Supporting information

Well-defined $CoSe_2$@$MoSe_2$ hollow heterostructured nanocubes with enhanced dissociation kinetics for overall water splitting

Zhiwen Chen,‡[a] Wenwen Wang,‡[a] Shoushuang Huang,[a,] * Ping Ning,[a] Ye Wu,[a] Chunyan Gao,[a] Thanh-Tung Le,[a] Jiantao Zai,[b] Yong Jiang,[a] Zhangjun Hu,[a, c] and Xuefeng Qian[b]

[a] School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, People's Republic of China

[b] Shanghai Electrochemical Energy Devices Research Center, School of Chemistry and Chemical Engineering and State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai, 200240, P. R. China

[c] Department of Physics, Chemistry and Biology, Linköping University, Linköping, 58183, Sweden

* Corresponding authors.

E-mail: sshuang@shu.edu.cn;

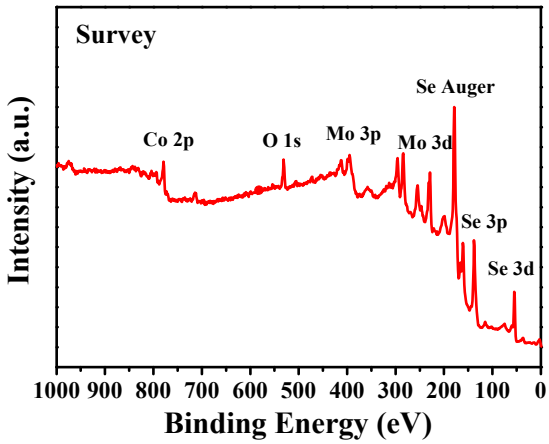

Fig. S1. The survey XPS spectrum of the as-synthesized $CoSe_2$@$MoSe_2$ heterostructures.

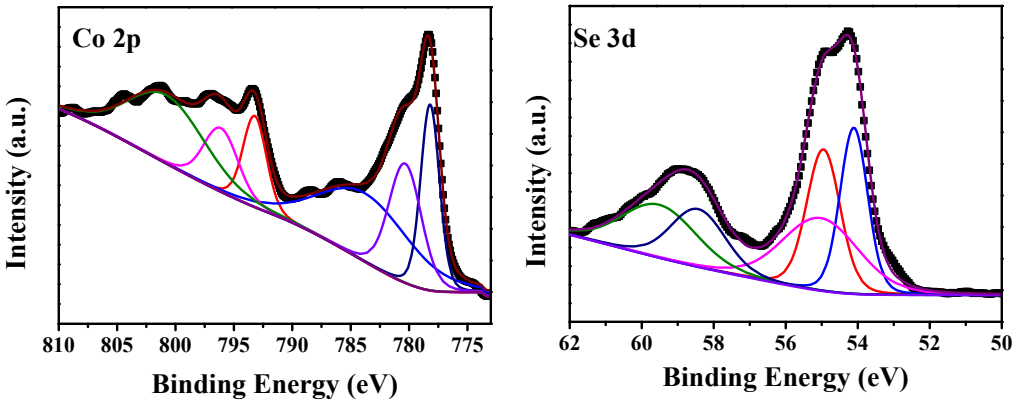

Fig. S2 XPS spectrum of the as-obtained $CoSe_2$ hollow nanocubes.

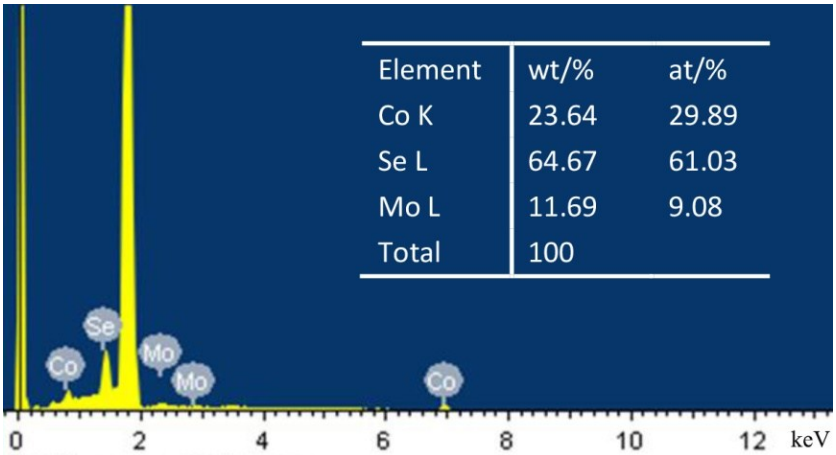

Fig. S3. The energy dispersive X-ray spectroscopy (EDX) of the as-synthesized $CoSe_2$@$MoSe_2$ heterostructures.

