Supporting Information

Mesoporous Hollow Nested Nanospheres of Ni, Cu, Co-Based Mixed Sulfides for Electrocatalytic Oxygen Reduction and Evolution

Xiaoyu Wu, Songmei Li,* Jianhua Liu, Mei Yu

Key Laboratory of Aerospace Advanced Materials and Performance of Ministry of Education, School of Materials Science and Engineering, Beihang University, Beijing, 100191, P. R. China

> S Counts (a.u.) Co Ni Co Ni Cu Co Cu Ni 4 6 2 8 10 Energy (keV)

Figure S1 EDX spectrum of the NiCuCo-sulfides nanospheres.

^{*} Corresponding author. Tel: +86 10 82317103; fax: +86 10 82317103. *E-mail address:* songmei_li@buaa.edu.cn.

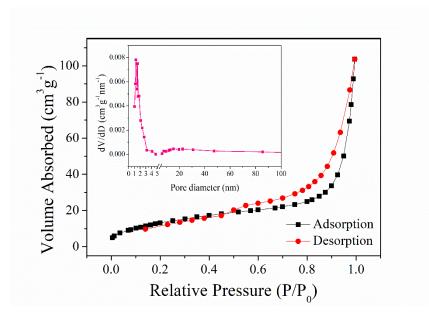


Figure S2 (a) N_2 adsorption-desorption isotherms of the NiCuCo-oxides nanospheres and the inset is the pore size distribution plot.

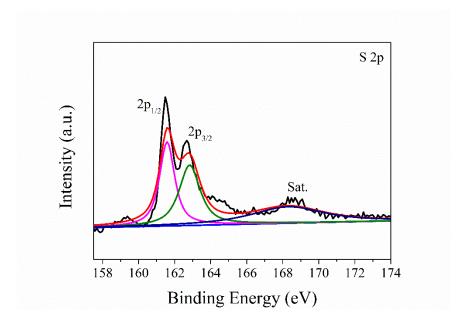


Figure S3 XPS spectrum of S 2p for the NiCuCo-sulfides nanospheres.

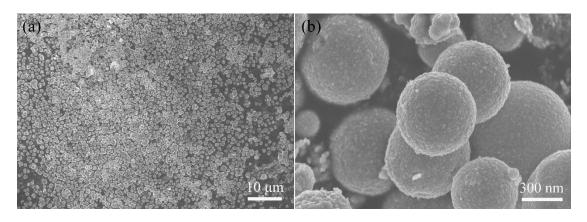
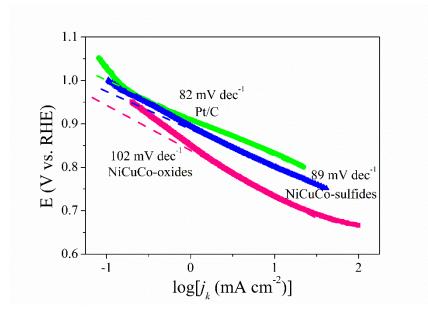


Figure S4 SEM images of the NiCuCo-sulfides nanospheres with Nafion additives in



glassy carbon electrodes.

Figure S5 Comparison of Tafel plots of the NiCuCo-sulfides, NiCuCo-oxides and Pt/C obtained from the ORR LSV curves at 1600 rpm.

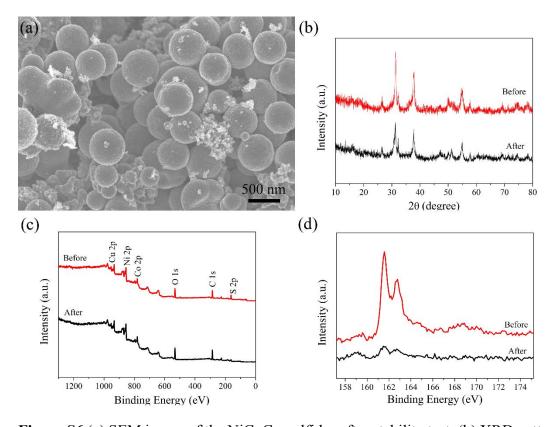


Figure S6 (a) SEM image of the NiCuCo-sulfides after stability test; (b) XRD patterns, (c) XPS survey scans and (d) XPS spectra of S 2p of the NiCuCo-sulfides before and after cyclic stability test.

