Supporting Information

CoS₂@N-doped Carbon Core-Shell Nanorod Array Grown on Ni Foam for Enhanced Electrocatalytic Water Oxidation

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DFT Calculation.

The calculations were performed using density functional theory with the Perdew-Burke-Ernzerbof (PBE) form of generalized gradient approximation functional (GGA)[1]. The Vienna ab-initio simulation package (VASP) was adopted[2-5]. The electron wave functions were expanded using the plane waves with a cutoff energy of 400 eV. The electron occupancies were determined according to the Fermi scheme with the energy smearing of 0.1 eV. The first Brillouin zone was sampled in the Gamma

centered Monkhorst−Pack grid[6]. The 3×3×1 k-point mesh for the calculations of layered models. To avoid periodic interactions, a vacuum layer as large as 15 Å was used along the c direction normal to the surface. The energy (converged to 1.0×10^{-6} eV/atom) and force (converged to 0.01eV/Å) were set as the convergence criterion for geometry optimization. To describe the vdw interaction, the dispersion corrections DFT-D3 was employed in this work. The spin polarization was considered in all calculations due to the existence of magnetism atom. To reduce the lattice mismatch between graphene and CoS_2, one layer and (3×3) supercell of graphene randomly doped with one N atom, and three layers and (2×2) supercell of CoS_2 (111) were chosen to construct the complex structures in our model.

According to the method developed by Nørskov et al[7], the Gibbs free energy change (ΔG_{ads}) for OER steps in this work is calculated as follows:

$$\Delta G_{ads} = \Delta E + \Delta ZPE - T\Delta S$$

where ΔE is the energy difference between two intermediates on the catalyst, ΔZPE is the difference in zero-point energy between two intermediates. ΔS is the entropy change of two intermediates and T is room temperature (298.15 K). ZPE values could be derived after frequency calculation by:[8]

$$ZPE = \frac{1}{2}\sum hv_i$$

TS values of adsorbed species were calculated after obtaining the vibrational frequencies:[9]

$$TS_v = k_B T \left[\sum\nolimits_K \ln(\frac{1}{1-e^{-hv/k_B T}}) + \sum\nolimits_K \frac{hv}{k_B T} \frac{1}{(e^{hv/k_B T}-1)} \right]$$

where K_B is the Boltzmann constant, v is vibrational frequency for the intermediates, which are obtained from DFT calculations using VASP.
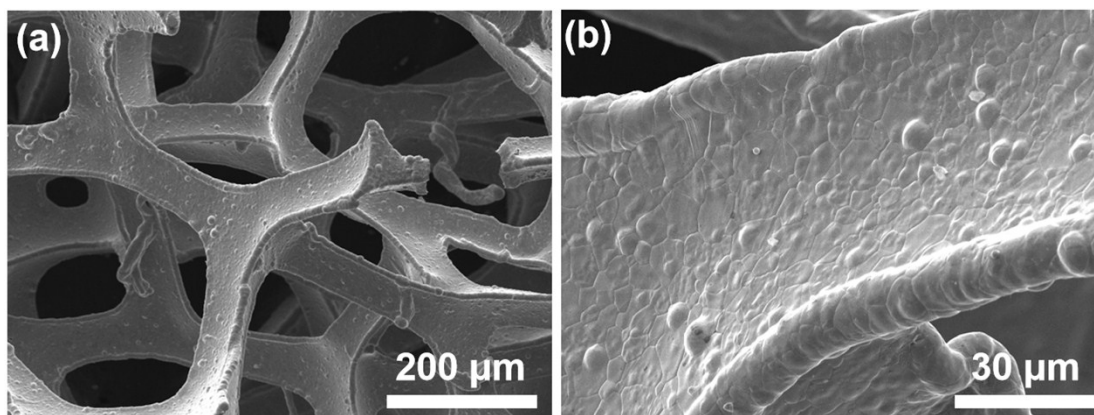
Additional Tables and Figures

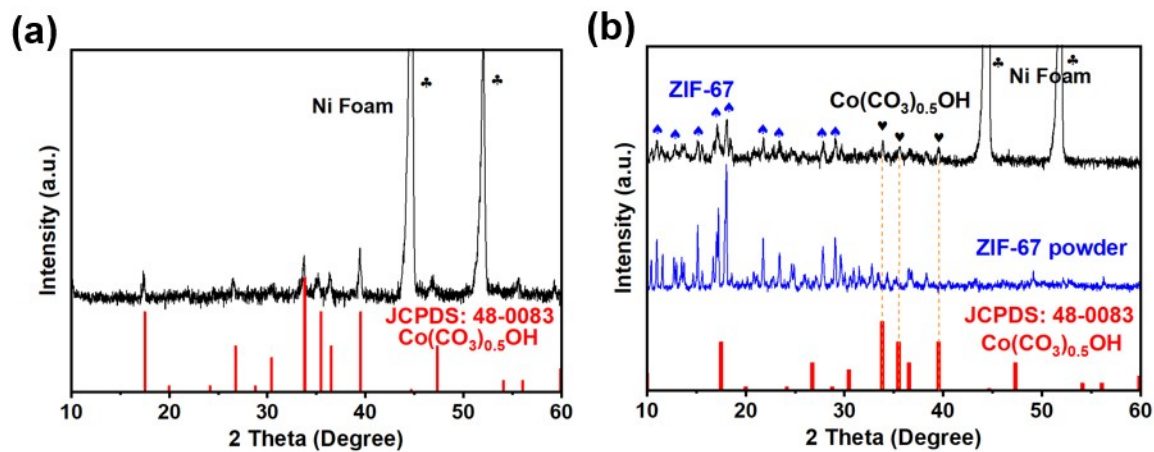**Fig. S1.** SEM images of the electrode surface of Ni foam after published procedure.

