Multi-dimensional hierarchical CoS₂@MXene as trifunctional electrocatalysts for zinc-air batteries and overall water splitting

Silin Han¹, Yu Chen¹, Yanan Hao¹, Yaoyi Xie¹, Dengyu Xie¹, Ying Chen¹, Yixing Xiong¹, Zhengyao He¹, Feng Hu^{1*}, Linlin Li¹, Jixin Zhu² and Shengjie Peng^{1*}

ABSTRACT The demanding all-in-one electrocatalyst system for oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) in zinc-air batteries or water splitting requires elaborate material manufacturing, which is usually complicated and time-consuming. Efficient interface engineering between MXene and highly active electrocatalytic species (CoS₂) is, herein, achieved by an *in situ* hydrothermal growth and facile sulfurization process. The CoS₂@MXene electrocatalyst is composed by one-dimensional CoS₂ nanowires and two-dimensional MXene nanosheets, which lead to a hierarchical structure (large specific surface area and abundant active sites), a spatial electron redistribution (high intrinsic activity), and high anchoring strength (superior performance stability). Therefore, the electrocatalyst achieves enhanced catalytic activity and long-time stability for ORR (a half-wave potential of 0.80 V), OER (an overpotential of 270 mV at 10 mA cm⁻², i.e., η_{10} = 270 mV) and HER (η_{10} = 175 mV). Furthermore, the asymmetry water splitting system based on the CoS₂@MXene composites delivers a low overall voltage of 1.63 V at 10 mA cm⁻². The solid-state zinc-air batteries using CoS₂@MXene as the air cathode display a small charge-discharge voltage gap (0.53 V at 1 mA cm⁻²) and superior stability (60 circles and 20-h continuous test). The energy interconversion between the chemical energy and electricity can be achieved by a self-powered system *via* integrating the water splitting system and quasi-solid-state zinc-air batteries. Supported by *in situ* Raman analyses, the formation of cobalt oxyhydroxide species provides the active sites for water oxidation. This study paves a

promising avenue for the design and application of multi-functional nanocatalysts.

Keywords: hierarchical structure, sulfides, multiple functionalities, water splitting, zinc-air batteries

INTRODUCTION

Sustainable production and efficient storage of energy have attracted extensive attention due to the growing environmental pollution and global energy crisis. Electrochemistry provides a viable method for the interconversion between chemical energy and electricity under the ambient condition. Of particular interest is the integrated energy system, for example, the electrolytic water splitting [1–3] powered by lithium storage units [4] or metal-air batteries [5–10], which holds promise in the next-generation of power supply, conversion, and distribution featured with high efficiency, low cost, sustainability, and environmental benignity. In particular, hydrogen (H₂), the product of electrolytic water splitting [11], is an infinitely renewable and relatively pollution-free fuel source to alleviate the reliance on traditional fuels. Meanwhile, metal-air batteries have been intensely focused upon as promising next-generation high-energy devices. The core technology of such combined system lies on three redox reactions involving the hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) [12–16]. Although both the required thermodynamic voltage to drive the electrolytic water splitting (HER and OER) and

¹ Jiangsu Key Laboratory of Electrochemical Energy Storage Technologies, College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

² Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), Nanjing 211816, China

* Corresponding authors (emails: pengshengjie@nuaa.edu.cn (Peng S); fenghu@nuaa.edu.cn (Hu F))

the equilibrium potential to initiate the reversible oxygen conversion (OER and ORR) are 1.23 V *versus* reversible hydrogen electrode (RHE), in practice an overpotential is always necessary to carry out any of these reactions in order to overcome their sluggish kinetics, which in turn calls for high-performance electrocatalysts to maximize the energy efficiency and improve the reaction kinetics. To date, although noble metal electrocatalysts, such as Pt/C for ORR, HER, and RuO₂ or IrO₂ for OER, showcase the state-of-the-art performance, their global-scale commercial deployment is dramatically impeded by their high price, scarcity, and poor stability. Thus, developing multifunctional electrocatalysts with low cost, high performance, and long-time duration is imperative for the future implementation of integrated energy systems [17,18].

