Supporting Information (SI):

Vanadium-mediated ultrafine Co/Co_9S_8 nanoparticles anchored on Co-N-doped mesoporous carbon enable efficient hydrogen evolution and oxygen reduction reactions

*Danyang He,[a] Liyun Cao,[*a] Jianfeng Huang[a], Linlin Wang,[a] Guodong Li,[b] Zhenting Liu,[a] Yongqiang Feng,[a] Yijun Liu,[c] Limin Pan[c] and Liangliang Feng[*a]*

[a] *School of Materials Science & Engineering, International S&T Cooperation Foundation of Shaanxi Province, Xi'an Key Laboratory of Green Manufacture of Ceramic Materials, Shaanxi Key Laboratory of Green Preparation and Functionalization for Inorganic Materials, Key Laboratory of Auxiliary Chemistry and Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science & Technology, Xi'an Shaanxi, 710021, P.R. China*

[b] *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China.*

[c] *Guangdong Mona Lisa Group Co. Ltd., Foshan, Guangdong 528211, PR China.*

** Corresponding authors, E-mail address: 2644245930@qq.com (L. Cao), fengll@sust.edu.cn (L. Feng)).*

Number of pages: S15

Number of Figures: S17

Number of tables: 2

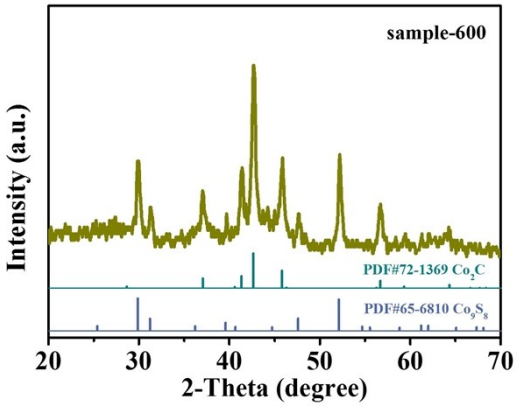

Fig. S1 XRD pattern of sample-600 catalyst.

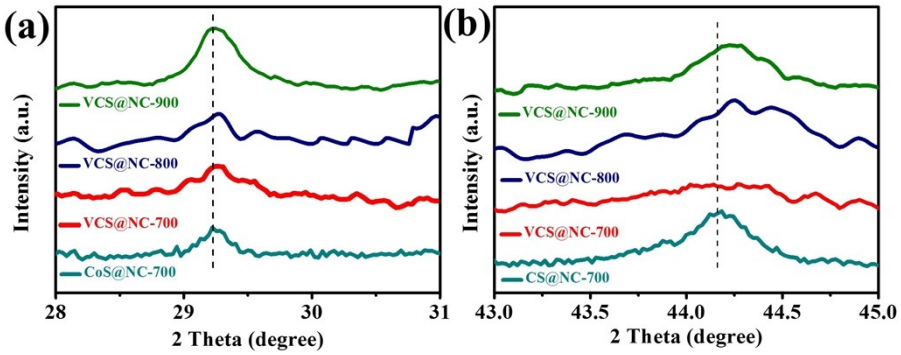

Fig. S2 XRD patterns of as-prepared samples with zoomed-in image.

