Supporting Information

Copper confined in vesicle-like BCN cavity promotes electrochemical reduction of nitrate to ammonia in water

Xue Zhao[a,b], Guangzhi Hu[b,c,*], Fang Tan[b], Shusheng Zhang[c], Xinzhong Wang[d], Xun Hu[e], Artem V. Kuklin[f,g], Glib V. Baryshnikov[h*], Hans Ågren[g], Xiaohai Zhou[a] and Haibo Zhang[a,*]

[a] College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China.

[b] Institute for Ecological Research and Pollution Control of Plateau Lakes, School of Ecology and Environmental Science, Yunnan University, Kunming 650504, China

[c] College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450000, China.

[d] Shenzhen Institute of Information Technology, Shenzhen 518172, China.

[e] School of Materials Science and Engineering, University of Jinan, Jinan, 250022, China

[f] International Research Center of Spectroscopy and Quantum Chemistry (IRC SQC), Siberian Federal University, 79 Svobodny pr., 660041 Krasnoyarsk, Russia

[g] Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden

[h] Laboratory of Organic Electronics, ITN, Linköping University, 601 74 Norrköping, Sweden

*** Corresponding authors**

guangzhihu@ynu.edu.cn; **ORCID: 0000-0003-0324-2788**

glib.baryshnikov@liu.se; **ORCID: 0000-0002-0716-3385**

haibozhang@whu.edu.cn; **ORCID: 0000-0001-5965-5069**

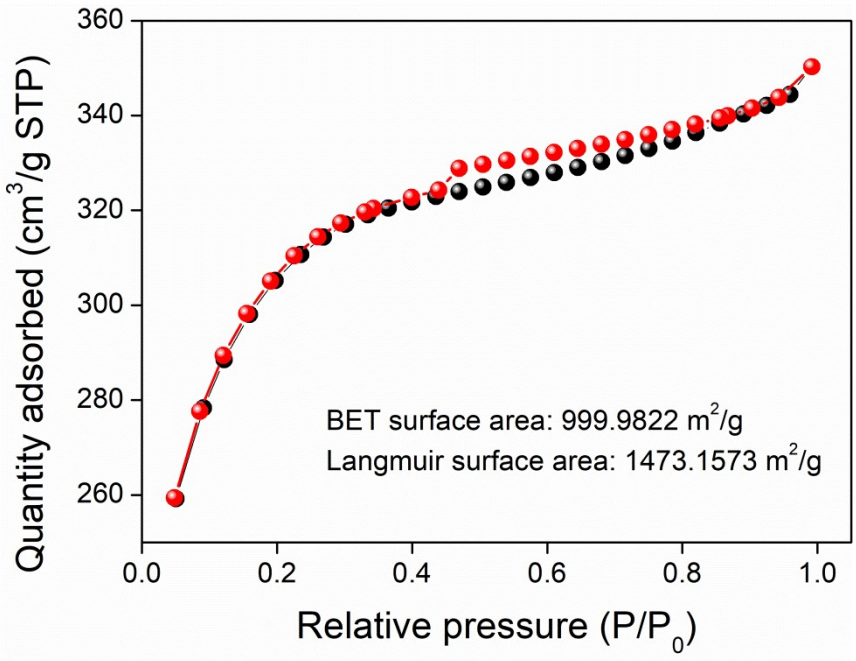


Figure S1. Nitrogen adsorption and desorption curve of BCN@Cu

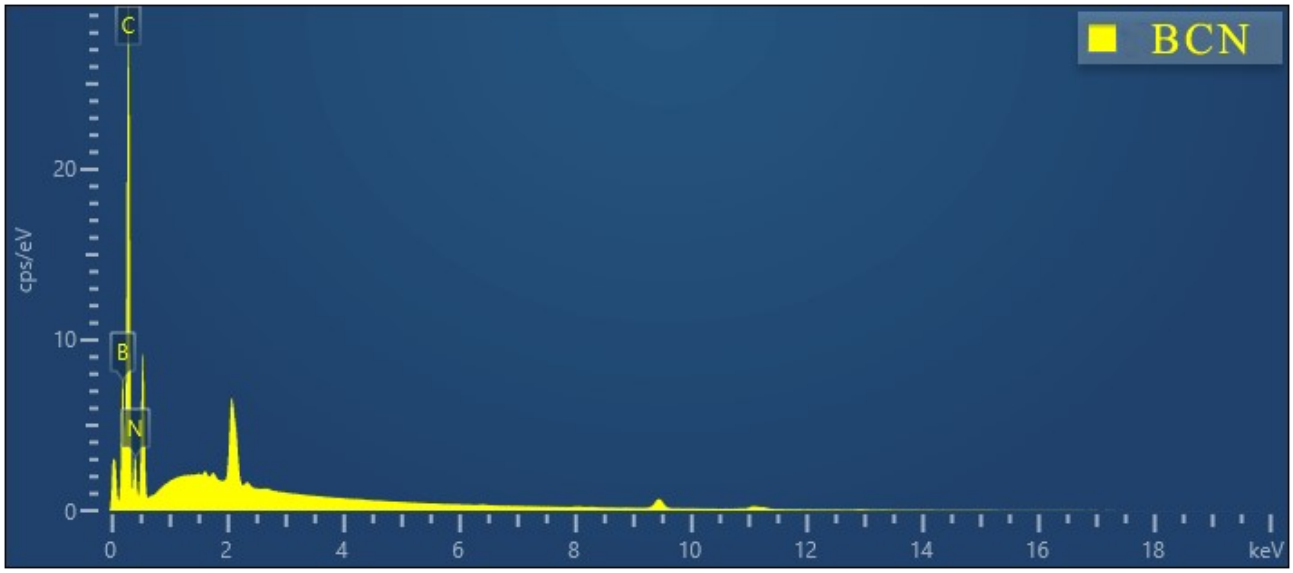


Figure S2. Energy dispersive spectroscopy (EDS) of BCN

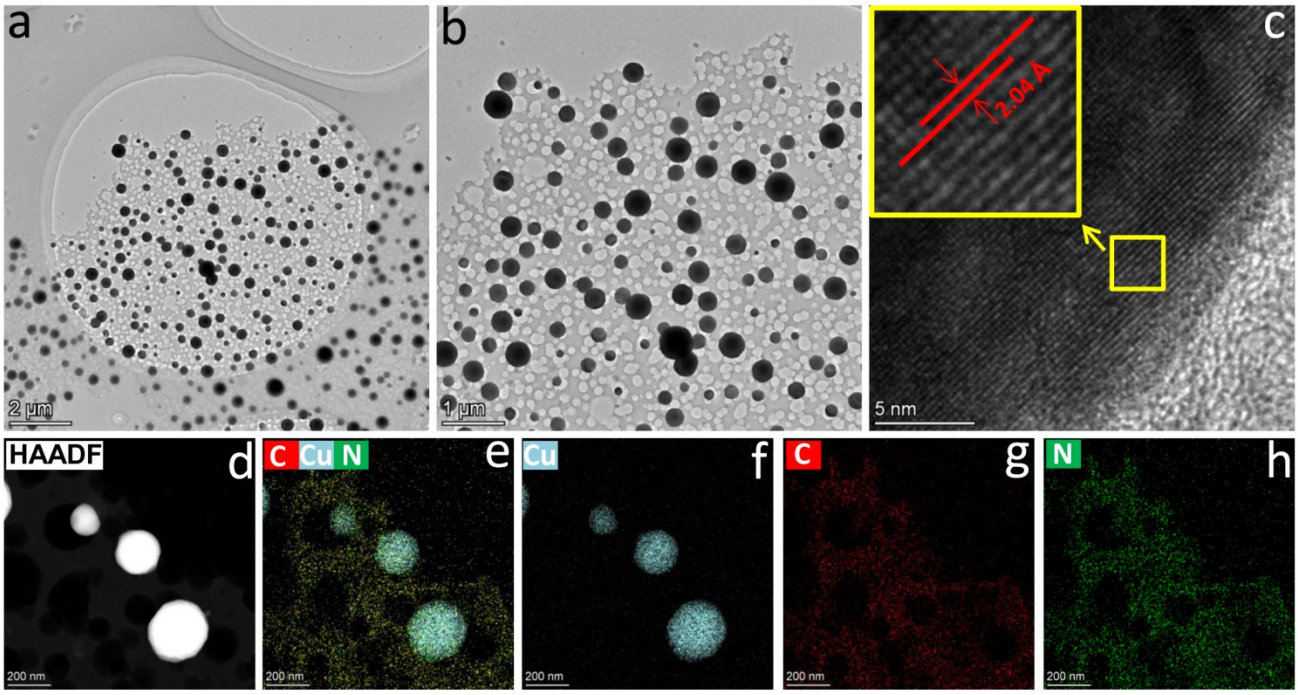


Figure S3. **a-b**) TEM images of CN@Cu; **c**) HRTEM image of CN@Cu; **d-h**) HAADF image of CN@Cu and corresponding element mapping

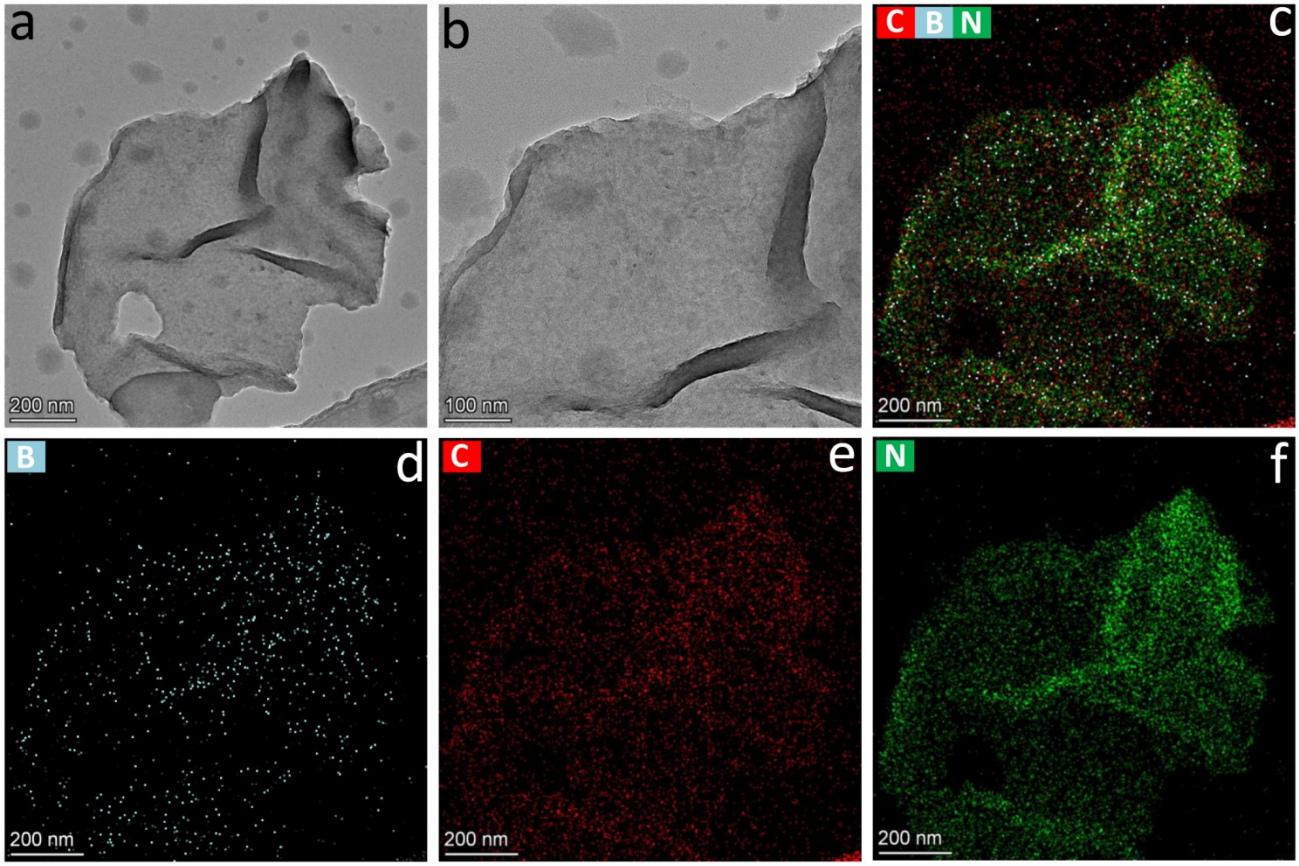


Figure S4. a-b) TEM images of BCN; d-f) Element mapping B, C, and N element in BCN