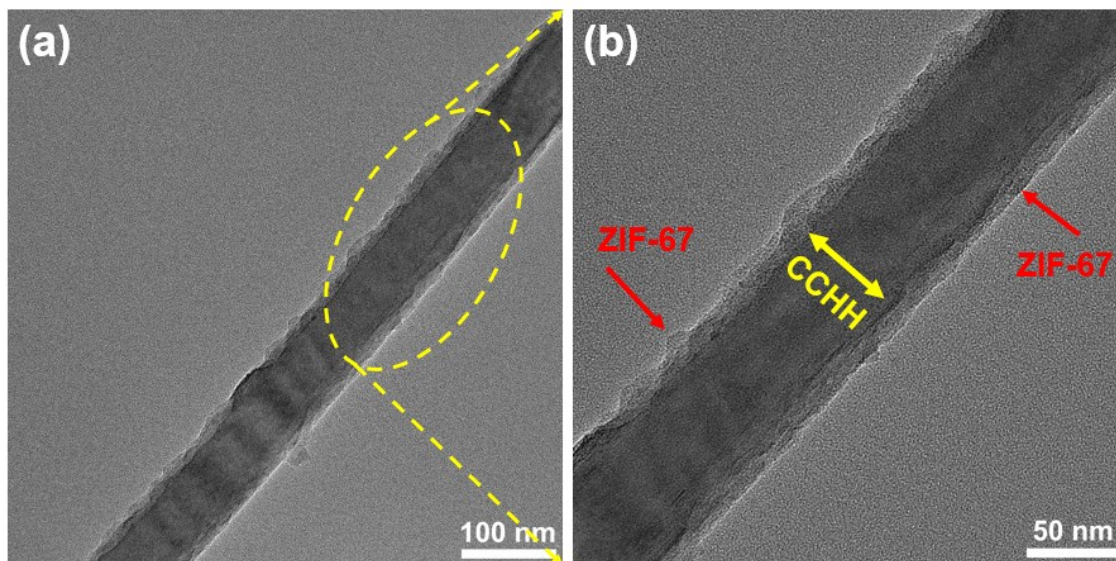**Fig. S2.** XRD patterns of (a) CCHH@NF and (b) ZIF-67@CCHH@NFs, respectively.
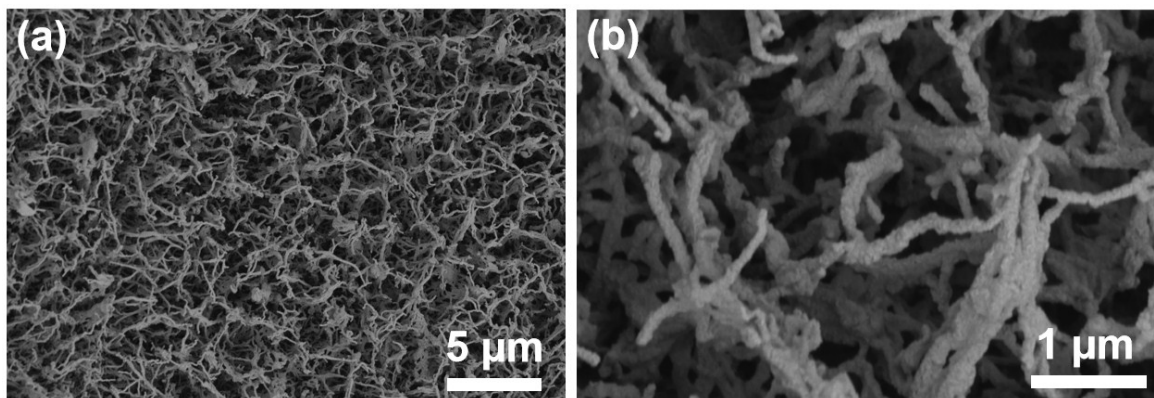

Fig. S3. TEM images of the ZIF-67@CCHH.
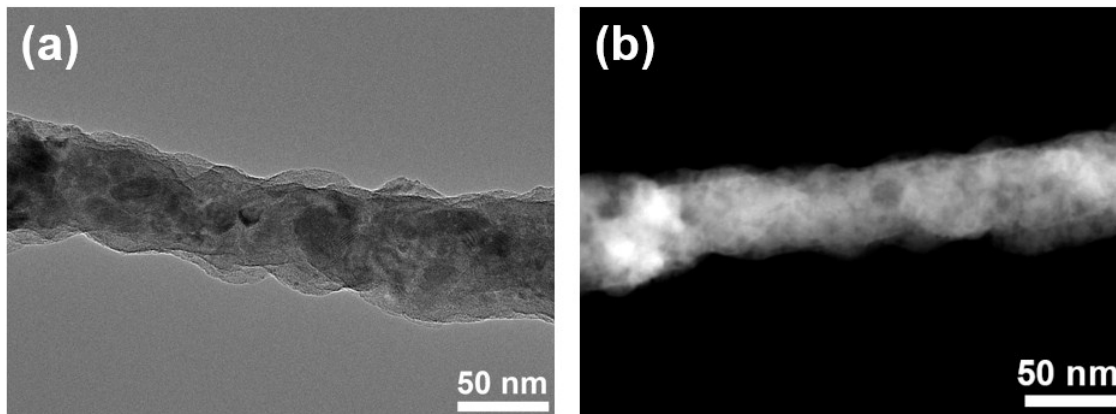
Fig. S4. SEM images of the CoS$_2$@NF.