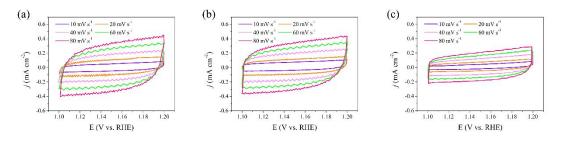


Figure S7 Cyclic voltammetry curves measured in a potential range (1.1-1.2 V vs. RHE) at scan rates from 10 to 80 mV/s for (a) NiCuCo-sulfides, (b) NiCuCo-oxides and (c) Pt/C.

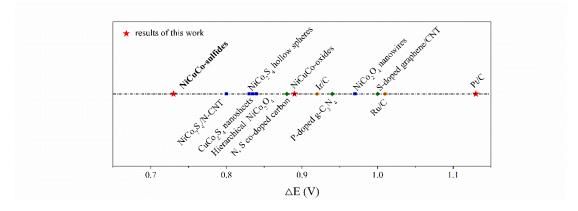


Figure S8 Comparison of ORR and OER bifunctional activities of samples in this work with representative electrocatalysts in references, which were evaluated by the potential difference ΔE ($\Delta E = E_{OER} - E_{ORR} = E_{j=10} - E_{1/2}$) between the potential under the OER current density of 10 mA cm⁻² ($E_{j=10}$) and the half-wave potential of ORR ($E_{1/2}$).¹⁻⁹

REFERENCES

- Gorlin, Y.; Jaramillo, T. F., A Bifunctional Nonprecious Metal Catalyst for Oxygen Reduction and Water Oxidation. *Journal of the American Chemical Society* 2010, 132, 13612-13614.
- (2) Prabu, M.; Ketpang, K.; Shanmugam, S., Hierarchical nanostructured NiCo2O4 as an efficient bifunctional non-precious metal catalyst for rechargeable zinc-air batteries. *Nanoscale* 2014, 6, 3173-81.
- (3) Jin, C.; Lu, F.; Cao, X.; Yang, Z.; Yang, R., Facile synthesis and excellent electrochemical properties of NiCo2O4 spinel nanowire arrays as a bifunctional catalyst for the oxygen reduction and evolution reaction. *Journal of Materials Chemistry A* 2013, 1, 12170-12177.
- (4) Zhao, S.; Wang, Y.; Zhang, Q.; Li, Y.; Gu, L.; Dai, Z.; Liu, S.; Lan, Y.-Q.; Han, M.; Bao, J., Two-dimensional nanostructures of non-layered ternary thiospinels and

their bifunctional electrocatalytic properties for oxygen reduction and evolution: the case of CuCo2S4 nanosheets. *Inorganic Chemistry Frontiers* 2016, 3, 1501-1509.

- (5) Han, X.; Wu, X.; Zhong, C.; Deng, Y.; Zhao, N.; Hu, W., NiCo 2 S 4 nanocrystals anchored on nitrogen-doped carbon nanotubes as a highly efficient bifunctional electrocatalyst for rechargeable zinc-air batteries. *Nano Energy* 2017, 31, 541-550.
- (6) Feng, X.; Jiao, Q.; Cui, H.; Yin, M.; Li, Q.; Zhao, Y.; Li, H.; Zhou, W.; Feng, C., One-Pot Synthesis of NiCo2S4 Hollow Spheres via Sequential Ion-Exchange as an Enhanced Oxygen Bifunctional Electrocatalyst in Alkaline Solution. *ACS applied materials & interfaces* 2018, 10, 29521-29531.
- (7) Ma, T. Y.; Ran, J.; Dai, S.; Jaroniec, M.; Qiao, S. Z., Phosphorus-Doped Graphitic Carbon Nitrides Grown In Situ on Carbon-Fiber Paper: Flexible and Reversible Oxygen Electrodes. *Angewandte Chemie International Edition* 2015, 54, 4646-4650.
- (8) El-Sawy, A. M.; Mosa, I. M.; Su, D.; Guild, C. J.; Khalid, S.; Joesten, R.; Rusling, J. F.; Suib, S. L., Controlling the Active Sites of Sulfur-Doped Carbon Nanotube– Graphene Nanolobes for Highly Efficient Oxygen Evolution and Reduction Catalysis. *Advanced Energy Materials* 2016, 6, 1501966.
- (9) Qu, K.; Zheng, Y.; Dai, S.; Qiao, S. Z., Graphene oxide-polydopamine derived N, S-codoped carbon nanosheets as superior bifunctional electrocatalysts for oxygen reduction and evolution. *Nano Energy* 2016, 19, 373-381.