One-dimensional Co_9S_8 - V_3S_4 heterojunctions as bifunctional electrocatalysts for highly efficient overall water splitting

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ABSTRACT Development of cost-effective, active and durable electrocatalysts for overall water splitting is still a huge challenge. Herein, we have constructed one-dimensional (1D) cobalt sulfide and vanadium sulfide heterojunction nanowires arranged on carbon cloth (Co_9S_8 - V_3S_4 /CC) as bifunctional electrocatalysts for the efficient overall water splitting. The 1D wire-structured Co_9S_8 - V_3S_4 heterojunctions possess large surface area, plentiful active sites and rapid transport of electrons/reactants and the release of gas. Importantly, the electron transfer from Co_9S_8 to V_3S_4 occurs at the interface due to the strong electronic coupling effect in Co_9S_8 - V_3S_4 heterojunction, in which the electron-attracting V_3S_4 (V^{2+}) optimizes the adsorption of H^+ active species for hydrogen evolution reaction (HER), while the electron-losing Co_9S_8 (Co^{3+}) responds to the enhancement of oxygen evolution reaction (OER) activity. Co_9S_8 - V_3S_4 /CC exhibits low overpotentials of 85 and 232 mV at 10 mA cm^{-2} and small Tafel slopes of 51 and 59 mV dec^{-1} for HER and OER, respectively. Especially, the electrolyzer with Co_9S_8 - V_3S_4 /CC as both the anode and cathode requires low onset voltage of 1.35 V and cell voltage of 1.53 V at 10 mA cm^{-2} and exhibits high Faradaic efficiencies and robust stability. It can be driven by a solar cell (1.53 V) for continuous production of hydrogen and oxygen. This study highlights the design of 1D sulfide heterojunction in pursuit of highly efficient electrocatalysts for overall water splitting.

Keywords: overall water splitting, heterojunction, cobalt sulfide, vanadium sulfide, electronic structure

INTRODUCTION

Electrocatalytic water splitting to produce hydrogen (H_2) with renewable energies input is envisioned as an attractive route to tackle energy shortage and environ-

mental pollution caused by massive burning of traditional fossil fuels [1]. It involves two half reactions of the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER) [2–5]. However, the electrocatalytic water splitting is difficult to trigger due to the sluggish kinetics of both two half-reactions [6–9]. To reduce the consumption of energy and improve the efficiency of overall water splitting, the efficient and stable catalysts for HER and OER are required to improve the reaction rates [10]. Pt-based catalysts are the superb catalysts for HER, and Ru/Ir-based oxides are the benchmark OER catalysts, but their commercial application is hindered by the expensive price and low abundance [11,12]. In this regard, much endeavors have been devoted to developing cheap transition metal (TM)-based oxides, sulfides, nitrides, and phosphides as substitute materials of precious metal catalysts [13,14].

Recently, cobalt sulfides (e.g., Co_9S_8 [15], CoS_2 [16] and CoS_x [17]) have been considered as the promising electrocatalysts for HER, OER and overall water splitting. For example, Peng *et al.* [18] fabricated a flexible CoS_2 /reduced graphene oxide-carbon nanotube electrode, which exhibited the catalytic HER activity. Liu *et al.* [19] reported that ultrathin Co_3S_4 nanosheets showed excellent OER performance under neutral solution *via* engineering spin states and exposing polyhedra in thin nanosheets. Huang *et al.* [20] fabricated Co_9S_8 /N-, O- and S-tridoped carbon materials based on a simple pyrolysis strategy, which showed catalytic activity for overall water splitting in 1.0 mol L^{-1} KOH with a voltage of 1.6 V at 10 mA cm^{-2} . However, in water splitting, compared with the outstanding OER performance, cobalt sulfides often present an undistinguished HER activity, which limits the

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efficiency of overall water splitting performance. To improve the HER performance of cobalt sulfides, some effects have been devoted to constructing the nanostructures, e.g., nanoparticles, nanosheets and nanowires [21–23]. Particularly, one-dimensional (1D) nanowires are exceptionally promising for electrocatalysis, because 1D nanowires can provide the large surface area with plentiful active sites in the radial direction, and favor the electron transfer in the axial dimension [24,25]. Nevertheless, the HER activity of cobalt sulfides is intrinsically restricted by its weak H-binding, which limits the adsorption of active H^* species. Engineering heterojunction is considered as a feasible approach to regulate the electronic structure and optimize the absorption of active species [26–28]. Particularly, the hybridization of early-transition metals (W, Mo, V) with Co-based composites can promote the HER kinetics owing to the synergistic effect of the two components [29–31]. Vanadium (V) has rich reserves, low price and atomic radius close to Co [32]. Moreover, the multivalent state of V permits it to flexibly tailor the electronic structure, and thus to improve the catalytic activity of the whole materials [33,34]. Some reports and our previous studies have verified that V-Co (Ni)-based hybrid materials perform excellent HER and OER performances because of the synergistic effects, such as the synergism occurring in the V-doped Co_4N [35], $CoVO_x$ [36] and Ni_3N -VN composites [37]. Therefore, it is exceedingly expected that the rational integration of Co- and V-based sulfides can promote the HER and OER dynamics, thereby upgrading the performance of overall water splitting. However, related reports on 1D Co-V-based sulfide heterojunctions for overall water splitting are rare.

