

Electronic Supplementary Information

Room temperature thiosulfate ion redox reaction-driven robust and porous copper-cobalt-sulfur-oxygen nanowire coating on copper foam for highly-efficient and low-cost oxygen evolution reaction

Yanqing Wang^a, Yuemeng Li^a, Liping Ding^b, Aaron Ong^a, Jun Ding^{a,*}

^a Department of Materials Science & Engineering, National University of Singapore, 117575,

Singapore

^b School of Chemistry and Chemical Engineering, Nantong University, Nantong 226007, China

Experimental Section

Materials

Cu foam(CF) conductive support was bought from Latech Scientific Supply Pte. Ltd. $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, KOH, H_2SO_4 (95-98wt%) and ethyl alcohol were purchased from Sigma-Aldrich Chemical Reagent Co.

Preparation of Cu-Co-S-O nanowire coating(Cu-Co-S-O NWC)

Cu-Co-S-O nanowire coating(Cu-Co-S-O NWC) was fabricated as follows. In a typical synthesis, a piece of CF($1 \times 1 \text{cm}^2$) was dipped into ethyl alcohol at room temperature for 2 min to remove the oil. To remove the oxide of CF surface, then CF was immersed in 5 volume% H_2SO_4 for 2min at room temperature. Finally, CF was dipped into thiosulfate metal solution for 2h at room temperature. Thiosulfate metal solution contains 140g/L $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 45g/L $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$. Notably, CF was cleaned by deionized water for a few times among the above two processes. At last, the mass loading of catalyst is about 2.23 mg/cm^2 .

Characterizations

ZEISS SEM Supra 40 was used to observe the microscopic morphology of samples. Transmission electron microscopy (TEM) of samples was measured on a JEOL-3010 (300 kV acceleration voltage). XRD patterns were carried out by Bruker D8 Advanced Diffractometer System. X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD) was employed to determine the element analysis of surface layer of

samples. ICP (Perkin Elmer Optima 5300DV) test was conducted to detect the element analysis of the bulk phase of samples. The CHNS analyzer (Elementar vario MICRO cube) test was determined to detect the sulphur element analysis of the bulk phase of samples.

Electrochemical measurements

OER process was investigated in a typical three-electrode cell connected to a Bio-logic VMP 3. In this cell, the Cu-Co-S-O NWC/CF, Pt and Hg/HgO were used as the working electrode ($1 \times 1 \text{ cm}^2$), a counter electrode and a reference electrode, respectively. The electrolyte is 1M KOH (pH=14). According to $E(\text{RHE}) = E_{\text{Hg}/\text{HgO}} + 0.059\text{pH} + 0.098 \text{ V}$, the measured potentials were all converted to reversible hydrogen electrodes (RHE). LSV curves were measured with the scan rates of 1mV/s. All the tafel slopes of the experiments were derived from LSV curves. Please note that all the electrochemical datas were shown with 100% IR compensation.

Table S1 element atomic content of the surface layer of Cu-Co-S-O NWC by XPS analysis.

