Supporting Information

Coupling of nonstoichiometric $Cu_{2-x}Se$ with stable Cu_2Se berzelianite for efficient synergistic electrocatalytic hydrazine-assisted water splitting

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Supplementary figures

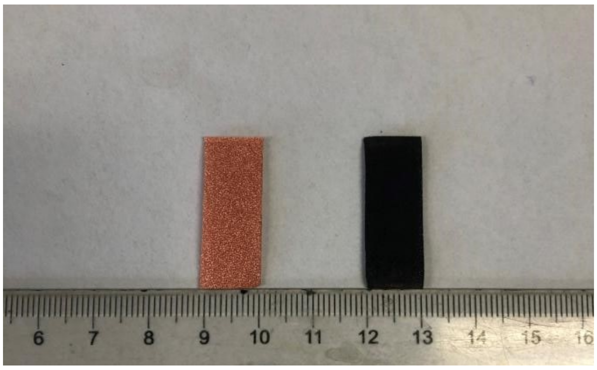

Figure S1. Digital photographs of pristine Cu foam and Cu_xSe/CF samples.

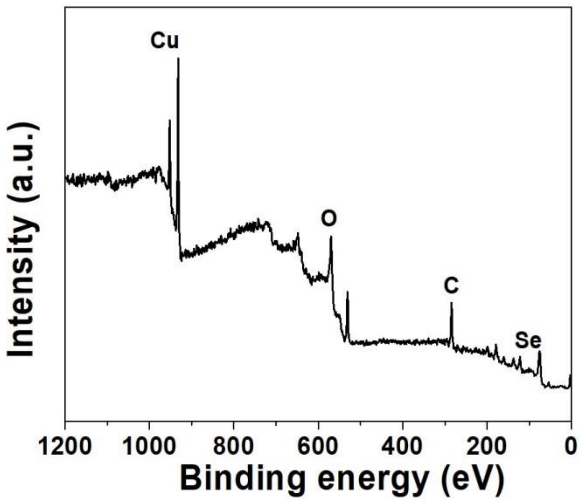

Figure S2. XPS survey spectra of Cu_xSe/CF.

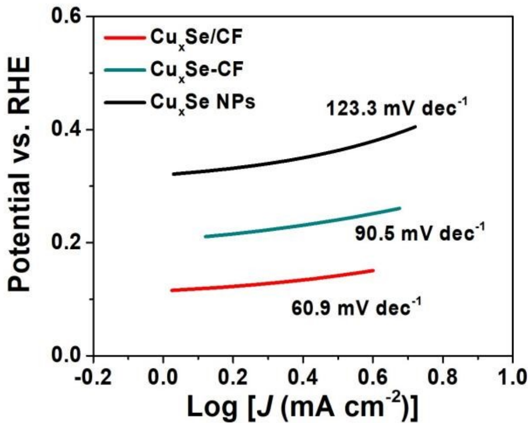

Figure S3. The Tafel slopes of Cu_xSe/CF, Cu_xSe-CF, and Cu_xSe NPs toward the HzOR.

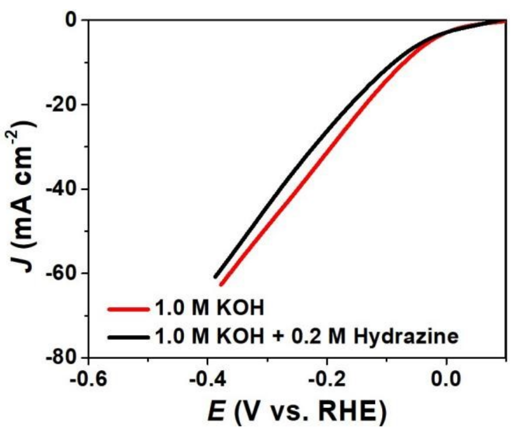

Figure S4. LSV curve of Cu_xSe/CF towards HER at a scan rate of 10 mV s^{-1} in 1.0 M KOH electrolyte with and without 0.2 M hydrazine.

