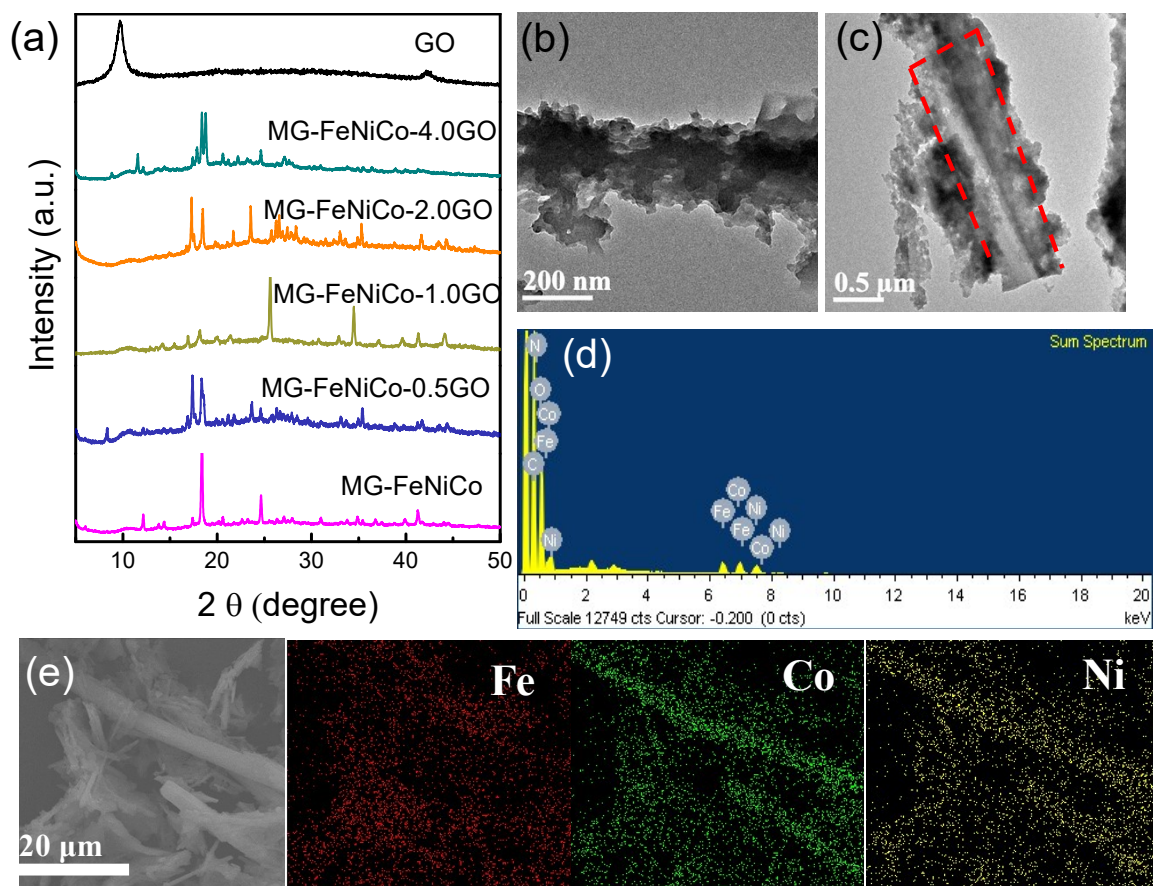


**Fig. S13** (a) LSV polarization curve, (b) Tafel plot, and (c) Nyquist EIS plot of the mechanical mixture of Fe-BTC MOG, Co-BTC MOG and Ni-BTC MOG aerogels.

