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Hierarchical Co-FeS₂/CoS₂ heterostructures as a superior bifunctional electrocatalyst[†]

Ka Wang, Weilan Guo, Shancheng Yan, ** Haizeng Song and Yi Shi**

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.

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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 alloys13-17 have been investigated widely as electrocatalysts over the past decades. Among them, the low-cost, earthabundant 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

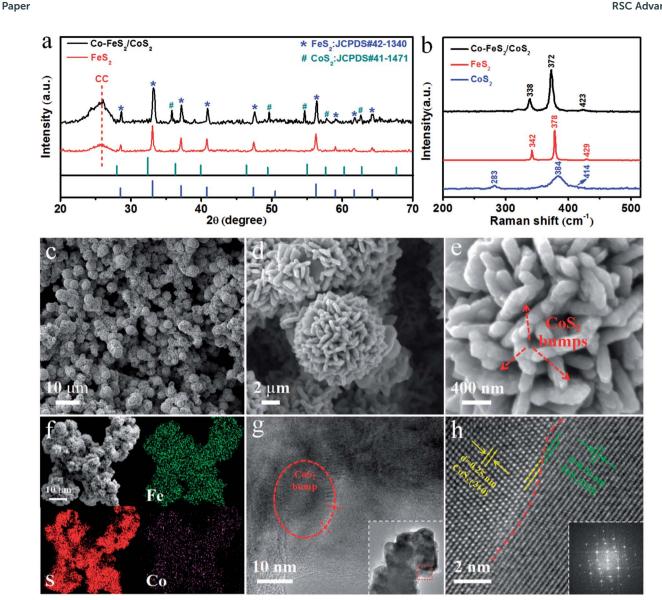
WOS1009 carbon cloth (CC) was supplied by CeTech Co., Ltd. FeSO $_4$ ·7H $_2$ O, was purchased from Shanghai Titan Scientific Co., Ltd. CH $_3$ CSNH $_2$ was purchased from Aladdin Ltd. Co(NO $_3$)·6H $_2$ O, sulfur power (S), thiourea (SC(NH $_2$) $_2$), Na $_2$ S·9H $_2$ O, C $_2$ H $_5$ OH, H $_2$ SO $_4$, 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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(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/CoS₂ nanopetals; (h) HRTEM image of Co-FeS₂/CoS₂ heterostructures, the inset is corresponding SAED pattern of Co-FeS₂/CoS₂ heterostructures.

Synthesis of Co-FeS₂/CoS₂ heterostructures

In this experiment, the carbon cloth (1.8 cm \times 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), $Co(NO_3)_2 \cdot 6H_2O$ (0.156 mM), and $SC(NH_2)_2$ (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.

Materials characterization

The crystal phase properties of the samples were analyzed with a Bruker D8 Advance X-ray diffractometer (XRD) using Cu Kα 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 μW 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).

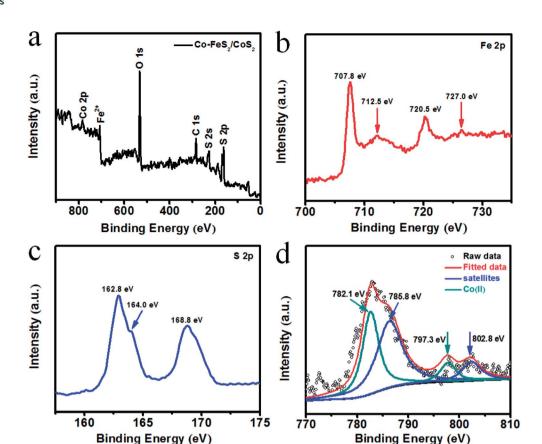


Fig. 2 (a) XPS survey spectrum for $Co-FeS_2/CoS_2$; XPS spectra of the $Co-FeS_2/CoS_2$ from (b) Fe 2p, (c) S 2p, (d) Co 2p

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 (Co^{3+}) .⁴⁵

We further analyzed the main process of formation of Co– FeS_2/CoS_2 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 Fe^{2+} , Co^{2+} , and S^{2-} . Co^{2+} was incorporated into the reaction of Fe^{2+} , S^{2-} , and sulfur powder droplets (S^0). When $Co-FeS_2$ was formed, Co^{2+} further reacted with sulfur powder droplets (S^0)/ S^{2-} to form CoS_2 , thus forming the $Co-FeS_2/CoS_2$ 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

