Supporting Information

Interface engineering and heterometal doping FeOOH/Ga-Ni_3S_2 nanosheet arrays for efficient electrocatalytic oxygen evolution

Rui Wang,[a] Yang Yang,[c] Xiaocheng Xu,[a] Sijie Chen,[a] Alex Trukhanov,[d] Lianyi Shao,*[a, b] Ruiying Wang, *[e] Xia Lu,*[c] Hui Pan,*[b] and Zhipeng Sun *[a]

[a]*School of Materials and Energy, Guangdong University of Technology, No. 100 Waihuan Xi Road, Guang zhou Higher Education Mega Center, Panyu District, Guangzhou 510006, China.*

[b]*Institute of Applied Physics and Materials Engineering, University of Macau, Macao SAR 999078, China.*

[c]*School of Materials, Sun Yat-Sen University, Guangzhou, 510006, China.*

[d]*Functional Materials Centre, SSPA "Scientific and Practical Materials Research Centre of NAS of Belarus", 19 P. Brovki St., 220072, Minsk, Belarus.*

[e]*State Key Laboratory of Chemistry and Utilization of Carbon-Based Energy Resources; College of Chemistry, Xinjiang University, Urumqi, 830017 China.*

**Corresponding author:*

*E-mail: zpsunxj@gdut.edu.cn (Zhipeng Sun); wangry9581@sina.com (*Ruiying Wang*)*

shaolianyi@gdut.edu.cn(Lianyi Shao); luxia3@mail.sysu.edu.cn (Xia Lu);

huipan@um.edu.mo (Hui Pan).

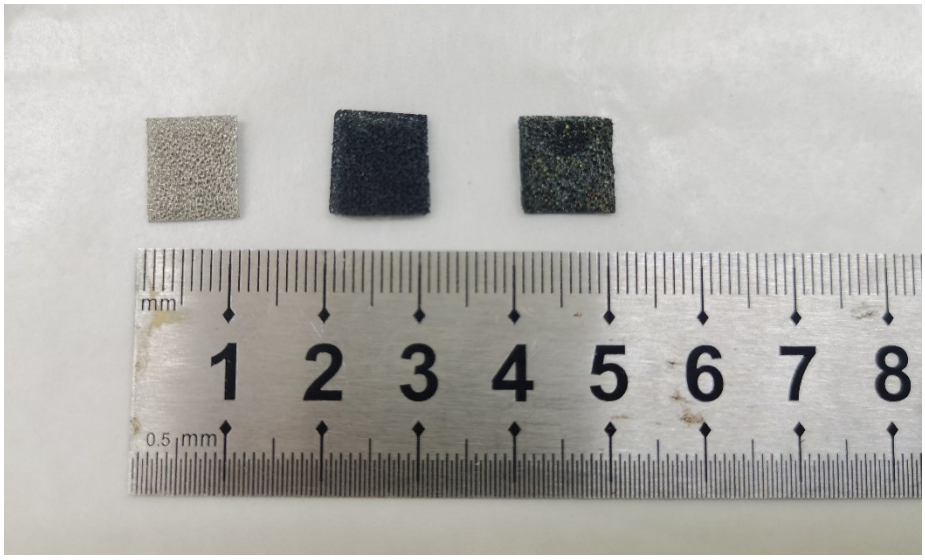

Figure S1. The digital photographs of NF, Ga-Ni_3S_2 and FeOOH/Ga-Ni_3S_2 (from left to right)