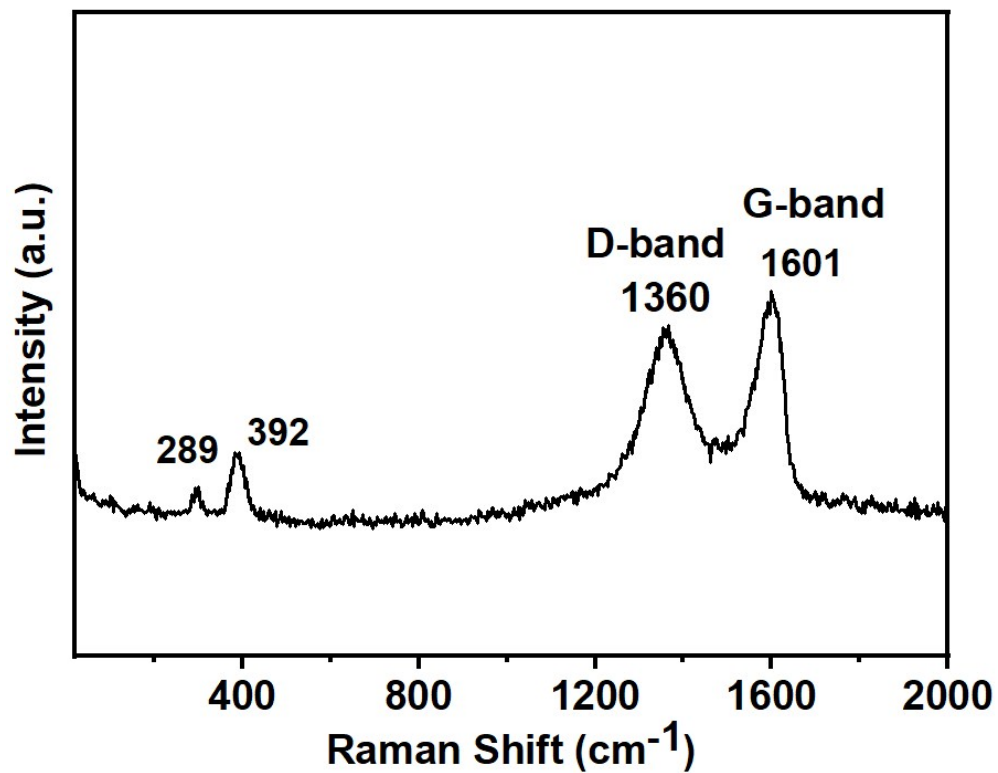**Fig. S5**. (a) TEM and (b) HAADF-STEM images of CoS$_2$@NGC.

Fig. S6. Raman spectra of CoS$_2$@NGC.
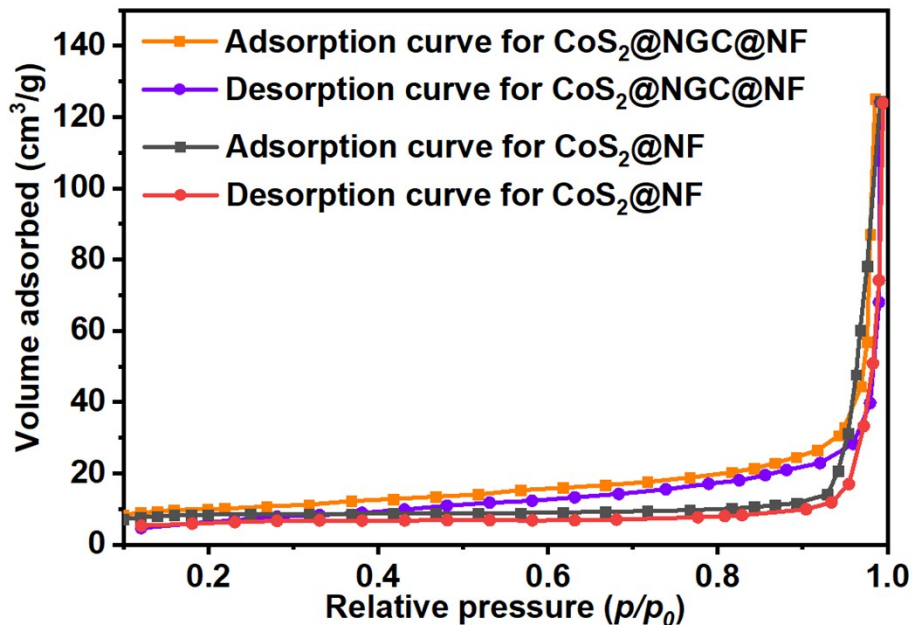
Fig. S7. Nitrogen adsorption/desorption isotherms of the CoS_2@NGC@NF and CoS_2@NF, respectively.

Catalyst	Overpotential (mV) @10 mA mg^{-2}	Current density (mA mg^{-2}) @1.53 V. RHE
NF	395	3.4
CCHH@NF	358	23.5
ZIF-67@CCHH@NF	303	9.53
CoS_2@NF	277	54.7
CoS_2@NGC@NF	246	103.0

Fig. S8. (a) LSV curves (Figure 4a in the main text) normalized by the loading amount, (b) the OER catalytic performance of the different electrodes.

