



Cite this: *RSC Adv.*, 2018, 8, 28684

Hierarchical Co–FeS₂/CoS₂ heterostructures as a superior bifunctional electrocatalyst†

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The traditional method of preparing hydrogen and oxygen as efficient clean energy sources mainly relies on the use of platinum, palladium, and other precious metals. However, the high cost and low abundance limit wide application of such metals. As such, one challenging issue is the development of low-cost and high-efficiency electrocatalysts for such purposes. In this study, we synthesized Co–FeS₂/CoS₂ heterostructures via a hydrothermal method for efficient hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Benefitting from their unique three-dimensional hierarchical nanostructures, Co-doped FeS₂ and CoS₂ formed heterostructures on Co–FeS₂ petals, which bestowed remarkable electrocatalytic properties upon Co–FeS₂/CoS₂ nanostructures. Co–FeS₂/CoS₂ effectively catalyzed the OER with an overpotential of 278 mV at a current density of 10 mA cm^{−2} in 1 M KOH solution, and also is capable of driving a current density −10 mA cm^{−2} at an overpotential of −103 mV in 0.5 M H₂SO₄ solution. The overpotential of the OER and HER only decreased by 5 mV and 3 mV after 1000 cycles. Our Co–FeS₂/CoS₂ materials may offer a promising alternative to noble metal-based electrocatalysts for water splitting.

Received 19th June 2018
Accepted 7th August 2018

DOI: 10.1039/c8ra05237a

rsc.li/rsc-advances

1. Introduction

In response to global energy and environmental problems, researchers have made tremendous efforts to explore and develop high-performance and low-cost electrocatalysts for HER and OER to replace platinum, palladium and other precious metals.^{1–5} Non-noble metal electrocatalysts such as Fe, Co, Ni, Mo, and their sulfides,^{6–8} phosphides^{9–12} or their alloys^{13–17} have been investigated widely as electrocatalysts over the past decades. Among them, the low-cost, earth-abundant iron sulfide has attracted much attention as an electrocatalytic material due to its excellent catalytic activity.^{7,18} However, the catalytic performance of iron sulfide is limited by its low surface area and lack of active sites.¹⁹ If the non-noble metals electrocatalysts are grown on carbon material substrates, doping with homologous elements not only reduces the catalytic resistance but also exposes more active sites.^{20–22} Furthermore, the formation of epitaxial heterostructures can regulate the energy barrier between the two interfaces to reduce the catalytic kinetic energy.^{23–25}

In this work, we prepared Co–FeS₂/CoS₂ heterostructures electrocatalysts on a carbon cloth (CC) by using sulfur powder and thiourea as sulfur sources and show that they have excellent catalytic performance. The unique 3D hierarchical nanostructures give it a high surface area and the doping of cobalt reduced the kinetic energy barrier of the catalytic reaction of FeS₂. The bumps heterostructures of CoS₂ further exposed more active sites and adjusted the kinetic energy barrier for catalytic reaction at the two interface junctions, which led to the remarkable electrocatalytic properties. The as-synthesized Co–FeS₂/CoS₂ materials has an exceptional overpotential of 278 mV at a current density of 10 mA cm^{−2} in 1 M KOH solution and the Tafel slope is only 73 mV dec^{−1}. The overpotential is −103 mV at a current density of −10 mA cm^{−2} in 0.5 M H₂SO₄ solution, and the Tafel slope is only 56 mV dec^{−1}. In addition, the overpotential of OER and HER only decreased by 5 mV and 3 mV after 1000 cycles. Our Co–FeS₂/CoS₂ materials may be a promising alternative to noble metal-based electrocatalysts for water splitting applications.

2. Experimental section

2.1 Chemicals and materials

WOS1009 carbon cloth (CC) was supplied by CeTech Co., Ltd. FeSO₄·7H₂O, was purchased from Shanghai Titan Scientific Co., Ltd. CH₃CSNH₂ was purchased from Aladdin Ltd. Co(NO₃)·6H₂O, sulfur power (S), thiourea (SC(NH₂)₂), Na₂S·9H₂O, C₂H₅OH, H₂SO₄, and KOH were purchased from Nanjing Chemical Reagent Co., Ltd. Ultrapure water was obtained using a Millipore pure water filter (Millipore Q, USA).