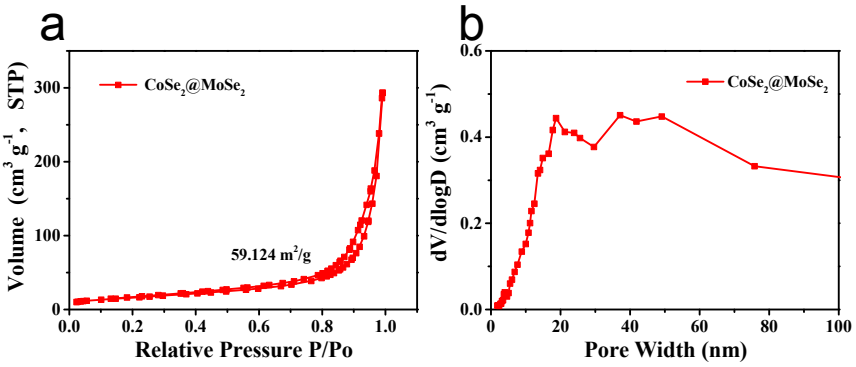

Fig. S4 (a) Nitrogen adsorption/desorption isotherms of $CoSe_2$@$MoSe_2$. (b) Pore size distribution plots of $CoSe_2$@$MoSe_2$.