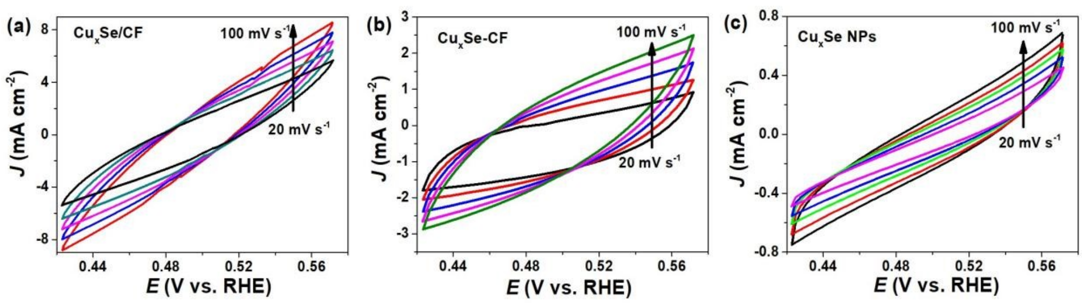

Figure S5. Cyclic voltammograms of (a) Cu_xSe/CF, (b) Cu_xSe-CF, and (c) Cu_xSe NPs measured at different scan rates from 20 to 100 mV s^{-1}.

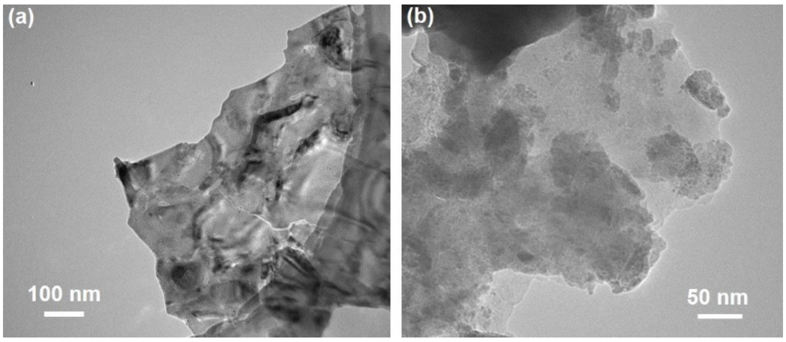

Figure S6. TEM images of Cu_2Se/CF control samples.

Supplementary videos

Video S1. Video of displaying the generation of hydrogen bubbles during hydrazine-assisted water splitting.

Supplementary tables

Table S1. Comparison of HER performance of some recently reported Cu-based catalysts.

Catalyst	Electrolyte	$E_{j=10}$ (mV) vs. RHE	Tafel slop ($mV \cdot dec^{-1}$)	Reference
Cu_xSe/CF	1.0 M KOH	79	106	This work
Cu-Ni nanocages	1.0 M KOH	140	79	1
Cu-Co-P20 foam	1.0 M KOH	138	48	2
Ni/Cu/CF	1.0 M KOH	38	42.7	3
GDY/CuS	1.0 M KOH	106	63.8	4
Cu@WC	1.0 M KOH	119	88.7	5
Ni-Se-Cu	1.0 M KOH	136	117.5	6
Ni-Cu B	1.0 M KOH	202	82	7
CuNPs/CNFs	0.5 M H_2SO_4	200	152	8
CuS@C	0.5 M H_2SO_4	128	44	9
3% CoS2-7% CuS	0.5 M H_2SO_4	62	46	10

Table S2. Comparison of electrocatalytic performance of some recently reported HzOR catalysts in alkaline electrolyte solution.