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ra05237a



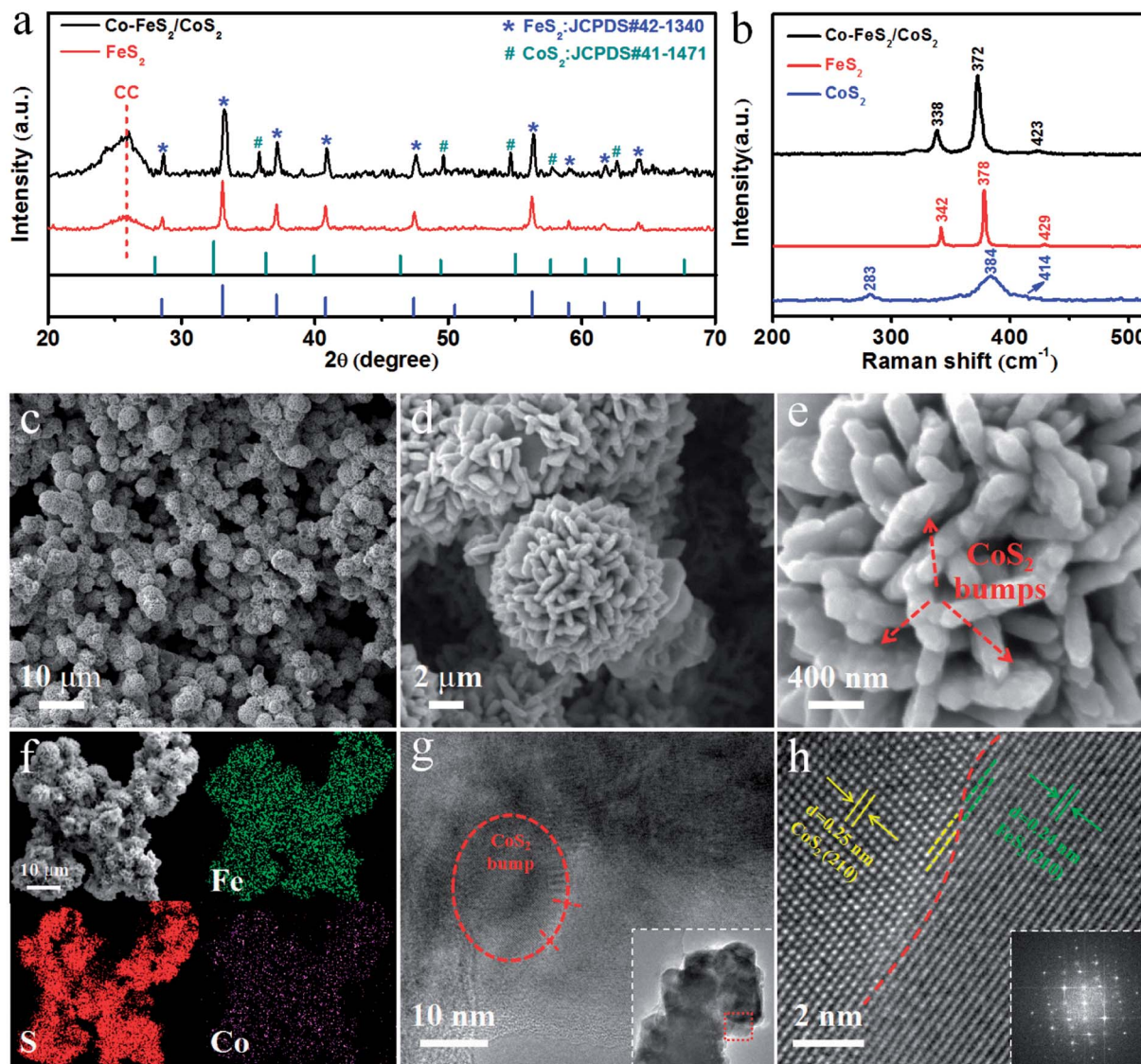


Fig. 1 (a) XRD patterns for Co-FeS₂/CoS₂ and FeS₂; (b) Raman spectra for Co-FeS₂/CoS₂, FeS₂ and CoS₂; (c)–(e) progressively enlarged SEM images of Co-FeS₂/CoS₂; (f) SEM image and corresponding EDX elemental mapping images of Fe, S, Co for Co-FeS₂/CoS₂; (g) TEM image of Co-FeS₂/CoS₂ heterostructures, the inset is TEM image of Co-FeS₂ nanopetals; (h) HRTEM image of Co-FeS₂/CoS₂ heterostructures, the inset is corresponding SAED pattern of Co-FeS₂/CoS₂ heterostructures.

2.2 Synthesis of Co-FeS₂/CoS₂ heterostructures

In this experiment, the carbon cloth (1.8 cm × 2.2 cm) was first ultrasonically clean for 15 minutes using ultrapure water and anhydrous ethanol and then dried. Subsequently, FeSO₄·7H₂O (1.2 mM), Co(NO₃)₂·6H₂O (0.156 mM), and SC(NH₂)₂ (1.8 mM) were added to a 30 mL reaction kettle followed by 25 mL of ultrapure water and stirred for 15 minutes to form a transparent homogeneous solution. Sulfur powder (0.72 mM) was then introduced to the above reactor and stirred at a low speed for 15 minutes. After the stirring was stopped, the magnetic stirrer was removed and sulfur powder film was formed on the liquid surface. The clean and dried carbon cloth was inserted vertically into reaction kettle solution and maintained at 180 °C for 8 hours. After the reactor cooled down to room temperature, the solution was removed, and then samples were washed using ultrapure water and absolute ethanol.

2.3 Materials characterization

The crystal phase properties of the samples were analyzed with a Bruker D8 Advance X-ray diffractometer (XRD) using Cu K α radiation at 40 kV and 40 mA, for 2θ ranging from 20° to 70°, with a scan rate of 0.1° per second. Raman spectra were obtained by Raman spectroscopy (JY T64000) excited at 514.5 nm of a 100 μ W Ar⁺ laser. Scanning electron microscopy (FE-SEM; JSM-7000F) was used to obtain the surface morphology of the sample. The energy dispersive spectrometer (EDS; Inca x-stream 034A0) was used to confirm the elemental composition of the sample. Transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) images were obtained by using a JEOL type JEM2100 instrument at an accelerating voltage of 200 kV. The chemical compositions of samples were determined by using X-ray photoelectron spectroscopy (XPS) analysis (PHI5000 Versaprobe).