Herein, we have designed and fabricated novel 1D cobalt sulfide and vanadium sulfide heterojunction nanowires grown on carbon cloth (Co_9S_8 - V_3S_4 /CC), through sulfurization treatment of cobalt-vanadium precursors on CC (Co-V precursor/CC) *via* a facile and controllable strategy. The Co_9S_8 - V_3S_4 /CC heterostructures with well-defined 1D architecture show large area surface, abundant active sites and rapid transport of electrons/reactants as well as the release of gas. Particularly, the electrons transfer from Co_9S_8 to V_3S_4 at the Co_9S_8 - V_3S_4 interface, in which the electron-attracting V_3S_4 (V^{2+}) optimizes the adsorption of H^* active species for HER, while the electron-losing Co_9S_8 (Co^{3+}) responds to the elevation of OER activity. The Co_9S_8 - V_3S_4 /CC catalyst delivers low overpotentials (η_{10}) of 85 and 232 mV at 10 mA cm^{-2} and small Tafel slopes of 51 and 59 mV dec^{-1} for HER and OER, respectively. Intriguingly, the electrolyzer as-

sembled by Co_9S_8 - V_3S_4 /CC as both anode and cathode requires low onset voltage of 1.35 V and cell voltage of 1.53 V at 10 mA cm^{-2} , and exhibits high Faradaic efficiencies and robust stability. It can be driven by a solar cell (1.53 V) for continuous production of hydrogen and oxygen, implying its large potential for practical applications.

EXPERIMENTAL SECTION

Synthesis

In a typical synthesis, 0.05 mmol of NH_4VO_3 , 0.95 mmol of $Co(NO_3)_2 \cdot 6H_2O$, 5 mmol of $CO(NH_2)_2$, and 2 mmol of NH_4F were dissolved in 25 mL of deionized water and stirred for 30 min to form a homogeneous solution. Afterward, the mixture was transferred to a 50-mL Teflon-lined stainless steel autoclave containing CC ($3 \times 3\text{ cm}^2$) and hydrothermally treated at 120°C for 4 h. After cooling to the room temperature, the Co-V precursors grown on the CC (Co-V precursor/CC, the mole ratio of V and Co in the preparation of Co-V precursor was 1:19) were ultrasonically cleaned with deionized water and ethanol for several times and dried in an oven at 60°C overnight. Finally, 25 mg of sulfur powder and Co-V precursor/CC were placed on the upstream and downstream of the quartz tube, respectively. Before sulfurization, N_2 was purged for 20 min to remove the air. The Co-V precursor/CC was heated at 350°C with a ramp rate of 2°C min^{-1} and maintained at 350°C for 3 h. After cooling to room temperature, the Co_9S_8 - V_3S_4 /CC was harvested. For comparison, V_3S_4 /CC and Co_9S_8 /CC were prepared with similar processes to that employed for the fabrication of Co_9S_8 - V_3S_4 /CC, except that one metal (V or Co) was included. Additionally, a series of control experiments were performed. Specifically, the corresponding sulfurization products with other hydrothermal times of 2 and 6 h were prepared (labeled as Co_9S_8 - V_3S_4 /CC-2 and Co_9S_8 - V_3S_4 /CC-6). The Co_9S_8 - V_3S_4 /CC samples were also prepared with other V/Co mole ratios of 0.5:19 and 2:19 (named as Co_9S_8 - V_3S_4 /CC (0.5:19) and Co_9S_8 - V_3S_4 /CC (2:19)). The Co-V precursor/CC was sulfurized for 2 and 4 h and tagged as Co_9S_8 - V_3S_4 /CC-T2 and Co_9S_8 - V_3S_4 /CC-T4. The Co-V precursor/CC was treated at the sulfurization temperatures of 250 and 450°C and labeled as Co_9S_8 - V_3S_4 /CC-T250 and Co_9S_8 - V_3S_4 /CC-T450.

Characterizations

The phase of the samples were analyzed by Bruker D8 diffractometer X-ray powder diffraction (XRD, with Cu $K\alpha$ radiation and the acceleration voltage of 40 kV). The

scanning electron microscopy (SEM) images were obtained by a Hitachi s-4800 electron microscope. The transmission electron microscopy (TEM) images and energy dispersive X-ray spectroscopy (EDX) elemental mapping images were acquired on the JEM-2100 TEM microscope with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) characterization was performed on a VG ESCALAB MK II with the excitation source of Mg K α (1253.6 eV) achromatic X-ray radiation. Scanning Kelvin probe measurements were performed in a Scottish SKP5050 system, and the N₂ adsorption-desorption isotherms of the samples were determined by Micromeritics Tristar II.