The development of multifunctional electrocatalysts typically relies on the rational integration of each component together with a synergic improvement of both morphological and electronic structures favorable for each reaction. However, achieving the high intrinsic activity, large density, and long-term stability of reaction sites together always meets with inevitable interferences. For example, high-index facets or boundaries of nanostructures usually showcase improved electrocatalytic activity but poor stability due to the incident surface reconstruction. Manufacturing ultrathin nanostructures with large specific surface area and abundant reaction sites typically suffers from stacking effects. More importantly, single active site favors multiple redox reactions (i.e., HER, OER, and ORR), which has hardly been realized. Transition metal chalcogenides (TMCs) have shown a wide application prospect in various fields due to their tunable nanostructures, superior electrocatalytic activities, and enormous active sites [19–24]. Among those, cobalt disulfide is an emerging electrocatalyst for multiple reactions with the merits of controllable morphology, metallic conductivity, and favorable 3d-electron configuration [25,26]. However, the CoS₂ alone still underperforms regarding the multifunctionality required simultaneously for ORR, OER, and HER [27]. Although heteroatom doping and defect engineering have been employed to improve their electrocatalytic performance [28–31], a facile synthesis strategy for the high-performance trifunctional electrocatalysts is urgently desired to accelerate the realistic application of such integrated energy systems.

Two-dimensional (2D) MXene, the selective etching product of the MAX phase by removing Al element [32–34], with fascinating physicochemical properties includ-

ing element diversity, rich surface terminations (e.g., –OH and –O), and high conductivity show a promising potential in electrochemistry [35–40]. With abundant anchoring sites, 2D MXene works well for conducting substrate for electrocatalytically active nanoparticles to achieve hybrid electrocatalysts with well-dispersed and stable reaction sites, and more importantly creates an intimate interface for the electron redistribution and optimized electrocatalysis [41–47].

In this study, we rationally design a multidimensional TMC-MXene heterostructure composed by 1D CoS₂ nanowires grafted on 2D MXene nanosheets (denoted as CoS₂@MXene) through a facile hydrothermal reaction followed by a sulfurization process. The large specific surface area and rich surface functions enable the strong-grafted CoS₂ nanowires; in turn, the *in situ* growth of CoS₂ prevents the stacking and agglomeration of MXene nanosheets. Moreover, MXene exhibits a higher electronegativity and results in the electron transfer from Co atoms to MXene. Therefore, the multidimensional CoS₂@MXene affords the superior catalytic performance simultaneously for OER, HER and ORR. The assembled zinc-air batteries with CoS₂@MXene air cathode show a low voltage gap (0.73 V) with a long-time stability by 20-h continuous test. The CoS₂@MXene electrode entails a voltage of 1.63 V at 10 mA cm^{–2} for overall water splitting. The overall water-splitting system can be self-powered by two series-connected zinc-air batteries. This study enlightens the design of trifunctional electrocatalysts which have a great potential for the wide application of integrated energy systems.

EXPERIMENTAL SECTION

Preparation of MXene nanosheets by selective etching and exfoliation

The Ti₃C₂T_x MXene was obtained by an etching process of Ti₃AlC₂ *via* removing the Al layer using HF. Typically, the etching solution was firstly prepared by adding LiF (2.0 g) to 30 mL HCl solution (9 mol L^{–1}) followed by 5-min stirring. Then, the pristine Ti₃AlC₂ (2.0 g) was added into the etching solution at 40°C. After 30-h reaction, the Al layer was entirely removed. The bulk Ti₃C₂T_x MXene was collected by centrifugation and washed with water until the final pH reached about 6. The collected powder was dried under vacuum. For the preparation of MXene nanosheets, the obtained bulk MXene powder was dispersed in 250 mL water followed by sonication at Ar atmosphere for 2 h. After centrifugation, the collected supernatant was the MXene nanosheet suspension. The

concentration of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in the supernatant was about 3 mg mL^{-1} .

Preparation of CoS_2 @MXene

The CoS_2 @MXene was synthesized by sulfurization of the $\text{Co}(\text{OH})_2$ @MXene precursor. To prepare the $\text{Co}(\text{OH})_2$ @MXene, 1.5 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 3 mmol of NH_4F and 7.5 mmol of $\text{CO}(\text{NH}_2)_2$ were added in the mixed solution of H_2O (50 mL) and MXene (10 mL) under stirring. Then, the mixed solution was transferred to a Teflon-lined stainless-steel autoclave and kept at 110°C for 5 h. The $\text{Co}(\text{OH})_2$ @MXene was finally obtained after centrifugation followed by the freeze drying process. For the sulfurization treatment, 200 mg of sulfur powder and 40 mg of $\text{Co}(\text{OH})_2$ @MXene were placed in an upstream and downstream porcelain boat, respectively. The temperature was increased by 5°C min^{-1} and maintained at 450°C for 2 h. As a consequence, CoS_2 @MXene was obtained, which was also referred as CoS_2 @10MXene. For comparison, the CoS_2 @MXene with different concentrations of CoS_2 were prepared simply by changing the amount of MXene precursor to 5 mL and 15 mL, with other conditions kept the same, and the obtained products were labeled as CoS_2 @5MXene and CoS_2 @15MXene, respectively.