Element	Atomic/%
Cu K	25.2
Co K	12.1
S K	5.1
O K	57.6
Total	100.00

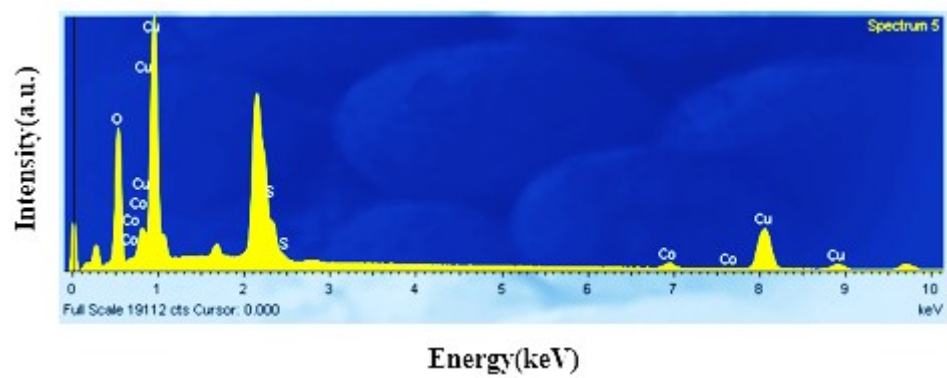


Figure S1 EDS test results of Cu-Co-S-O NWC

Table S2. ICP and CHNS test of the bulk phase of Cu-Co-S-O NWC

Materials	Test type	Cu/ppm	Co/ppm	S/%
Cu-Co-S-O NWC	ICP	297	41	-
	CHNS	-	-	8.49

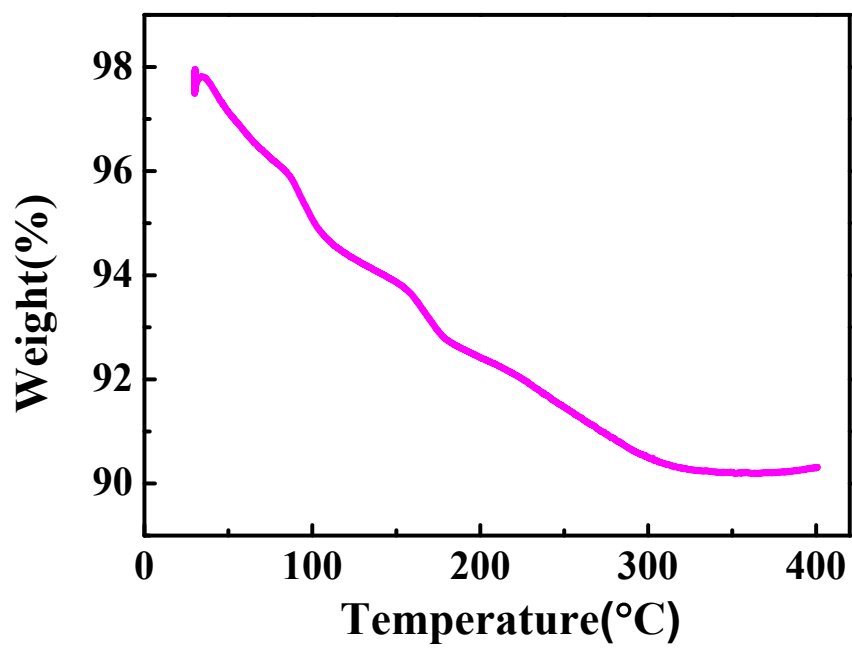


Figure S2 TGA test results of Cu-Co-S-O NWC

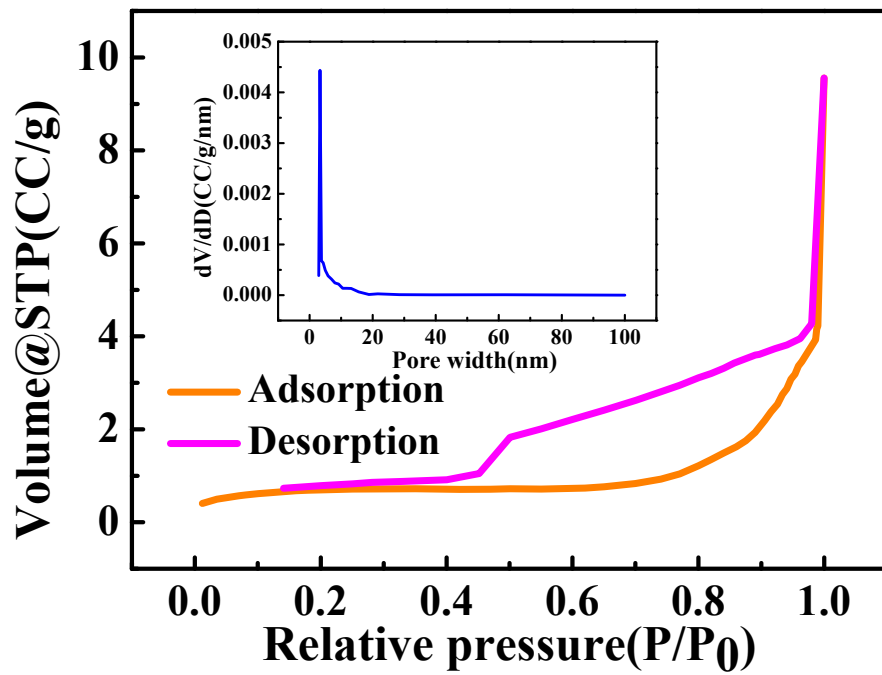


Figure S3 Nitrogen sorption isotherms with the corresponding pore size distribution curve for