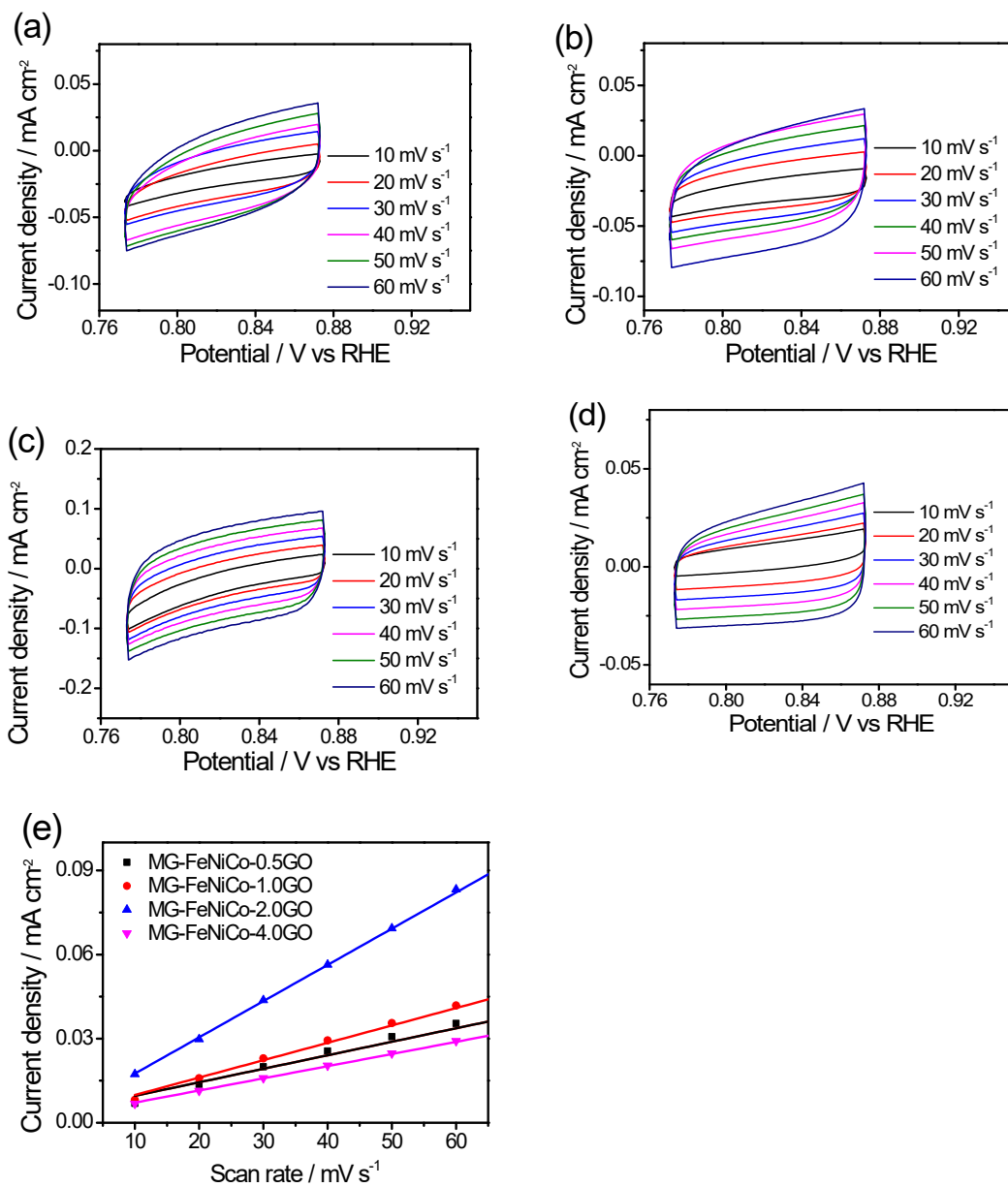


**Fig. S14** CV curves of (a) MG-FeCo, (b) MG-FeNi, (c) MG-NiCo, (d) MG-Fe<sub>1</sub>Ni<sub>2</sub>Co<sub>3</sub>, and (e) MG-Fe<sub>1</sub>Ni<sub>3</sub>Co<sub>8</sub> at various scan rates at a given overpotential of +0.823 V vs. RHE in 1.0 mol L<sup>-1</sup> KOH.