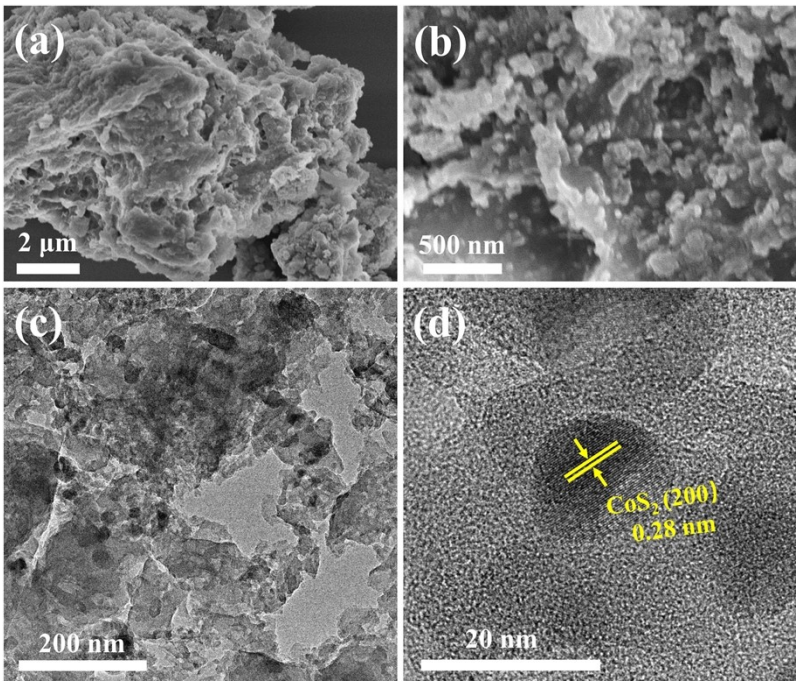

Fig. S3 Structural and morphologic characterization of CoS_2@g-C_3N_4: (a, b) SEM images with different magnifications; (c) low magnification TEM image; (d) HRTEM image.

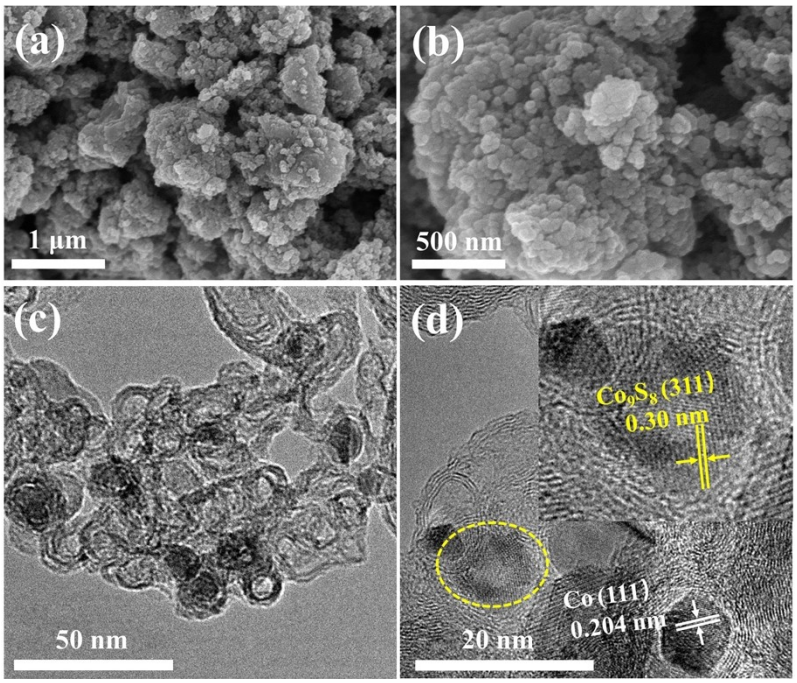

Fig. S4 Structural and morphologic characterization of CS@NC-700: (a, b) SEM images with different magnifications; (c) low magnification TEM image; (d) HRTEM image.

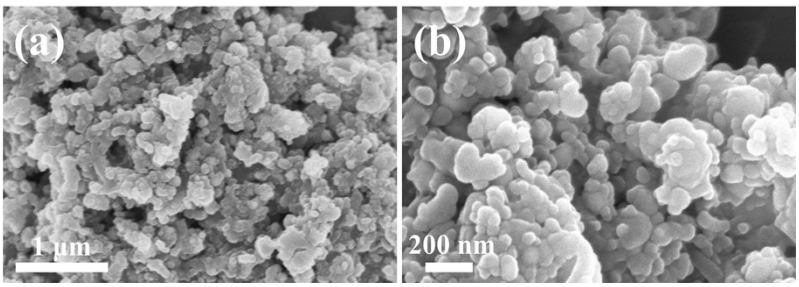

Fig. S5 SEM images of VCS@NC-700 sample with different magnifications: (a) ×30 k; (b) ×100 k.