Characterization

The crystalline structures were characterized by X-ray diffractometer (XRD, Bruker D8 ADVANCE). The morphologies were observed using scanning electron microscopy (SEM, Regulus 8100) under 5.0–20.0 kV and transmission electron microscopy (TEM, FEI Tecnai G2 F20) at an accelerating voltage of 200 kV. The surface area analysis was carried out using the Brunauer-Emmett-Teller (BET) method from N_2 adsorption-desorption isotherms (V-Sorb 2800P). The inductively coupled plasma optical emission spectroscopy (ICP-OES) was measured on an Optima 4300 DV spectrometer (Perkin-Elmer). The elemental composition and chemical state were confirmed by X-ray photoelectron spectroscopy (XPS Escalab 250Xi). The Raman spectra were collected by RENISHAW equipped with an excitation wavelength of 633 nm.

Electrochemical measurements

The electrocatalytic performances were evaluated by the three-electrode system with a potentiostat. Carbon rod and Ag/AgCl (saturated KCl) electrode were used as a counter electrode and reference electrode, respectively. The catalyst ink was prepared with a mass ratio of cata-

lyst:carbon black:Nafion of 7:2:1 in the mixed solution of ethanol/water (volume ratio of 4:6). Then, the ink was coated onto a nickel foam (1 cm^2) which was used as a working electrode for OER and HER measurements. ORR measurement was carried out in N_2 or O_2 -saturated 0.1 mol L^{-1} KOH solution using an ink-coated glassy carbon disk (0.196 cm^2) as the working electrode. The linear scan voltammeter (LSV) was measured under 5 mV s^{-1} . Cyclic voltammograms (CV) were recorded within a non-Faradaic potential window ($0.92\text{--}1.02 \text{ V vs. RHE}$) at increasing scan rates ($10\text{--}140 \text{ mV s}^{-1}$) to obtain the electrochemical surface areas (ECSA). The turnover frequency (TOF) was calculated by the following equation: $\text{TOF} = JA/4Fm$, where J (mA cm^{-2}) is the current density at each overpotential, A is the geometric surface area of the electrode, F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), and m is the mole number of Fe and Ni atoms in the catalyst.

Fabrication of quasi-solid-state zinc-air batteries

The quasi-solid-state zinc-air battery was constructed by a zinc foil, a hydrogel electrolyte and an air cathode. The hydrogel electrolyte was prepared as follows: 10 mg of N,N' -methylene-bisacrylamide was added into 2.2 g of acrylic acid solution under sonication. After full dissolution, the above solution was added into 10 mL of KOH solution (8.4 mol L^{-1}) under stirring. Then, $80 \mu\text{L}$ of $\text{K}_2\text{S}_2\text{O}_8$ solution (0.1 mol L^{-1}) was added. The solution was then poured into the glass mold. The hydrogel can finally form after a spontaneous polymerization process. The catalyst ink was made by mixing catalysts, 5 wt% Nafion and ethanol. The air electrode was obtained by dropping catalyst ink onto the carbon cloth ($1 \text{ cm} \times 1 \text{ cm}$) with a final loading concentration of 0.6 mg cm^{-2} .

RESULTS AND DISCUSSION

Materials manufacturing

The CoS_2 @MXene heterostructure was prepared through the hydrothermal reaction and subsequent sulfurization treatment as shown in Fig. 1a. The MXene sheets were obtained by the typical etching and exfoliation processes (Figs S1 and S2). The morphologies in the SEM (Fig. 1b–e) and TEM (Fig. 1f) images confirm that the CoS_2 nanowires were parallelly anchored on the isolated MXene nanosheets without obvious aggregation and restacking. The heterostructure could enhance the interface effect between the electrolyte and electrode by providing rich reaction sites and promoting the mass transport of reactants. The clear lattice fringe of 0.26 nm is corre-