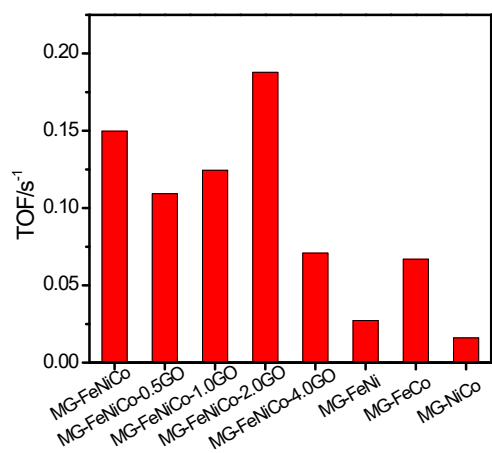


**Fig. S15** (a) XRD patterns of multimetallic MG-FeNiCo- $x$ GO aerogels, (b, c) TEM images, (d) EDX spectrum, and (e) mapping images of MG-FeNiCo-2.0GO.

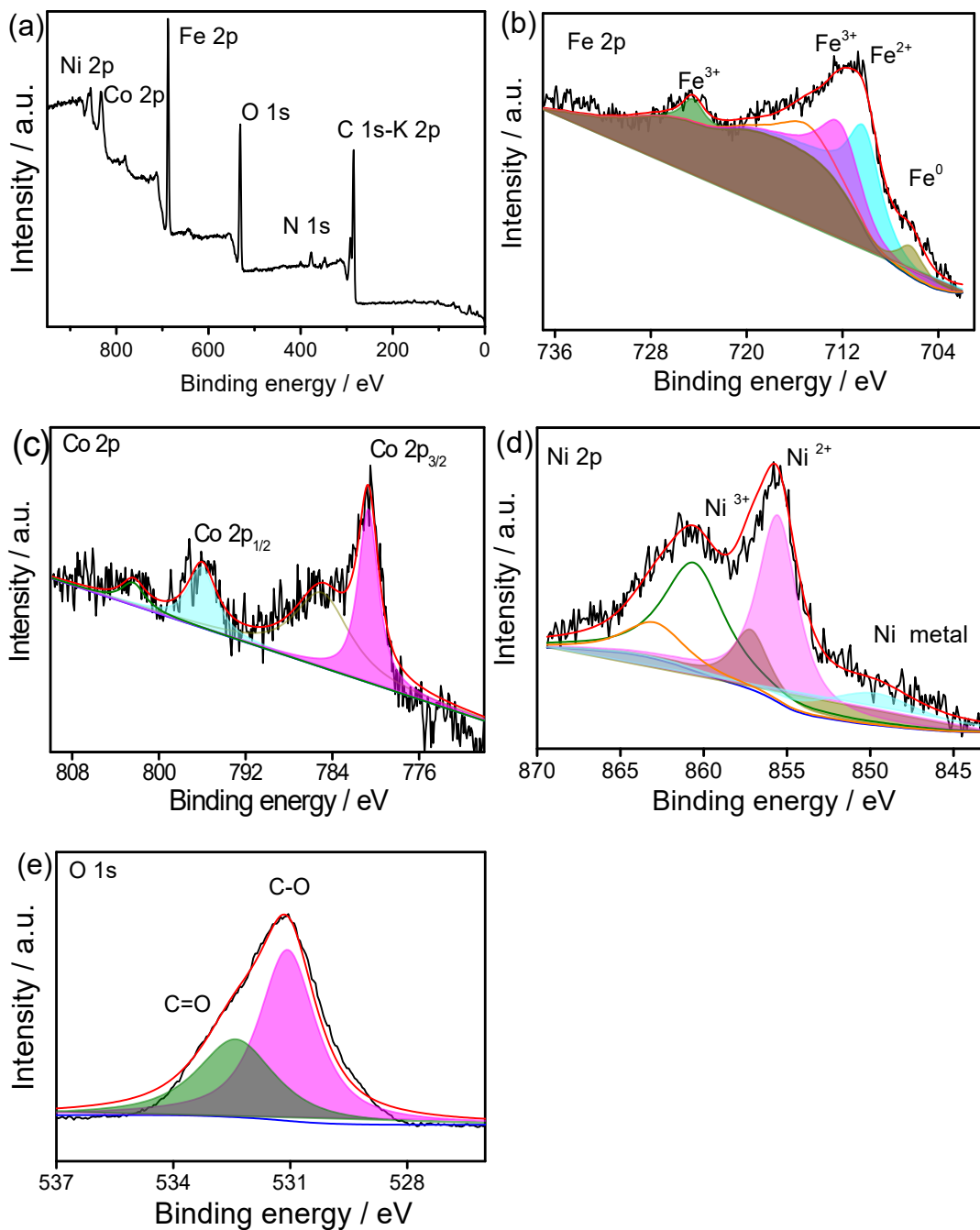


**Fig. S16** CV curves of (a) MG-FeNiCo-0.5GO, (b) MG-FeNiCo-1.0GO, (c) MG-FeNiCo-2.0GO and (d) MG-FeNiCo-4.0GO, and (e) linear fitting of  $\Delta_j$  ( $\Delta_j = j_a - j_c$ ) vs. scan rates at various scan rates at a given overpotential of +0.823 V vs. RHE in 1.0 mol L<sup>-1</sup> KOH.