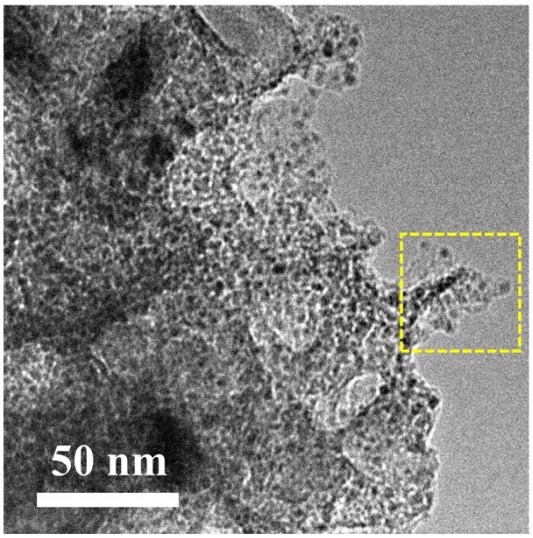

Fig. S6 TEM image of VCS@NC-700 sample.

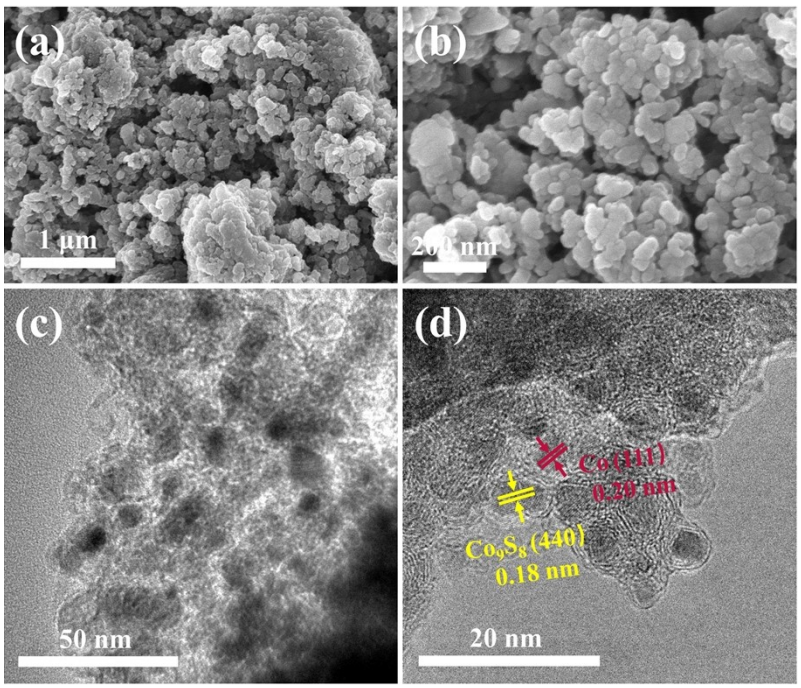

Fig. S7 Structural and morphologic characterization of VCS@NC-800: (a, b) SEM images with different magnifications; (c) low magnification TEM image; (d) HRTEM image.

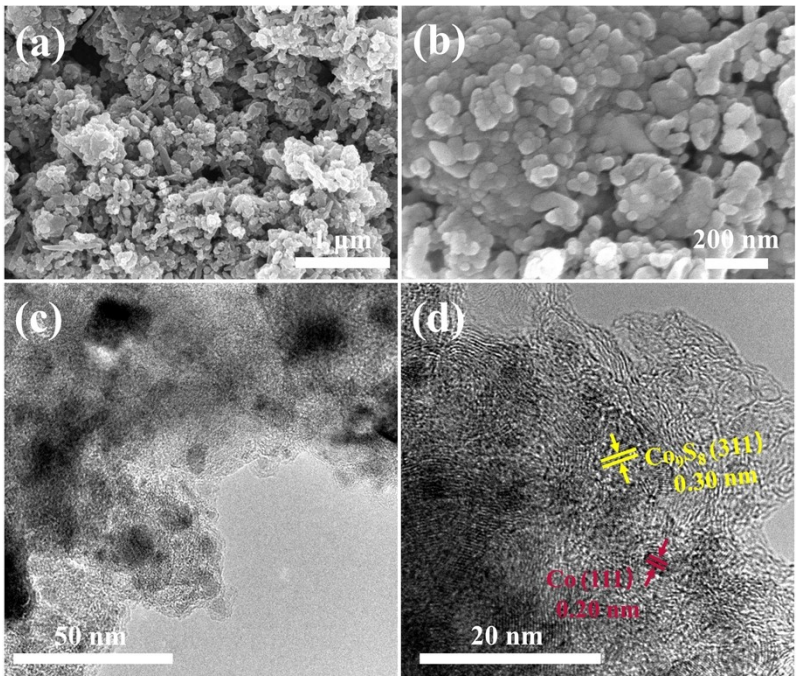

Fig. S8 Structural and morphologic characterization of VCS@NC-900: (a, b) SEM images with different magnifications; (c) low magnification TEM image; (d) HRTEM image.