Catalyst	Electrolyte	$E_{j=20}$ (V) vs. SCE	Tafel slop (mV·dec^{-1})	Reference
Cu_xSe/CF	1.0 M KOH, 0.2 M N_2H_4	0.53	60.9	This work
$Ni_{0.43}Cu_{0.57}$	3.0 M NaOH, 0.1 M N_2H_4	-0.6 ($E_{j=300}$)	N.A.	11
Cu-SA/PCN	1.0 M KOH, 0.1 M N_2H_4	0.336 ($E_{j=100}$)	142	12
SeNCM-1000	1.0 M KOH, 0.1 M N_2H_4	0.34 (onset potential)	N.A.	13
MnO/N-C	0.1 M KOH, 0.1 M N_2H_4	-0.43	N.A.	14
Fe_2O_3/ECP-15	1.0 M KOH, 0.1 M N_2H_4	0.664 vs. RHE ($E_{j=10}$)	179.2	15
Ni(Cu) CNPs	1.0 M KOH, 0.5 M N_2H_4	0.233 ($E_{j=300}$)	50.2	16

Table S3. Comparison of some recently reported bifunctional Cu-based catalysts for hydrazine-assisted water splitting in 1.0 M KOH.

Catalyst	Substrates	$E_{j=25}$ (V) vs. RHE	Reference
Cu_xSe/CF	Cu foam	0.49	This work
Ni(Cu) CNPs	Ni foam	1.0 ($E_{j=504}$)	16
Ni(Cu)/NF	Ni foam	0.41 ($E_{j=100}$)	17
Ni(Cu)@NiFeP/NM	Ni foam	0.491 ($E_{j=100}$)	18
Cu_3P/CF	Ni foam	0.72 ($E_{j=100}$)	19
Ni-Cu-P@ Ni-Cu	Ni foam	125 mV ($E_{j=10}$)	20

References

[1] Z. Li, C. Yu, Y. Wen, Y. Gao, X. Xing, Z. Wei, H. Sun, Y.-W. Zhang, W. Song, Mesoporous hollow Cu–Ni alloy nanocage from core–shell Cu@ Ni nanocube for efficient hydrogen evolution reaction, ACS Catal., 9 (2019) 5084-5095.

[2] Y.S. Park, W.-S. Choi, M.J. Jang, J.H. Lee, S. Park, H. Jin, M.H. Seo, K.-H. Lee, Y. Yin, Y. Kim, Three-dimensional dendritic Cu–Co–P electrode by one-step electrodeposition on a hydrogen bubble template for hydrogen evolution reaction, ACS Sustain. Chem. Eng., 7 (2019) 10734-10741.

[3] S. Li, M. Li, Y. Ni, Grass-like Ni/Cu nanosheet arrays grown on copper foam as efficient and non-precious catalyst for hydrogen evolution reaction, Appl. Catal. B: Environ., 268 (2020) 118392.

[4] G. Shi, Z. Fan, L. Du, X. Fu, C. Dong, W. Xie, D. Zhao, M. Wang, M. Yuan, In situ construction of graphdiyne/CuS heterostructures for efficient hydrogen evolution reaction, Mater. Chem. Front., 3 (2019) 821-828.

[5] M. Yao, B. Wang, B. Sun, L. Luo, Y. Chen, J. Wang, N. Wang, S. Komarneni, X. Niu, W. Hu, Rational design of self-supported Cu@ WC core-shell mesoporous nanowires for pH-universal hydrogen evolution reaction, Appl. Catal. B: Environ., 280 (2021) 119451.

[6] Y. Gao, Y. Wu, H. He, W. Tan, Potentiostatic electrodeposition of Ni–Se–Cu on nickel foam as an electrocatalyst for hydrogen evolution reaction, J. Colloid Interf. Sci., 578 (2020) 555-564.

[7] N. Lotfi, T. Shahrabi, Y. Yaghoubinezhad, G.B. Darband, Surface modification of Ni foam by the dendrite Ni-Cu electrode for hydrogen evolution reaction in an alkaline solution, J. Electroanal. Chem., 848 (2019) 113350.

[8] J. Wang, H. Zhu, J. Chen, B. Zhang, M. Zhang, L. Wang, M. Du, Small and well-dispersed Cu nanoparticles on carbon nanofibers: self-supported electrode materials for efficient hydrogen evolution reaction, Int. J. Hydrogen Energ., 41 (2016) 18044-18049.