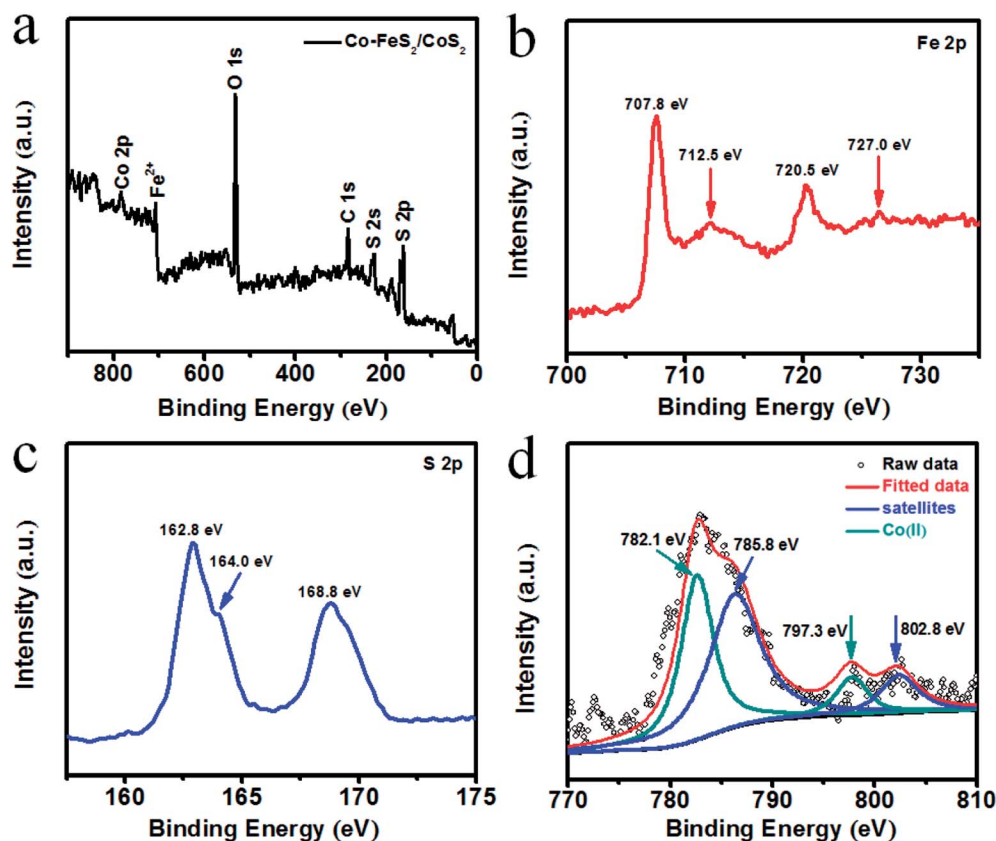


Fig. 2 (a) XPS survey spectrum for Co-FeS₂/CoS₂; XPS spectra of the Co-FeS₂/CoS₂ from (b) Fe 2p, (c) S 2p, (d) Co 2p.

2.4 Electrochemical measurements

Electrochemical measurements were performed with a CHI760E electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China). A conventional three-electrode cell was used, including the sample as a working electrode, a calomel electrode as a reference electrode, and a graphite rod as a counter electrode. 1 M KOH and 0.5 M H₂SO₄ solution were used as the electrolyte solution, nitrogen was bubbled into the solution for 30 minutes before testing. In this paper, the positive scan curve is selected as the LSV curve (between 0 and 0.8 V, 2 mV s⁻¹) for OER and the negative scan curve is selected as the LSV curve for HER (between -0.8 and -0.2 V, 2 mV s⁻¹). The Tafel slope is calculated from the logarithmic relationship between overpotential and current density based on the LSV curve. The electrochemical active surface areas (ECSA) were calculated from the double layer charging curves using cyclic voltammograms (CVs) at different scan rates of 2–160 mV s⁻¹ in potential range from 0 to 0.20 V vs. RHE for HER. Electrochemical impedance spectroscopy (EIS) was performed with a frequency range of 10⁵–0.1 Hz. The stability assessment was performed by 1000 cycles of the testing at a scan rate of 100 mV s⁻¹.

3. Results and discussion

In the experiment, we prepared Co-FeS₂/CoS₂ heterostructures with superior electrocatalytic performance through the selection of sulfur sources, regulation of cobalt content,

optimization of loading, addition and optimization of dual sulfur sources (as can be seen in ESI†). Fig. 1a shows the X-ray diffraction (XRD) patterns for Co-FeS₂/CoS₂ heterostructures and FeS₂. The peaks at 28.5°, 33.1°, 37.1°, 40.8°, 47.5° and 56.3° can be indexed to the (111), (200), (210), (211), (220), (311) planes of FeS₂ (JCPDS#42-1340).^{19,26} The peaks at 35.9°, 49.5°, 54.7°, 57.7° and 62.7° correspond to the planes of (210), (221), (311), (222) and (321) of CoS₂ (JCPDS#41-1471).^{8,27} From the XRD pattern, it can be seen that the Co-FeS₂/CoS₂ heterostructures exhibit good crystallinity. Fig. 1b shows the Raman spectra of the Co-FeS₂/CoS₂ heterostructures, FeS₂ and CoS₂. The Raman spectrum for the Co-FeS₂/CoS₂ heterostructures shows a broad primary peak centered around 372 cm⁻¹, which is likely the result of contributions from the most intense FeS₂ peaks at 378 cm⁻¹ and the primary CoS₂ peak at 384 cm⁻¹.²⁸

As shown in Fig. 1c, Co-FeS₂/CoS₂ exhibits a microflower-like morphology with diameters ranging from 4 to 6 micrometer. Fig. 1d shows the nano-petals structures on the Co-FeS₂/CoS₂ heterostructures, the nano-petals crosslinked together to form a 3D microflower-like structures,²⁹ which not only increase the specific surface area but also accelerate the outward diffusion rate of the generated gas in the solution for water splitting.^{30,31} Fig. 1e is a high-resolution SEM image showing the bumps of CoS₂ on the nano-petals of the Co-FeS₂/CoS₂ heterostructures; Co-doped FeS₂ decreased the kinetic energy barrier of the catalytic reaction, synergistic catalysis by heterostructures of Co-FeS₂/CoS₂ further improves electrocatalytic activity.^{10,32-34} Fig. 1f shows the SEM image and the energy-dispersive X-ray



(EDX) spectrum elemental mapping images of Fe, S and Co, for the Co-FeS₂/CoS₂ heterostructures, revealing the distribution of the three elements. Fig. 1g is a TEM image of Co-FeS₂/CoS₂ heterostructures, the inside of the ellipse is a bump of CoS₂ which further increased the surface area of the sample and adjusted the kinetic energy. Fig. 1h is a high resolution TEM (HRTEM) image of Co-FeS₂/CoS₂ heterostructures, the interplanar spacing (210) of FeS₂ is 0.24 nm,^{19,35} the interplanar spacings (210) of the CoS₂ bump are 0.25 nm,^{36,37} and the inset showed the selected area electron diffraction (SAED) pattern, which shows the monocrystallinity of the sample. All these potentially explain the excellent electrocatalytic performance of the Co-FeS₂/CoS₂ heterostructures.