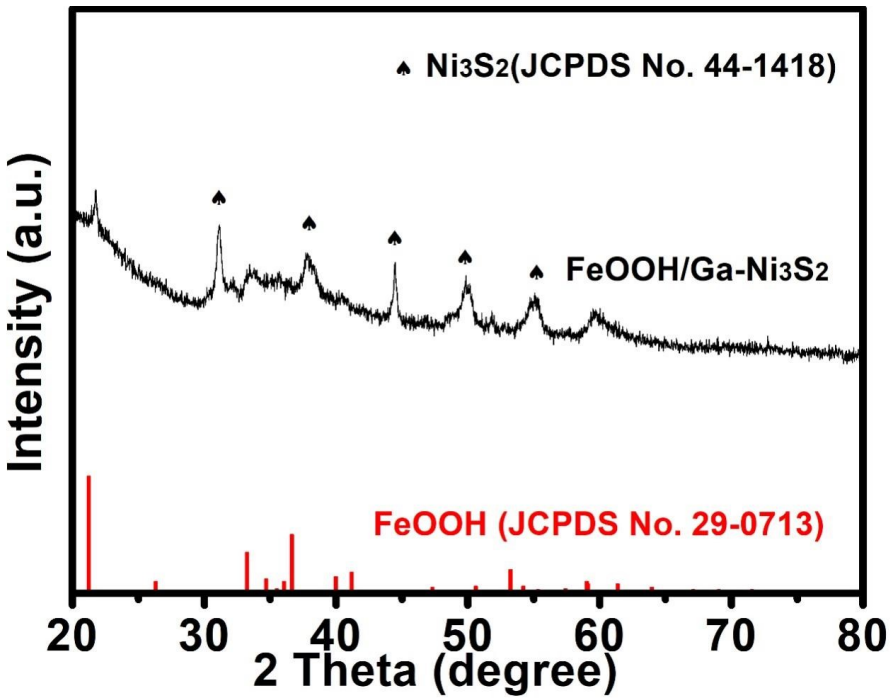

Figure S2. XRD patterns of the FeOOH/Ga-Ni_3S_2

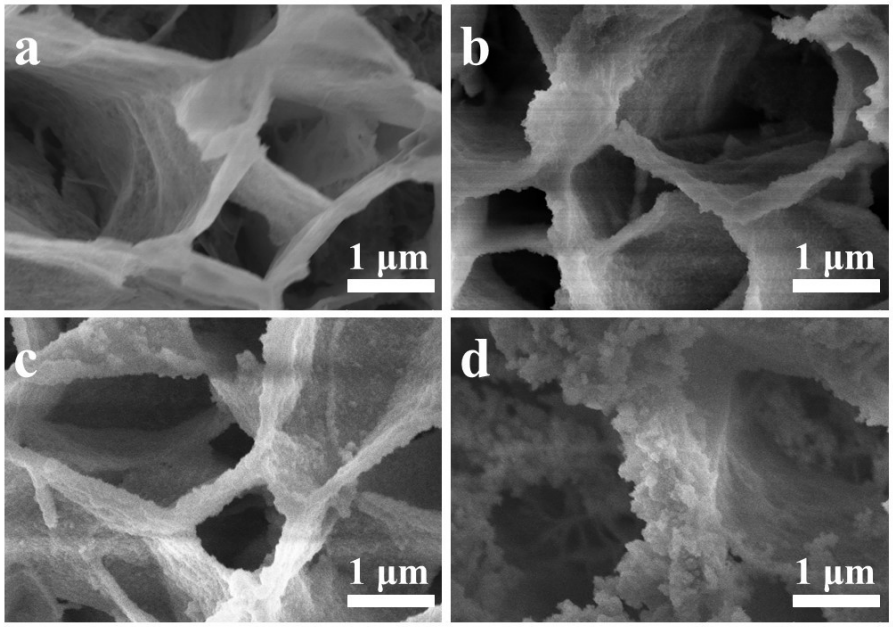

Figure S3. The SEM images of (a) Ga-Ni_3S_2, and samples with different electrodeposition durations of (b) 60 s, (c) 300 s and (d) 600 s