Fig. S9. The polarization curves before and after the durability test for 20 h in 1.0 M KOH.

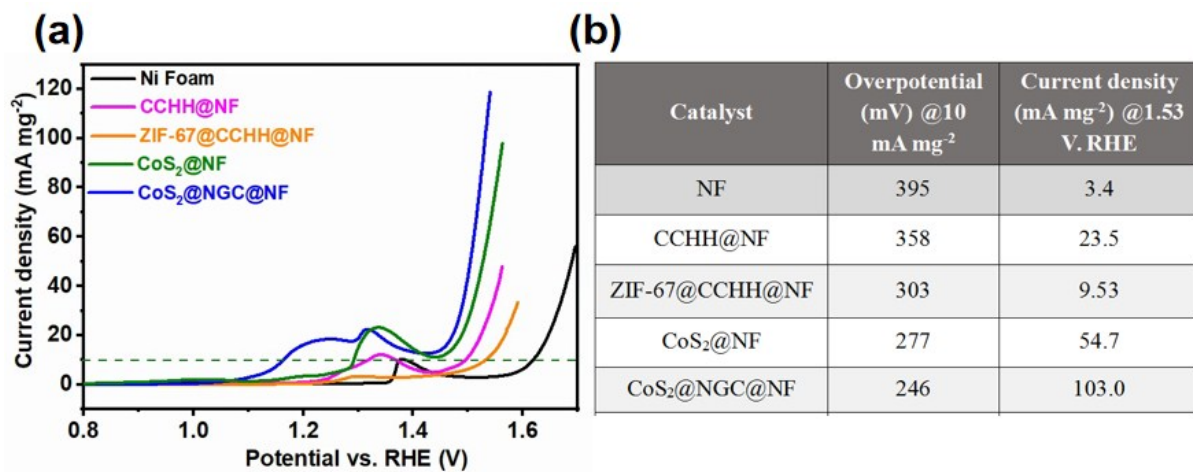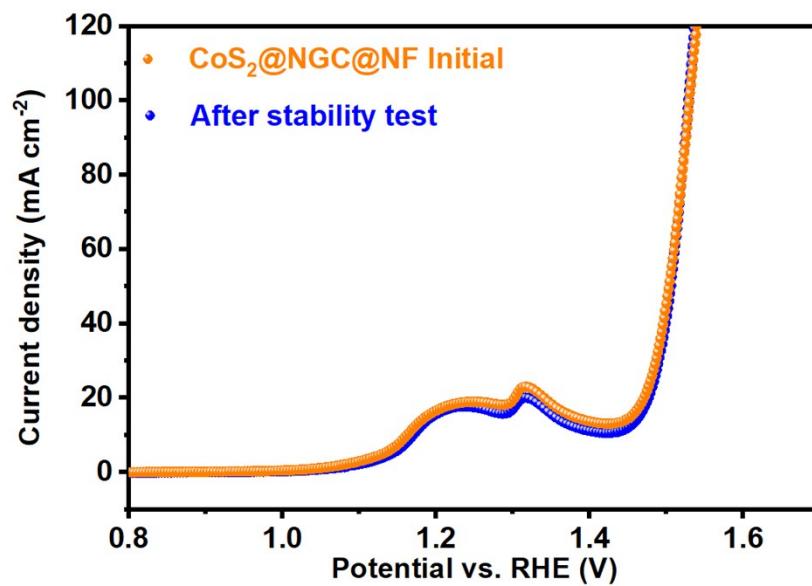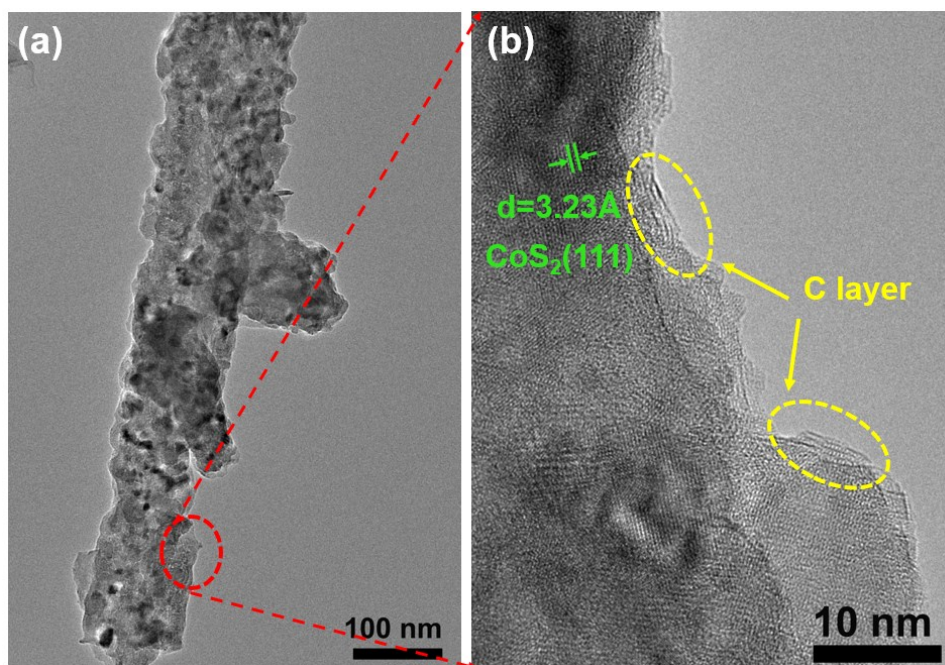
Fig. S10. (a,b) TEM image of CoS$_2$@NGC@NF after the durability test for 20 h in 1.0 M KOH.
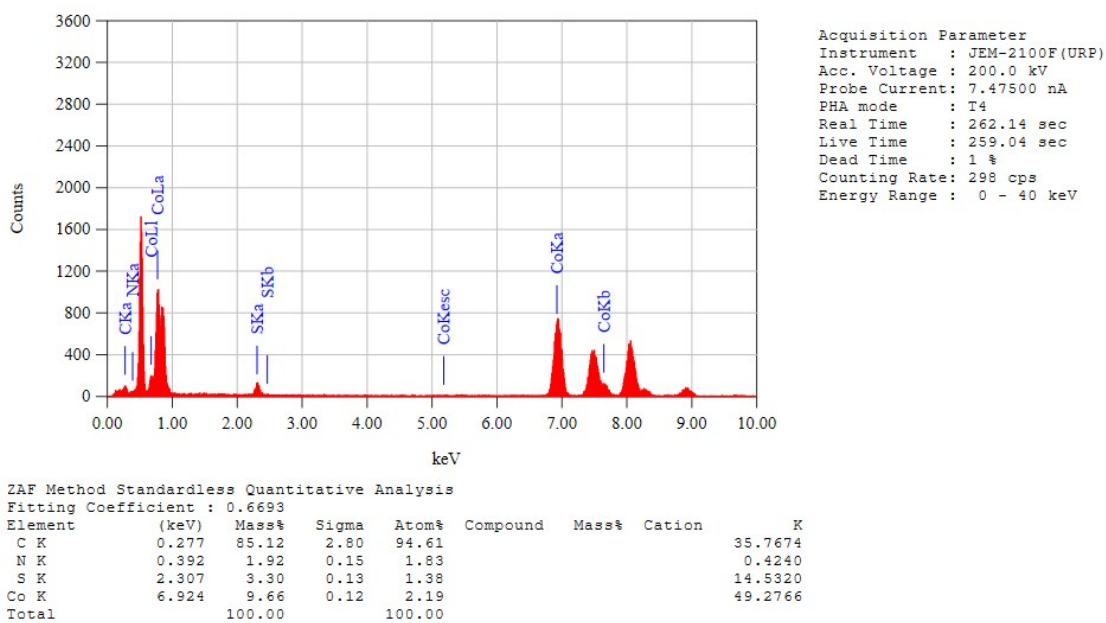
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                                              Acquisition Parameter
                                              Instrument   : JEM-2100F(URP)
                                              Acc. Voltage : 200.0 kV
                                              Probe Current: 7.47500 nA
                                              PHA mode     : T4
                                              Real Time    : 262.14 sec