Fig. 2a presents the full XPS survey spectrum of the Co-FeS₂/CoS₂ heterostructures, also confirming the presence of Fe, S and Co elements. Fig. 2b shows the XPS spectrum of Fe (2p); the characteristic peaks of Co-FeS₂/CoS₂ were detected at 707.8 (Fe 2p_{3/2}) and 720.5 eV (Fe 2p_{1/2}) due to the Fe²⁺ of the FeS₂ structure.⁷ The peaks at 712.5 and 727.0 eV can be attributed to a small amount of Fe²⁺ being oxidized to Fe³⁺.³⁸ The XPS spectra of Co-FeS₂/CoS₂ were measured in the S (2p) region, as shown in Fig. 2c. The binding energies of S (2p) at 162.8 and 164.0 eV belong to S₂²⁻ of FeS₂.^{39,40} There were some oxidized S species found (168.8 eV) in Co-FeS₂/CoS₂.^{41,42} As shown in Fig. 2d, the Co 2p spectrum can be deconvoluted into four peaks: the Co 2p_{3/2} and Co 2p_{1/2} peaks at 782.1 and 797.3 eV can be attributed to Co²⁺ bound to oxygen,^{43,44} while another two peaks at 785.8

and 802.8 eV are ascribed to higher oxidized cobalt species (Co³⁺).⁴⁵

We further analyzed the main process of formation of Co-FeS₂/CoS₂ heterostructures. We speculate the following reaction process: solid sulfur powder attached to the carbon cloth at 180 °C is melted into small droplets. At the sulfur powder droplets and solution interface, due to the severe excess in sulfur powder compared to Fe²⁺, Co²⁺, and S²⁻. Co²⁺ was incorporated into the reaction of Fe²⁺, S²⁻, and sulfur powder droplets (S⁰). When Co-FeS₂ was formed, Co²⁺ further reacted with sulfur powder droplets (S⁰)/S²⁻ to form CoS₂, thus forming the Co-FeS₂/CoS₂ heterostructures.

To our knowledge, Co-FeS₂/CoS₂ heterostructures has not yet been explored for the electrocatalytic splitting of water into hydrogen and oxygen. Unique 3D hierarchical nanostructures not only increase the surface area but also facilitates the release of hydrogen and oxygen from the electrode surface. The superior oxygen evolution performance of the Co-FeS₂/CoS₂ heterostructures were mainly attributed to the presence of the CoS₂ phase and the formation of heterostructures with the Co-FeS₂.⁴⁶ In addition, density functional theory calculation revealed that sulfur was responsible for the active sites for proton adsorption and reduction; the high catalytic activity was stemmed from a large reduction of the kinetic energy barrier of H atom adsorption on FeS₂ surface upon Co doping in the iron pyrite structure.^{18,19} The formation of heterostructures for Co-FeS₂ and CoS₂ further lowers the kinetic

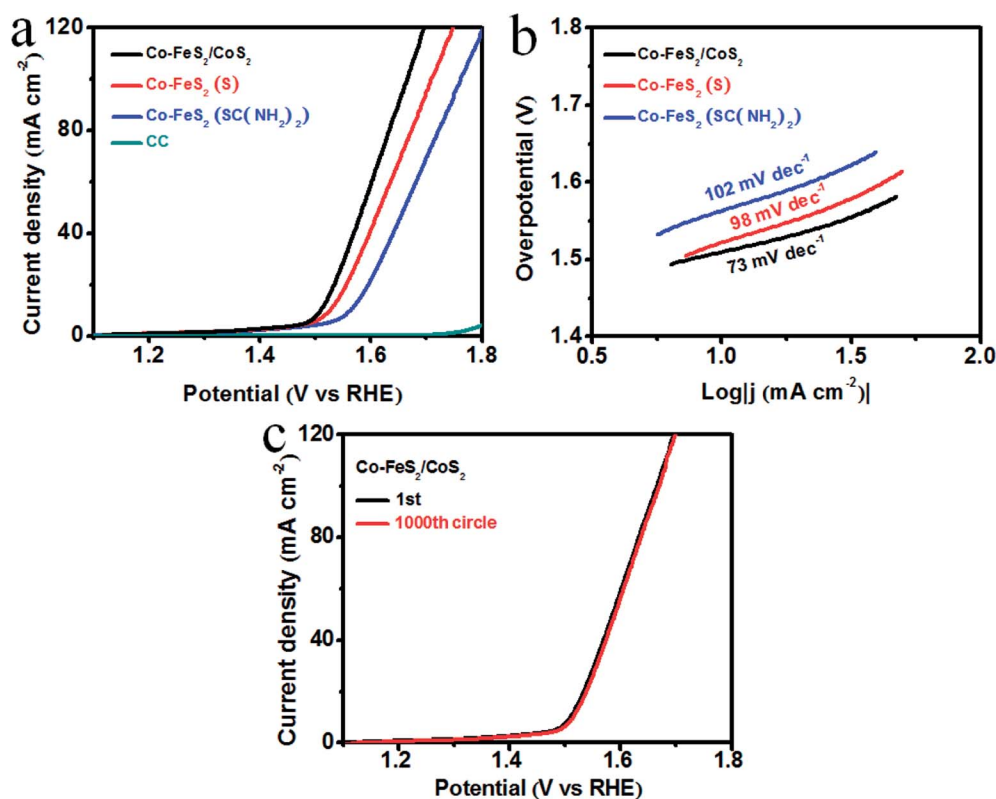


Fig. 3 (a) LSV curves of Co-FeS₂/CoS₂, Co-FeS₂ (S), Co-FeS₂ (SC(NH₂)₂), and bare CC for OER in 1 M KOH solution; (b) corresponding Tafel plots; (c) LSV curves of Co-FeS₂/CoS₂ before and after 1000 CV cycles.