Electrochemical tests

All the electrochemical tests were conducted by using the CHI electrochemistry workstation (CHI-760E) at room temperature. The catalysts grown on CC were directly used as working electrode. Carbon rod and Hg/HgO served as the counter electrode and reference electrode, respectively. In addition, the commercial Pt/C and RuO₂ were coated on the CC with the loading of 3 mg for comparison. All values were calculated relative to the reversible hydrogen electrode (RHE) based on the formula $E_{(\text{RHE})} = E_{\text{Hg/HgO}} + 0.098 + 0.059\text{pH}$. In addition, all polarization curves were corrected for removing the 90% iR interference. Electrochemical performance was conducted by linear scanning voltammetry (LSV) at a scan rate of 2 mV s⁻¹. Before the test, the working electrode was pre-activated by cyclic voltammogram (CV) scans at a scan rate of 100 mV s⁻¹ for 10 cycles. For HER, the LSV curves were measured from 0 to -1 V vs. RHE. While for OER, the LSV curves were recorded in the range of 1–2 V vs. RHE. The double-layer capacitance values were obtained from the CVs with different scan rates, which varied from 2 to 12 mV s⁻¹. The potential range of HER was 0–0.2 V vs. RHE, and that of OER was 1–1.2 V vs. RHE. Electrochemical impedance spectroscopy (EIS) test was performed with the frequency ranging from 100 kHz to 0.01 Hz. Overall water splitting was performed in a two-electrode cell, where Co₉S₈-V₃S₄/CC was employed as the anode and cathode. The voltage range for overall water splitting was tested from 1 to 2 V. I - t tests at a constant overpotential to afford the current density of 10 and 20 mA cm⁻² were carried out. The Faradaic efficiencies for HER and OER during overall water splitting were measured by comparing the experimental and theoretical amounts of H₂ and O₂. In the test, potentiostatic electrolysis was employed at 1.53 V for 1 h. The amounts of gas generated were determined by gas chromatography

(GC, Aglient, 7820A).

Theoretical calculation

The projector augmented-wave (PAW) technique was utilized and the plane-wave energy cutoff was set to 500 eV [38]. Perdew-Burke-Ernzerhof (PBE) functional was applied to treat the correlation-exchange energies of the systems [39]. In addition, the sampling over Brillouin zone was treated by a (2 × 2 × 1) Monkhorst-Pack grid, and a vacuum slab with the length of 15 Å was placed along z axis on each slab to avoid the pseudo interactions between periodic images. Geometry optimization was repeated until the total energy tolerance was converged to 1 × 10⁻⁵ eV and the changes of the force on the atoms less than 0.03 eV Å⁻¹.

The adsorption energy of X (X = H or H₂O) of the catalysts was defined as:

$$\Delta E = (E_{\text{X/surface}} - 2E_{\text{X}} - E_{\text{surface}})/2. \quad (1)$$

The adsorption energy of H* (ΔG_{H^*}) was calculated by the equation:

$$\Delta G_{\text{H}^*} = \Delta E_{\text{H}^*} + \Delta E_{\text{ZPE}} - T\Delta S, \quad (2)$$

where ΔE_{H^*} , ΔE_{ZPE} and ΔS are the adsorption energy of atomic hydrogens on the given unit cell, the difference corresponding to the zero point energy between the adsorbed hydrogen and hydrogen in the gas phase and the entropy change of H* adsorption, respectively. ΔS can be obtained by $\Delta S = S(\text{H}^*) - 1/2S_0(\text{H}_2)$ (S_0 is the entropy of H₂ in the gas phase at standard conditions).

RESULTS AND DISCUSSION

Morphology and structure characterization

The synthetic route of Co₉S₈-V₃S₄/CC nanowires is schematically depicted in Fig. 1. Briefly, the uniform 1D Co-V precursor/CC can be harvested by a hydrothermal treatment of Co(NO₃)₂, NH₄VO₃, CO(NH₂)₂ and NH₄F at 120°C for 4 h. Subsequently, the Co-V precursor/CC were converted into Co₉S₈-V₃S₄/CC heterostructure by the controllable sulfurization at 350°C for 3 h. A host of control experiments were conducted to comprehend the relationship between structure and performance, and the naming rules of the samples are summarized in Table S1. SEM image of bare CC shows the smooth surface of carbon fiber with ca. 10 μm in diameter (Fig. S1). After hydrothermal treatment, the Co-V precursors are uniformly grown on the surface of CC (Fig. S2). Due to the importance of hydrothermal time on the structure of precursors, the precursors treated by different hydrothermal times (2, 4 and 6 h) were detailedly investigated. As shown in Fig. S2a, the X-ray diffraction (XRD) peaks

Figure 1 Schematic diagram of the synthesis of 1D $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ nanowires.

of the Co-V precursors correspond to vanadium oxyhydroxide, cobalt oxyhydroxide, ammonium vanadate and ammonium F-substituted vanadate. The existence of ammonium vanadate and ammonium F-substituted vanadate is attributed to the hydrolytic residues of $\text{CO}(\text{NH}_2)_2$ and NH_4F on the surface of the Co-V precursors. With the extension of hydrothermal time, the diffraction intensity of the peaks gradually increases. The result illustrates that the crystallinity and structure of precursors can be tuned by changing the hydrothermal time. SEM images of these samples show that all the

precursors have the wire-like morphology (Fig. S2b–d).

