

## Electronic Supplementary Information

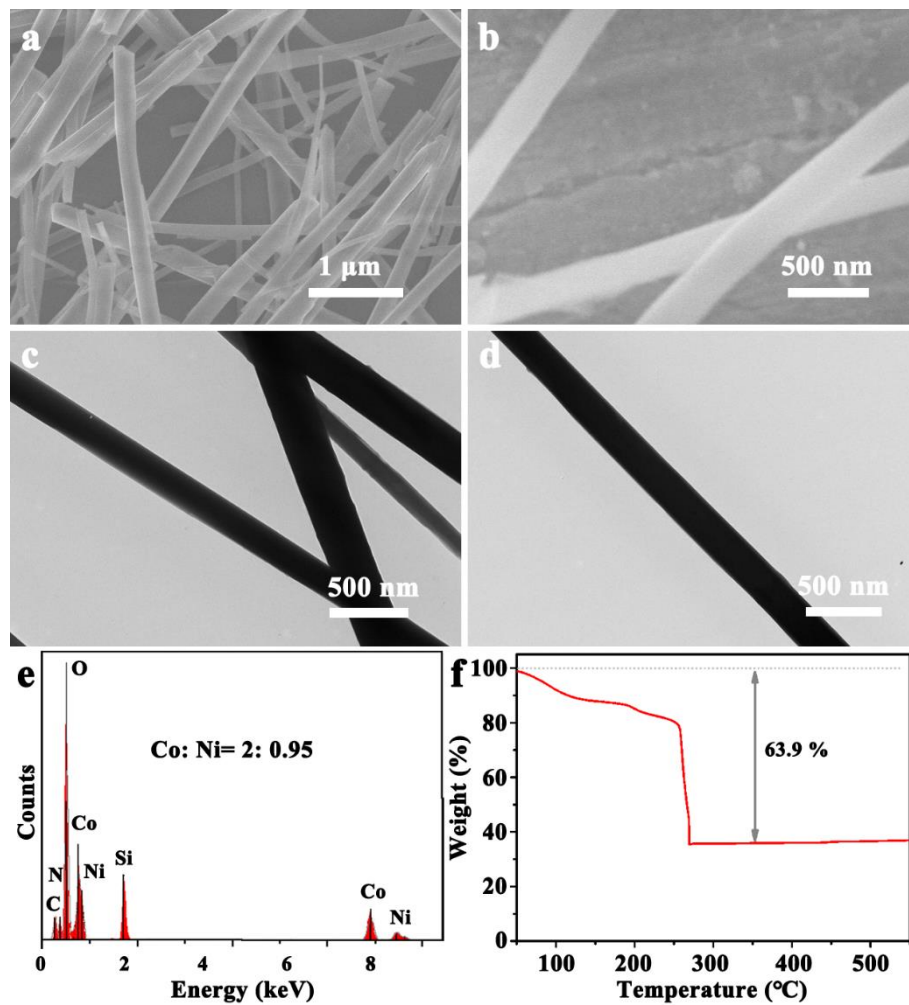
### **Controllable synthesis of CoFe<sub>2</sub>Se<sub>4</sub>/NiCo<sub>2</sub>Se<sub>4</sub> hybrid nanotubes with heterointerfaces and improved oxygen evolution reaction performance**

Huan Wang, ‡ Zhonghua Sun, ‡ Xiaoran Zou, ‡ Jianhai Ren, and Chun-yang Zhang \*

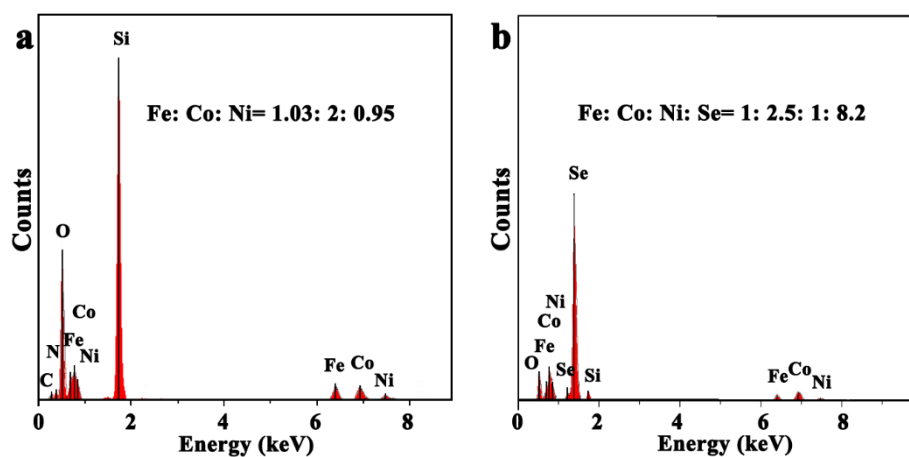
College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Shandong Normal University, Jinan 250014, China.