Cu-Co-S-O NWC

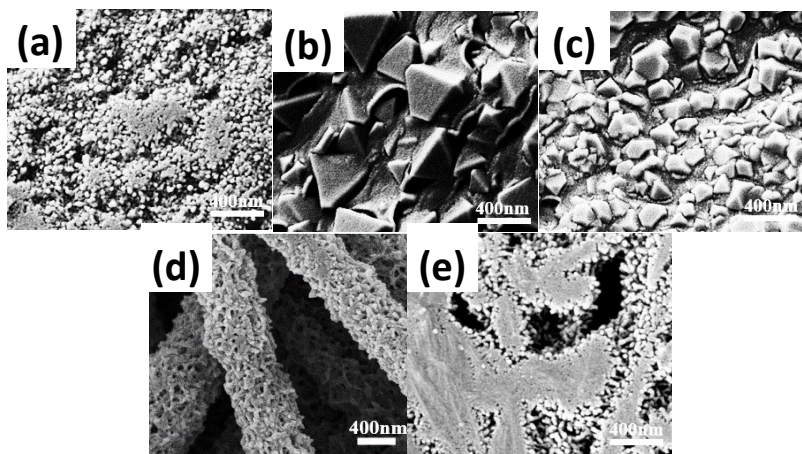


Figure S4 The influence of different reaction time on the morphology of Cu-Co-S-O NWC (a)