[9] J. Rong, J. Xu, F. Qiu, Y. Fang, T. Zhang, Y. Zhu, 2D metal-organic frameworks-derived preparation of layered CuS@ C as an efficient and stable electrocatalyst for hydrogen evolution reaction, Electrochim. Acta, 323 (2019) 134856.

[10] M. Li, Y. Qian, J. Du, H. Wu, L. Zhang, G. Li, K. Li, W. Wang, D.J. Kang, CuS nanosheets decorated with CoS2 nanoparticles as an efficient electrocatalyst for enhanced hydrogen evolution at all pH values, ACS Sustain. Chem. Eng., 7 (2019) 14016-14022.

[11] M. Sun, Z. Lu, L. Luo, Z. Chang, X. Sun, A 3D porous Ni–Cu alloy film for high-performance hydrazine electrooxidation, Nanoscale, 8 (2016) 1479-1484.

[12] C. Zhang, W. Yuan, Q. Wang, X. Peng, X. Liu, J. Luo, Single Cu Atoms as Catalysts for Efficient Hydrazine Oxidation Reaction, ChemNanoMat, 6 (2020) 1474-1478.

[13] T. Wang, Q. Wang, Y. Wang, Y. Da, W. Zhou, Y. Shao, D. Li, S. Zhan, J. Yuan, H. Wang, Atomically dispersed semimetallic selenium on porous carbon membrane as an electrode for hydrazine fuel cells, Angew. Chem. Int. Ed., 131 (2019) 13600-13605.

[14] J. Ding, P. Kannan, P. Wang, S. Ji, H. Wang, Q. Liu, H. Gai, F. Liu, R. Wang, Synthesis of nitrogen-doped MnO/carbon network as an advanced catalyst for direct hydrazine fuel cells, J. Power Sources, 413 (2019) 209-215.

[15] Y. Wang, Z. Chen, H. Wu, F. Xiao, E. Cao, S. Du, Y. Wu, Z. Ren, Self-assembly-induced mosslike Fe2O3 and FeP on electro-oxidized carbon paper for low-voltage-driven hydrogen production plus hydrazine degradation, ACS Sustain. Chem. Eng., 6 (2018) 15727-15736.

[16] Q. Sun, Y. Li, J. Wang, B. Cao, Y. Yu, C. Zhou, G. Zhang, Z. Wang, C. Zhao, Pulsed electrodeposition of well-ordered nanoporous Cu-doped Ni arrays promotes high-efficiency overall hydrazine splitting, J. Mater. Chem. A, 8 (2020) 21084-21093.

[17] Q. Sun, L. Wang, Y. Shen, M. Zhou, Y. Ma, Z. Wang, C. Zhao, Bifunctional copper-doped nickel catalysts enable energy-efficient hydrogen production via hydrazine oxidation and hydrogen evolution reduction, ACS Sustain. Chem. Eng., 6 (2018) 12746-12754.

[18] Q. Sun, M. Zhou, Y. Shen, L. Wang, Y. Ma, Y. Li, X. Bo, Z. Wang, C. Zhao, Hierarchical nanoporous Ni(Cu) alloy anchored on amorphous NiFeP as efficient bifunctional electrocatalysts for hydrogen evolution and hydrazine oxidation, J. Catal., 373 (2019) 180-189.

[19] M. Liu, R. Zhang, L. Zhang, D. Liu, S. Hao, G. Du, A.M. Asiri, R. Kong, X. Sun, Energy-efficient electrolytic hydrogen generation using a Cu_3P nanoarray as a bifunctional catalyst for hydrazine oxidation and water reduction, Inorgan. Chem. Front., 4 (2017) 420-423.

[20] G.B. Darband, N. Lotfi, A. Aliabadi, S. Hyun, S. Shanmugam, Hydrazine-assisted electrochemical hydrogen production by efficient and self-supported electrodeposited Ni-Cu-P@Ni-Cu nano-micro dendrite catalyst, Electrochim. Acta, 382 (2021) 138335.