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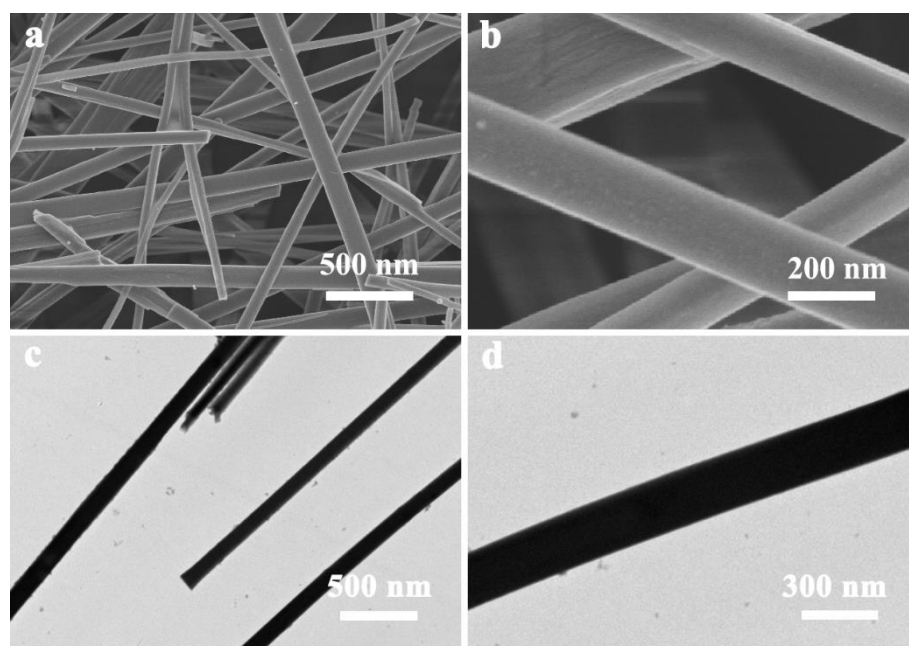
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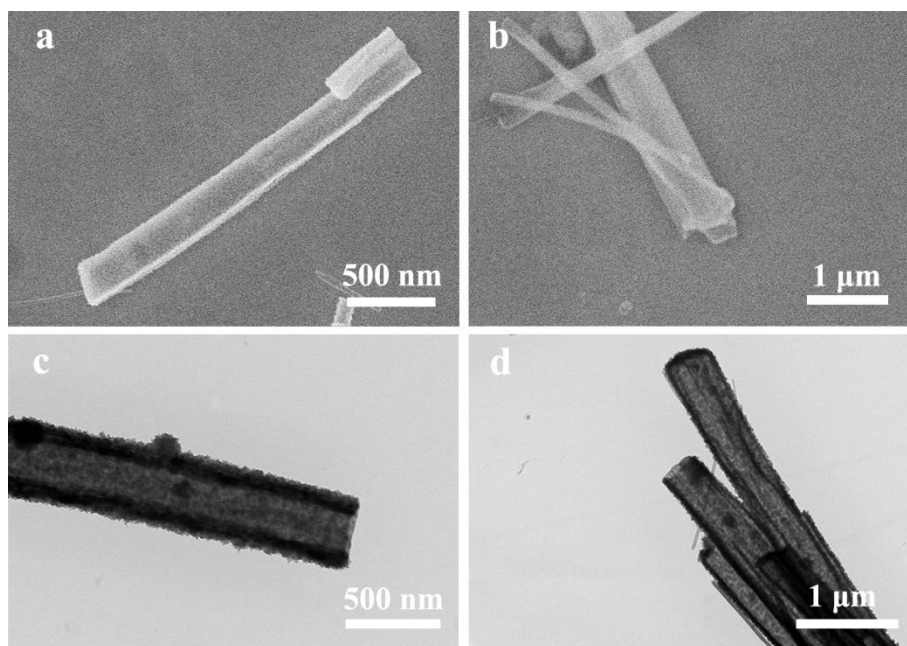
**Fig. S1.** (a, b) SEM images, (c, d) TEM images, (e) EDS image and (e) TGA result of NiCo-Asp NFs. The EDS and TGA results confirm that the as-prepared nanofibers are composed by metals and organics. And the atomic ratio of Co and Ni is 2: 0.95, which is close to the experimental proportion.