0.25h (b) 0.5h (c) 1h (d) 2h (e) 4h

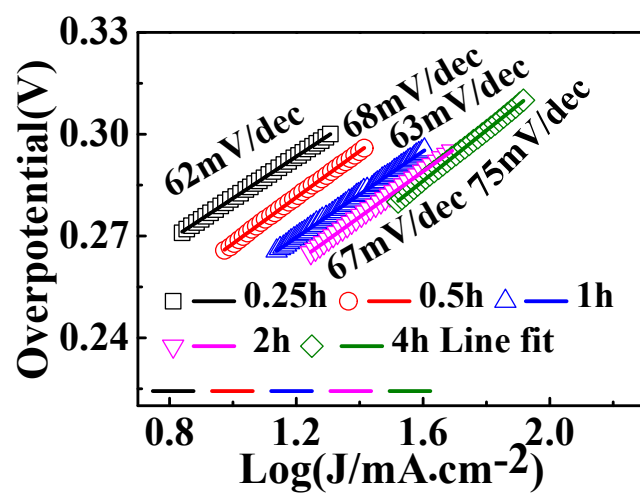


Figure S5 The tafel performance of Cu-Co-S-O NWC under different reaction time

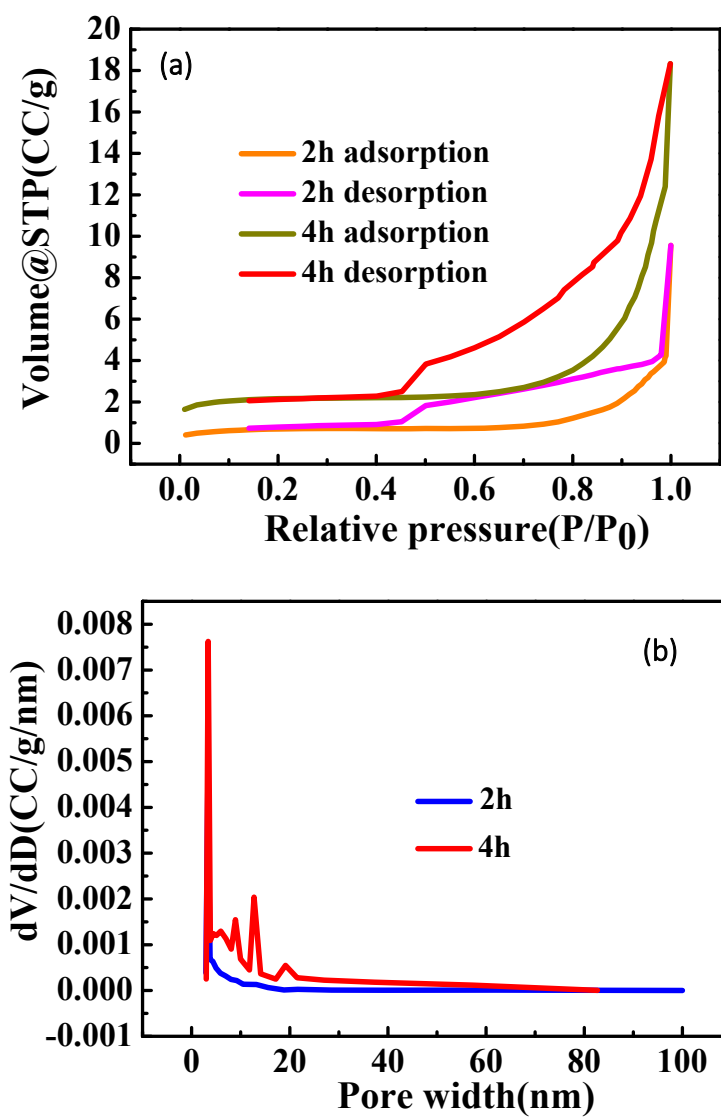


Figure S6 The comparison of Nitrogen sorption isotherms with the corresponding adsorption desorption curve(a) and pore size distribution curve(b) for Cu-Co-S-O NWC under 2h and 4h reaction time.

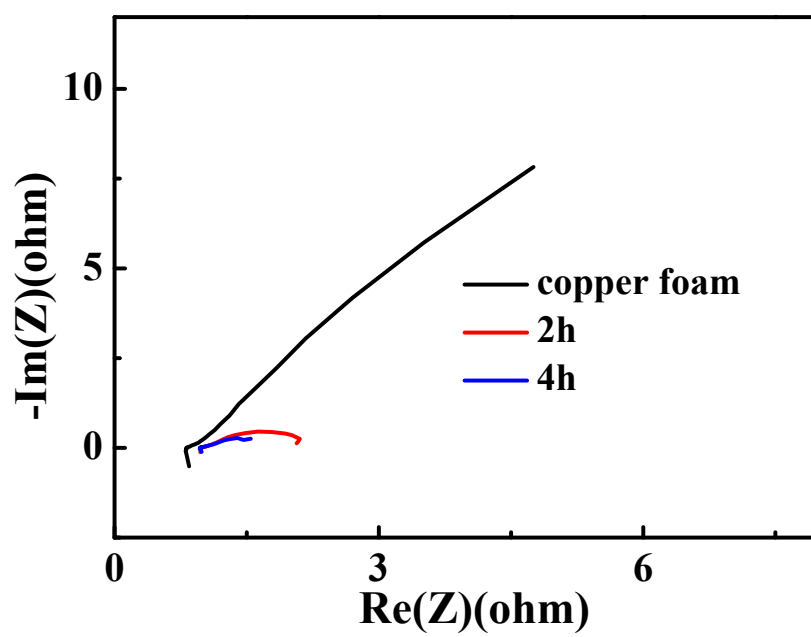


Figure S7 The comparison of the conductivity of copper foam, Cu-Co-S-O NWC under 2h and 4h reaction time by EIS test at 300mV overpotential.