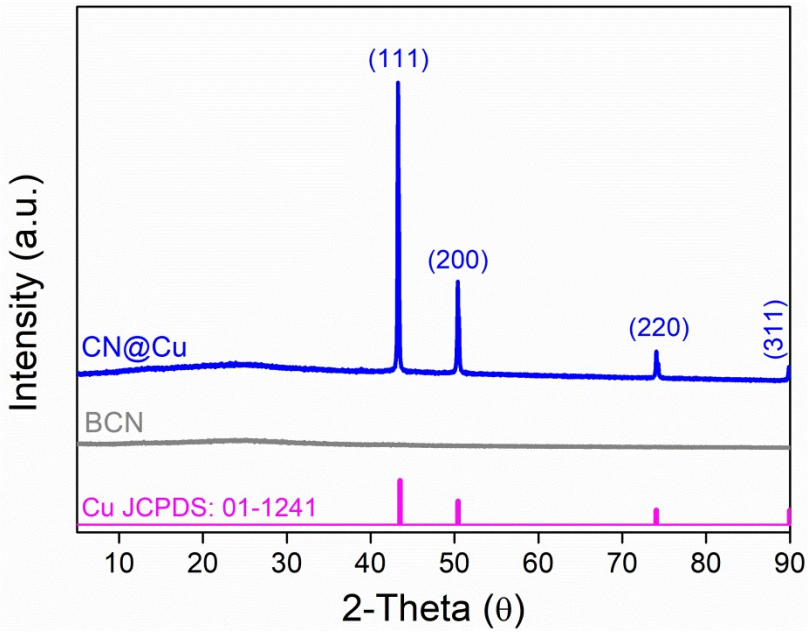


Figure S5. PXRD patterns of CN@Cu and BCN

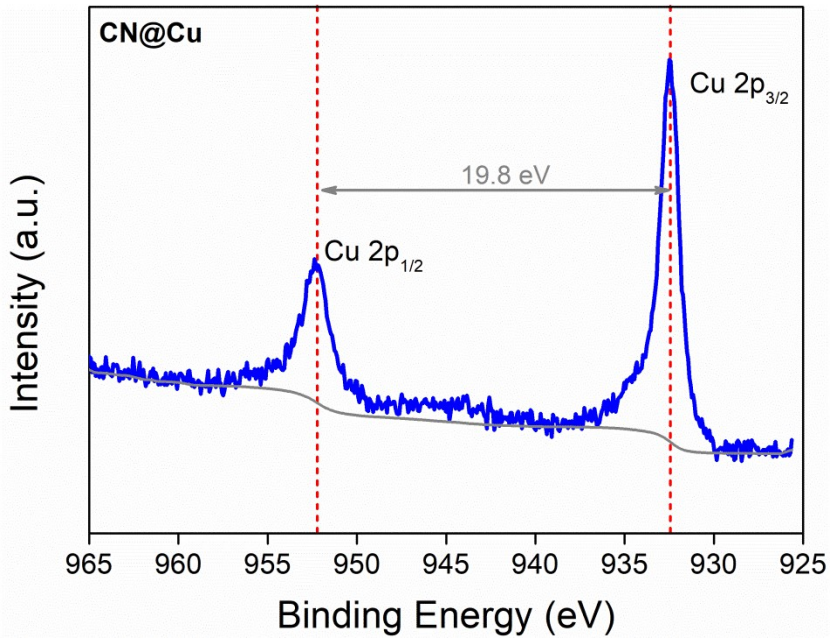


Figure S6. XPS spectrum (Cu binding energy region) of CN@Cu

Table S1. Crystal data and structure refinement for M-BOPs-2.

Identification code	3
Empirical formula	$C_{16}H_{38}B_{12}CuN_8O$
Formula weight	551.80
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.56466(18)
b/Å	12.78559(15)
c/Å	18.7204(3)
α/°	90
β/°	107.7291(16)
γ/°	90
Volume/Å^3	2864.53(7)
Z	4
ρ_{calc}g/cm^3	1.279
μ/mm^{-1}	1.273
F(000)	1148.0
Crystal size/mm^3	0.17 × 0.16 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.386 to 132.018
Index ranges	$-12 \leq h \leq 14$, $-15 \leq k \leq 10$, $-19 \leq l \leq 22$
Reflections collected	8478
Independent reflections	4952 [R_{int} = 0.0420, R_{sigma} = 0.0489]
Data/restraints/parameters	4952/78/405
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0463, wR_2 = 0.1257
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.1299
Largest diff. peak/hole / e Å^{-3}	0.47/-0.71

Table S2. Comparison of the electrocatalytic ammonia production activity of some recently reported catalysts and BCN@Cu

Entry	Catalyst	Electrolyte	Potential (vs RHE)	FE (%)	Mass activity $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	Area activity $\mu g\ h^{-1}\ cm^{-2}$	Ref.
1	Cu nanosheets	0.1 M KOH	-0.15 V	99.70	390.1	390.1	1
2	Bi nanosheets	0.1 M Na_2SO_4	-0.8 V	10.46	13.23	2.54	2
3	Bi nanoplates	0.2 M Na_2SO_4	-0.6 V	11.68	5.453	-	3
4	VN	Nafion	-0.1 V	6	-	20.2	4
5	CoS_2/NS-G	0.05 M H_2SO_4	-0.2 V	7	25	-	5
6	B_4C	0.1 M HCl	-0.75 V	15.95	26.57	-	6
7	Pd/C	0.1 M PBS	0.1 V	8.20	4.5	-	7
8	B-graphene	0.05 M H_2SO_4	-0.5 V	10.80	-	9.8	8
9	Ti_3C_2Tx	-	-0.2 V	5.78	-	0.26	9
10	Polyimide/C	Li^+/H^+	-0.4 V	2.91	-	0.47	10
11	Black P	0.01 M HCl	-0.6 V	5.07	31.37	-	11
12	$Bi_4V_2O_{11}/CeO_2$	0.1 M HCl	-0.2 V	10.16	23.21	-	12
13	PdCu/rGO	0.1 M KOH	-0.2 V	0.70	2.8	-	13
14	SA-Mo/NPC	0.1 M KOH	-0.3 V	14.60	34	-	14
15	VN	0.1 M HCl	-0.3 V	3.58	-	15.18	15
16	Rh nanosheets	0.1 M KOH	-0.2 V	0.22	23.88	-	16
17	Iron Oxide	0.1 M KOH	-0.9 V	6.04	-	0.46	17
18	Au	0.5 M $LiClO_4$	-0.5 V	15	-	3.9	18
19	Ru nanoclusters	1 M KOH	-0.2 V	100	94520	19890	19
20	PTCDA/O-Cu	0.1 M PBS	-0.4 V	85.9	1411	436	20
21	BCN@Cu	0.1 M KOH	-0.1 V	56.441	153.5	122.8	**This work**
22	BCN@Cu	0.1 M KOH	-0.2 V	71.282	1427.2	1141.8	
23	BCN@Cu	0.1 M KOH	-0.3 V	91.146	4609.1	3687.3	
24	BCN@Cu	0.1 M KOH	-0.4 V	87.522	6031.9	4825.5	
25	BCN@Cu	0.1 M KOH	-0.5 V	59.826	7404.7	5923.7	
26	BCN@Cu	0.1 M KOH	-0.6 V	31.321	9794.8	7835.8	