Figure 1 (a) The schematic synthesis process for $\text{Co(OH)}_2\text{/MXene}$ and $\text{CoS}_2\text{/MXene}$ hybrids. SEM images of (b) MXene sheets, (c) $\text{Co(OH)}_2\text{/MXene}$ and (d, e) $\text{CoS}_2\text{/MXene}$ hybrids. (f, g) TEM and HRTEM images of $\text{CoS}_2\text{/MXene}$. (h) The distributions of Co, S, Ti, and C elements.

sponding to the (210) plane of CoS_2 in Fig. 1g. The elemental mapping of $\text{CoS}_2\text{/MXene}$ confirms the homogenous distribution of Co, S, Ti, and C throughout the composite structure, implying the uniform growth of CoS_2 on MXene nanosheets. The surface area was further confirmed by the N_2 adsorption/desorption isotherms (Fig. S3). The $\text{CoS}_2\text{/MXene}$ shows a higher surface area ($46.2 \text{ m}^2 \text{ g}^{-1}$) than that of only CoS_2 ($6.4 \text{ m}^2 \text{ g}^{-1}$) and MXene ($15.1 \text{ m}^2 \text{ g}^{-1}$). The larger surface area demonstrates the successful growth of $\text{CoS}_2\text{/MXene}$ composites with less aggregation and restacking structure. Therefore, the above results demonstrate that MXene nanosheet as a conductive substrate to provide anchoring sites for electrocatalytic active centers and therefore the hybrids with an open structure show larger specific surface area. Identified by ICP-OES, the molar ratio of CoS_2 to MXene can be reflected by the atomic ratio of Co to Ti (e.g., 2.6 for $\text{CoS}_2\text{/MXene}$, Fig. S4), which increases with more addition of MXene, consistent with the results of XPS.

The phase of the products was identified by the XRD analysis. In the XRD pattern of $\text{CoS}_2\text{/MXene}$, the diffraction peaks confirm the crystalline structure of CoS_2 (PDF No. 41-1471) in Fig. 2a and Fig. S5. To study the surface element species and electronic structure, XPS analyses were conducted for pristine CoS_2 and $\text{CoS}_2\text{/MXene}$ composite. Compared with pure CoS_2 , the full-range spectrum of $\text{CoS}_2\text{/MXene}$ presents the obvious signals of Ti, F and O, which are inherited from successful addition of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (Fig. 2d, e and Fig. S6). The high-resolution XPS spectrum of S 2p in Fig. 2c shows two splitting peaks of S 2p_{3/2} and S 2p_{1/2} at 162.9 and 164.1 eV, respectively, indicating the existence of metal-S bonds. The transition metal element of Co is considered as the active site for electrocatalytic reactions. The signals of Co could be deconvoluted to Co^{2+} and Co^{3+} species in Fig. 2b. More importantly, the Co and S peaks of $\text{CoS}_2\text{/MXene}$ shift to a high bind energy compared with CoS_2 . The strong electronegative property of MXene

Figure 2 (a) XRD patterns of CoS₂, MXene, and CoS₂@MXene. XPS spectra of (b) Co 2p, (c) S 2p, (d) Ti 2p, (e) C 1s and (f) O 1s spectra of the CoS₂ and CoS₂@MXene hybrid.

induces the charge transfer from CoS₂ to MXene. The consequently increased valence of Co centers can facilitate the adsorption of anionic intermediates (e.g., -OH). The XPS results show the electron coupling effect between CoS₂ and Ti₃C₂T_x. The optimized electronic environment is expected to improve the intrinsic activity in OER, HER, and ORR processes.

Electrocatalytic activity

The performance of CoS₂@MXene for OER was evaluated in 0.1 mol L⁻¹ KOH solution in the conventional three-electrode system. The as-prepared CoS₂@MXene and referenced materials including pure CoS₂, MXene, and commercial RuO₂ or Pt/C were homogeneously coated onto 3D nickel foams as the working electrodes. Among the series of hybrid electrocatalysts with different ratios of CoS₂ to MXene, CoS₂@MXene synthesized with 10 mL of MXene solution exhibits the best OER performance with the lowest overpotential of 270 mV at 10 mA cm⁻² (Fig. S7). In particular, the overpotential is smaller than those of other samples including CoS₂ (323 mV), MXene (431 mV) and RuO₂ (302 mV) in Fig. 3a. The mixed CoS₂ and MXene (CoS₂+MXene) shows a higher overpotential than that of CoS₂@MXene indicating that the electronic interaction facilitates the OER reaction. Compared with the reported catalysts, CoS₂@MXene is one of the best

OER catalysts in an alkaline medium (Table S1). The Tafel slope and electrochemical impedance spectroscopy (EIS) results highly correlate to the reaction kinetics. Tafel slope of CoS₂@MXene (92 mV dec⁻¹) is smaller than that of CoS₂ (96 mV dec⁻¹) and MXene (204 mV dec⁻¹) (Fig. 3b). The integration of CoS₂ and MXene clearly improves its reaction kinetics. The EIS was conducted to investigate the charge transport in the frequency range from 100 kHz to 0.1 Hz for all samples (Fig. S8). The CoS₂@MXene electrode shows a smaller charge-transfer resistance (R_{ct}) value, implying the improved kinetics of the composite.