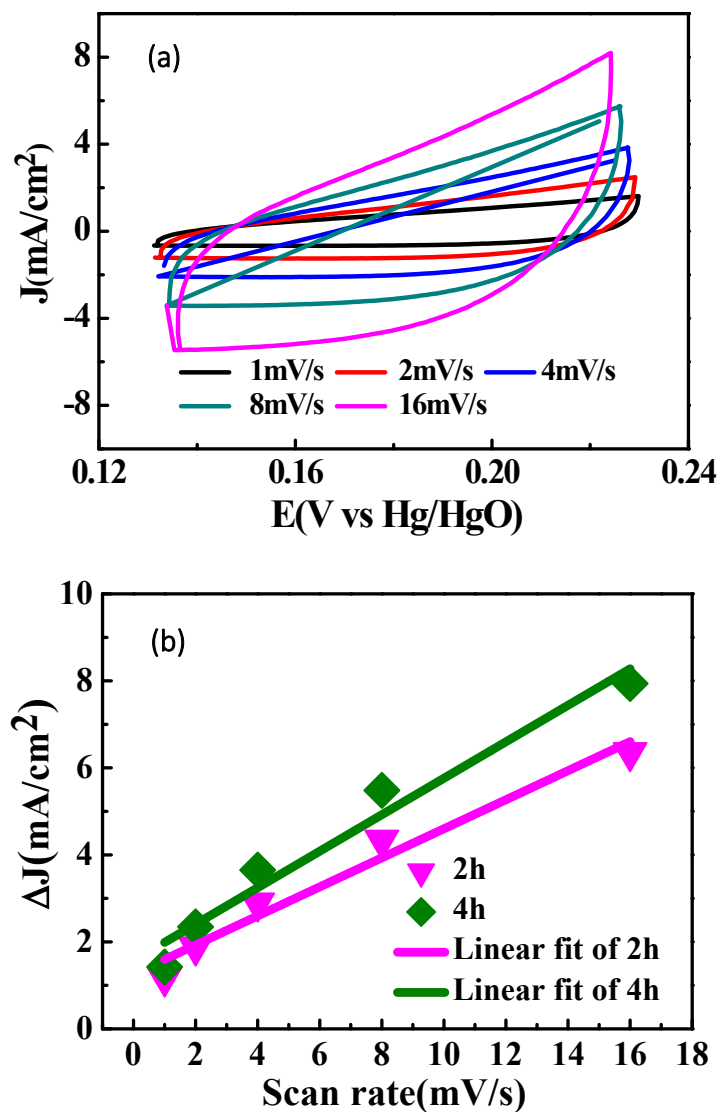


Figure S8 The ECAS performance of Cu-Co-S-0 coating under different reaction time (a) CV curves at different scan rates in the non-Faradaic capacitance current range for Cu-Co-S-O NWC under 4h (b) corresponding capacitive current differences at 0.18V vs. Hg/HgO as a function of scan rates for Cu-Co-S-O NWC under 2h and 4h.

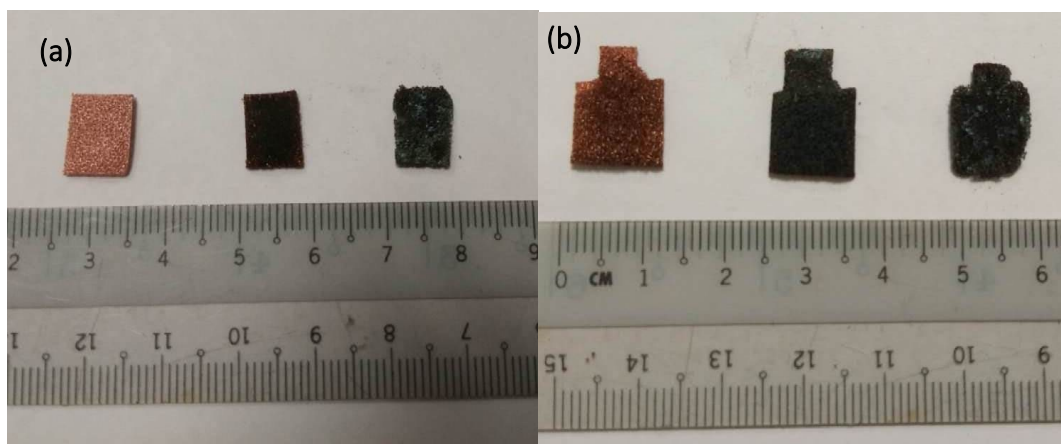


Figure S9 The digital photographs of different catalytic electrode materials before (a) and after OER (b). Note: the catalytic electrode materials are copper foam, copper foam/Cu-Co-S-O coating under 2h, copper foam/Cu-Co-S-O coating under 4h from left to right direction, respectively.

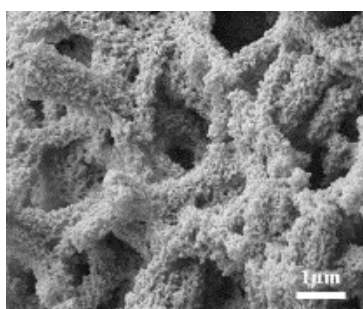


Figure S10 SEM image of Cu-Co-S-O NWC after OER stability test($50\text{mA}/\text{cm}^2 \times 10\text{h}$).

Supplementary METHODS

Calculation of electrochemically active surface area (*ECAS*)

The electrochemical double-layer capacitance C_{dl} is calculated according to the below equation:

$$C_{dl} = J_c \div \nu \quad (1)$$

The charge current J_c was derived from CV curves in the non-Faradaic capacitance current range. ν is the scan rate as shown in **Fig 3d**.

As shown in **Fig 3e**, C_{dl} value of Cu-Co-S-O NWC is 333.9mF.

The electrochemically active surface area *ECAS* is calculated as the below equation according to the previous reports:

$$ECAS = C_{dl} \div C_s \quad (2)$$

According to the literatures, the specific capacitance value of the sample C_s is 0.040 mF/cm², so the *ECAS* of Cu-Co-S-O NWC/CF electrode is 8348 cm².