energy barrier of the reaction to gain superior electrocatalytic performance.^{23–25}

We used a typical three-electrode system with a sweeping rate of 2 mV s^{-1} to test the OER electrocatalytic activity and stability of the Co-FeS₂/CoS₂ heterostructures. For comparison study, the electrocatalytic activity of Co-FeS₂ synthesized using sulfur powder or thiourea was also tested. Fig. 3a shows the linear sweep voltammetry (LSV) curves, showing that bare CC almost has no OER activity. Co-FeS₂/CoS₂ heterostructures shows superior OER activity, with an overpotential of only 278 mV required to drive 10 mA cm^{-2} . This is better than the overpotential of 292 mV for Co-FeS₂ (S) and 333 mV for Co-FeS₂ (SC(NH₂)₂). Fig. 3b shows that the Tafel slope of Co-FeS₂/CoS₂ is 73 mV dec^{-1} , which is superior to the measured 98 mV dec^{-1} of Co-FeS₂ (S) and 102 mV dec^{-1} of Co-FeS₂ (SC(NH₂)₂). As shown in Fig. 3c, the overpotential of Co-FeS₂/CoS₂ is only 283 mV after 1000 cycles, which signifies Co-FeS₂/CoS₂ heterostructures have good electrochemical stability in strongly alkaline solutions.

HER activity was analyzed by measuring the LSV curves of Co-FeS₂/CoS₂ and bare CC in $0.5 \text{ M H}_2\text{SO}_4$ solution. In the polarization curve of Fig. 4a, the blank substrate of CC shows negligible HER activity over the measured voltage range, indicating that the HER performance of the CC has little contribution. The Co-FeS₂/CoS₂ heterostructures grown on the CC substrate achieved geometric current densities of -10 mA cm^{-2} at much lower overpotential of -103 mV versus the reversible hydrogen electrode (RHE) compared to that of Co-FeS₂

(-161 mV for (S) and -173 mV for SC(NH₂)₂). As shown in Fig. 4b, Co-FeS₂/CoS₂ heterostructures have a Tafel slope of 56 mV dec^{-1} , smaller than those for Co-FeS₂ 70 mV dec^{-1} for (S) and 68 mV dec^{-1} for SC(NH₂)₂. To investigate the origin of the superior activity of Co-FeS₂/CoS₂ heterostructures, we further estimated the ECSA by calculating its non-faradaic double-layer capacitance using cyclic voltammetry measurement, since ECSA value is linearly proportional to C_{dl} .^{46–48} As shown in Fig. S10a–d,† cyclic voltammograms were measured in the non-faradaic capacitance current range, the C_{dl} value of hierarchical Co-FeS₂/CoS₂ is 86 mF cm^{-2} is larger than that of Co-FeS₂(S) (37 mF cm^{-2}) and Co-FeS₂(SC(NH₂)₂) (20 mF cm^{-2}). The result indicates that hierarchical architecture and bump feature can maximize the exposure of accessible active sites, which contributes to excellent electrocatalytic performance of Co-FeS₂/CoS₂ heterostructures. In addition, as shown in Fig. S10e,† the reaction kinetics is verified by EIS, the hierarchical Co-FeS₂/CoS₂ heterostructures present a smaller semicircle than Co-FeS₂(S) and Co-FeS₂(SC(NH₂)₂), which can be associated with interfacial charge transfer process, a lower value corresponds to a faster electron transfer rate. This result demonstrated further the faster catalytic kinetics of Co-FeS₂/CoS₂ heterostructures.^{49–51} In addition to catalytic activity, stability is another critical factor to evaluate a good electrocatalyst, we investigated the stability of Co-FeS₂/CoS₂ heterostructures *via* 1000 cycles scanning. As shown in Fig. 4c, the Co-FeS₂/CoS₂ electrode lost only 3 mV of overpotential at -10 mV cm^{-2} after