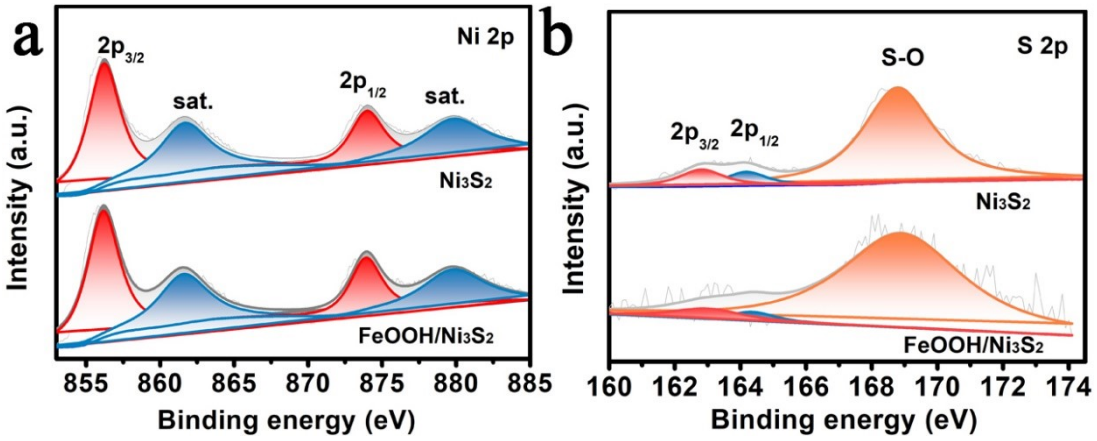

Figure S4. (a) Ni 2p and (b) S 2p XPS spectra of FeOOH/Ni_3S_2 and Ni_3S_2

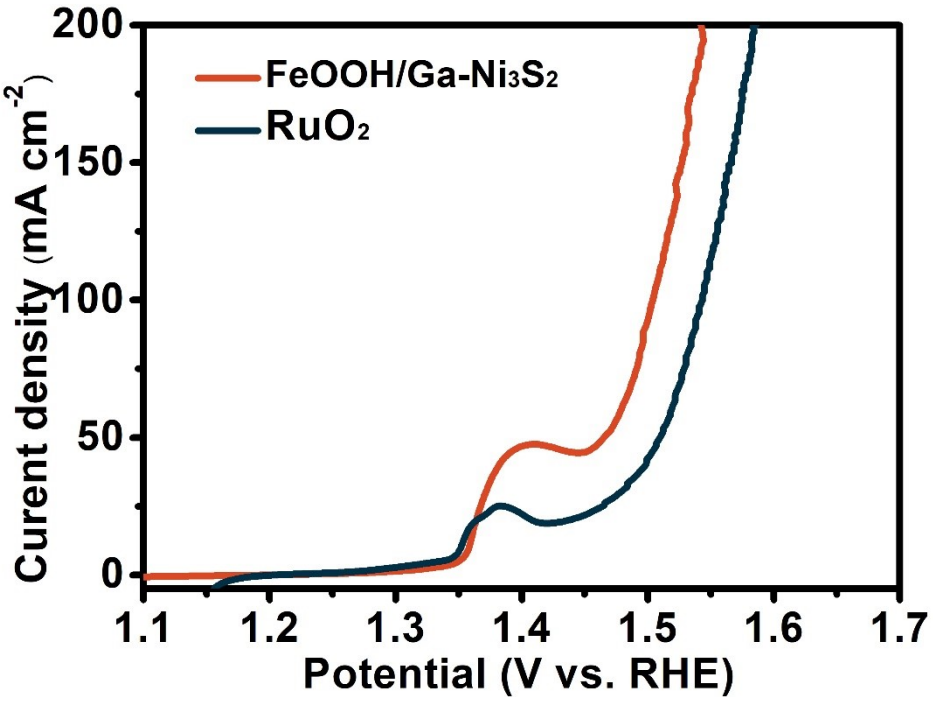

Figure S5. LSV curves of FeOOH/Ga-Ni_3S_2 and RuO2.