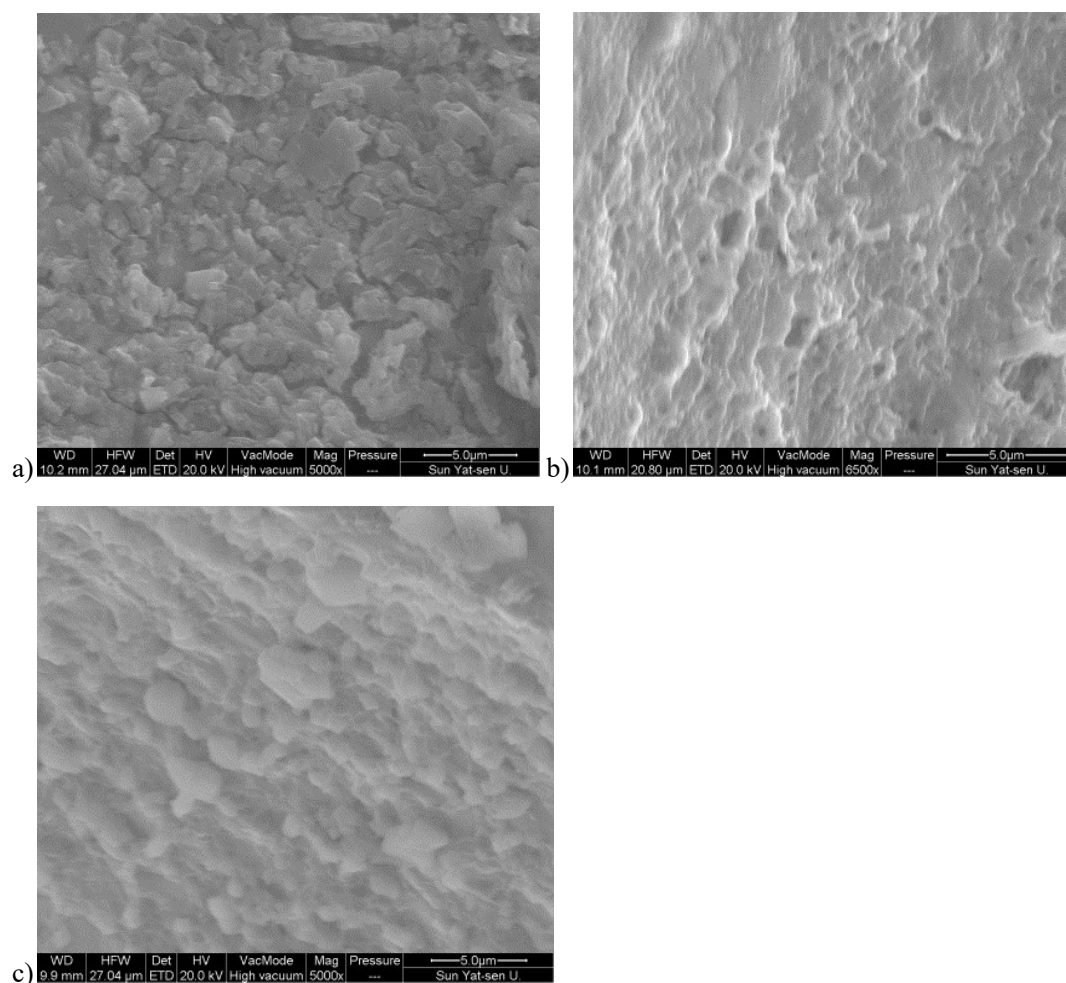




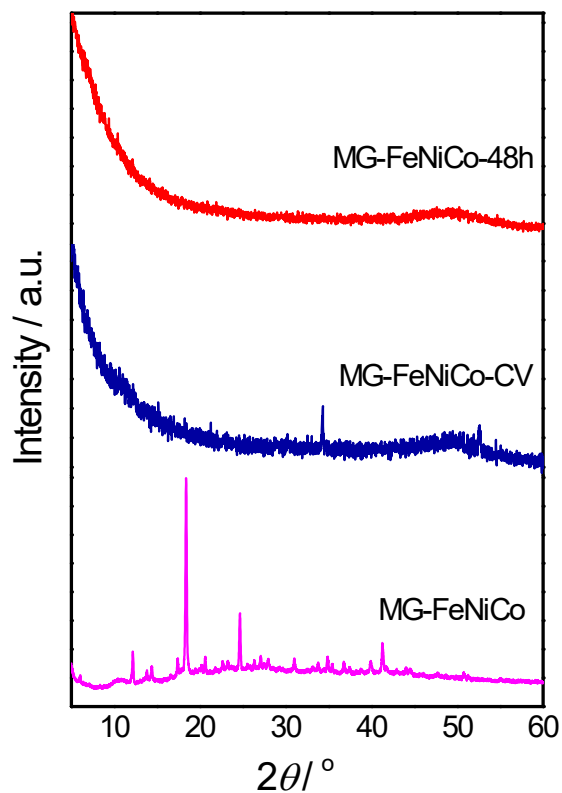
**Fig. S17** TOF comparison of bimetallic aerogels MG-FeNi, MG-FeCo, MG-NiCo and multimetallic aerogels MG-FeNiCo, MG-FeNiCo-0.5GO, MG-FeNiCo-1.0GO, MG-FeNiCo-2.0GO and MG-FeNiCo-4.0GO at the overpotential of 300 mV.



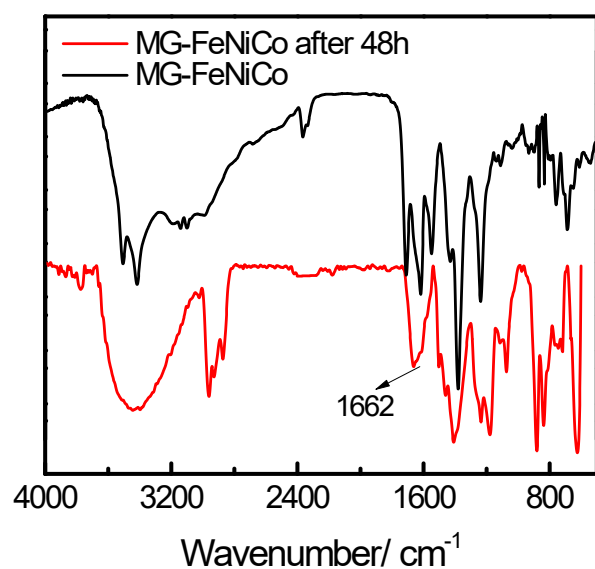
**Fig. S18** XPS spectra of (a) survey, (b) Fe 2p, (c) Co 2p, (d) Ni 2p, (e) O 1s of MG-FeNiCo after electrocatalysis for 48 h by chronoamperometry.



**Fig. S19** SEM images of (a) MG-FeNiCo-NF, (b) MG-FeNiCo-NF cyclic voltammetry activation for 20 cycles, and (c) MG-FeNiCo-NF CP 48 h. The samples contained PVDF and were collected from the nickel foam (NF) for SEM tests after cyclic voltammetry activated for 20 cycles and after stability test for 48 h.



**Fig. S20** XRD patterns of MG-FeNiCo-NF, MG-FeNiCo-NF cyclic voltammetry activation for 20 cycles, and (c) MG-FeNiCo-NF CP 48 h. The samples contained PVDF and were collected from the nickel foam (NF) for XRD tests.



**Fig. S21** FT-IR spectra of MG-FeNiCo before and after stability test for 48 h. After the stability test for 48 h, the nickel foam supporting MG-FeNiCo was directly taken and washed by distilled water for three times, then dried in vacuum, and used for the IR test.