After sulfurization, the diffraction peaks of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ can be well indexed to V_3S_4 (PDF No. 18-1456) and Co_9S_8 (PDF No. 02-1459) phases (Fig. 2a). No other peaks of impurities can be found, indicating the decomposition of ammonium vanadate and ammonium F-substituted vanadate impurities after calcination and the successful conversion from Co-V precursor/CC to $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$. SEM image of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ reveals the well-maintained nanowire arranged on the CC (Fig. 2b, c). Such 1D nanostructure can enlarge the active area and facilitate the rapid transport of electrons/reactants and the release of gas, which can greatly improve the catalytic performance [40]. For comparison, single V_3S_4 or Co_9S_8 grown on CC (tagged as $\text{V}_3\text{S}_4/\text{CC}$ and $\text{Co}_9\text{S}_8/\text{CC}$) were prepared by the similar procedure of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ in the presence of only vanadium salt or cobalt salt. The single $\text{Co}_9\text{S}_8/\text{CC}$ and $\text{V}_3\text{S}_4/\text{CC}$ samples show irregular granule morphology, while $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ shows the morphology of nanowire. This result indicates that the formation of nanowire is the co-contribution of both Co_9S_8 and V_3S_4 . (Fig. S3). The corresponding products obtained from different hydrothermal times after sulfurization were also studied. As shown in Fig. S4, with prolonging hydrothermal time, the morphology of the samples changes, in which the hierarchical nanospheres appear instead of

Figure 2 (a) XRD pattern and (b, c) SEM images of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ arranged on CC. (d) TEM and (e) HRTEM images of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ scrapped from CC. (f) TEM image of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ scrapped from CC and the corresponding EDX mapping images of (g) Co, (h) V and (i) S elements.

nanowires. This phenomenon further demonstrates the important role of hydrothermal time on the structure of the catalysts. A further examination with TEM (Fig. 2d) further confirms the structure of the $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ nanowire with the diameter and length of ~ 100 and $2\ \mu\text{m}$, respectively. The high-resolution TEM (HRTEM) image of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ displays the formation of heterojunction with well-defined lattice fringes and close contact of Co_9S_8 (222) (0.29 nm) and V_3S_4 (112) (0.26 nm) (Fig. 2e). The TEM and the corresponding EDX elemental mapping images manifest the uniform distributions of Co, V and S elements in $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$. (Fig. 2f–i). All of above results verify the formation of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ heterojunction grown on CC.

XPS was carried out to deeply comprehend the composition and the interaction effect between Co_9S_8 and V_3S_4 in $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$. The survey spectrum (Fig. 3a) shows the presence of Co, V, S and O elements in the $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$. The presence of O element would be ascribed to the oxidation of the metal elements (Co or V) in air. The high-resolution Co 2p spectrum of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$ presents three doublet peaks corresponding to Co^{3+} (784.2/800.1 eV), Co^{2+} (787.5/803.7 eV) and satellite signals (790.3/806.3 eV) of Co $2p_{3/2}$ and Co $2p_{1/2}$ cores, respectively (Fig. 3b) [41]. The V spectrum of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$

CC shows that V^{2+} (514.3/522.1 eV) is the predominant component in $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$ [42], and a lower amount of V^{3+} and V^{4+} at 515.9/517.6 and 524.3/526.2 eV, respectively (Fig. 3c) [43]. The S 2p spectrum (Fig. 3d) shows five peaks, corresponding to Co–S bonds (161.4/163.1 eV) and V–S bonds (162.3/164.4 eV) of the S $2p_{3/2}$ and S $2p_{1/2}$ cores and a broad peak of sulfate species (169.5 eV) caused by the oxidation of sulphur [44]. Above findings further confirm the formation of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ heterojunction. Notably, the Co peaks of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$ shift towards the positive position (0.8 eV) in comparison with those of $\text{Co}_9\text{S}_8\text{/CC}$. Comparatively, the V peaks of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$ show the negative shift of 0.6 eV relative to those of $\text{V}_3\text{S}_4\text{/CC}$. These results indicate that the strong electronic interaction effect occurs at the interface, in which V_3S_4 works as the electron attracting effect and draws the electrons from Co_9S_8 , resulting in a higher valence Co (Co^{3+}) and a lower valence V (V^{2+}) in $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$ [45,46]. Previous reports confirm that the Co^{3+} species is the active site for OER [47–50]. Meanwhile, a low valence V (V^{2+}) can supply more electrons for bonding with proton to form H_2 and thereby fasten HER kinetics. Therefore, we deduce that the strong electronic interaction between Co_9S_8 and V_3S_4 in $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$ can tailor the electronic structures of Co and V in $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$.

Figure 3 (a) XPS survey spectrum of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$. High resolution XPS spectra of (b) Co 2p of $\text{Co}_9\text{S}_8\text{/CC}$ and $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$, (c) V 2p of $\text{V}_3\text{S}_4\text{/CC}$ and $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$. (d) S 2p of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$. (e) N_2 sorption isotherms of $\text{V}_3\text{S}_4\text{/CC}$, $\text{Co}_9\text{S}_8\text{/CC}$ and $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$ (inset: pore size distribution). (f) WF drawings of $\text{V}_3\text{S}_4\text{/CC}$, $\text{Co}_9\text{S}_8\text{/CC}$, $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4\text{/CC}$ and Pt black.