Table S3. Summary of OER catalysis activity of Cu-Co-S-O nanowire coating and as-reported Co-based or Cu-based catalysts in 1M KOH electrolyte

Catalyst	j [mA /cm ²]	Overpotential [mV] @ j	Tafel slope (mV /dec)	Substrate	Ref
Cu-Co-S-O NWC	50	296	67	CF	This work
	100	318			
	200	346			
	300	366			
Co@Co ₉ S ₈	10	350	55	Cobalt foam	<i>Chem. Eur. J.</i> 2017, 23, 8749.
A-CoS _{4.6} O _{0.6} PNCs	10	290	67	GCE	<i>Angew. Chem. Int. Ed.</i> 2017, 56, 4858.
N-doped graphene-CoO	10	340	71	GCE	<i>Energy Environ. Sci.</i> 2014, 7, 609.
Co ₃ O ₄ /N-doped-graphene	10	310	67	NF	<i>Nat. Mater.</i> 2011, 10, 780.
Co-Bi NS/G nanosheet	10	290	53	GCE	<i>Angew. Chem. Int. Ed.</i> 2016, 55, 2488.
Co-P	50	420	47	rotating disk GCE	<i>Angew. Chem. Int. Ed.</i> 2015, 54, 6251.
Co ₃ O ₄ /NiCo ₂ O ₄ DSNCs	50	~418	88	NF	<i>J. Am. Chem. Soc.</i> 2015, 137, 5590.
Co ₃ O ₄ -MTA	150	360	84	NF	<i>Angew. Chem. Int. Ed.</i> 2017, 56, 1324.
Co ₃ O ₄ nanoparticles	50	~496	-	HOPG	<i>ACS Catal.</i> 2013, 3, 2497.

Co-B@CoO	50	290	78	TM	<i>Small</i> 2017, 13, 1700805.
	100	310			
Co ₃ O ₄ nanocrystal /carbon paper	50	420	101	CFP	<i>Chem. Commun.</i> 2015, 51, 8066.
Co(OH) ₂ -TCNQ/CF	25	276	101	CF	<i>Adv. Mater.</i> 2018, 30, 1705366
	50	315			
P-doped-Co@NC-3/1	10	340	85	GCE	<i>Adv. Energy Mater.</i> 2018, 8, 1702048
Co ₂ V ₂ O ₇	10	340	62	GCE	<i>Nano Energy</i> , 2017, 34, 1.
	100	452			
Co/VN	10	320	55	GCE	<i>Nano Energy</i> , 2017, 34, 1.
	100	385			
	200	412			
HS-CuO/C NDs	10	286	66.3	Cu foil	<i>ACS Appl. Mater. Interfaces</i> 2018, 10, 23807.
	50	422			
	100	482			
2D CuO nanosheet	10	350	59	Stainless	<i>J. Mater. Chem. A</i> , 2017, 5, 12747
	50	393			
CuCo ₂ O ₄ /NrGO	10	360	64	GC-RDE	<i>J Power Sources</i> , 2015, 281, 243.
Cu _{0.3} Co _{2.7} O ₄ nanochains (0.2)	10	351	63.3	GC-RDE	<i>ACS Appl. Mater. Interfaces</i> 2017, 9, 22378
	50	432			
CuCo ₂ S ₄ nanosheets	10	310	86	GCE	<i>ACS Catal.</i> 2017, 7, 5871.

Co-Cu7S4-0.07	10	270	130	Carbon paper	<i>ACS Nano</i> 2017, 11, 12230
	50	397			
Fe(OH) ₃ : Cu(OH) ₂	10	365	42	CF	<i>Chem. Commun.</i> , 2016, 52, 14470
	50	399			
	100	407			
CuO-TCNQ/CF	25	317	85	CF	<i>Chem. Commun.</i> , 2018, 54, 1425.
	50	355			
Cu ₂ S/CF	10	290	101	CF	<i>ACS Catal.</i> 2018, 8, 3859.
	20	336			
	50	378			
IrO ₂ /C(52 wt%)	10	250	87	Cu foil	<i>J. Am. Chem. Soc.</i> , 2014, 136, 13925.