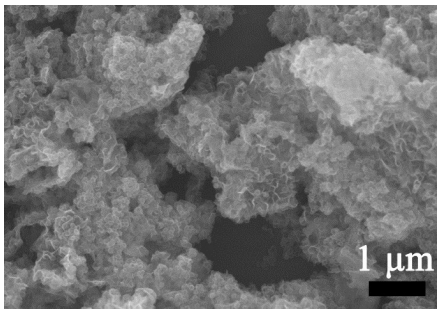

Fig S5. SEM image of the as-synthesized $MoSe_2$ microspheres

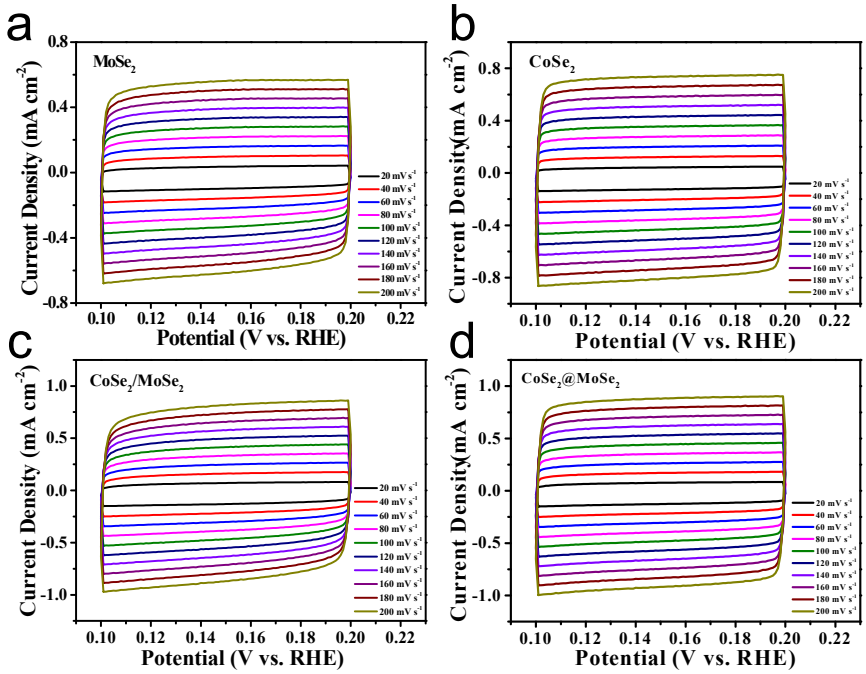

Fig S6. Cyclic voltammograms of the as-synthesized (a) $CoSe_2$, (b) $MoSe_2$, (c) $CoSe_2$/$MoSe_2$ and (d) $CoSe_2$@$MoSe_2$ heterostructures in 0.1~0.2 V *vs.* RHE at different scan rates from 20 mV s^{-1} to 200 mV s^{-1} in 0.5 M H_2SO_4 by Ni foam.

Tab S1 Comparison of HER Performance of Metal Sulfide Catalysts under Alkaline Conditions

Catalysts	electrolyte	Electrode	η_{10} (mV)	Tafel slop (mV/dec)	Reference
$CoSe_2$@$MoSe_2$	1.0 M KOH	NF	183	87.69	This work
CoS_2@N-GN	1.0 M KOH	GCE	204	108	1
Ni_3S_2/NiS	1.0 M KOH	GCE	180	83	2
$CoNi_2S_4$	1.0 M KOH	NF	54	129	3
$Co_{0.85}Se$@NC	1.0 M KOH	NF	230	125	4
$NiCo_2Se_4$	1.0 M KOH	NF	150	122	5
Ni_3S_2	1.0 M KOH	NF	223	/	6
Co_3S_4	1.0 M KOH	NF	199	91	7
NiS_2	1.0 M KOH	GS	190	80	8

GCE: Glassy carbon electrode; GS: Graphite substrate; NF: Ni foam

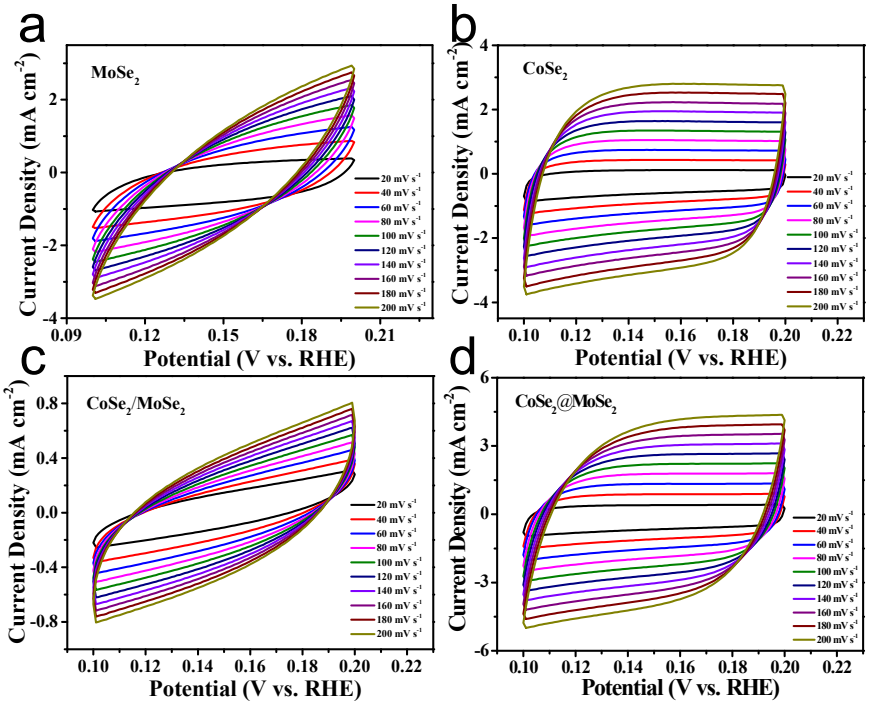

Fig S7. Cyclic voltammograms of the as-synthesized (a) $CoSe_2$, (b) $MoSe_2$, (c) $CoSe_2/MoSe_2$ and (d) $CoSe_2$@$MoSe_2$ heterostructures in 0.1~0.2 V *vs.* RHE at different scan rates from 20 mV s^{-1} to 200 mV s^{-1} in 1.0 M KOH.