As we know, the number of active sites and intrinsic activity are two main factors for electrochemical performance. The ECSA experiment was conducted by CV measurements under different scan rates, by which the number of active sites from the electrochemical double-layer capacitance (C_{dl}) can be calculated. Figs S9–S11 show a larger C_{dl} value for CoS₂@MXene (28 mF cm⁻²) which is higher than that of CoS₂ (9 mF cm⁻²) and MXene (2 mF cm⁻²). As mentioned from BET and ECSA measurements, heterostructure engineering can improve the surface area to expose more electrochemically active area. As expected, the CoS₂@MXene shows higher TOF value than CoS₂ and CoS₂+MXene, indicating the improvement of the intrinsic activity (Fig. S12).

Figure 3 (a) The OER polarization curves of CoS₂, MXene, mixed CoS₂+MXene, CoS₂@MXene, and Pt/C. (b) The corresponding Tafel plots. (c) The chronopotentiometric test at 10 mA s⁻¹ of CoS₂@MXene (inset: OER LSV curves before and after 1000 cycles). (d) The HER polarization curves and (e) Tafel plots of CoS₂, MXene, mixed CoS₂+MXene, CoS₂@MXene, and Pt/C. (f) The chronopotentiometric test at 10 mA s⁻¹ of CoS₂@MXene (inset: HER LSV curves before and after 1000 cycles).

For any commercial electrochemical system, stability is also another crucial criterion, apart from electrocatalytic activities. The stability of CoS₂@MXene was firstly tested by chronoamperometric measurements at the current density of 10 mA cm⁻², and only slightly increase in the applied potential can be observed after 30-h test in Fig. 3c. Furthermore, the LSV curves show no appreciable change after successive 1000 CV cycles, indicating the superior durability of CoS₂@MXene.

Besides the superior OER performance, CoS₂@MXene also achieves electrocatalytic HER activity in the same measurement condition. The CoS₂@MXene composite displays a smaller overpotential of 175 mV than CoS₂ (225 mV) and MXene (260 mV) at 10 mA cm⁻² in Fig. 3d, which is ascribed to the synergistic effect between CoS₂ and MXene. The Tafel plot was also used to evaluate the kinetics and mechanism for the HER process in Fig. 3e. For the HER reaction, Tafel slopes of CoS₂@MXene, CoS₂, MXene, mixed CoS₂+MXene and Pt/C were determined to gain more insight into the HER mechanism. The CoS₂@MXene exhibits a higher Tafel slope of 97 mV dec⁻¹ than Pt/C (36 mV dec⁻¹), indicating the HER on this catalyst may undergo a Volmer-Heyrovsky

mechanism. While the HER on CoS₂, MXene and mixed CoS₂+MXene proceeded *via* sluggish Volmer step, yielding much larger Tafel slope of 132, 148, and 138 mV dec⁻¹, respectively. Apparently, the improvement of CoS₂@MXene in HER may be associated with the acceleration of Volmer step in HER. The Volmer step (H₂O + e⁻ → H⁺ + OH⁻) is a crucial but sluggish step for HER in alkaline solution. Strong adsorption and fast dissociation of water are primarily important to accelerate this step and guarantee high coverage of H_{ads} on the catalyst surface in the next Heyrovsky or Tafel step. On this basis, the water adsorption and electrode wetting can be further improved in the presence of highly hydrophilic MXene, which is proved in previous reports [47]. Enhanced water adsorption and dissociation may greatly accelerate the Volmer step on CoS₂@MXene in alkaline electrolyte, thereby prompting the HER activity.