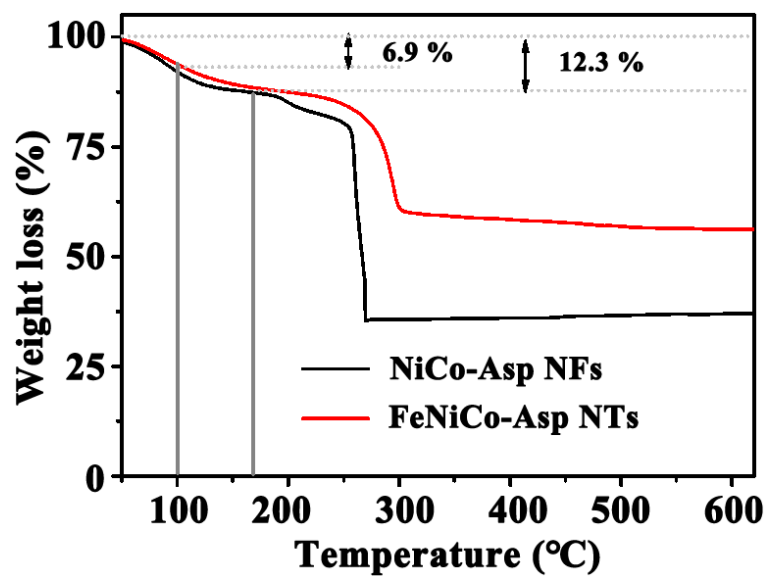
**Fig. S2.** EDS images of (a) FeNiCo-Asp NTs and (b) CFSe/NCSe HNTs.



**Fig. S3.** (a, b) SEM images and (c, d) TEM images of Co-Asp NFs.



**Fig. S4.** (a, b) SEM images and (c, d) TEM images of CoFe-Asp NTs.



**Fig. S5.** TGA curves of NiCo-Asp NFs and FeNiCo-Asp NTs. The TGA measurements of NiCo-Asp NFs and FeNiCo-Asp NTs were performed under air flow at a heating rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  from  $30\text{ }^{\circ}\text{C}$  to  $700\text{ }^{\circ}\text{C}$ . The weight loss of 12.3% below  $170\text{ }^{\circ}\text{C}$  can be attributed to the evaporation of the absorbed organic residues (e.g., ethanol) or the bound water on the surface of samples. The NiCo-Asp NFs and FeNiCo-Asp NTs were completely decomposed at  $270\text{ }^{\circ}\text{C}$  and  $300\text{ }^{\circ}\text{C}$ , respectively.