CC to generate dual-functional active sites (Co^{3+} for OER and V^{2+} for HER) in the heterostructure. The specific surface area of the catalysts were determined by Micromeritics Tristar II and calculated by Brunauer-Emmett-Teller (BET) method. The N_2 adsorption-desorption isotherms indicate that the BET specific surface area of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ is about $143.4 \text{ m}^2 \text{ g}^{-1}$, 2.14 and 3.89 times that of $\text{Co}_9\text{S}_8/\text{CC}$ ($67.1 \text{ m}^2 \text{ g}^{-1}$) and $\text{V}_3\text{S}_4/\text{CC}$ ($36.9 \text{ m}^2 \text{ g}^{-1}$), respectively (Fig. 3e). The pore size of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ is $\sim 10 \text{ nm}$ due to the piled pore of nanowire array while $\text{Co}_9\text{S}_8/\text{CC}$ and $\text{V}_3\text{S}_4/\text{CC}$ (inset in Fig. 3e) do not show obvious pores. The high specific surface area of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ is related to its 1D nanowires, which is beneficial to exposing more active sites. In addition, the scanning Kelvin probe (SKP) method was executed to calculate the work function (WF) value of the catalysts. As shown in Fig. 3f, the WF values of $\text{V}_3\text{S}_4/\text{CC}$, $\text{Co}_9\text{S}_8/\text{CC}$, $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ and Pt black are 5.47, 5.52, 5.56 and 5.60 eV, respectively. The WF value of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ approaches to that of Pt, suggesting the vast potential of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ as promising Pt-like catalyst for electrocatalytic water splitting.

HER

To evaluate the electrocatalytic HER activity of the cata-

lysts, the as-prepared $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ was directly used as the working electrode. The electrochemical measurements were conducted in a typical three-electrode configuration with an electrolyte of 1.0 mol L^{-1} KOH solution and a scan rate of 2 mV s^{-1} . For comparison, the activities of bare CC, $\text{V}_3\text{S}_4/\text{CC}$ and $\text{Co}_9\text{S}_8/\text{CC}$, along with that of the benchmark Pt-C coated on CC (Pt-C/CC) were measured. Fig. 4a shows the LSV curves of bare CC, $\text{Co}_9\text{S}_8/\text{CC}$, $\text{V}_3\text{S}_4/\text{CC}$ and $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ with 90% iR compensation. Bare CC shows the inferior activity. The $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ catalyst displays a low onset potential (η_{onset}) of $\sim 8 \text{ mV}$, which is smaller than that of $\text{V}_3\text{S}_4/\text{CC}$ (120 mV) and $\text{Co}_9\text{S}_8/\text{CC}$ (51 mV) and comparable to that of Pt-C/CC (0 mV) (Table S2). Besides the low η_{onset} , $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ only requires smaller overpotentials of 85 (η_{10}) and 219 mV (η_{100}) to afford 10 and 100 mA cm^{-2} , respectively, superior to $\text{V}_3\text{S}_4/\text{CC}$ (432 and 562 mV) and $\text{Co}_9\text{S}_8/\text{CC}$ (255 and 359 mV) (Fig. 4b). Even at a higher current density of 200 mA cm^{-2} , the overpotential (η_{200}) employed on $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ merely increases to 254 mV, still far lower than that of $\text{V}_3\text{S}_4/\text{CC}$ (583 mV) and $\text{Co}_9\text{S}_8/\text{CC}$ (375 mV). As further compared with the recently reported HER electrocatalysts, $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ displays the best HER catalytic activity (Table S3). The noticeable enhancement in HER activity of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ is as-

Figure 4 (a) Polarization curves of bare CC, $\text{V}_3\text{S}_4/\text{CC}$, $\text{Co}_9\text{S}_8/\text{CC}$, $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ and Pt-C/CC catalysts with a scan rate of 2 mV s^{-1} in 1.0 mol L^{-1} KOH for HER. (b) Comparison of the overpotentials required to achieve current densities of 10, 100 and 200 mA cm^{-2} and (c) Tafel plots of $\text{V}_3\text{S}_4/\text{CC}$, $\text{Co}_9\text{S}_8/\text{CC}$, $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ and Pt-C/CC. (d) Nyquist plots (inset: the equivalent circuit) and (e) capacitive currents at 0.1 V as a function of the scan rate for $\text{V}_3\text{S}_4/\text{CC}$, $\text{Co}_9\text{S}_8/\text{CC}$ and $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ catalysts. (f) Polarization curves of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ before and after 3000 cycles. Inset: time dependence of the catalytic current for $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ during HER process for 40 h.

cribed to the feasible 1D nanowire structure, together with the favorable synergy of Co_9S_8 - V_3S_4 heterojunction, where V_3S_4 draws the electrons from Co_9S_8 to produce much lower valence V (V^{2+}) that can supply more electrons for bonding with proton to form H_2 and thereby fasten HER kinetics. The Tafel analysis was conducted to investigate the reaction kinetics for HER. Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ presents a small Tafel slope of 51 mV dec^{-1} (Fig. 4c), which is superior to that of $\text{V}_3\text{S}_4/\text{CC}$ (95 mV dec^{-1}) and $\text{Co}_9\text{S}_8/\text{CC}$ (80 mV dec^{-1}), and close to that of $\text{Pt-C}/\text{CC}$ (32 mV dec^{-1}). The small Tafel slope of Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ suggests a fast rate of hydrogen generation with applied overpotential, coinciding with the high activity exhibited in the LSV curves. EIS test shows that Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ delivers a smaller charge transfer resistance (R_{ct}) of 6.8Ω than $\text{V}_3\text{S}_4/\text{CC}$ (10.4Ω) and $\text{Co}_9\text{S}_8/\text{CC}$ (8.3Ω), further suggesting the rapid electron transport on the 1D Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ nanostructure (Fig. 4d).