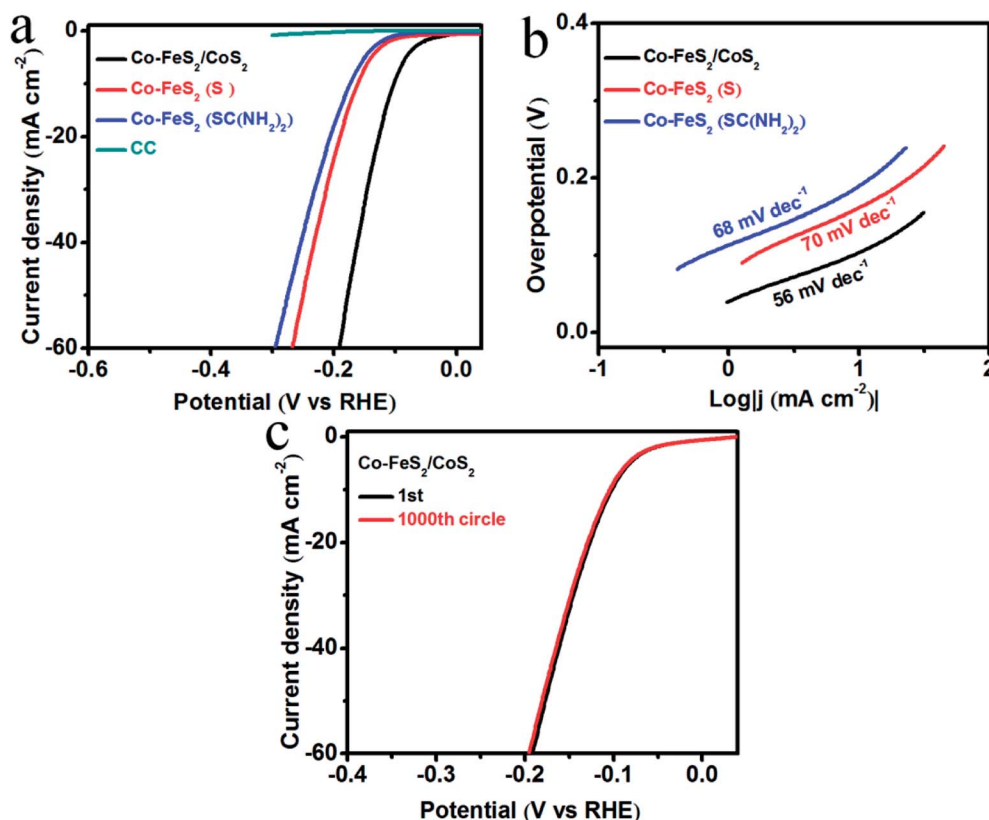


Fig. 4 (a) LSV curves of Co-FeS₂/CoS₂, Co-FeS₂/CoS₂ (S), Co-FeS₂ (SC(NH₂)₂), and bare CC for HER in $0.5 \text{ M H}_2\text{SO}_4$ solution; (b) corresponding Tafel plots; (c) LSV curves of Co-FeS₂/CoS₂ before and after 1000 cycles.



Table 1 Summary of HER and OER activity of electrocatalysts

Catalyst	Electrolyte	η_j (mV vs. RHE)	Tafel slope (mV dec ⁻¹)	η_j (mV vs. OER)	Reference
FeS ₂	0.1 M KOH	$\eta_{-10} = -96$	78	—	19
FeS ₂	0.5 M H ₂ SO ₄	$\eta_{-10} = -139$	66	—	7
Fe _{0.68} Co _{0.32} S ₂	0.5 M H ₂ SO ₄	$\eta_{-10} = -166$	51	—	38
CoS ₂	0.5 M H ₂ SO ₄	$\eta_{-10} = -145$	51.6	—	8
CoS ₂	0.5 M H ₂ SO ₄	$\eta_{-100} = -140$	70.1	—	27
CoS ₂	0.1 M KOH	—	—	$\eta_{10} = 290$	52
Co-FeS ₂ /CoS ₂	0.5 M H ₂ SO ₄	$\eta_{-10} = -103$	56	$\eta_{10} = 278$	This work

1000 cycles. Furthermore, we analyzed the characterization results of the Co-FeS₂/CoS₂ heterostructures before and after the 1000 cycles. As shown in Fig. S11,[†] it was found that the XRD patterns, XPS spectra, SEM, and TEM images of Co-FeS₂/CoS₂ heterostructures did not significantly changed. The Co-FeS₂/CoS₂ heterostructures also has excellent electrochemical stability in 0.5 M H₂SO₄ solution, which is better than the previously reported non-noble metal-based sulfide electrocatalyst, presented in Table 1.

4. Conclusions

In summary, by optimizing experiment conditions, Co-FeS₂/CoS₂ heterostructures were successfully prepared by the hydrothermal route with excellent OER and HER electrocatalytic performance. Their unique three-dimensional structure not only increases the surface area but also facilitates the release of hydrogen and oxygen from the electrode surface. Co-doped FeS₂ and CoS₂ formed heterostructures on the petals of Co-FeS₂, which change the energy barrier of the catalytic reaction to gain excellent electrocatalytic performance. This study not only provides a low-cost, stable and earth-abundant iron-based electrocatalyst for efficient water splitting, it will also provide an exciting new method for the rational design and scalable preparation of three-dimensional polynary heterostructures as electrocatalysts.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Basic Research Program of China (2018YFA0209101), the National Science Foundations of China (No. 61205057, No. 11574136), Qing Lan Project, the '1311 Talent Plan' Foundation of Nanjing University of Posts and Telecommunications, Six Talent Peaks Project in Jiangsu Province (JY-014), and State Key Laboratory of High Performance Computing, National University of Defense Technology.

References

- 1 C. Tang, L. Gan, R. Zhang, W. Lu, X. Jiang and A. M. Asiri, Ternary Fe_xCo_{1-x}P nanowire array as a robust hydrogen

evolution reaction electrocatalyst with pt-like activity: experimental and theoretical insight, *Nano Lett.*, 2016, **16**, 6617–6621.

- 2 W. Xiong, Z. Guo, H. Li, R. Zhao and X. Wang, Rational bottom-up engineering of electrocatalysts by atomic layer deposition: a case study of Fe_xCo_{1-x}S_y-based catalysts for electrochemical hydrogen evolution, *ACS Energy Lett.*, 2017, **2**, 2778–2785.
- 3 X. Zou and Y. Zhang, Noble metal-free hydrogen evolution catalysts for water splitting, *Chem. Soc. Rev.*, 2015, **44**, 5148–5180.
- 4 J. Wang, W. Cui, Q. Liu, Z. Xing, A. M. Asiri and X. Sun, Recent progress in cobalt-based heterogeneous catalysts for electrochemical water splitting, *Adv. Mater.*, 2016, **28**, 215–230.
- 5 Y. Li, H. Zhang, M. Jiang, Q. Zhang, P. He and X. Sun, 3D self-supported Fe-doped Ni₂P nanosheet arrays as bifunctional catalysts for overall water splitting, *Adv. Funct. Mater.*, 2017, **27**, 1702513.
- 6 X. Yu, Y. Feng, Y. Jeon, B. Guan, X. W. Lou and U. Paik, Formation of Ni-Co-MoS₂ nanoboxes with enhanced electrocatalytic activity for hydrogen evolution, *Adv. Mater.*, 2016, **28**, 9006–9011.
- 7 Y. Chen, S. Xu, Y. Li, R. J. Jacob, Y. Kuang and B. Liu, FeS₂ Nanoparticles embedded in reduced graphene oxide toward robust, high-performance electrocatalysts, *Adv. Energy Mater.*, 2017, **7**, 1700482.
- 8 M. S. Faber, R. Dziejic, M. A. Lukowski, N. S. Kaiser, Q. Ding and S. Jin, High-performance electrocatalysis using metallic cobalt pyrite (CoS₂) micro-and nanostructures, *J. Am. Chem. Soc.*, 2014, **136**, 10053–10061.
- 9 Y. Wang, B. Kong and D. Zhao, Strategies for developing transition metal phosphides as heterogeneous electrocatalysts for water splitting, *Nano Today*, 2017, **15**, 26–55.
- 10 X. Q. Lu, X. Yan and S. Devaramani, Self-supported rectangular CoP nanosheet arrays grown on carbon cloth as an efficient electrocatalysts for hydrogen evolution reaction over a variety of pH values 1, *New J. Chem.*, 2017, **41**, 2436–2442.
- 11 C. Ouyang, X. Wang and S. Wang, Phosphorus-doped CoS₂ nanosheet arrays as ultra-efficient electrocatalysts for the hydrogen evolution reaction, *Chem. Commun.*, 2015, **51**, 14160–14163.