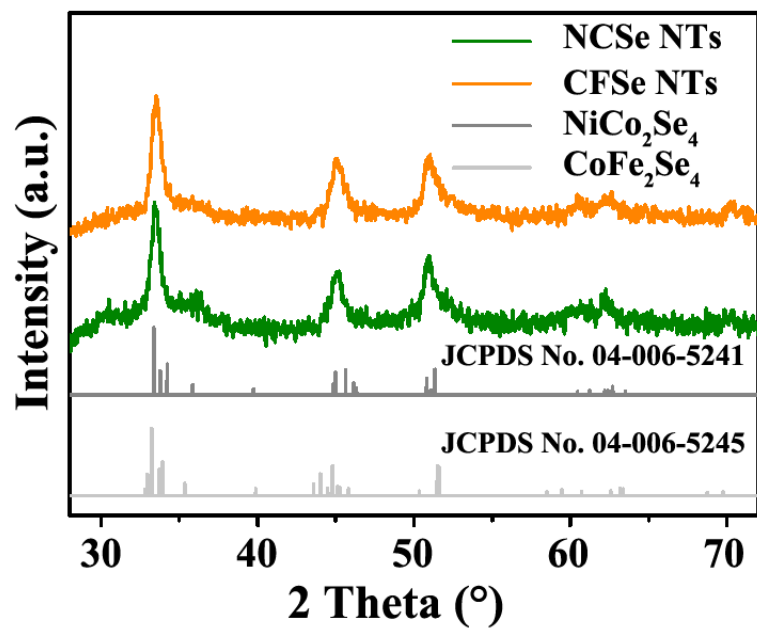
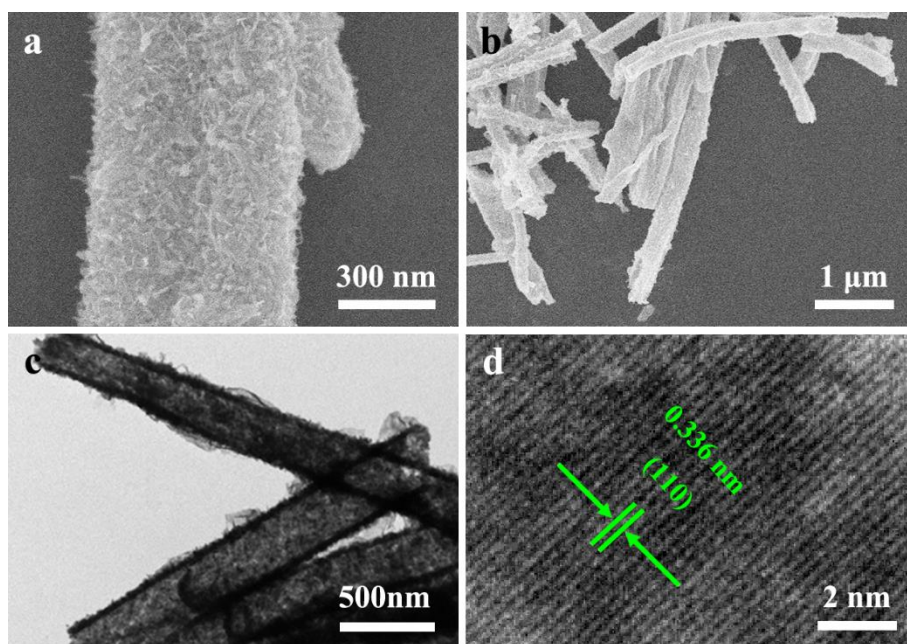
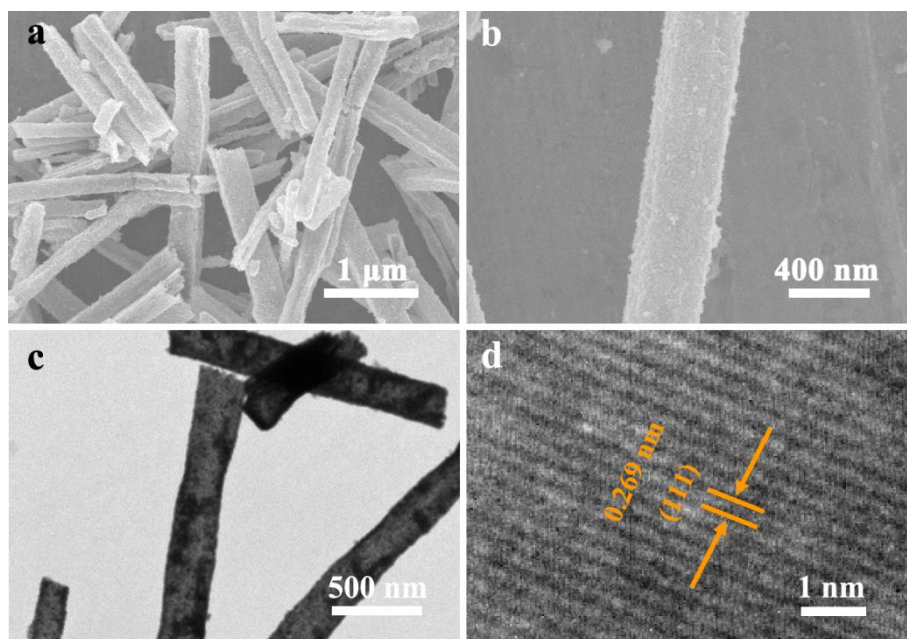


Fig. S6. XRD pattern of CFSe and NCSi NTs.