The influence of hydrothermal time on the activity was also studied. The Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ catalyst (obtained from hydrothermal time of 4 h) shows the best HER activity (Fig. S5). Too short or too long hydrothermal time cannot harvest the high HER activity of catalyst. The results demonstrate that high crystalline at long hydrothermal time may be beneficial for high HER activity, whereas too long hydrothermal time results in the damage of nanowire and inferior electrical conductivity. This result can be further verified by the electrochemical impedance of the catalysts with different hydrothermal times. As shown in the Fig. S6, the Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ catalyst obtained from hydrothermal time of 4 h delivers the smallest R_{ct} among them, indicating the best electronic conductivity of Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$. We also examined the effects of ratio of V/Co in Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$, sulfuration time and sulfuration temperature on the catalytic performance (Figs S7–S9). The Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ catalyst with V/Co ratio of 1/19, sulfuration time of 3 h and sulfuration temperature of 350°C exhibits the highest activity. These results indicate that the suitable V/Co ratio and sulfuration time are important to optimization of the performance of the catalyst.

The electrochemical surface area (ECSA) performed by a typical CV measurement in a potential range from 0 to 0.2 V, which was proportional to the double-layer capacitance (C_{dl}), was measured to explore the merits of the Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ (Fig. S10 and Fig. 4e). Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ shows the largest C_{dl} of 393 mF cm^{-2} , which is 2.91 and 1.12 times that of $\text{V}_3\text{S}_4/\text{CC}$ (135 mF cm^{-2}) and $\text{Co}_9\text{S}_8/\text{CC}$ (350 mF cm^{-2}). The value is also higher than that of Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ -2 and Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ -6 (Fig. S11). The

high C_{dl} implies additional exposed active sites on Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ for HER. Moreover, the HER activities normalized by BET and ECSA for Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ are also much higher than that for $\text{V}_3\text{S}_4/\text{CC}$ and $\text{Co}_9\text{S}_8/\text{CC}$ (Fig. S12). The exchange current density (j_0) of Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ is $40 \mu\text{A cm}^{-2}$, larger than that of $\text{Pt-C}/\text{CC}$ ($13 \mu\text{A cm}^{-2}$), and much larger than that of $\text{Co}_9\text{S}_8/\text{CC}$ ($6.3 \mu\text{A cm}^{-2}$) and $\text{V}_3\text{S}_4/\text{CC}$ ($0.25 \mu\text{A cm}^{-2}$) (Fig. S13). This finding illustrates the higher catalytic activity of Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ towards HER than the other counterparts. To better get insights into the intrinsic activity, the conversion frequency (TOF) of HER was estimated. As depicted in Fig. S14, the TOF value of Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ is 0.281 s^{-1} at 100 mV in 1.0 mol L^{-1} KOH, which is higher than that of $\text{V}_3\text{S}_4/\text{CC}$ (0.075 s^{-1}) and $\text{Co}_9\text{S}_8/\text{CC}$ (0.056 s^{-1}). The high TOF of Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ corresponds with its superb activity toward HER. Besides the catalytic activity, long-term stability is also a vital criterion for a good catalyst. The Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ catalyst was handled 3000 cycles using a successive CV measurement between 0 and -1 V . The polarization curves of Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ present a negligible loss after the stability test, demonstrating the optimum stability of the Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ catalyst (Fig. 4f). I - t curve displays no noticeable attenuation during 40 h (inset of Fig. 4f). Additionally, the XPS analysis shows a negligible change of Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ after HER (Fig. S15), further confirming the excellent stability for HER.

OER

The Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ catalyst was further investigated with respect to the catalytic OER in 1.0 mol L^{-1} KOH. Fig. 5a exhibits the polarization curves for bare CC, $\text{V}_3\text{S}_4/\text{CC}$, $\text{Co}_9\text{S}_8/\text{CC}$, Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ and RuO_2 coated on CC (RuO_2/CC) with 90% iR compensation and scan rate of 2 mV s^{-1} . Bare CC shows the negligible OER activity. The Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ catalyst shows a low η_{onset} of 60 mV, which is much better than $\text{Co}_9\text{S}_8/\text{CC}$ (72 mV) and $\text{V}_3\text{S}_4/\text{CC}$ (179 mV), and even superior to RuO_2/CC (109 mV) (Table S2). To achieve the current density of 10, 100 and 200 mA cm^{-2} , the required overpotentials for Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ are 232 (η_{10}), 312 (η_{100}) and 329 mV (η_{200}), respectively, much lower than those of $\text{V}_3\text{S}_4/\text{CC}$, $\text{Co}_9\text{S}_8/\text{CC}$ and RuO_2 (Fig. 5b and Table S2). Particularly, the current density of Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ increases sharply at the potential of 1.5 V, implying the rapid evolution of oxygen. These results demonstrate that Co_9S_8 - V_3S_4 heterojunction responds to the enhanced OER activity. The good performance can be ascribed to the more Co^{3+} species in the Co_9S_8 - $\text{V}_3\text{S}_4/\text{CC}$ compared with individuals, which can access the deprotonation of intermediates and formation

Figure 5 (a) Polarization curves of bare CC, V_3S_4/CC , Co_9S_8/CC , $Co_9S_8-V_3S_4/CC$ and RuO_2/CC catalysts with a scan rate of 2 mV s^{-1} in 1.0 mol L^{-1} KOH for OER. (b) Comparison of the overpotentials required to achieve current densities of 10, 100 and 200 mA cm^{-2} and (c) Tafel plots of V_3S_4/CC , Co_9S_8/CC , $Co_9S_8-V_3S_4/CC$ and RuO_2/CC . (d) Nyquist plots (inset: the equivalent circuit) and (e) capacitive currents at 1.1 V as a function of the scan rate of V_3S_4/CC , Co_9S_8/CC and $Co_9S_8-V_3S_4/CC$ catalysts. (f) Polarization curves of $Co_9S_8-V_3S_4/CC$ before and after 3000 cycles. Inset: time dependence of the catalytic current for $Co_9S_8-V_3S_4/CC$ during the OER process for 40 h.

of O_2 because of its lower coordination number and higher H_2O adsorption energy.