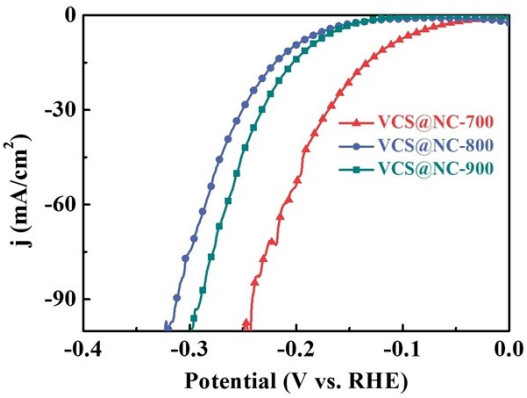

Fig. S9 LSV polarization curves of VCS@NC-700, VCS@NC-800 and VCS@NC-900 catalysts in 1.0 M KOH solution.

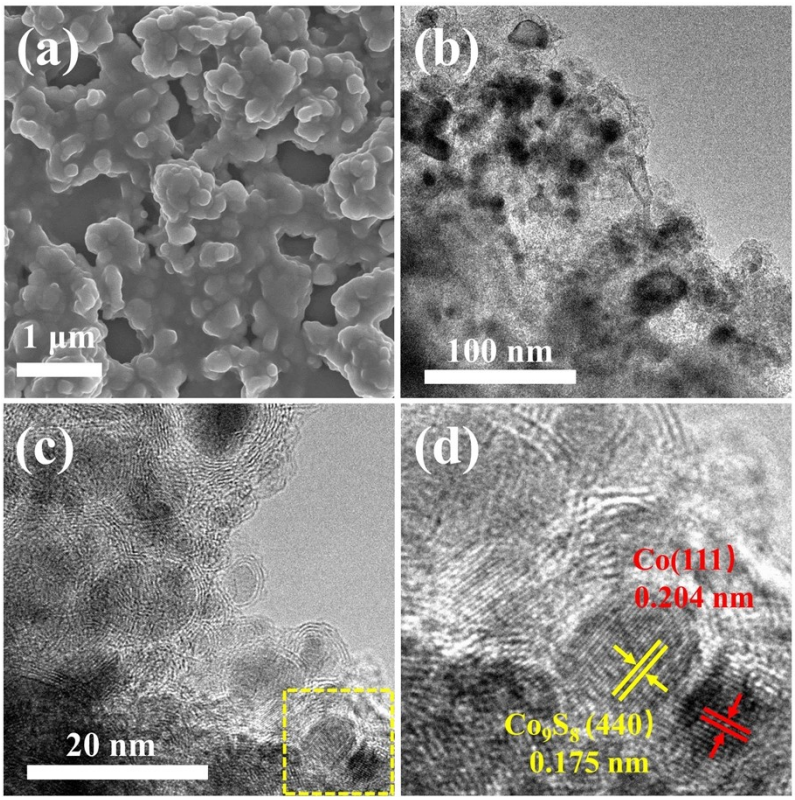

Fig. S10 Structural and morphologic characterization of VCS@NC-700 after durability test for 100 h in 1.0 M KOH: (a) SEM image; (b) low magnification TEM image; (c) HRTEM image and (d) the magnified area of the corresponding lattice fringes.