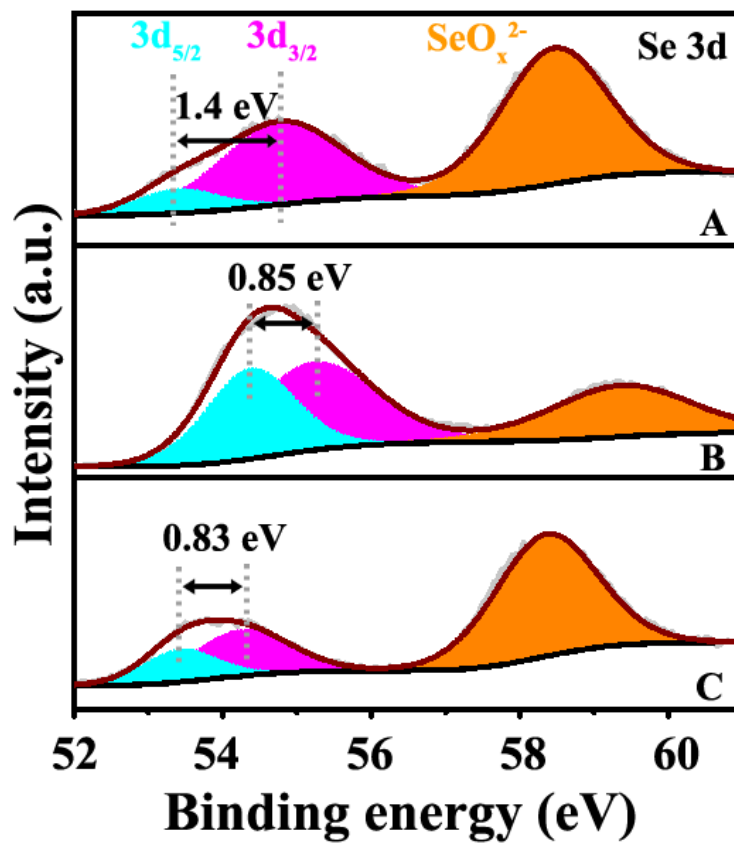


**Fig. S7.** (a, b) SEM images, (c) TEM image and (d) HRTEM image of CFSe NTs. The lattice fringe spacing of 0.336 nm is corresponding to (110) plane of  $\text{CoFe}_2\text{Se}_4$ .

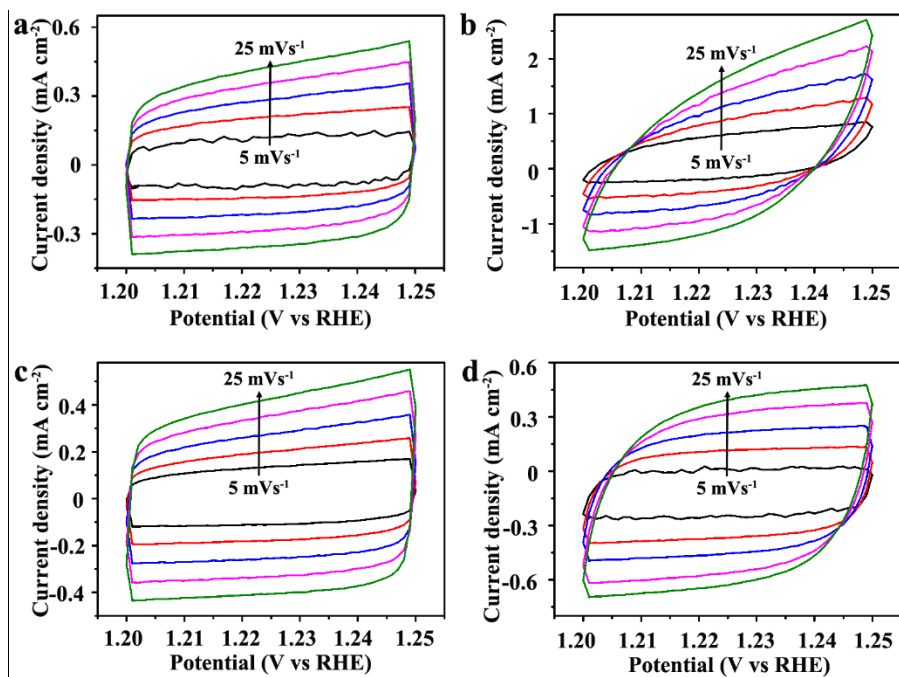


**Fig. S8.** (a, b) SEM images, (c) TEM image and (d) HRTEM image of NCSe NTs. The lattice fringe spacing of 0.269 nm is corresponding to (111) plane of  $\text{NiCo}_2\text{Se}_4$ .