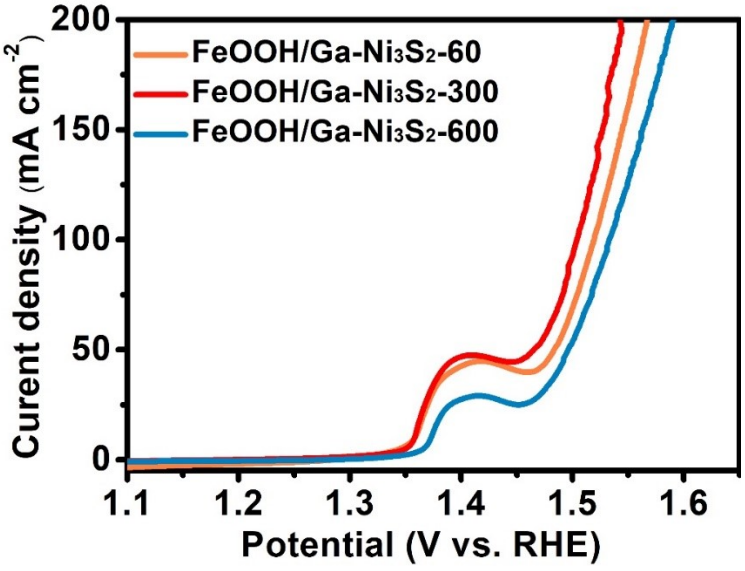

Figure S6. LSV curves of as-synthesized FeOOH/Ga-Ni_3S_2 catalysts with different electrodeposition durations: 60 s, 300 s and 600 s.