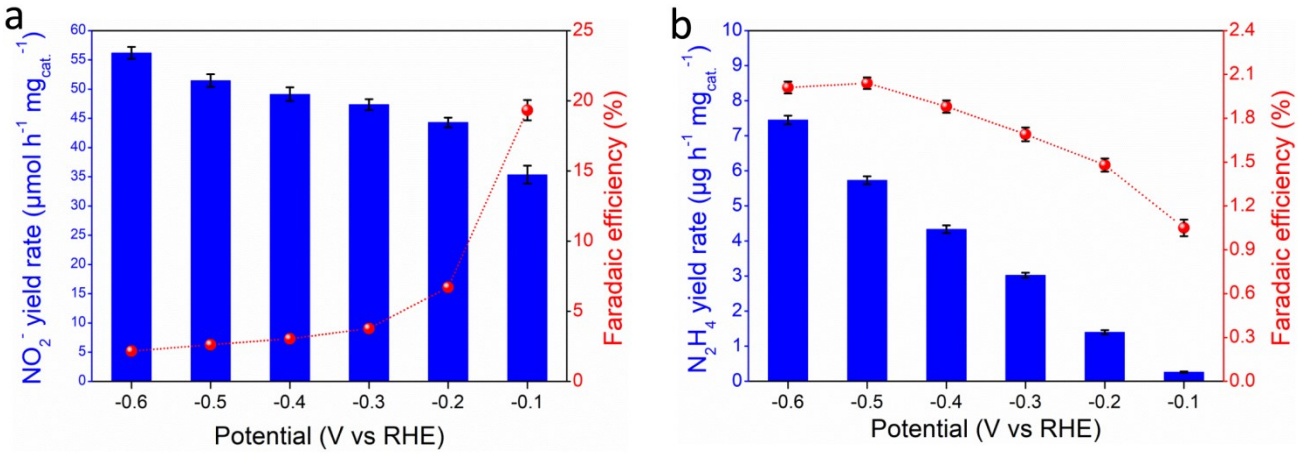


Figure S7. a) When BCN@Cu as a working electrode catalyzes the reduction of NO_3^- to NH_3 in 0.1 M KOH electrolyte, the yield rate and Faraday efficiency of NO_2^-; b) When BCN@Cu as a working electrode catalyzes the reduction of NO_3^- to NH_3 in 0.1 M KOH electrolyte, the yield rate and Faraday efficiency of N_2H_4

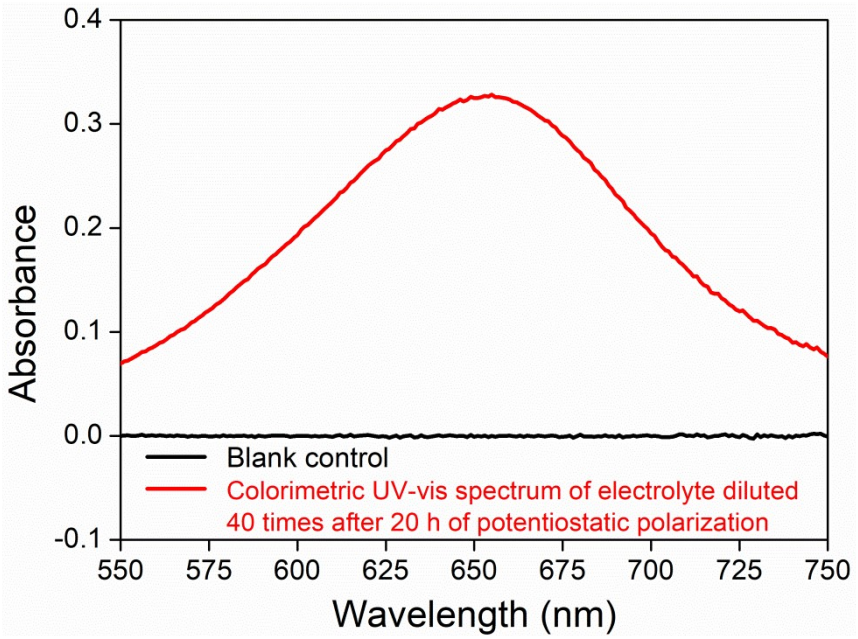


Figure S8. UV-vis spectra of electrolyte (after indophenol blue colorimetry) after 20 h constant potential (at -0.4 V vs RHE) electrolysis