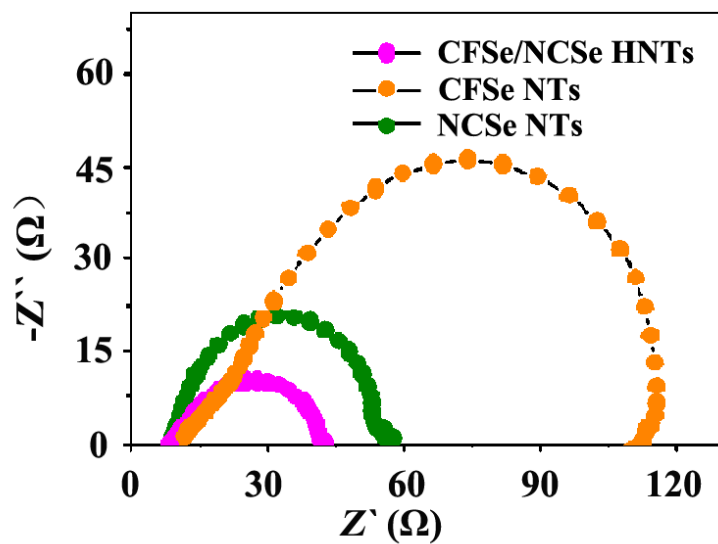




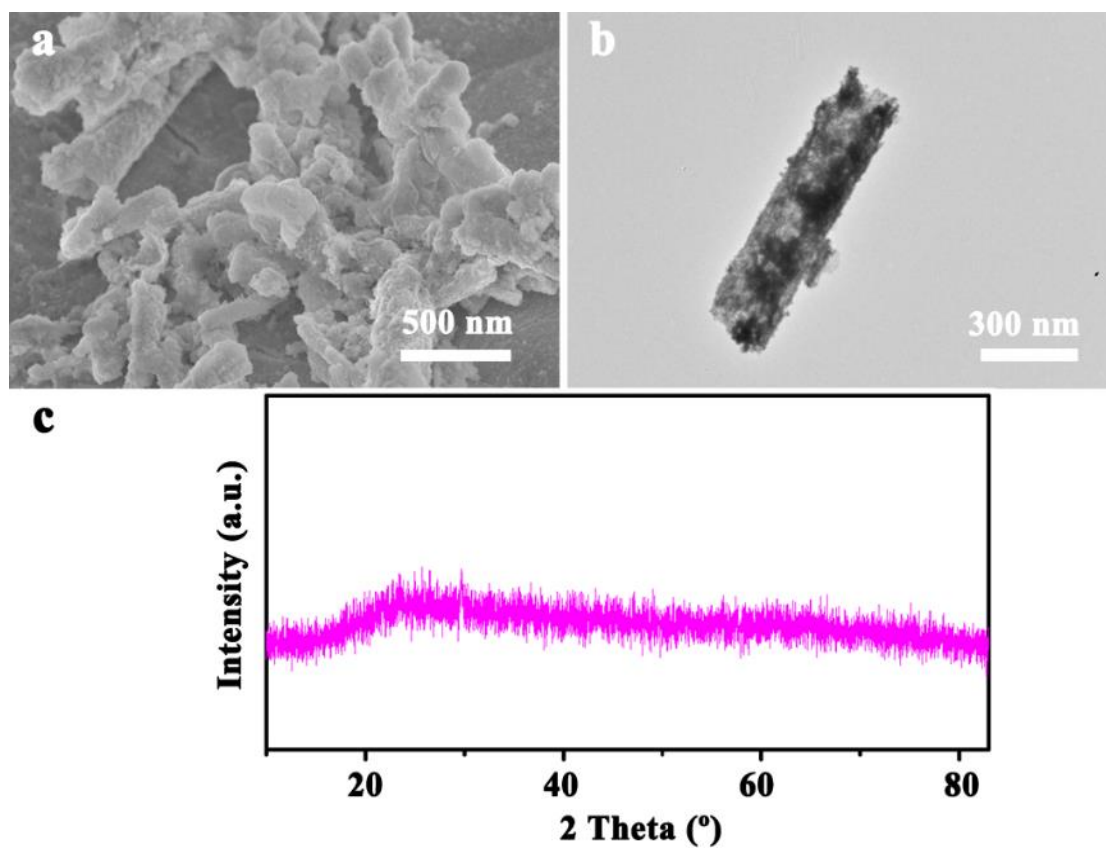
**Fig. S9.** Se 3d XPS spectra of CFSe/NCSe HNTs (A), CFSe NTs (B) and NCSe NTs (C). The peaks covered by cyan and magenta are assigned to Se  $3d_{5/2}$  and Se  $3d_{3/2}$ , respectively.<sup>1</sup> The difference value for CFSe/NCSe HNTs is larger than that of CFSe NTs, and NCSe NTs, indicating the strong interaction in the interface of CFSe-NCSe in CFSe/NCSe HNTs.



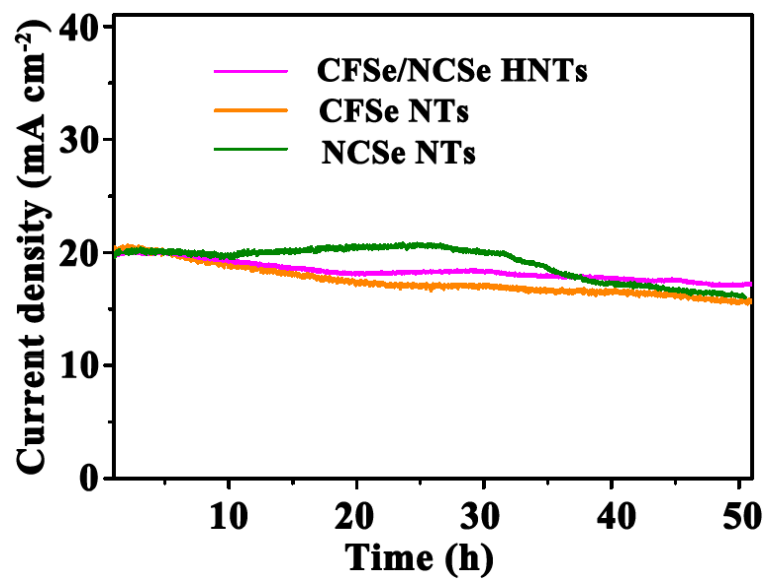
**Fig. S10.** CV curves of (a) RuO<sub>2</sub> NPs, (b) CFSe/NCSe HNTs, (c) NCSe NTs and (d) CFSe NTs at different scan rates.