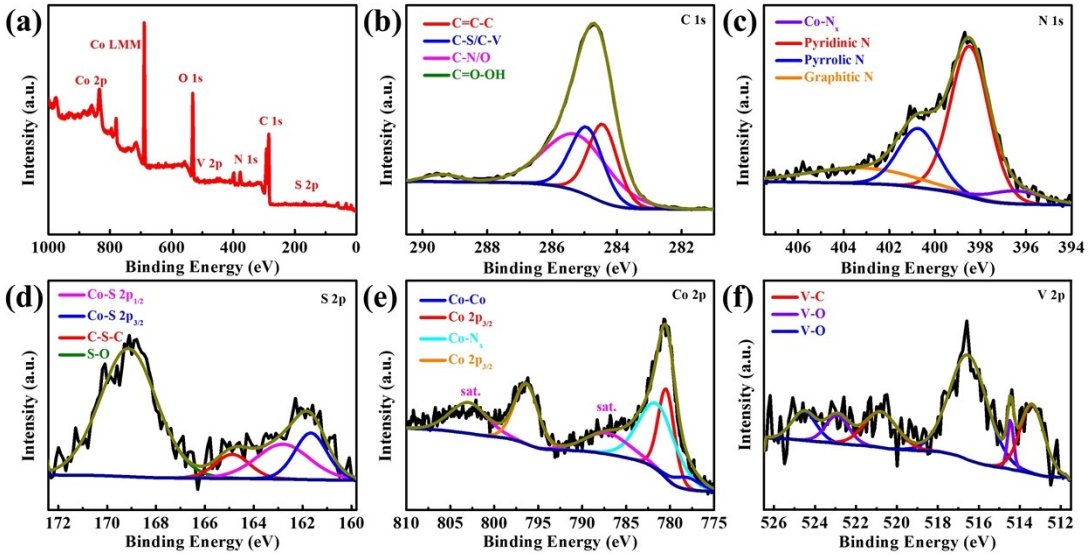

Fig. S11 XPS spectra of the VCS@NC-700 after HER electrochemical test in 1.0 M KOH:

(a) survey; (b) C 1s; (c) N 1s; (d) S 2p; (e) Co 2p; (f) V 2p.

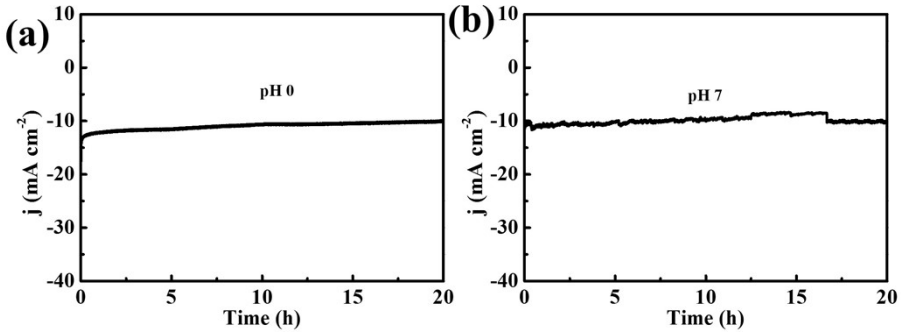

Fig. S12 Chronoamperometric profiles of VCS@NC-700 in (a) acidic and (b) neutral solutions.

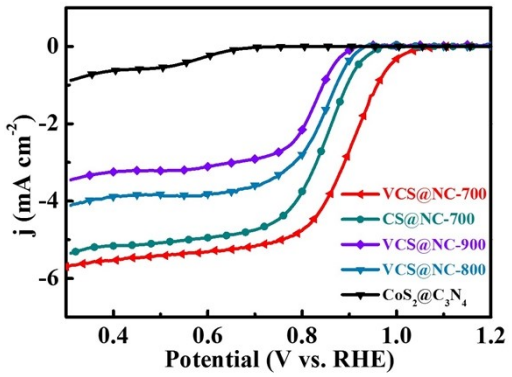

Fig. S13 LSV curves of the as-synthesized samples in O_2-saturated 0.1 M KOH with the sweep rate of 5 mV s^{-1} at 1600 rpm.

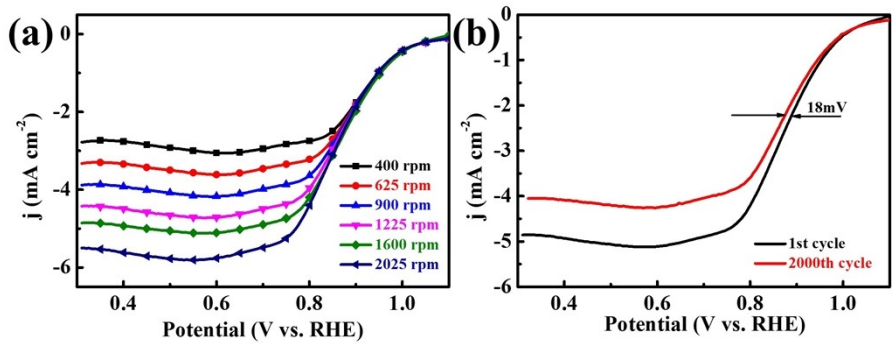

Fig. S14 LSV curves of the 20wt% Pt/C catalyst at a sweep rate of 5 mV s^{-1} with the different rotation speeds ranging from 400 to 2025 rpm and (b) the stability test of 20wt% Pt/C after 2000 cycles in O_2-saturated 0.1 M KOH solution.