                                              Live Time    : 259.04 sec
                                              Dead Time    : 1 %
                                              Counting Rate: 298 cps
                                              Energy Range :  0 - 40 keV
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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.6693
Element    (keV)   Mass%   Sigma   Atom%  Compound  Mass%  Cation        K
 C K       0.277   85.12   2.80    94.61                              35.7674
 N K       0.392    1.92   0.15     1.83                               0.4240
 S K       2.307    3.30   0.13     1.38                              14.5320
Co K       6.924    9.66   0.12     2.19                              49.2766
Total             100.00          100.00
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Fig. S11. The energy-dispersive X-ray spectrum of CoS_2@NGC@NF after the durability test for 20 h in 1.0 M KOH.
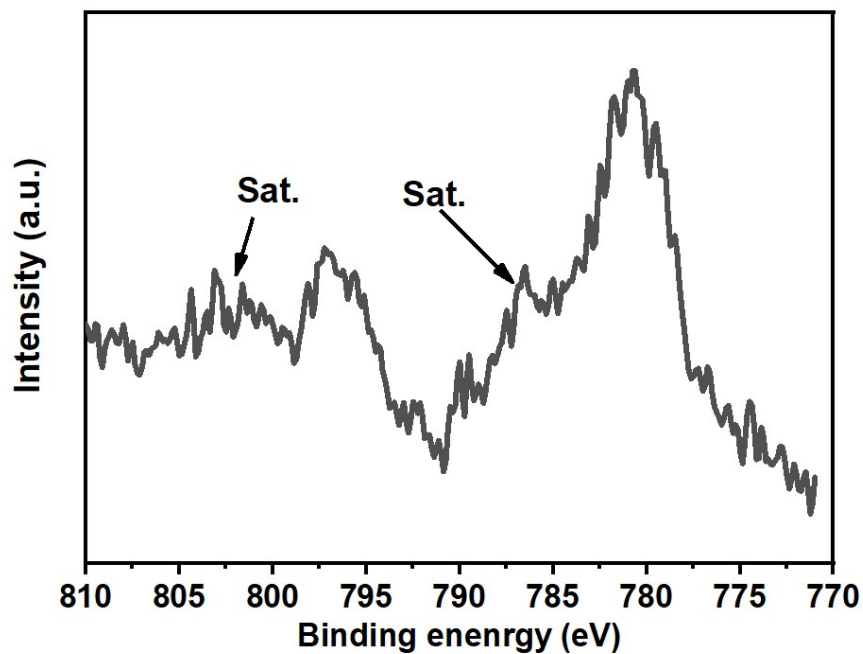
Fig. S12. The Co 2p XPS spectrum of CoS_2@NGC@NF after the durability test for 20 h in 1.0 M KOH. The two typical satellite peaks show decreased signal after durability test, which is likely due to the in situ generated partial Co oxide species (e.g., Co_3O_4 and CoOOH) during the OER. However, it is difficult to distinguish the typical Co^{3+} core level singles from Co^{2+} by fitting treatment because they are too close.
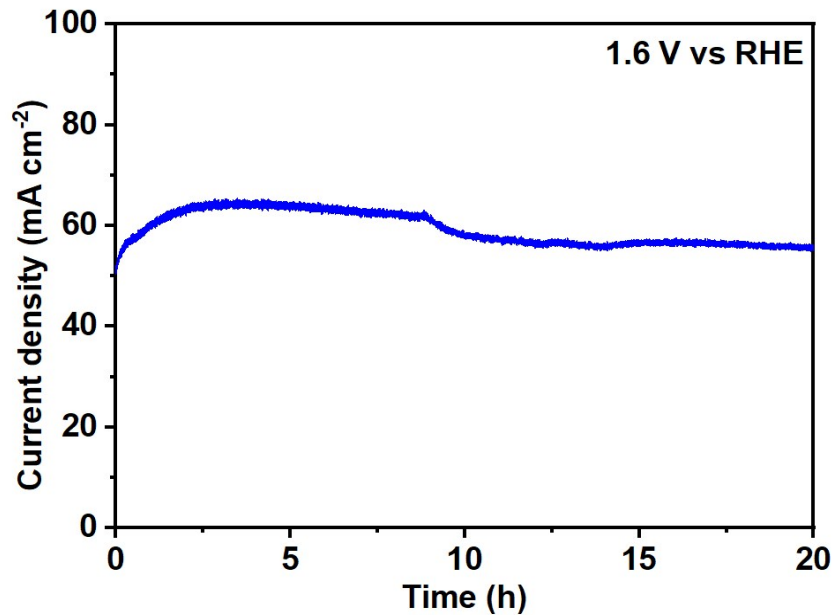
Fig. S13. The chronoamperometric durability test for CoS$_2$@NF under a constant bias of 1.6 V versus RHE.
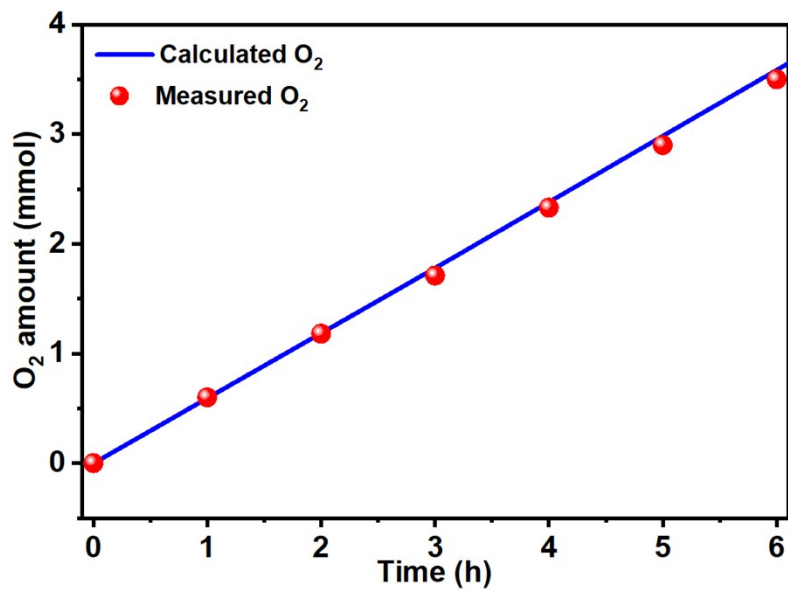