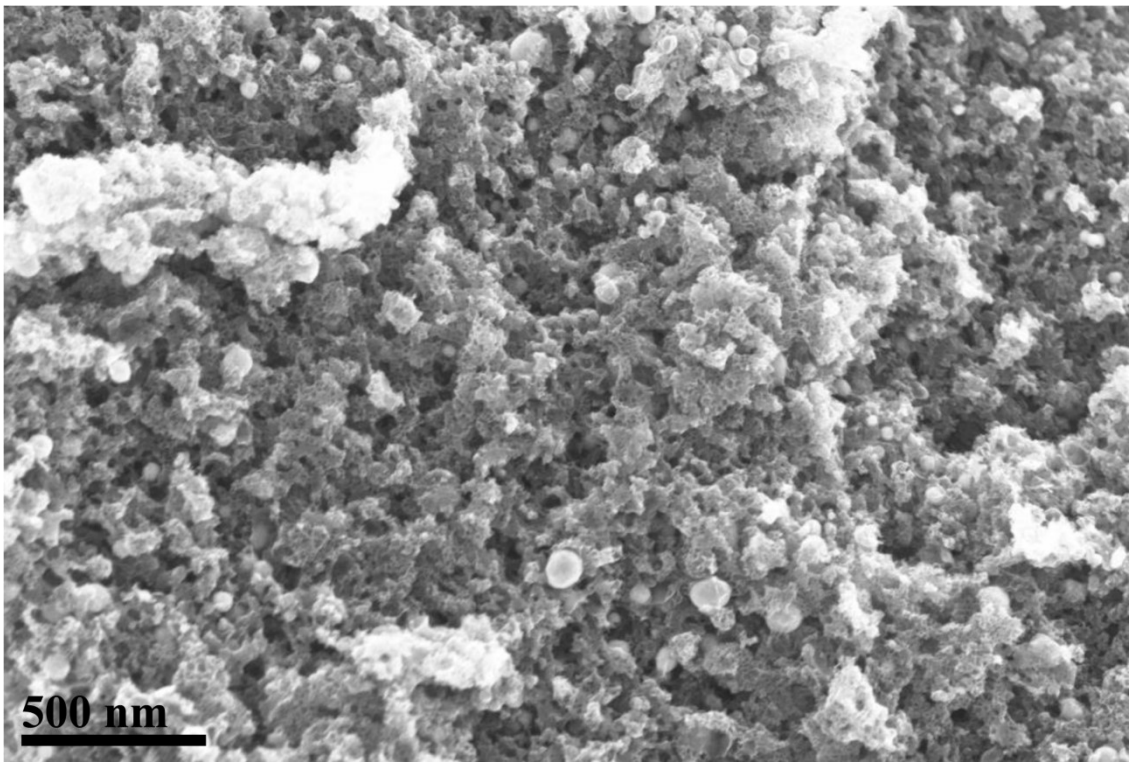


Figure S9. SEM image of BCN@Cu after reused

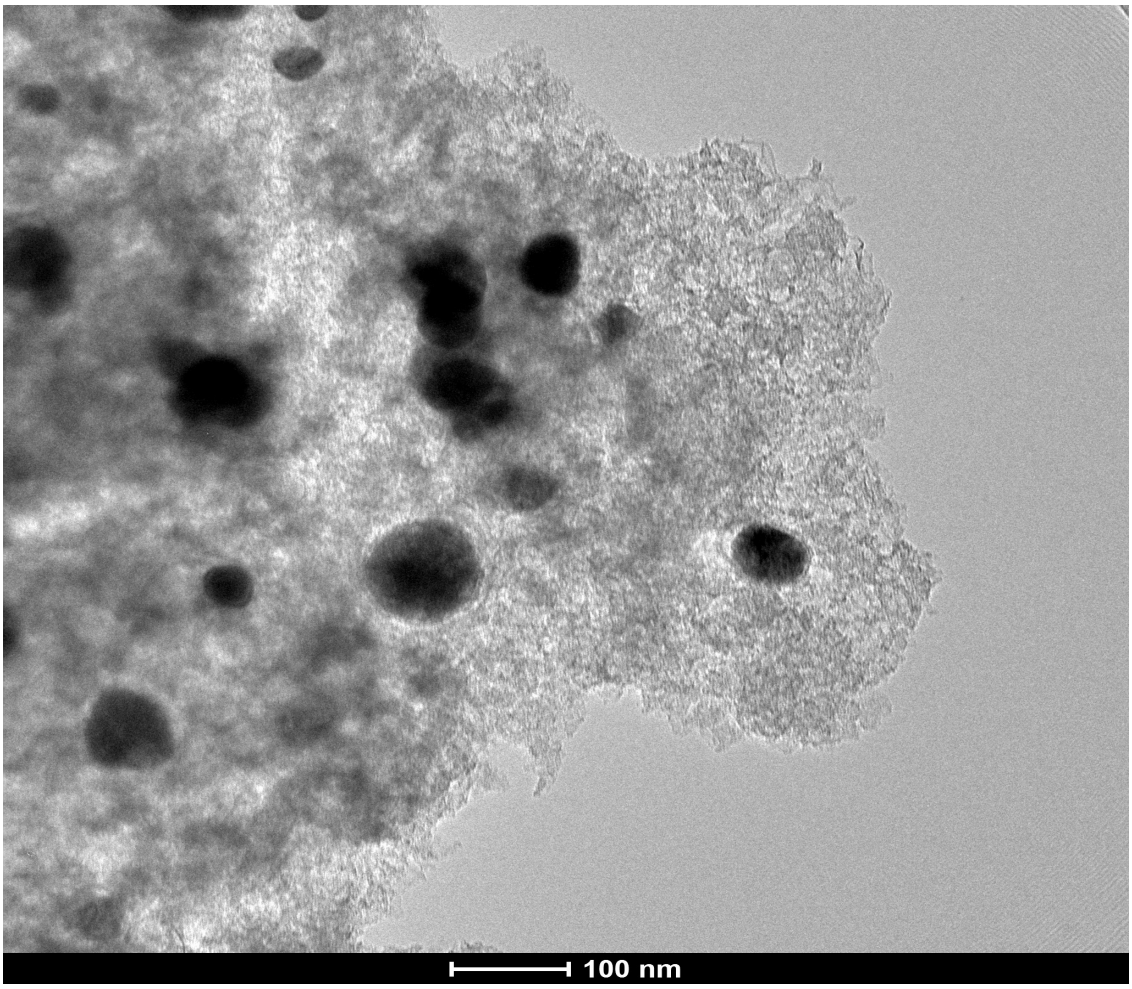


Figure S10. TEM image of BCN@Cu after reused

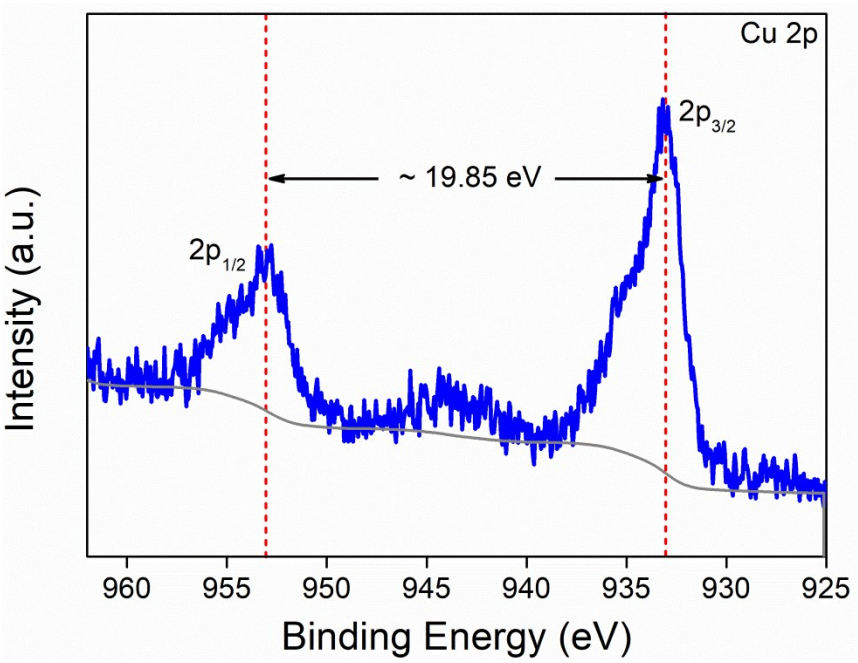


Figure S11. XPS of Cu in BCN@Cu after reused

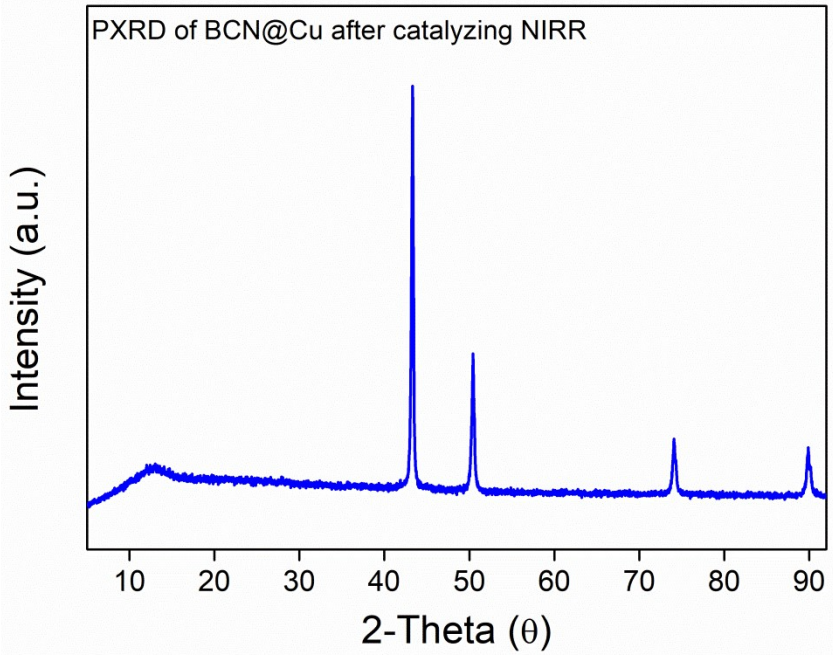
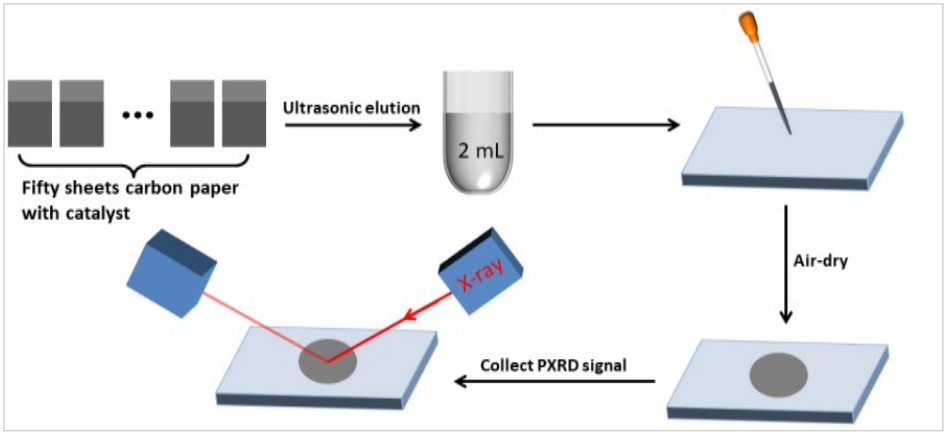


Figure S12. PXRD of BCN@Cu after reused.

Note

The BCN@Cu after used was enriched according to the following method to collect its PXRD signal:

1) Carry out 50 CA experiments under -0.4 V vs RHE potential, and then the catalyst on 20 pieces of carbon paper was ultrasonic dispersed into 2 mL ultra-pure water;
2) 2) Drop the catalyst dispersion liquid onto the platform used to collect XRD (a circular black spot with a diameter of about 1 cm is formed), and the PXRD signal was collected after natural air drying.