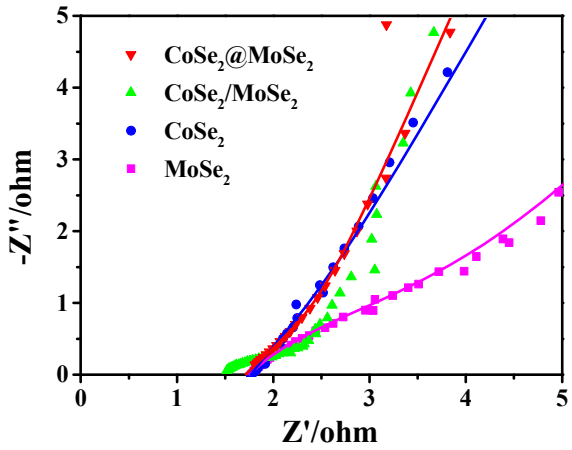

Fig S8. Nyquist plots and the corresponding simulated equivalent circuit diagram of the samples.

References

1. Zhang, W.; Ma, X. Y.; Zhong, C.; Ma, T. Y.; Deng, Y. D.; Hu, W. B.; Han, X. P., Pyrite-Type CoS_2 Nanoparticles Supported on Nitrogen-Doped Graphene for Enhanced Water Splitting. *Frontiers in Chemistry* **2018,** *6*.

2. Cao, Y. F.; Meng, Y. Y.; Huang, S. C.; He, S. M.; Li, X. H.; Tong, S. F.; Wu, M. M., Nitrogen-, Oxygen- and Sulfur-Doped Carbon-Encapsulated Ni_3S_2 and NiS Core Shell Architectures: Bifunctional Electrocatalysts for Hydrogen Evolution and Oxygen Reduction Reactions. *ACS Sustain. Chem. Eng.* **2018,** *6* (11), 15582-+.

3. Li, J. W.; Zhuang, Q. N.; Xu, P. M.; Zhang, D. W.; Wei, L. C.; Yuan, D. S., Three-dimensional lily-like $CoNi_2S_4$ as an advanced bifunctional electrocatalyst for hydrogen and oxygen evolution reaction. *Chin. J. Catal.* **2018,** *39* (8), 1403-1410.

4. Meng, T.; Qin, J. W.; Wang, S. G.; Zhao, D.; Mao, B. G.; Cao, M. H., In situ coupling of $Co_{0.85}Se$ and N-doped carbon via one-step selenization of metal-organic frameworks as a trifunctional catalyst for overall water splitting and Zn-air batteries. *J. Mater. Chem. A* **2017,** *5* (15), 7001-7014.

5. Fang, Z. W.; Peng, L. L.; Qian, Y. M.; Zhang, X.; Xie, Y. J.; Cha, J. J.; Yu, G. H., Dual Tuning of Ni-Co-A (A = P, Se, O) Nanosheets by Anion Substitution and Holey Engineering for Efficient Hydrogen Evolution. *J. Am. Chem. Soc.* **2018,** *140* (15), 5241-5247.

6. Feng, L. L.; Yu, G. T.; Wu, Y. Y.; Li, G. D.; Li, H.; Sun, Y. H.; Asefa, T.; Chen, W.; Zou, X. X., High-Index Faceted Ni_3S_2 Nanosheet Arrays as Highly Active and Ultrastable Electrocatalysts for Water Splitting. *J. Am. Chem. Soc.* **2015,** *137* (44), 14023-14026.

7. Tang, S. S.; Wang, X.; Zhang, Y. Q.; Courte, M.; Fan, H. J.; Fichou, D., Combining Co_3S_4 and $Ni:Co_3S_4$ nanowires as efficient catalysts for overall water splitting: an experimental and theoretical study. *Nanoscale* **2019,** *11* (5), 2202-2210.

8. Ma, X. Y.; Zhang, W.; Deng, Y. D.; Zhong, C.; Hu, W. B.; Han, X. P., Phase and composition controlled synthesis of cobalt sulfide hollow nanospheres for electrocatalytic water splitting. *Nanoscale* **2018,** *10* (10), 4816-4824.