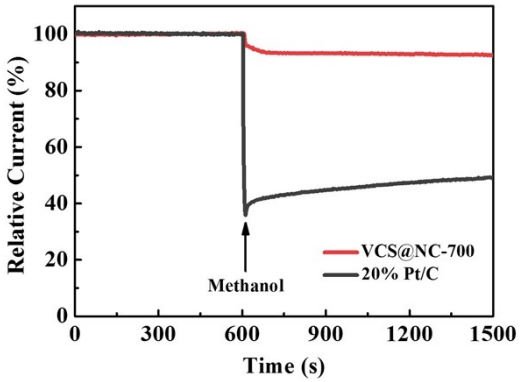

Fig. S15 Chronoamperometric response of VCS@NC-700 and 20% Pt/C before and after addition of 10 ml 3.0 M methanol at 600 s.

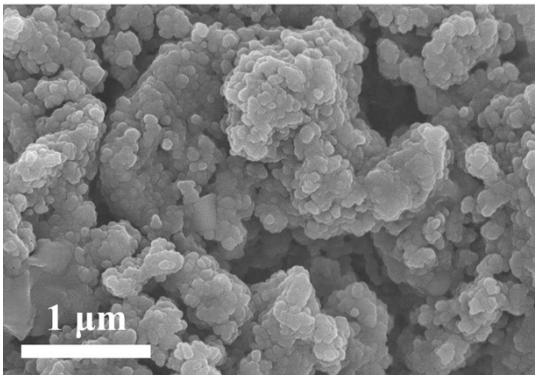

Fig. S16 SEM image of VCS@NC-700 after 2000 cycles in O_2-saturated 0.1 M KOH solution.

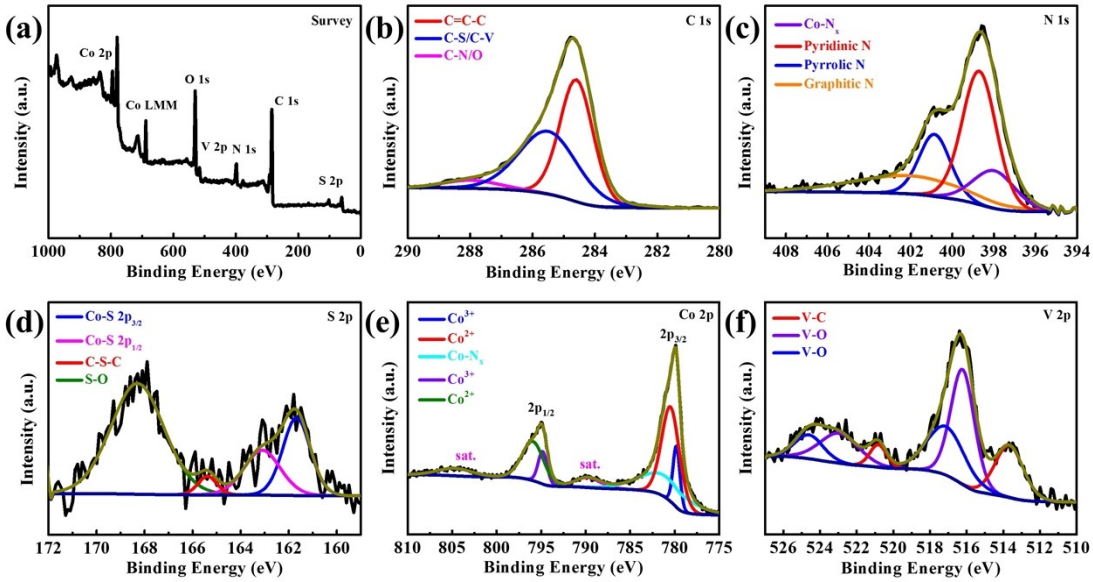

Fig. S17 XPS spectra of the VCS@NC-700 after ORR electrochemical stability test in 0.1M KOH: (a)Survey; (b) C 1s; (c) N 1s; (d) S 2p; (e) Co 2p; (f) V 2p.