Fig. S14. The amount of O$_2$ (theoretically calculated and experimentally measured at 1.6 V versus RHE) vs. time for oxygen evolution reaction.
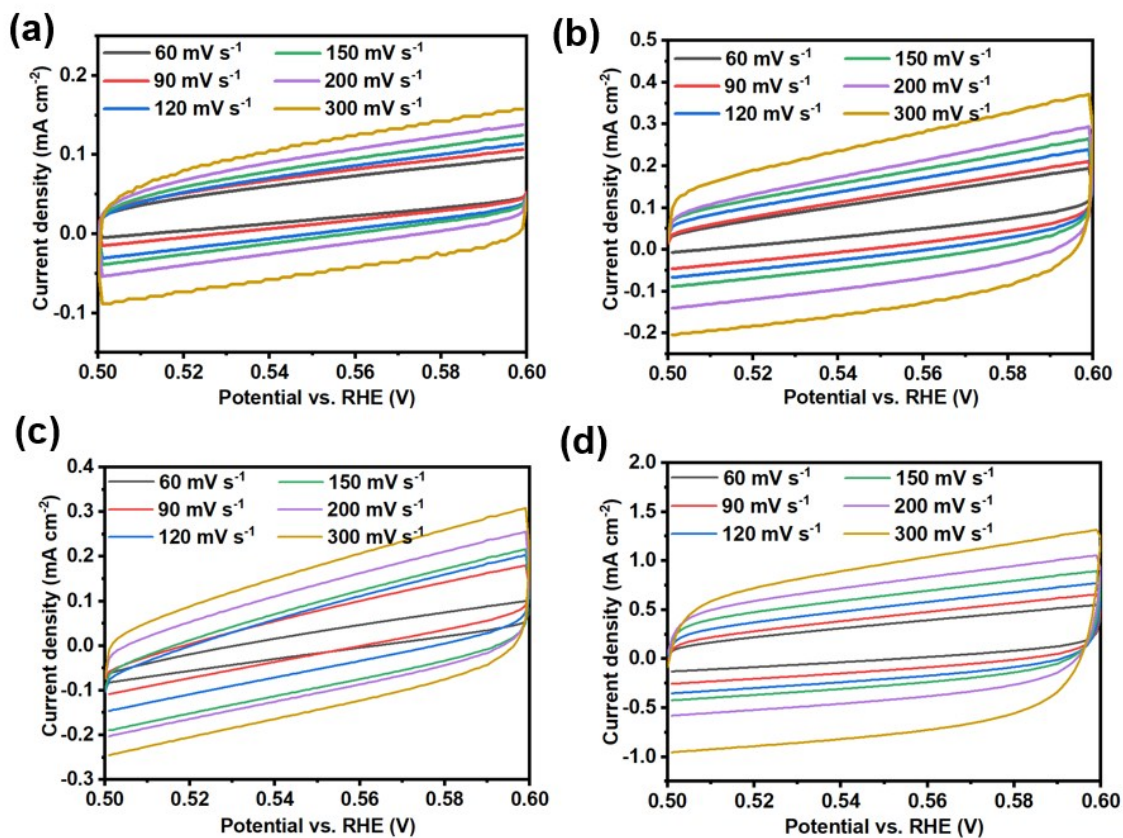
Fig. S15 Typical cyclic voltammogram shows the capacitive current for the (a) CCHH@NFs, (b) ZIF@CCHH@NFs, (c) CoS$_2$@NFs, and CoS$_2$@NGC@NF at six different scan rates from 60 to 300 mV/s.
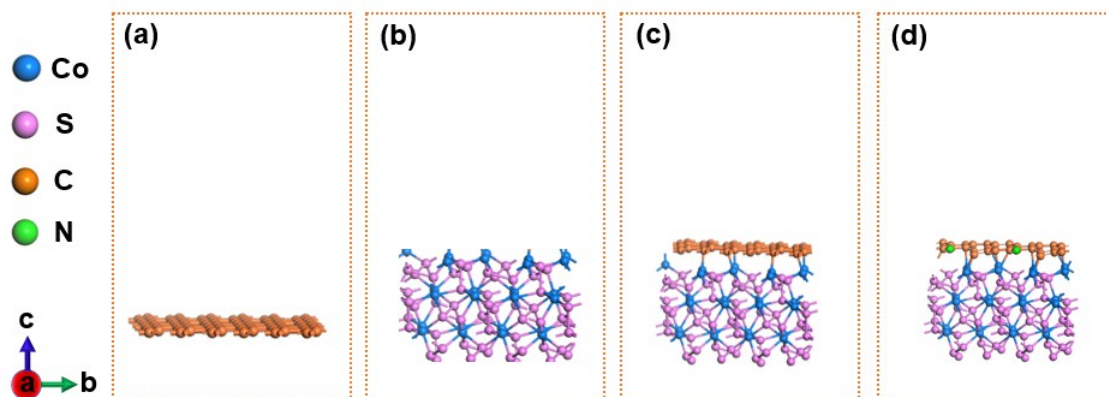
Fig. S16. Atomic structure of (a) C, (b) CoS_2, (c) CoS_2/C, and (d) CoS_2/NG for DFT calculations.
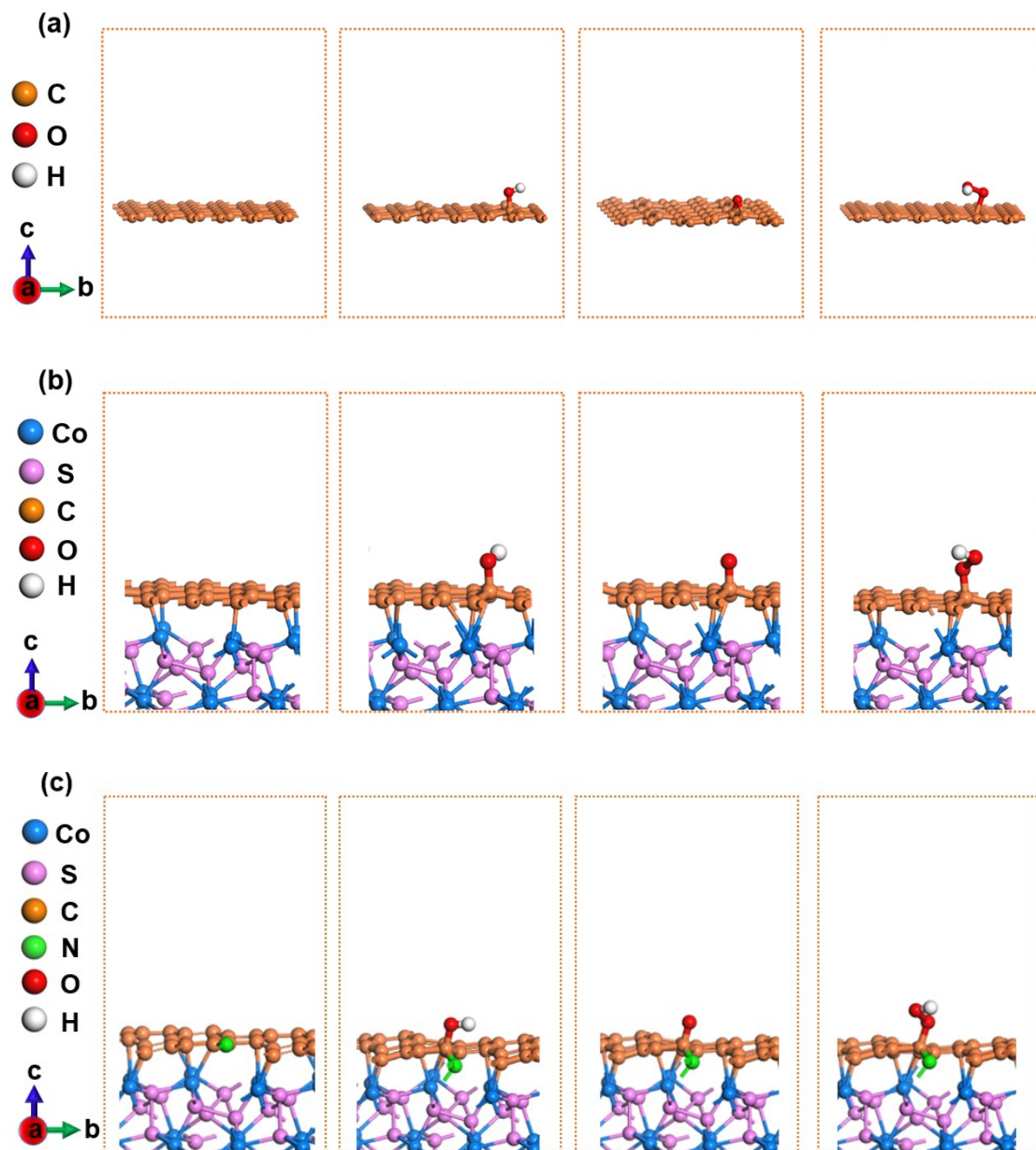