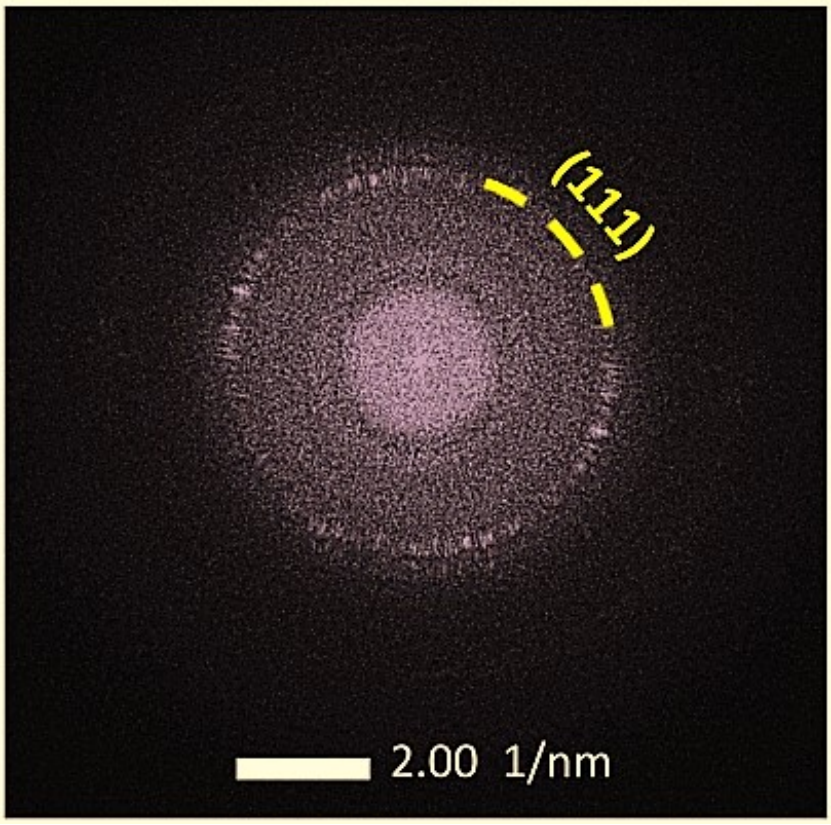


Figure S13. Selected area electron diffraction (SAED) pattern of BCN@Cu

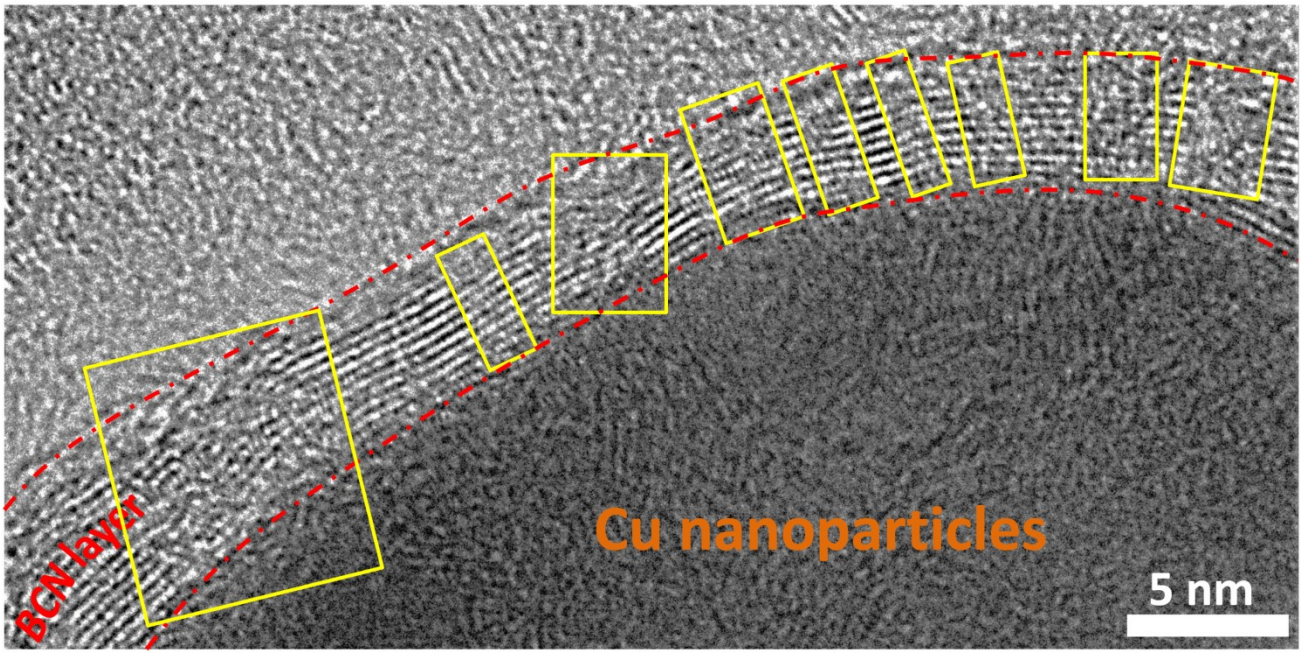


Figure S14. There are a large number of lattice defects (cracks) in the vesicle-like BCN shell covering Cu nanoparticle.

Pre-elimination procedures for extraneous ammonia pollution

(1) The entire electrolyzer (without CP and catalyst) was tested at an open circuit potential for 2 h to determine if ammonia was introduced during the production of the device, and the device without ammonia contamination was washed with ultrapure water at least five times before each use.

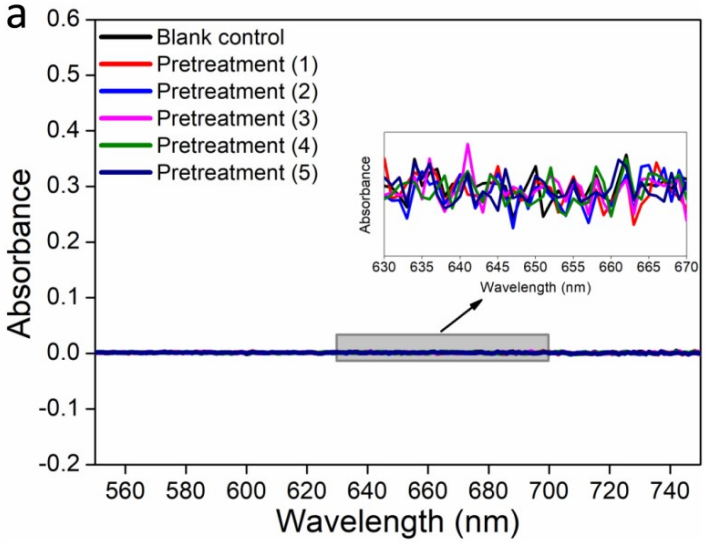
(2) Using 0.1 M KOH without NO_3^- as the electrolyte, BCN@Cu coated on carbon paper as the working electrode, and high-purity Ar gas as the filling gas, electrolysis was carried out at an applied potential of 1 V for 2 h. No ammonia signal was detected in the electrolyte.

(3) Carbon paper (CP) was alternate soaked for several times with a large amount of 0.1 M HCl and 0.1 M KOH until the presence of ammonia could not be detected in the last soaking solution by indophenol blue colorimetry, and then it was electrolyzed for 2 h at the open circuit voltage (Ar filling) until no ammonia colud be detected in the electrolyte, which was used for catalyst load after continuous vacuum drying.

(4) The catalyst was washed with a large amount of 0.1 M HCl and 0.1 M KOH for several times in advance, until the presence of ammonia could not be detected in the washing solution, so as to prevent the interference of raw materials not completely removed in the preparation process.

(5) The nafion proton exchange membrane treated with H_2O_2, H_2SO_4, and ultrapure water was washing with a large amount of ultrapure water and electrolyzed at an open circuit voltage for 2 h (under Ar flow). The above two processes were alternated until it was difficult to detect ammonia.

a



b

Pretreatment project	Ammonia concentration
Pretreatment (1)	~ 0
Pretreatment (2)	~ 0
Pretreatment (3)	~ 0
Pretreatment (4)	~ 0
Pretreatment (5)	~ 0

Figure S15. a) UV-vis spectrum of the solution produced by each pretreatment procedure (using indophenol blue colorimetry); b) Ammonia concentration calculated by UV-vis spectrum