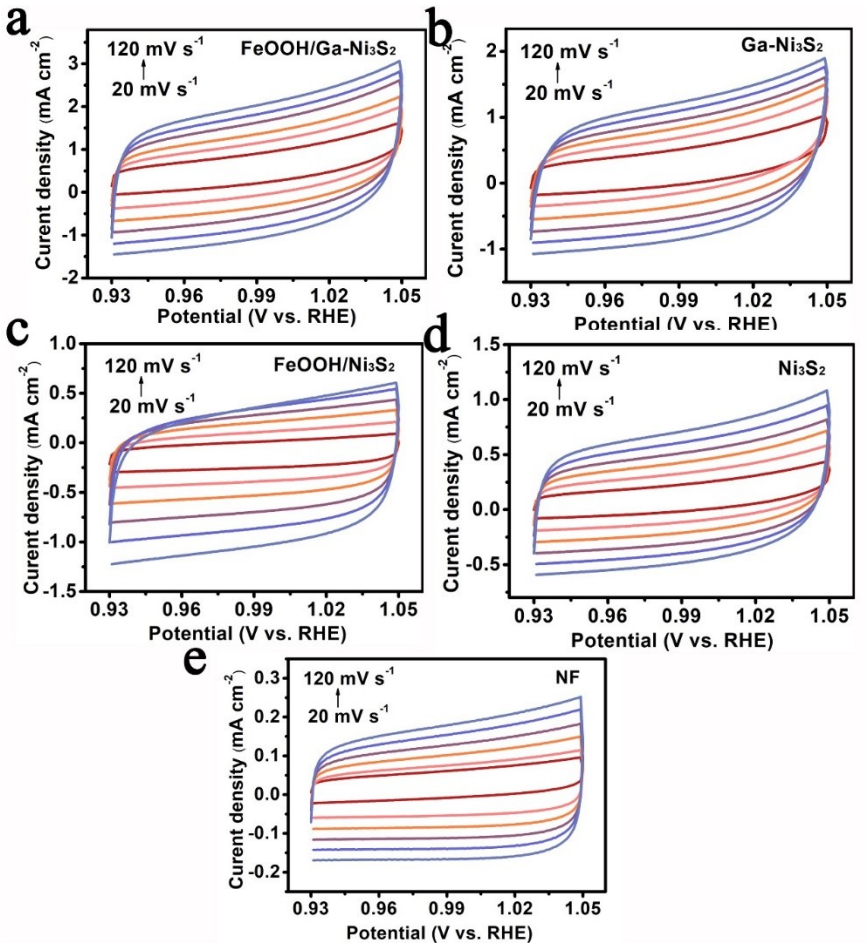

Figure S7. CV curves of (a) FeOOH/Ga-Ni_3S_2, (b) Ga-Ni_3S_2, (c) FeOOH/Ni_3S_2, (d) Ni_3S_2 and (e) NF obtained in a potential window of 0.93 to 1.05V (versus RHE) at different scan rates.

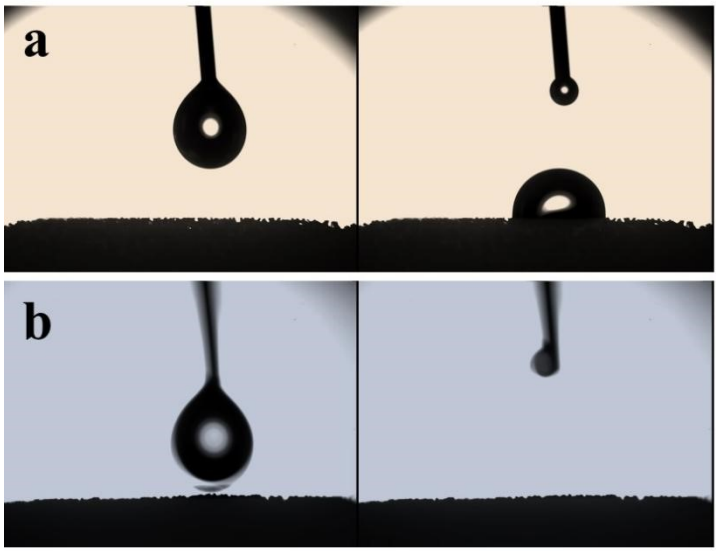

Figure S8. The wetting contact angle with a drop of water on the surface of (a) NF and (b) FeOOH/Ga-Ni_3S_2.

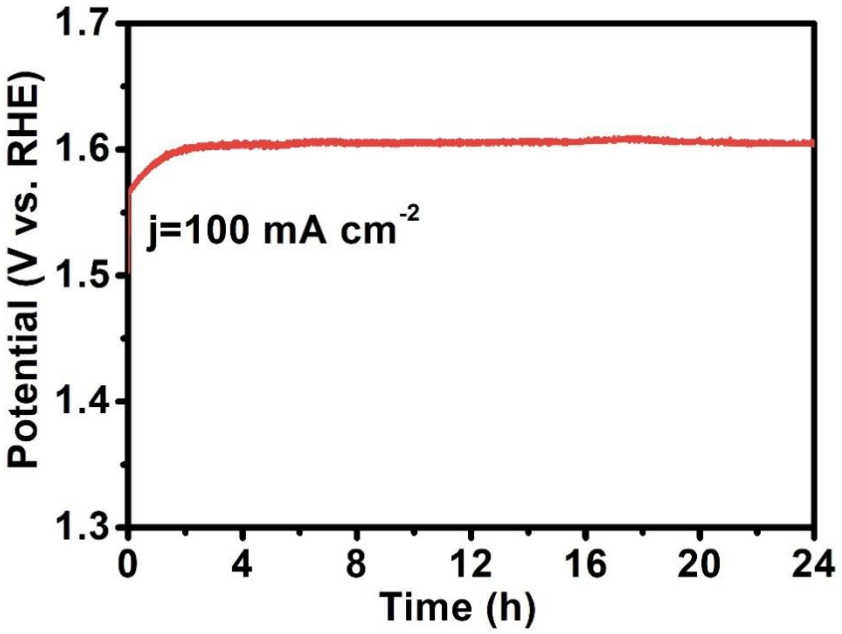

Figure S9. Chronopotentiometry curves of the FeOOH/Ga-Ni_3S_2 in 1 M KOH at a current density of 100 mA cm^{-2}

