Electronic Supplementary Information

Cobalt-based phosphide supported on carbon nanotubes for HER: Effect of phosphating degree on HER performance

Xianpei Ren[a, b], Baocai Pan[b], Shujun Li[b], Yuehong Peng[c]∗, Fei Li[a]∗

[a]Applied Nuclear Technology in Geosciences Key Laboratory of Sichuan Province，Chengdu University of Technology, Chengdu 610000, China

[b]School of Physics and Electronic Engineering, Sichuan University of Science and Engineering, Zigong 643000, China

[c]School of Physics and Electronical Science, Chuxiong Normal Unniversity, Chuxiong 675000, China.

∗Corresponding author: E-mail: renxianpei@163.com; pyh@cxtc.edu.cn; lifei17@cdut.edu.cn

Experimental Section

Reagents and materials

Cobalt acetate ($(CH_3COO)_2Co$) and Sodium hypophosphite ($NaPO_2H_2 \cdot H_2O$) were purchased from Macklin. Carbon nanotubes (CNT) were purchased from Nanjing XFNANO Materials Tech Co., Ltd. Nafion solution was purchased from Sigma-Aldrich. Platinum wire and glassy carbon electrodes were purchased from Tianjin Aidahengsheng Technology. Co. Ltd. 20% platinum carbon catalyst (20% Pt/C) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. All chemicals in this work were commercially obtained and without further purification.

Characterization

Powder X-ray diffraction (XRD) tests were detected by using a Bruker D8 ADVANCE. X-ray photoelectron spectroscopy (XPS) measurements were performed on aThermo-VG Scientific Escalab 250 electron spectrometer using Al Kα radiation. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained by a FEI Tecnai G2 F20 microscope. The elemental mapping of the samples was obtained using an energy-dispersive X-ray spectroscope (EDX) attached to the FEI Tecnai G2 F20 TEM instrument. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed using a ThermoFisher ESCALAB 250Xi spectrometer equipped with a He I (21.2 eV) as ultraviolet excitation source.

Electrochemical characterization

All electrochemical measurements were conducted on a CHI 604E electrochemical workstation with a standard three-electrode system. A glassy carbon electrode (diameter 3 mm), a platinum wire and an Ag/AgCl (in saturated KCl solution) electrode were used as the working electrode, counter electrode and reference electrode, respectively.

The working electrodes were prepared as follows: 4 mg catalyst powder and 80 μL Nafion solution (5 wt% Dupont) were dispersed in a mixture of 1 mL ethanol and distilled water (volume ratio 1:4) and treated by ultrasound for at least 30 minutes to form a uniform ink. Thereafter, 5 μL of catalyst ink was dropped onto the surface of the glassy carbon electrode. Finally, all the catalyst-loaded electrodes were air-dried at room temperature and used for electrochemical testing.

The HER performance was measured in 0.5 M H_2SO_4 at a scan rate of 5 $mV\cdot s^{-1}$ and the potential was converted by the use of equation: $E_{RHE}=E_{Ag/AgCl}+(0.205+0.0591\times pH)$ V. The electrochemical impedance spectroscopy (EIS) results were evaluated with a modulation amplitude of 5 mV in the frequency range of 100 kHz to 1 Hz. Cyclic voltammetry (CV) measurements for estimating the double-layer capacitance (C_{dl}) were conducted in the potential range of 0.10 V to 0.20 V at different scan rates ranging from 20 to 100 $mV\cdot s^{-1}$. Number of active sites and turnover frequency (TOF) of different samples were calculated according to the methods reported previously [1, 2].

Table S1. Comparison of HER performance for S4 with other CoP-based HER electrocatalysts in 0.5 M H_2SO_4 solution.

Catalysts	Overpotential (mV) @10 mA·cm^{-2}	References
CoP@NG	158	*Electrochim. Acta*, 2019, 307: 543e552
CoP/CC	130.6	*J. Colloid. Interf. Sci.*, 2023, 652: 989-996.
CoP@NPC	218	*J. Colloid. Interf. Sci.*, 2023, 631:147-153
CoP/DCS	136	*Carbon Energy*, 2023, 5:e268.
CoP/o-CC	118	*Int. J. Hydrogen Energ.*, 2022, 47: 9209-9219
Co/Co_2P@LGC	150	*Int. J. Hydrogen Energ.*, 2024, 60: 909-916
CoP/rGO	159	*Sci. China. Mater.*, 2022, 65: 1225-1236.
CoP-WP/rGO	130	*Sci. China. Mater.*, 2022, 65: 1225-1236.
CoP/NF	74.0	*ACS Appl. Nano Mater.*, 2024, 7: 17868-17876
Mo-CoP/NF	78.7	*ACS Appl. Nano Mater.*, 2024, 7: 17868-17876
CoP@CC	78	*Surf. Interface*s, 2024, 53: 105043
CoP/Co_2P	87	*J. Power Sources*, 2021, 486: 229351
CoP	139	*Mater. Design*, 2021, 211: 110165
CoP@MoS_2	119	*Mater. Design*, 2021, 211: 110165
CoP@CNT (S4)	109	This work