Table S1. Electrocatalytic HER performance of the VCS@NC-700 electrode compared with those of reported Co_9S_8-based carbon electrocatalysts in pH-universal electrolytes.

Catalysts	Electrolytes	Loading amount(mg cm^{-2})	Current density (j, mA cm^{-2})	Overpotential at corresponding j (mV)	Stability test	Reference
VCS@NC-700	1.0 M KOH	2.80	10	117	100 h	This work
	0.5 M H_2SO_4			178	20 h	
	1.0 M PBS			210	20 h	
Co_9S_8/MoS_2@NSOC	1.0 M KOH	2.80	10	194	12 h	J. Energy Chem., 2020, 44, 90-96
	0.5 M H_2SO_4			233	12 h	
Co_9S_8@N-S-HPC	1.0 M KOH	0.26	10	173	1000 cycles	Appl. Catal, B-Environ., 2019, 254, 186-193
CFP@Co_9S_8@C	1.0 M KOH	1.61	10	290	30 h	J. Mater. Chem. A, 2018, 6, 14752-14760
CoS_x	1.0 M KOH	/	10	127	36 h	J. Mater. Chem. A, 2018, 6, 7592-7607
Co-MOFs@GO	1.0 M KOH	0.31	10	~310	1000 cycles	Nano Energy, 2016, 30, 93-102
Co_9S_8/WS_2/Ti foil	1.0 M KOH	2.20	10	138	24 h	J. Mater. Chem. A, 2017, 5, 23361-23368
Co_9S_8-Ni_xS_y/NF	1.0 M KOH	9.00	10	163	70 h	J. Mater. Chem. A, 2016, 4, 9744-9749
Co_9S_8/CC	1.0 M PBS	0.40	10	175	100 h	J. Mater. Chem. A, 2016, 4, 6860-6867
CoP/Co_9S_8	1.0 M KOH	/	10	155	10 h	ACS Appl. Mater. Interfaces, 2019, 11, 9023-9032
Co_9S_8-NSC@Mo_2C	1.0 M KOH	0.43	10	89	50000s	ACS Appl. Mater. Interfaces, 2018, 10, 22291-22302
	0.5 M H_2SO_4			74	48 h	
	1.0 M PBS			121	20 h	
Co_9S_8/NC@MoS_2	1.0 M KOH	0.28	10	67	12 h	ACS Appl. Mater.

	0.5 M H_2SO_4			117	12 h	Interfaces, 2017, 9, 28394-28405
	1.0 M PBS			261	12 h	
Co_9S_8@C	1.0 M KOH	0.30	10	250	10 h	ACS Appl. Mater. Interfaces, 2015, 7, 980-988
	0.5 M H_2SO_4			240	10 h	
	1.0 M PBS			280	10 h	
Co_9S_8-MoS_2@N-CNAs@CNFs	1.0 M KOH	/	10	163	2000 cycles	ACS Appl. Mater. Interfaces, 2020, 12, 10280-10290
Co_9S_8/NSG	0.5 M H_2SO_4	2.00	10	247	16 h	ACS Sustainable Chem. Eng., 2019, 7, 19442-19452
CoS_2 HNSs	1.0 M KOH	1.50	10	193	12 h	Nanoscale, 2018, 10, 4816-4824
Co/Co_9S_8@NSOC-T	1.0 M KOH	0.64	10	216	10 h	Chem. Commun., 2019, 55,3203-3206
Co_9S_8 HMs-140/C	0.1 M KOH	0.80	10	250	200 cycles	Electrochim. Acta, 2017, 246, 380-390
Co_9S_8	0.5 M H_2SO_4	0.55	10	178	2000 cycles	Electrochim. Acta, 2018, 281, 198-207

Table S2. Electrocatalytic ORR performance of the VCS@NC-700 electrode compared with those of reported Co_9S_8-based carbon electrocatalysts in 0.1 M KOH electrolyte.