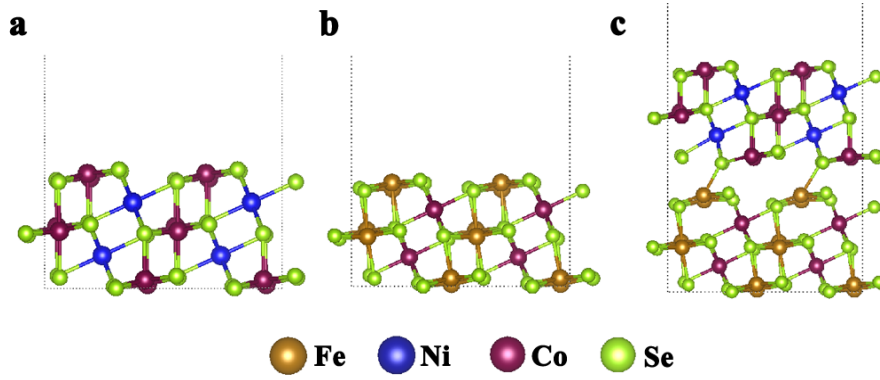
**Fig. S11.** Nyquist plots of the CFSe/NCSe HNTs, CFSe NTs and NCSe NTs.



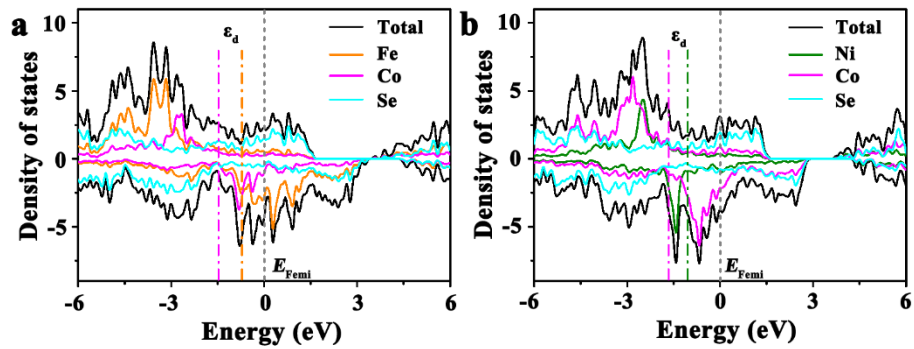
**Fig. S12.** (a) SEM image and (b) TEM image and XRD pattern of CFSe/NCSe HNTs after OER testing.



**Fig. S13.** Chronoamperometric (i-t) curve of the CFSe/NCSe HNTs, CFSe NTs and NCSe NTs at the current density of about 20 mA cm<sup>-2</sup>. After testing for 50 h, the current density of the three samples still can maintain more than 80 %.



**Fig. S14.** Optimized structure of (a) NiCo<sub>2</sub>Se<sub>4</sub>, (b) CoFe<sub>2</sub>Se<sub>4</sub> and (c) CoFe<sub>2</sub>Se<sub>4</sub>/ NiCo<sub>2</sub>Se<sub>4</sub>.



**Fig. S15.** (a) The DOSs of CFSe NTs, the  $\epsilon_d$  of Fe and Co in CFSe NTs are -0.69 and -1.46 eV, respectively. (b) The DOSs of NCSe NTs, the  $\epsilon_d$  of Ni and Co in NCSe NTs are -1.06 and -1.62 eV, respectively.

**Table S1.** Comparison of the electrochemical OER properties of the CFSe/NCSe HNTs with those of the reported transition metal chalcogenides.