- 12 D. Wang, D. Zhang, C. Tang, P. Zhou and Z. Wu, Hydrogen evolution catalyzed by cobalt promoted molybdenum phosphide nanoparticles, *Catal. Sci. Technol.*, 2016, **6**, 1952–1956.
- 13 X. Zhu, T. Jin, C. Tian, C. Lu, X. Liu and M. Zeng, *In situ* coupling strategy for the preparation of FeCo alloys and Co₄N hybrid for highly efficient oxygen evolution, *Adv. Mater.*, 2017, **29**, 1704091.
- 14 W. Fang, D. Liu, Q. Lu, X. Sun and A. M. Asiri, Nickel promoted cobalt disulfide nanowire array supported on carbon cloth: an efficient and stable bifunctional electrocatalyst for full water splitting, *Electrochem. Commun.*, 2016, **63**, 60–64.
- 15 V. Bachvarov, E. Lefterova and R. Rashkov, Electrodeposited NiFeCo and NiFeCoP alloy cathodes for hydrogen evolution reaction in alkaline medium, *Int. J. Hydrogen Energy*, 2016, **41**, 12762–12771.
- 16 X. Zhang, X. Zhang, H. Xu, Z. Wu, H. Wang and Y. Liang, Iron-doped cobalt monophosphide nanosheet/carbon nanotube hybrids as active and stable electrocatalysts for water splitting, *Adv. Funct. Mater.*, 2017, **27**, 1606635.
- 17 X. P. Han, X. Y. Wu, C. Zhong and Y. d. Deng, NiCo₂S₄ nanocrystals anchored on nitrogen-doped carbon nanotubes as a highly efficient bifunctional electrocatalyst for rechargeable zinc-air batteries, *Nano Energy*, 2017, **31**, 541–550.
- 18 D. Y. Wang, M. Gong and H. L. Chou, Highly active and stable hybrid catalyst of cobalt-doped FeS₂ nanosheets-carbon nanotubes for hydrogen evolution reaction, *J. Am. Chem. Soc.*, 2015, **137**, 1587–1592.
- 19 R. Miao, B. Dutta, S. Sahoo, J. He, W. Zhong and S. A. Cetegen, Mesoporous iron sulfide for highly efficient electrocatalytic hydrogen evolution, *J. Am. Chem. Soc.*, 2017, **139**, 13604–13607.
- 20 J. Yu, G. Cheng and W. Luo, Ternary nickel-iron sulfide microflowers as a robust electrocatalyst for bifunctional water splitting, *J. Mater. Chem. A*, 2017, **5**, 15838–15844.
- 21 Z. Wu, X. Wang, J. Huang and F. Gao, A Co-doped Ni-Fe mixed oxide mesoporous nanosheet array with low overpotential and high stability towards overall water splitting, *J. Mater. Chem. A*, 2018, **6**, 167–178.
- 22 K. Ao, D. Li and Y. Yao, Fe-doped Co₉S₈ nanosheets on carbon fiber cloth as pH-universal freestanding electrocatalysts for efficient hydrogen evolution, *Electrochim. Acta*, 2018, **264**, 157–165.
- 23 T. Kuo, W. Chen and H. Liao, Improving hydrogen evolution activity of earth-abundant cobalt-doped iron pyrite catalysts by surface modification with phosphide, *Small*, 2017, **13**, 1603356.
- 24 C. Zhu, A. L. Wang, W. Xiao, D. Chao and X. Zhang, *In situ* grown epitaxial heterojunction exhibits high-performance electrocatalytic water splitting, *Adv. Mater.*, 2018, **30**, 1705516.
- 25 P. Ganesan, A. Sivanantham and S. Shanmugam, CoS₂-TiO₂ hybrid nanostructures: efficient and durable bifunctional electrocatalysts for alkaline electrolyte membrane water electrolyzers, *J. Mater. Chem. A*, 2018, 1075–1085.
- 26 L. Xu, Y. Hu and H. Zhang, Confined synthesis of FeS₂ nanoparticles encapsulated in carbon nanotube hybrids for ultrastable lithium-ion batteries, *ACS Sustainable Chem. Eng.*, 2016, **4**, 4251–4255.
- 27 H. Zhang, Y. Li, G. Zhang, T. Xu, P. Wan and X. Sun, A metallic CoS₂ nanopyramid array grown on 3D carbon fiber paper as an excellent electrocatalyst for hydrogen evolution, *J. Mater. Chem. A*, 2015, **3**, 6306–6310.
- 28 M. S. Faber, M. A. Lukowski, Q. Ding, N. S. Kaiser and S. Jin, Earth-abundant metal pyrites (FeS₂, CoS₂, NiS₂, and their Alloys) for highly efficient hydrogen evolution and polysulfide reduction electrocatalysis, *J. Phys. Chem. C*, 2014, **118**, 21347–21356.
- 29 Z. Z. Wu, C. Y. Tang, P. Zhou and Z. H. Liu, Enhanced hydrogen evolution catalysis from osmotic swelled ammoniated MoS₂, *J. Mater. Chem. A*, 2015, **3**, 13050–13056.
- 30 J. Yu, G. Cheng and W. Luo, Hierarchical NiFeP microflowers directly grown on Ni foam for efficient electrocatalytic oxygen evolution, *J. Mater. Chem. A*, 2017, **5**, 11229–11235.
- 31 X. Y. Wu, X. P. Han, X. Y. Ma and W. Zhang, Morphology-Controllable Synthesis of Zn-Co-Mixed Sulfide Nanostructures on Carbon Fiber Paper Toward Efficient Rechargeable Zinc-Air Batteries and Water Electrolysis, *ACS Appl. Mater. Interfaces*, 2017, **9**, 12574–12583.
- 32 H. Zhang, X. Li, A. Hähnel, V. Naumann, C. Lin and S. Azimi, Bifunctional heterostructure assembly of NiFe LDH nanosheets on NiCoP nanowires for highly efficient and stable overall water splitting, *Adv. Funct. Mater.*, 2018, **28**, 1706847.
- 33 H. Song, S. Oh, H. Yoon, K. H. Kim, S. Ryu and J. Oh, Bifunctional NiFe inverse opal electrocatalysts with heterojunction Si solar cells for 9.54%-efficient unassisted solar water splitting, *Nano Energy*, 2017, **42**, 1–7.
- 34 H. Yu, Y. Xue, L. Hui, C. Zhang, Y. Li and Z. Zuo, Efficient hydrogen production on a 3D flexible heterojunction material, *Adv. Mater.*, 2018, 1707082.
- 35 L. Zhu, B. J. Richardson and Q. Yu, Anisotropic growth of iron pyrite FeS₂ nanocrystals *via* oriented attachment, *Chem. Mater.*, 2015, **27**, 150427111020001.
- 36 Y. Guo, L. Gan and C. Shang, A cake-style CoS₂@MoS₂/RGO hybrid catalyst for efficient hydrogen evolution, *Adv. Funct. Mater.*, 2017, **27**, 1602699.
- 37 H. Zhang, Y. Li and G. Zhang, Highly crystallized cubic cattierite CoS₂ for electrochemically hydrogen evolution over wide pH range from 0 to 14, *Electrochim. Acta*, 2014, **148**, 170–174.
- 38 S. Y. Huang, D. Sodano, T. Leonard, S. Luiso and P. S. Fedkiw, Cobalt-doped iron sulfide as an electrocatalyst for hydrogen evolution, *J. Electrochem. Soc.*, 2017, **164**, 276–282.
- 39 M. Zheng, Y. Ding, L. Yu, X. Du and Y. Zhao, *In situ* grown pristine cobalt sulfide as bifunctional photocatalyst for hydrogen and oxygen evolution, *Adv. Funct. Mater.*, 2017, 1605846.
- 40 X. Y. Ma, W. Zhang, Y. D. Deng and C. Zhong, Phase and composition controlled synthesis of cobalt sulfide hollow