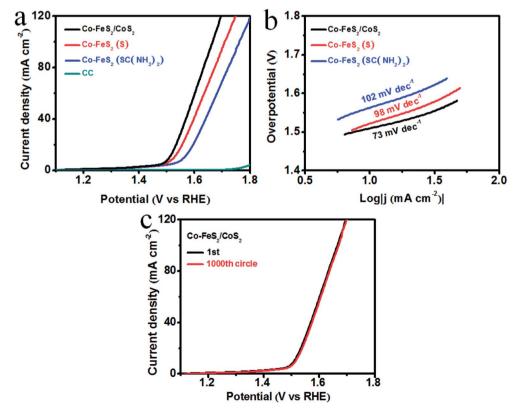


Fig. 3 (a) LSV curves of $Co-FeS_2/CoS_2$, $Co-FeS_2$ (S), $Co-FeS_2$ (SC(NH₂)₂), and bare CC for OER in 1 M KOH solution; (b) corresponding Tafel plots; (c) LSV curves of $Co-FeS_2/CoS_2$ before and after 1000 CV cycles.

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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 $Co-FeS_2$ (S) and 102 mV dec^{-1} of $Co-FeS_2$ (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–FeS $_2$ /CoS $_2$ and bare CC in 0.5 M H $_2$ 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–FeS $_2$ /CoS $_2$ 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–FeS $_2$

 $(-161 \text{ mV for (S)} \text{ and } -173 \text{ mV for } SC(NH_2)_2)$. 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 $C_{\rm dl}$. 46-48 As shown in Fig. S10ad,† cyclic voltammograms were measured in the non-faradaic capacitance current range, the Cdl value of hierarchical Co- FeS_2/CoS_2 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

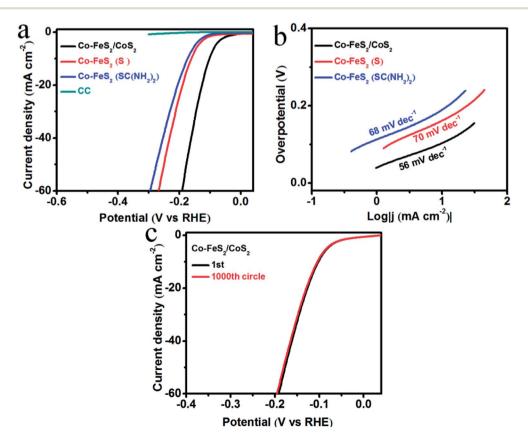


Fig. 4 (a) LSV curves of Co $-FeS_2/CoS_2$, Co $-FeS_2/CoS_2$ (S), Co $-FeS_2/CoS_2$ (SC(NH₂)₂), and bare CC for HER in 0.5 M H₂SO₄ solution; (b) corresponding Tafel plots; (c) LSV curves of Co $-FeS_2/CoS_2$ before and after 1000 cycles.

 Table 1
 Summary of HER and OER activity of electrocatalysts

Catalyst	Electrolyte	$\eta_{ m j}$ (mV vs. RHE)	Tafel slope (mV dec ⁻¹)	$\eta_{ m j}$ (mV vs. OER)	Reference
FeS_2	0.1 M KOH	$\eta_{-10} = -96$	78	_	19
FeS_2	$0.5 \text{ M H}_2\text{SO}_4$	$\eta_{-10} = -139$	66		7
$Fe_{0.68}Co_{0.32}S_2$	$0.5 \text{ M H}_2\text{SO}_4$	$\eta_{-10} = -166$	51	_	38
CoS_2	$0.5 \text{ M H}_2\text{SO}_4$	$\eta_{-10}=-145$	51.6	_	8
CoS_2	$0.5 \text{ M H}_2\text{SO}_4$	$\eta_{-100} = -140$	70.1	_	27
CoS_2	0.1 M KOH	_	_	$\eta_{10}=290$	52
$Co-FeS_2/CoS_2$	$0.5 \text{ M H}_2\text{SO}_4$	$\boldsymbol{\eta_{-10}} = -103$	56	$\eta_{10}=278$	This work

1000 cycles. Furthermore, we analyzed the characterization results of the $\text{Co-FeS}_2/\text{CoS}_2$ 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 $\text{Co-FeS}_2/\text{CoS}_2$ heterostructures did not significantly changed. The $\text{Co-FeS}_2/\text{CoS}_2$ heterostructures also has excellent electrochemical stability in 0.5 M H_2SO_4 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

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