GCE: glassy carbon electrode,
 NF: nickel foam,
 HOPG: highly-ordered pyrolytic graphite,
 CFP: Carbon fiber paper
 TM: Ti mesh
 CF: copper foam

REFERENCES

1. D. Xiong, Q. Zhang, S. M. Thalluri, J. Xu, W. Li, X. Fu and L. Liu, *Chem. Eur. J.* 2017, **23**, 8749.
2. P. Cai, J. Huang, J. Chen and Z. Wen, *Angew. Chem. Int. Ed.* 2017, **56**, 4858.
3. S. Mao, Z. Wen, T. Huang, Y. Hou and J. Chen, *Energy Environ. Sci.*, 2014, **7**, 609.
4. Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat Mater*, 2011, **10**, 780.
5. P. Chen, K. Xu, T. Zhou, Y. Tong, J. Wu, H. Cheng, X. Lu, H. Ding, C. Wu and Y. Xie, *Angew. Chem. Int. Ed.*, 2016, **55**, 2488.
6. N. Jiang, B. You, M. Sheng and Y. Sun, *Angew. Chem. Int. Ed.*, 2015, **54**, 6251.
7. H. Hu, B. Guan, B. Xia and X. W. (D.) Lou, *J. Am. Chem. Soc.*, 2015, **137**, 5590.
8. Y. P. Zhu, T. Y. Ma, M. Jaroniec and S. Z. Qiao, *Angew. Chem. Int. Ed.*, 2017, **56**,

- 1324.
9. J. D. Blakemore, H. B. Gray, J. R. Winkler and A. M. Müller, *ACS Catal.*, 2013, **3**, 2497.
 10. W. Lu, T. Liu, L. Xie, C. Tang, D. Liu, S. Hao, F. Qu, G. Du, Y. Ma, A. M. Asiri, and X. Sun, *small*, 2017, **13**, 1700805.
 11. S. Du, Z. Ren, J. Zhang, J. Wu, W. Xi, J. Zhu and H. Fu, *Chem. Commun.*, 2015, **51**, 8066.
 12. D. Wu, Y. Wei, X. Ren, X. Ji, Y. Liu, X. Guo, Z. Liu, A. M. Asiri, Q. Wei and X. Sun, *Adv. Mater.*, 2018, **30**, 1705366.
 13. Y. Li, B. Jia, Y. Fan, K. Zhu, G. Li and C. -Y. Su, *Adv. Energy Mater.*, 2018, **8**, 1702048.
 14. X. Peng, L. Wang, L. Hu, Y. Li, B. Gao, H. Song, C. Huang, X. Zhang, J. Fu, K. Huo and P. K. Chu, *Nano Energy*, 2017, **34**, 1.
 15. T. Y. Ma, S. Dai, M. Jaroniec and S. Z. Qiao, *J. Am. Chem. Soc.*, 2014, **136**, 13925.
 16. B. Zhang, C. Li, G. Yang, K. Huang, J. Wu, Z. Li, X. Cao, D. Peng, S. Hao and Y. Huang, *ACS Appl. Mater. Interfaces*, 2018, **10**, 23807.
 17. S. M. Pawar, B. S. Pawar, B. Hou, J. Kim, A. T. A. Ahmed, H. S. Chavan, Y. Jo, S. Cho, A. I. Inamdar, J. L. Gunjekar, H. Kim, S. Cha and H. Im, *J. Mater. Chem. A*, 2017, **5**, 12747.
 18. S. K. Bikkarolla and P. Papakonstantinou, *J Power Sources*, 2015, **281**, 243.
 19. A. Karmakar and S. K. Srivastava, *ACS Appl. Mater. Interfaces*, 2017, **9**, 22378.
 20. M. Chauhan, K. P. Reddy, C. S. Gopinath and S. Deka, *ACS Catal.*, 2017, **7**, 5871.
 21. Q. Li, X. Wang, K. Tang, M. Wang, C. Wang and C. Yan, *ACS Nano*, 2017, **11**, 12230.
 22. C. -C. Hou, C. -J. Wang, Q. -Q. Chen, X. -J. Lv, W. -F. Fu and Y. Chen, *Chem. Commun.*, 2016, **52**, 14470.
 23. X. Ren, X. Ji, Y. Wei, D. Wu, Y. Zhang, M. Ma, Z. Liu, A. M. Asiri, Q. Wei and X. Sun, *Chem. Commun.*, 2018, **54**, 1425.
 24. L. He, D. Zhou, Y. Lin, R. Ge, X. Hou, X. Sun and C. Zheng, *ACS Catal.*, 2018, **8**, 3859.