- nanospheres for electrocatalytic water splitting, *Nanoscale*, 2018, **10**, 4816–4824.
- 41 L. Fang, Y. Zhang, Y. Guan, H. Zhang, S. Wang and Y. Wang, Specific synthesis of CoS₂ nanoparticles embedded in porous Al₂O₃ nanosheets for efficient hydrogen evolution and enhanced lithium storage, *J. Mater. Chem. A*, 2017, **5**, 2861–2869.
- 42 J. Jiang, S. Lu, H. Gao, X. Zhang and H. Q. Yu, Ternary FeNiS₂ ultrathin nanosheets as an electrocatalyst for both oxygen evolution and reduction reactions, *Nano Energy*, 2016, **27**, 526–534.
- 43 R. Zhang, X. Wang and S. Yu, Ternary NiCo₂Px nanowires as pH-universal electrocatalysts for highly efficient hydrogen evolution reaction, *Adv. Mater.*, 2016, **29**, 1605502.
- 44 M. Nakayama, F. Kotaro and T. Kobayakawa, A binder-free thin film anode composed of Co²⁺-intercalated busenite grown on carbon cloth for oxygen evolution reaction, *Electrochim. Commun.*, 2017, **84**, 24–27.
- 45 M. Ma, G. Zhu, F. Xie, F. Qu, Z. Liu and G. Du, Homologous catalysts based on Fe-doped CoP nanoarrays for high-performance full water splitting under benign conditions, *ChemSusChem*, 2017, **10**, 3188–3192.
- 46 Y. Hua, H. Jiang and H. Jiang, Hierarchical porous CoS₂ microboxes for efficient oxygen evolution reaction, *Electrochim. Acta*, 2018, **278**, 219–225.
- 47 S. Hao, L. Yang and D. Liu, Integrating natural biomass electro-oxidation and hydrogen evolution: using a porous Fe-doped CoP nanosheet array as a bifunctional catalyst, *Chem. Commun.*, 2017, **53**, 5710–5713.
- 48 Y. Wang, Y. Ni and B. Liu, Vertically oriented CoO@FeOOH nanowire arrays anchored on carbon cloth as a highly efficient electrode for oxygen evolution reaction, *Electrochim. Acta*, 2017, **257**, 356–363.
- 49 X. Wang, F. Li and W. Li, Hollow bimetallic cobalt-based selenide polyhedrons derived from metal-organic framework: an efficient bifunctional electrocatalyst for overall water splitting, *J. Mater. Chem. A*, 2017, 17982–17989.
- 50 Y. Teng, X. D. Wang and H. Y. Chen, Iron-assisted engineering of molybdenum phosphide nanowires on carbon cloth for efficient hydrogen evolution in a wide pH range, *J. Mater. Chem. A*, 2017, 22790–22796.
- 51 Z. Gao, Q. Gao and Z. Liu, High-efficiency hydrogen evolution catalyzed by iron phosphide nanocrystals, *RSC Adv.*, 2016, **6**, 114430–114435.
- 52 J. Yang, Z. Yang and L. H. Li, Highly efficient oxygen evolution from CoS₂/CNT nanocomposites *via* a one-step electrochemical deposition and dissolution method, *Nanoscale*, 2017, **9**, 6886–6894.