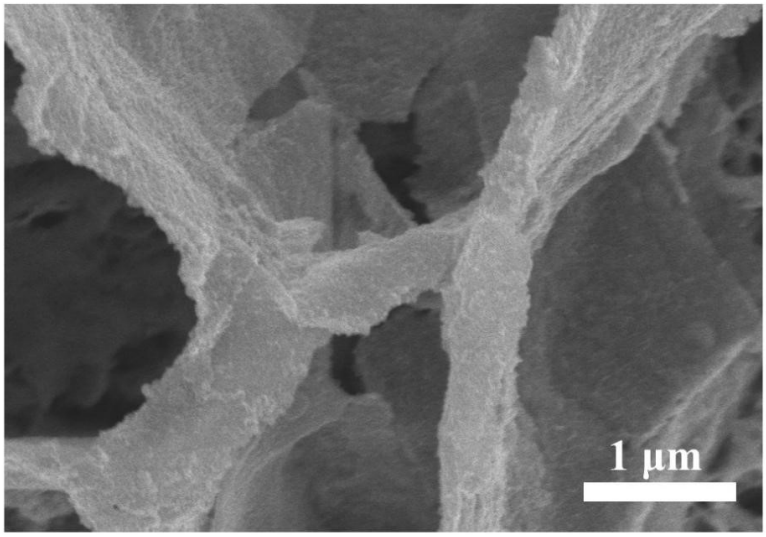

Figure S10. the SEM of FeOOH/Ga-Ni_3S_2 after the chronopotentiometry test.

Computational details

The Vienna Ab Initio Simulation Package (VASP)[1-2] was used to perform all first-principles calculations using density functional theory (DFT). In the parameterization of the Perdew Burke and Ernzerhof (PBE)[4] pseudopotential, the projector augmented wave (PAW)[3] potentials were employed in conjunction with the GGA functional to cope with the electronic exchange-correlation interaction. The wave function was represented as a plane wave with a cutoff energy of 450 eV. Geometry optimizations were carried out utilizing conjugate gradient reduction until all the forces acting on the ions were less than 0.02 eV/Å per atom. The slabs were separated using a 15 Å vacuum in the z direction. A k-point mesh with a spacing of ca. 0.03 $A^{\circ -1}$ was used in the calculations.

All calculations take long-range interactions (DFT-D3) into account as a correction[5-6]. For Fe 3d states, the U_{eff} (U - J) value of 3 eV was used. After the heterojunction is optimized and stabilized, we cut away half of the FeOOH so that we get the place where the catalysis takes place. The following equation was used to calculate free energy:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

ΔG, ΔE, ΔZPE and TΔS are the free energy, total energy from DFT calculations, zero point energy and entropic contributions (T was set to be 298.15K), correspondingly. The solvent effect is considered using VASPsol[7].

[1] Kresse G, Furthmuller J. Efficient iterative schemes forab initiototal-energy calculations using a plane-wave basis set. Phys. Rev. B 1996, 54, 11169-86.

[2] Kresse G, Furthmuller J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a planewave basis set. Comput. Mater. Sci. 1996, 6, 15-50.

[3] Kresse G, Joubert D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 1999, 59, 1758-75.

[4] Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865-8.

[5] Grimme S, Antony J, Ehrlich S, Krieg H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys., 2010, 132, 154104.

[6] Grimme S, Ehrlich S, Goerigk L, Effect of the Damping Function in Dispersion Corrected Density Functional Theory. J. Comput. Chem., 2011, 32, 1456-1465.

[7] Mathew K, Sundararaman R, Letchworth-Weaver, K, Arias T A, Hennig R G, Implicit Solvation Model for Density-Functional Study of Nanocrystal Surfaces and Reaction Pathways. J. Chem. Phys., 2014, 140, 084106.