The Tafel slopes for V_3S_4/CC , Co_9S_8/CC , $Co_9S_8-V_3S_4/CC$ and RuO_2/CC were calculated to be 80, 75, 59 and 62 mV dec^{-1} , respectively (Fig. 5c). $Co_9S_8-V_3S_4/CC$ shows the best OER catalytic activity among them. The largely boosted OER kinetics for $Co_9S_8-V_3S_4/CC$ should result from the rapid charge transfer, which is verified by the EIS (Fig. 5d). $Co_9S_8-V_3S_4/CC$ displays the smallest R_{ct} ($4\ \Omega$) compared with V_3S_4/CC ($54\ \Omega$) and Co_9S_8/CC ($6\ \Omega$), suggesting the outstanding electronic conductivity of $Co_9S_8-V_3S_4/CC$. Fig. S16 shows CVs of the catalysts at different sweep speeds recorded from 1 to 1.2 V . $Co_9S_8-V_3S_4/CC$ has the largest C_{dl} of 201 mF cm^{-2} (Fig. 5e), which is 11.82 and 1.14 times that of V_3S_4/CC (17 mF cm^{-2}) and Co_9S_8/CC (176 mF cm^{-2}), respectively. The highest catalytically relevant surface area of $Co_9S_8-V_3S_4/CC$ can be mainly attributed to the more exposed active sites of 1D nanowire heterostructure. The OER activities normalized by BET and ECSA for $Co_9S_8-V_3S_4/CC$ are also much higher than that for V_3S_4/CC and Co_9S_8/CC (Fig. S17). A series of tests showed that the

suitable hydrothermal time, V/Co ratio, sulfuration time and sulfuration temperature are also important for yielding an optimized catalyst for the OER (Figs S18–S23). Based on the above results, it is concluded that the enhanced OER performance of $Co_9S_8-V_3S_4/CC$ can be ascribed to the optimal electronic structure of $Co_9S_8-V_3S_4$ heterojunction derived from the strong electronic coupling effect of V_3S_4 and Co_9S_8 to produce the more Co^{3+} active species at the interfaces, which improve the intrinsic OER activity. Additionally, the performance of the $Co_9S_8-V_3S_4/CC$ is also superior to most of the recently reported non-noble metal OER electrocatalysts summarized in Table S4. After successive CV cycling for 3000 cycles (Fig. 5f), the curve presents a negligible change. Furthermore, the $I-t$ response shows the diminutive attenuation at η_{10} for 40 h (inset in Fig. 5f). Figs S24–S26 show the XPS, EDS and XRD analyses of $Co_9S_8-V_3S_4/CC$ after OER. The morphology and phase of $Co_9S_8-V_3S_4/CC$ after the OER show negligible changes, while the high valence species of all elements slightly increased for $Co_9S_8-V_3S_4/CC$, implying that synergistic effect of sulfide and oxide layer formed during the OER process is re-

sponsible for the OER activity [51].

Overall water splitting

For the easily practical application of the overall water splitting, a bifunctional HER/OER electrocatalyst is desirable for its facile manipulation and assembly. In view of the excellent HER and OER performances of the $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ catalyst, a two-electrode electrolyzer that used $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ as both the anode and cathode was assembled and measured to evaluate the overall water splitting performance. As shown in the Fig. 6a, the electrolyzer requires a low onset voltage of 1.35 V and cell voltage of 1.53 V at 10 mA cm^{-2} , which outperform that of $\text{Pt-C/CC}||\text{RuO}_2/\text{CC}$ (1.61 V) and the other reported bifunctional electrocatalysts for overall water splitting (Fig. 6a, Fig. S27 and Table S5). Additionally, $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ presents the Faradaic efficiencies (FE) close to 100% for both the HER and OER during the overall water splitting (Fig. 6b). $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ also shows robust stability for overall water splitting and has no noticeable deactivation at the constant voltage of 1.53 and 1.71 V for 48 h (Fig. 6c). Impressively, the electrolyzer can be driven by a solar cell with the voltage of 1.53 V and a large amount of hydrogen and oxygen bubbles are clearly observed on the surface of CC (Fig. 6d–f and Movie S1), implying its vast potential for converting the solar energy.