Catalysts	Electrolyte	Loading amount (mg cm^{-2})	Potential (V, at half peak)	Stability test	Reference
VCS@NC-700	0.1 M KOH	2.80	0.901	2000 cycles	This work
Co_9S_8-NSHPCNF	0.1 M KOH	0.30	0.82	2000 cycles	Appl. Catal. B- Environ., 2020, 268, 118437
IOSHs-NSC-Co_9S_8	0.1 M KOH	1.00	0.82	10000 cycles	Appl. Catal. B- Environ., 2020, 260, 118209
Co_9S_8@N-S-HPC	0.1 M KOH	0.26	~0.85	5000 cycles	Appl. Catal, B- Environ., 2019, 254, 186-193
Co9S8@G/NS-PCNFs	0.1 M KOH	/	0.82	/	Chem. Eng. J., 2019, 378, 122247
Co_9S_8@TDC-900	0.1 M KOH	1.70	0.78	3000 cycles	J. Mater. Chem. A, 2019,7, 7389-7395
Co_9S_8@NC	0.1 M KOH	/	0.861	12 h	ACS Appl. Mater. Interfaces, 2020, 12, 33740-33750
Co_9S_8-MoS_2@N-CNAs@CNFs	0.1 M KOH	/	0.82	40000 s	ACS Appl. Mater. Interfaces, 2020, 12, 10280-10290
Co_9S_8/N, P-APC	0.1 M KOH	0.25	0.78	/	Carbon, 2019, 144, 557-566
Co_9S_8/S-CNTs	0.1 M KOH	0.29	0.810	35000 s	Carbon, 2019, 144, 259-268
CE-Co_9S_8@N,SCM	0.1 M KOH	0.10	0.88	/	Catal. Sci. Technol., 2019, 9, 5757-5762
Co_9S_8@CT	0.1 M KOH	0.20	0.86	/	J. Mater. Chem. A, 2018, 6, 5935-5943
Co_9S_8/CNT	0.1 M KOH	0.20	0.82	7200 s	J. Mater. Chem. A, 2017, 5, 21353-21361
Co_9S_8/NHCS	0.1 M KOH	0.15	0.86	10000 s	J. Mater. Chem. A, 2016, 4, 11342-11350
Co_9S_8/CD@NSC	0.1 M KOH	/	0.84	40000 s	ACS Appl. Mater. Interfaces, 2019, 11, 14085-14094
Ni_3Fe-Co_9S_8/rGO	0.1 M KOH	0.25	0.80	/	ACS Appl. Mater. Interfaces, 2019, 11, 4028-4036
Co_9S_8@N−C	0.1 M KOH	/	0.83	20000 s	ACS Appl. Mater. Interface, 2018, 10, 25415-25421
Co_9S_8/NSC	0.1 M KOH	/	0.896	20000 s	ACS Appl. Mater. Interfaces,

					2017, 9, 36755-36761
Co/Co_9S_8/rGO/ MWCNT	0.1 M KOH	/	0.776	15000	Inorg. Chem. Front., 2019, 6, 2558-2565
Co_9S_8/C	0.1 M KOH	0.02	0.778	5000 cycles	Nanoscale, 2019,11, 901-907
Co_9S_8@Co_9S_8@MoS_2	0.1 M KOH	0.20	0.77	/	Inorg. Chem. Front., 2020, 7, 191
Co_9S_8 HMs-140/C	0.1 M KOH	0.8	0.82	2000 cycles	Electrochim. Acta, 2017, 246, 380-390
Co_9S_8/CS-800	0.1 M KOH	/	0.818	10 h	Electrochim. Acta, 2018, 265, 32-40
Co_9S_8@NS-3DrGO	0.1 M KOH	0.20	0.826	30000 s	Dalton T., 2018, 47 14992-15001
W-N/C_4@Co_9S_8 @WS_2	0.1 M KOH	/	~0.8456	12000 s	Electrochim. Acta, 2020, 351, 136249
Co_9S_8/Co-NCNT	0.1 M KOH	/	0.93	16 h	J. Colloid and Interf. Sci., 2019, 557, 291-300
Co_9S_8@NSC	0.1 M KOH	0.28	0.865	3000 cycles	ChemElectroChem, 2018, 5, 355-361
T-CCSNC	0.1 M KOH	/	0.78	10000 s	New J. Chem., 2020,44, 9522-9529