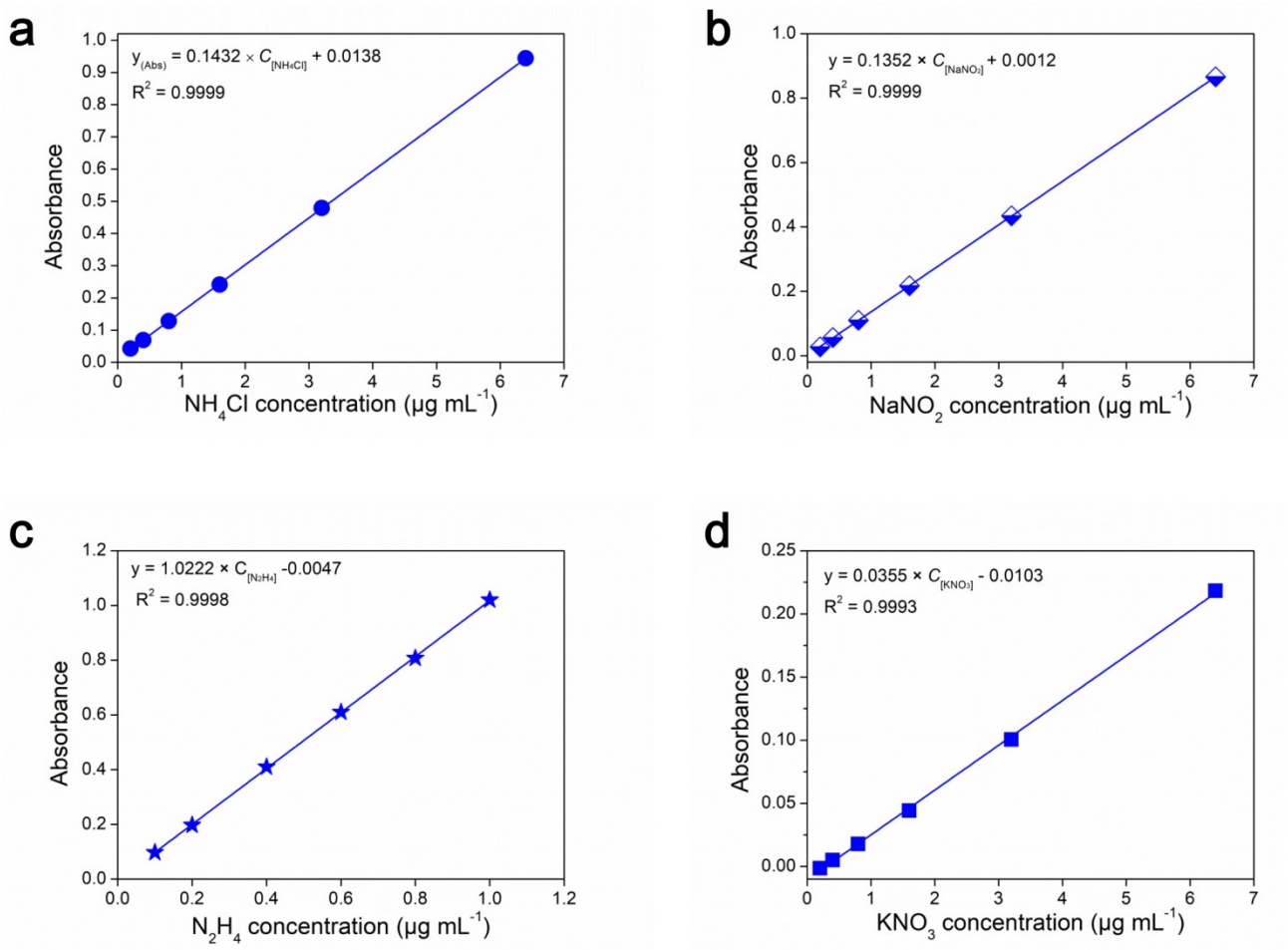


Figure S16. Standard curves based on concentration-absorbance. a) NH_4Cl; b) $NaNO_2$; c) N_2H_4; d) KNO_3

References

1. X. Fu, X. Zhao, X. Hu, K. He, Y. Yu, T. Li, Q. Tu, X. Qian, Q. Yue, M. R. Wasielewski and Y. Kang, *Applied Materials Today*, 2020, **19**, 100620.
2. L. Li, C. Tang, B. Xia, H. Jin, Y. Zheng and S.-Z. Qiao, *ACS Catal.*, 2019, **9**, 2902-2908.
3. Y. Wang, M.-m. Shi, D. Bao, F.-l. Meng, Q. Zhang, Y.-t. Zhou, K.-h. Liu, Y. Zhang, J.-z. Wang, Z.-w. Chen, D.-p. Liu, Z. Jiang, M. Luo, L. Gu, Q.-h. Zhang, X.-z. Cao, Y. Yao, M.-h. Shao, Y. Zhang, X.-B. Zhang, J. G. Chen, J.-m. Yan and Q. Jiang, *Angew. Chem., Int. Ed.*, 2019, **58**, 9464-9469.
4. X. Yang, J. Nash, J. Anibal, M. Dunwell, S. Kattel, E. Stavitski, K. Attenkofer, J. G. Chen, Y. Yan and B. Xu, *J. Am. Chem. Soc.*, 2018, **140**, 13387-13391.
5. P. Chen, N. Zhang, S. Wang, T. Zhou, Y. Tong, C. Ao, W. Yan, L. Zhang, W. Chu, C. Wu and Y. Xie, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, **116**, 6635.
6. W. Qiu, X.-Y. Xie, J. Qiu, W.-H. Fang, R. Liang, X. Ren, X. Ji, G. Cui, A. M. Asiri, G. Cui, B. Tang and X. Sun, *Nat. Commun.*, 2018, **9**, 3485.
7. J. Wang, L. Yu, L. Hu, G. Chen, H. Xin and X. Feng, *Nat. Commun.*, 2018, **9**, 1795.
8. X. Yu, P. Han, Z. Wei, L. Huang, Z. Gu, S. Peng, J. Ma and G. Zheng, *Joule*, 2018, **2**, 1610-1622.
9. Y. Luo, G.-F. Chen, L. Ding, X. Chen, L.-X. Ding and H. Wang, *Joule*, 2019, **3**, 279-289.
10. G.-F. Chen, X. Cao, S. Wu, X. Zeng, L.-X. Ding, M. Zhu and H. Wang, *J. Am. Chem. Soc.*, 2017, **139**, 9771-9774.
11. L. Zhang, L.-X. Ding, G.-F. Chen, X. Yang and H. Wang, *Angew. Chem., Int. Ed.*, 2019, **58**, 2612-2616.
12. C. Lv, C. Yan, G. Chen, Y. Ding, J. Sun, Y. Zhou and G. Yu, *Angew. Chem., Int. Ed.*, 2018, **57**, 6073-6076.
13. M.-M. Shi, D. Bao, S.-J. Li, B.-R. Wulan, J.-M. Yan and Q. Jiang, *Adv. Energy Mater.*, 2018, **8**, 1800124.
14. L. Han, X. Liu, J. Chen, R. Lin, H. Liu, F. Lü, S. Bak, Z. Liang, S. Zhao, E. Stavitski, J. Luo, R. R. Adzic and H. L. Xin, *Angew. Chem., Int. Ed.*, 2019, **58**, 2321-2325.
15. X. Zhang, R.-M. Kong, H. Du, L. Xia and F. Qu, *Chem. Commun.*, 2018, **54**, 5323-5325.
16. H.-M. Liu, S.-H. Han, Y. Zhao, Y.-Y. Zhu, X.-L. Tian, J.-H. Zeng, J.-X. Jiang, B. Y. Xia and Y. Chen, *J. Mater. Chem. A*, 2018, **6**, 3211-3217.
17. X. Cui, C. Tang, X.-M. Liu, C. Wang, W. Ma and Q. Zhang, *Chem. – A Eur. J.*, 2018, **24**, 18494-18501.
18. M. Nazemi, S. R. Panikkanvalappil and M. A. El-Sayed, *Nano Energy*, 2018, **49**, 316-323.
19. J. Li, G. Zhan, J. Yang, F. Quan, C. Mao, Y. Liu, B. Wang, F. Lei, L. Li, A. W. M. Chan, L. Xu, Y. Shi, Y. Du, W. Hao, P. K. Wong, J. Wang, S.-X. Dou, L. Zhang and J. C. Yu, *J. Am. Chem. Soc.*, 2020, **142**, 7036-7046.
20. G.-F. Chen, Y. Yuan, H. Jiang, S.-Y. Ren, L.-X. Ding, L. Ma, T. Wu, J. Lu and H. Wang, *Nat. Energy*, 2020, **5**, 605-613.