Notes: NG is nitrogen-doped graphene nanosheets; CC is carbon cloth; NPC is N, P co-doped carbon; DCS is rich-defect carbon shell; LGC is lignin-based carbon; rGO is reduced graphene oxide; NF is nickel foam.

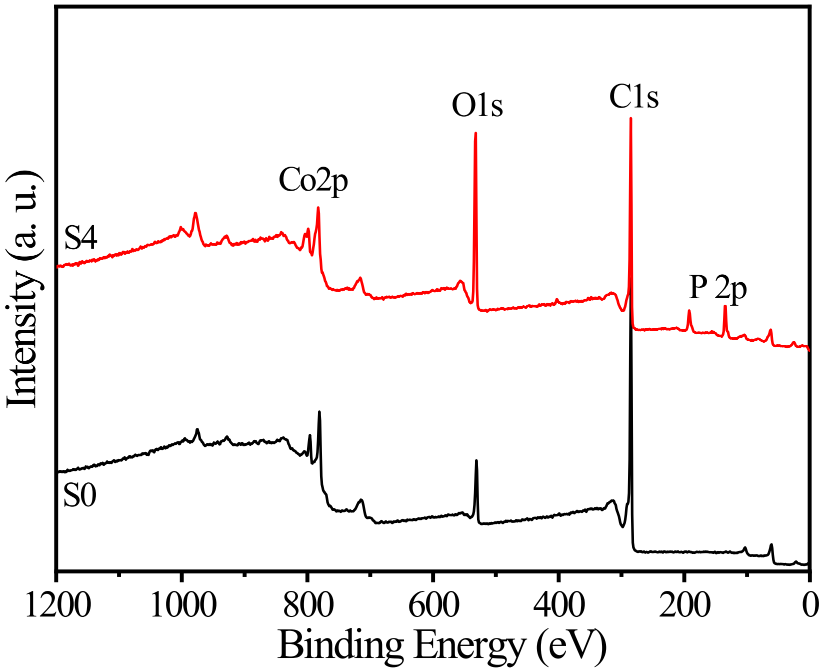

Fig. S1 XPS survey spectra of S0 and S4.