Electrocatalysts	$\eta$ value (mV) at 10 mA·cm <sup>-2</sup>	Tafel slopes (mV·dec <sup>-1</sup> )	Current collector	Ref.
(Ni, Co) <sub>0.85</sub> Se	255	79	carbon cloth	1
FeCoNi-NS 2D	251	58	glass carbon	2
(Ni,Co)Se <sub>2</sub>	256	74	carbon cloth	3
N-NiCo <sub>2</sub> S <sub>4</sub> /CoO	227	66.8	Ni foam	4
Co-Fe-P-Se/NC	270	39	glass carbon	5
CoSe <sub>2</sub> /FeSe <sub>2</sub>	240	44	Ni foam	6
Fe, Al-NiSe <sub>2</sub> /rGO	272	48	glass carbon	7
Ni <sub>3</sub> S <sub>4</sub>	257	67	Ni foam	8
Ni <sub>0.6</sub> Co <sub>0.4</sub> Se	249	53	Ni foam	9
O-CoSe <sub>2</sub> -HNT	252	60	glass carbon	10
NiFe/Co <sub>9</sub> S <sub>8</sub> /CC	219	55	carbon cloth	11
NiSe <sub>2</sub> /CoSe <sub>2</sub>	286	53	glass carbon	12
Fe-doped NiSe <sub>2</sub>	268	69	glass carbon	13
CoTe <sub>2</sub>	357	32	glass carbon	14
CoSe <sub>2</sub> -CoO/NCF	279	44.6	carbon cloth	15
CoSe/FeSe <sub>2</sub>	281	34.3	glass carbon	16
CFSe/NCSe HNTs	224	48.1	glass carbon	This work

## References:

1. C. Xia, Q. Jiang, C. Zhao, M. N. Hedhili and H. N. Alshareef, *Adv. Mater.*, 2016, **28**, 77-85.
2. J. Y. Jiang, L. Y. Chang, W. C. Zhao, Q. Y. Tian and Q. Xu, *Chem. Commun.*, 2019, **55**, 10174-10177.
3. W. J. Song, X. Teng, Y. Y. Liu, J. Y. Wang, Y. L. Niu, X. M. He, C. Zhang and Z. F. Chen, *Nanoscale*, 2019, **11**, 6401-6409.
4. B. He, J. J. Song, X. Y. Li, C. Y. Xu, Y. B. Li, Y. W. Tang, Q. L. Hao, H. K. Liu and Z. Su, *Nanoscale*, 2020, DOI: 10.1039/d0nr07120j
5. H. B. Wu, J. Wang, J. Yan, Z. X. Wu and W. Jin, *Nanoscale*, 2019, **11**, 20144-20150.
6. C. Y. Xu, Q. H. Li, J. L. Shen, Z. Yuan, J. Q. Ning, Y. J. Zhong, Z. Y. Zhang and Y. Hu, *Nanoscale*, 2019, **11**, 10738-10745.
7. L. Chen, H. Jang, M. G. Kim, Q. Qin, X. Liu and J. Cho, *Nanoscale*, 2020, **12**, 13680-13687.
8. W. K., L. J. S, Z. C., Z. T., A. J., Lu X. H., M. B.W., Z. X. and F. J., *Adv. Funct. Mater.*, 2019, **29**, 1900315.
9. Z. Feng, E. Wang, S. Huang and J. Liu, *Nanoscale*, 2020, **12**, 4426-4434.
10. B. M. Jia, Z. Q. Xue, Q. Liu, Q. L. Liu, K. Liu, M. Liu, T. S. Chan, Y. L. Li, Z. J. Li, C. Y. Su and G. Q. Li, *J. Mater. Chem. A*, 2019, **7**, 15073-15078.
11. C. Zhan, Z. Liu, Y. Zhou, M. Guo, X. Zhang, J. Tu, L. Ding and Y. Cao, *Nanoscale*, 2019, **11**, 3378-3385.
12. X. R. Zheng, X. P. Han, Y. H. Cao, Y. Zhang, D. Nordlund, J. H. Wang, S. L. Chou, H. Liu,

- L. L. Li, C. Zhong, Y. D. Deng and W. B. Hu, *Adv. Mater.*, 2020, **32**, 2000607.
13. C. Gu, S. J. Hu, X. S. Zheng, M. R. Gao, Y. R. Zheng, L. Shi, Q. Gao, X. Zheng, W. S. Chu, H. B. Yao, J. F. Zhu and S. H. Yu, *Angew. Chem. Int. Ed.*, 2018, **57**, 4020-4024.
14. Q. Gao, C. Q. Huang, Y. M. Ju, M. R. Gao, J. W. Liu, D. An, C. H. Cui, Y. R. Zheng, W. X. Li and S. H. Yu, *Angew. Chem. Int. Ed.*, 2017, **56**, 7769-7773.
15. T. Zhang, J. Yu, H. Guo, J. Y. Liu, Q. Liu, D. L. Song, R. R. Chen, R. M. Li, P. L. Liu and J. Wang, *Electrochimica Acta*, 2020, **356**, 136822.
16. Y. Zhang, J. Xu, L. Lv, A. Wang, B. Zhang, Y. Ding and C. Wang, *Nanoscale*, 2020, **12**, 10196-10204.