Fig. S17. The optimized atomic models for intermediates adsorptions on (a) C, (b) CoS_2/C, and (c) CoS_2/NC, respectively.

Table S1. Comparison of the OER catalytic performance of the CoS_2@NGC@NF electrode and the metal-based sulfides reported in literature (in 1.0 M KOH).

Catalyst	Overpotential (mV) @10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Stability	Substrate	References
CoS_2@NGC	**243**	**71**	**At 65 mA cm^{-2} for 20 h**	**Ni Foam**	**This work**
Co_3S_4/EC-MOF	226	120	At 1.65 V versus RHE for **20** h	Carbon Cloth	*Adv. Mater.* **2019**, 31, 1806672
Ni_3S_4	257	67	At 50 mA cm^{-2} for **300** h	Ni Foam	*Adv. Funct. Mater.* **2019**, 1900315.
Mo-Co_9S_8@C	200	95.6	At 10 mA cm^{-2} for **20** h	Carbon Cloth	*Adv. Energy Mater.* **2019**, 1903137.
Pt-CoS_2/CC	300	58	At 1.53 V versus RHE for **50** h	Carbon Cloth	*Adv. Energy Mater.* **2018**, 27, 1800935.
Fe-Ni_3S_2	214	42	At 1.5 V versus RHE for **20** h	Ni Foam	*ACS Catal.* **2018**, 8, 5431.
S, N-CNTs/ CoS_2@Co	340	76.1	–	Glassy Carbon	*Science Bulletin* **2018**, 63, 1130.
Co_9S_8/NSCNFs	302	54	At 1.55 V versus RHE for **10** h	Glassy Carbon	*Small* **2018**, 14, 1704035.
CeO_x/CoS/CC	232	50	At ~1.48 V versus RHE for **20** h	Carbon Cloth	*Angew. Chem., Int. Ed.* **2018**, 57, 8654.
Co_9S_8@N-doped Carbon	302	67	–	Glassy Carbon	*J. Mater. Chem. A* **2018**, 6, 10304
$Co_{1-x}Ni_xS_2$–graphene	330	47	At 1.6 V versus RHE for **7** h	Glassy Carbon	*ACS Catal.* **2018**, 8, 4091.
Fe-Ni_3S_2	214	42	At 1.5 V versus RHE for **20** h	Ni Foam	*ACS Catal.* **2018**, 8, 5431.
NiS_2/CoS_2–O NWs	235	31	At 10 mA cm^{-2}	Carbon	Adv. Mater.

			for **70** h	cloth	**2017**, 29, 1704681.
Cu@CoS$_x$/CF	160	–	At 100 mA cm^{-2} for **20** h	Copper foam	*Adv. Mater.* **2017**, 29, 1606200.
Amorphous CoS$_x$	290	67	At 1.56 V versus RHE for **5.56** h	Glassy Carbon	*Angew. Chem., Int. Ed.* **2017**, 56, 4858
NiCo$_2$S$_4$	260	40.1	At 10 mA cm^{-2} for **50** h	Ni Foam	*Adv. Funct. Mater.* **2016**, 26, 4661.
MoS$_2$/Ni$_3$S$_2$	218	88	At 10 mA cm^{-2} for **10** h	Ni Foam	*Angew. Chem.* **2016**, 128, 6814.

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