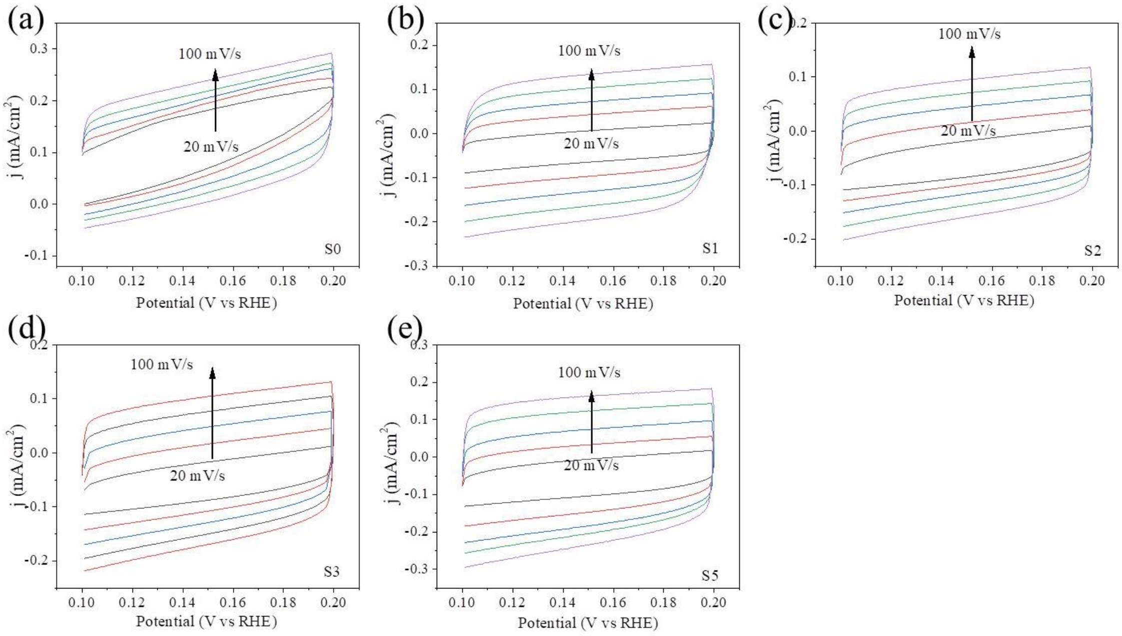

Fig. S2 (a-e) Electrochemical cyclic voltammogram of S0, S1, S2, S3 and S5 at different potential scanning rates. The scan rates are 20, 40, 60, 80 and 100 mV·s^{-1}. The selected potential range where no faradic current was observed is 0.10 to 0.20 V vs RHE.

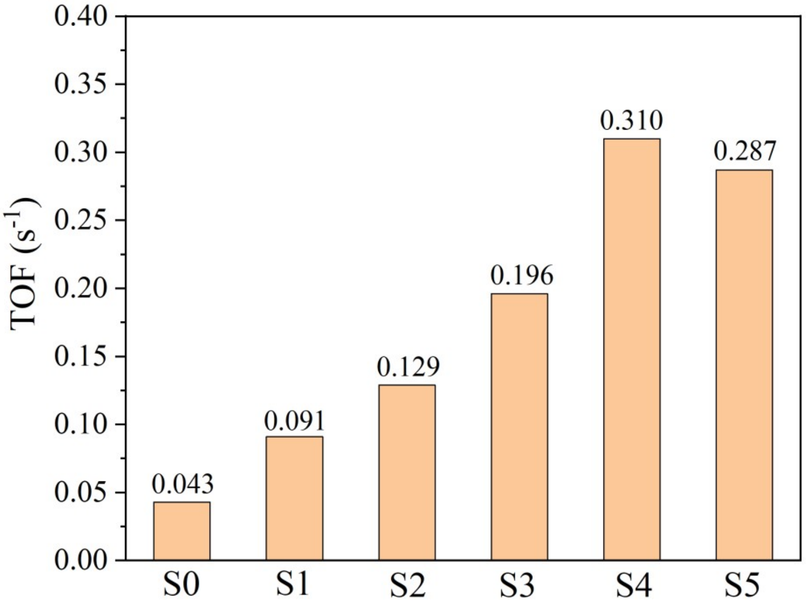

Fig. S3 Comparison graph of the turnover frequency (TOF) of the five samples (η=200 mV).

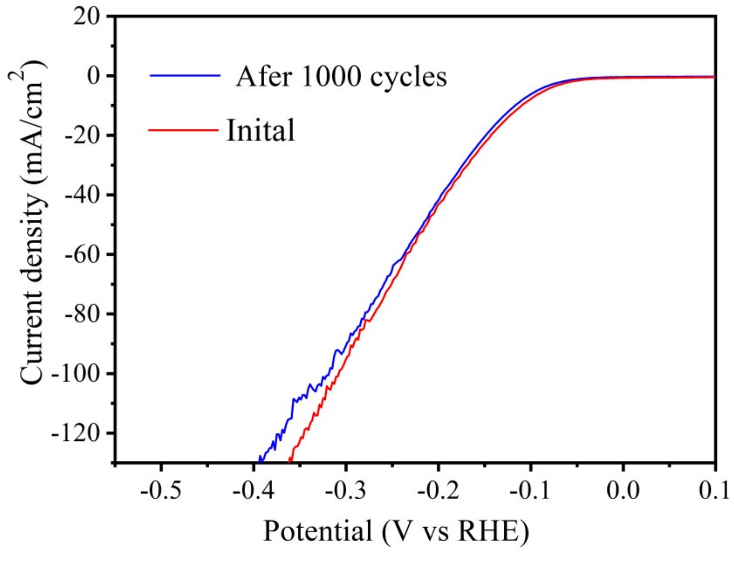

Fig. S4 Polarization curves of S4 electrocatalyst before and after 1000 CV cycles in 0.5 mol·L^{-1} H_2SO_4.

References

[1] W. Zhang, D. H. Li, L. Z. Zhang, X. L. She, D. J. Yang, J. Energy Chem., 2019, 39, 39-53.

[2] D. Merki, S. Fierro, H. Vrubel, X. Hu, Chem. Sci., 2011, 2, 1262-1267.