Comprehending active origin of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ with DFT calculations

To further unveil the effect of electronic structure of the $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ on the HER and OER activities, the density functional theory (DFT) calculations were performed. Fig. 7a shows the calculation models of single Co_9S_8 and V_3S_4 and $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ heterojunction. Density of states (DOS) of Co_9S_8 , V_3S_4 and $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ cross the Fermi level, indicating that all the catalysts show metallic behavior (Fig. 7b). Particularly, the DOS of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ is larger than that of V_3S_4 and Co_9S_8 near the Fermi level (dash curve), suggesting the increase of charge carrier density of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ heterojunction. This result is beneficial to the electron transfer during the electrocatalytic process. Moreover, the adsorption energies of H (ΔG_{H^+}) on the surfaces of V_3S_4 , Co_9S_8 and $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ were calculated and compared (Fig. 7c). The ΔG_{H^+} absolute value for $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ heterojunction is 0.297 eV, which is far smaller than that of V_3S_4 (1.069 eV) and Co_9S_8 (0.680 eV). The small ΔG_{H^+} of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ demonstrates a low energy barrier for H adsorption/desorption on $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ during the HER process. Additionally, the water adsorption energy ($\Delta E_{\text{H}_2\text{O}}$) of Co_9S_8 , V_3S_4 and $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ was calculated. $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ exhibits the higher water adsorption energy of -0.364 eV than V_3S_4 (-0.340 eV) and Co_9S_8 (-0.301 eV). This result manifests that the easy adsorption and dissociation of H_2O on the surface of $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$

Figure 6 (a) Polarization curve of overall water splitting for $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}||\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$. (b) Amount of H_2 and O_2 collected and amount calculated from the electric quantity for $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ during the overall water splitting. (c) Long-term stability test conducted at the constant voltages of 1.53 and 1.71 V for 48 h. (d–f) Demonstration of the overall water splitting system powered by a solar cell with a voltage of 1.53 V to produce H_2 and O_2 on $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}||\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$.

Figure 7 Theoretical calculations of V_3S_4 , Co_9S_8 and $Co_9S_8-V_3S_4$ systems. (a) Crystal structures, (b) DOS, (c) H^* adsorption energy and (d) water adsorption energy.

heterojunction facilitate the subsequent HER and OER processes (Fig. 7d), which coincides with the good electrochemical performance. The bifunctional activity of the $Co_9S_8-V_3S_4$ heterojunction was further elucidated by calculating the difference in the electron density (Fig. S28). The blue and yellow regions refer to the electron accumulation and electron depletion areas, respectively. Noticeably, the electrons ($1.8 e^-$) transfer from Co_9S_8 to V_3S_4 , which is in agreement with the XPS results. The electron accumulation on V_3S_4 favors the optimization of the H^* adsorption energy for HER, whereas the accumulation losing on Co_9S_8 is beneficial for improving OER performance. All above results noticeably demonstrate the enhanced HER and OER activities of the $Co_9S_8-V_3S_4/CC$ heterostructure originate from the synergistic effects of V_3S_4 and Co_9S_8 interface via well-defined 1D wire-like morphology, tailored electronic structure, increased charge carrier density and optimized adsorption energies of active species during water electrolysis.

CONCLUSIONS

In summary, a 1D $Co_9S_8-V_3S_4$ heterojunction with a well-

designed nanowire architecture grown on CC was successfully fabricated by a facile and controllable strategy. Such 1D nanostructure enlarges the active area, exposes more active sites and facilitates the rapid transport of electrons/reactants. The strong electronic effect between V_3S_4 and Co_9S_8 occurs at the interface and dual-functional active sites (Co^{3+} for OER and V^{2+} for HER) were generated in the heterostructure. $Co_9S_8-V_3S_4/CC$ exhibits excellent HER and OER activities with low overpotentials, small Tafel slopes, high j_0 and remarkable stability. Assembled as two-electrode electrolyzer, it only requires the onset voltage of 1.35 V and cell voltage of 1.53 V at 10 mA cm^{-2} , and exhibits high Faradaic efficiencies and robust stability. It can be driven by a solar cell with the voltage of 1.53 V. This study sheds a light on the guidance for the design of effective bifunctional electrocatalysts for overall water splitting.

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Supplementary information Supporting data are available in the online version of the paper.

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一维 $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ 异质结作为双功能电催化剂用于高效电催化分解水

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摘要 发展低成本、高活性和稳定的电催化分解水电催化剂, 仍然是一项巨大的挑战. 本研究工作中, 我们构建了一种在碳布基底上生长的一维硫化钴和硫化钒异质结纳米线($\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$)作为双功能电催化剂用于高效全解水. 一维线状结构的 $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ 具有大比表面积、丰富的活性位点和快速的质子/电子转移能力以及释放气体的能力. 更重要的是, 由于 $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4$ 异质结具有强电子耦合效应, 在界面处, Co_9S_8 的电子向 V_3S_4 转移, 即 $\text{V}_3\text{S}_4(\text{V}^{2+})$ 吸引电子, 有利于析氢反应中的 H^+ 活性位点的吸附, $\text{Co}_9\text{S}_8(\text{Co}^{3+})$ 失去电子, 有利于提高析氧反应催化活性. 在 10 mA cm^{-2} 的电流密度下, $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ 催化HER、OER的过电位分别是85和232 mV; Tafel斜率分别是51和59 mV dec^{-1} . 以 $\text{Co}_9\text{S}_8\text{-V}_3\text{S}_4/\text{CC}$ 分别作为阳极和阴极用于全解水, 起始电压仅为1.35 V, 达到 10 mA cm^{-2} 的电流密度所需电压仅为1.53 V, 且具有高法拉第效率和高稳定性. 此装置可被太阳能电池(1.53 V)驱动连续产生 H_2 和 O_2 . 这项工作提出了一种设计用于高效全解水的一维硫化物异质结电催化剂的新方法.