Meanwhile, the small charge-transfer resistance reveals faster kinetics of CoS₂@MXene from EIS in Fig. S13. The HER performance of CoS₂@MXene is comparable to other reported non-noble HER catalysts (Table S2). To assess the durability of CoS₂@MXene during HER catalysis, the chronopotentiometry test was firstly measured

at 10 mA cm^{-2} for 25 h. In Fig. 3f, only a slight increase of the applied potential was observed, implying its good long-term stability. After the continuous measurement with 1000 CV cycles, the polarization curve manifests a minor current decay in the whole potential range. Thus, the above results confirm the $\text{CoS}_2\text{@MXene}$ hybrids are attractive HER electrocatalysts in the alkaline solution. For the comparison of intrinsic activities, the electrocatalytic data for OER and HER are presented with carbon paper (CP) as a substrate rather than nickel foam (NF) in Fig. S14. While the CP was applied as the substrate, the $\text{CoS}_2\text{@MXene}$ -CP showed similar performance with $\text{CoS}_2\text{@MXene}$ -NF. However, the $\text{CoS}_2\text{@MXene}$ -CP showed smaller overpotential than CoS_2 -CP, MXene-CP and mixed $\text{CoS}_2\text{+MXene}$ -CP, implying the synergistic effect between CoS_2 and MXene.

Based on the electrochemical performance in both OER and HER processes, $\text{CoS}_2\text{@MXene}$ composites were adopted as bifunctional electrodes to assemble into the water splitting system. Remarkably, the constructed electrolyzer delivers an applied voltage of 1.63 V at 10 mA cm^{-2} , substantially lower than those based on CoS_2

and MXene (Fig. 4a and Figs S15, S16), which is rival to the reported MXene-based multi-functional materials in Table S3. Moreover, the constant 10 mA cm^{-2} was operated to test the durability with a negligible potential increase for 24-h water splitting (Fig. 4b). Therefore, the activity and stability render $\text{CoS}_2\text{@MXene}$ a great promising multi-functional catalyst for water electrolysis under alkaline conditions. The morphologies of 1D/2D hybrid nanostructure are also well maintained after OER and HER processes in Fig. 5a, b. the negligible change of morphology can confirm the stability of $\text{CoS}_2\text{@MXene}$. The chemical binding states of Co on the OER and HER electrode after long-time water electrolysis were exhibited at Fig. 5c, d and Fig. S17, indicating a higher content of Co^{3+} than Co^{2+} after OER. The peaks of S 2p retain in HER, while the peak disappears in OER, indicating the chemical structure of CoS_2 is well-maintained after the HER process. The peaks of C 1s maintain well before and after OER and HER (Fig. S18). The peaks of Ti 2p shift to lower binding energy. The change can be ascribed to the strong electronegative property of MXene, which induces the charge transfer from CoS_2 to MXene. After OER and

Figure 4 (a) LSV curves based on the bifunctional electrodes of CoS_2 , MXene and $\text{CoS}_2\text{@MXene}$ towards water splitting. (b) The chronopotentiometric test at 10 mA s^{-1} of $\text{CoS}_2\text{@MXene}$. (c) Water splitting device self-driven by two series zinc-air batteries fabricated by $\text{CoS}_2\text{@MXene}$. (d) Schematic illustration of the overall water splitting mechanism of $\text{CoS}_2\text{@MXene}$.

Figure 5 (a, b) SEM images; XPS spectra of (c) Co 2p and (d) S 2p after OER and HER processes for CoS₂@MXene. (e) *In situ* Raman spectra of CoS₂@MXene at various potentials for OER process.

HER, the stronger contact between CoS₂ and MXene can accelerate the charge transfer from CoS₂ to MXene, so the Ti 2p of MXene shifts to lower binding energy. *In situ* Raman spectroscopy of CoS₂@MXene was studied under various potentials (Fig. S19). The peaks at 394 cm⁻¹ are corresponding to the Co²⁺-O, which is due to the adsorption of OH species on the surface of CoS₂@MXene. The peak at 503 cm⁻¹ is ascribed to CoO(OH) (Fig. 5e) [48,49]. The reduction of Co²⁺-O peak and appearance of CoO(OH) peak confirm the change of chemical state of CoS₂@MXene, which is consistent with the XPS results.

The ORR performance of CoS₂@MXene was further explored in 0.1 mol L⁻¹ KOH solution. The CV curves in Fig. 6a show no cathode peak in the N₂-saturated KOH solution; in contrast, an obvious cathode peak appears at 0.68 V in the O₂-saturated KOH solution, which implies the pronounced ORR activity for the CoS₂@MXene catalysts. The CoS₂@MXene exhibits higher onset potential (0.87 V) and higher half-wave potential (0.80 V) than CoS₂ and MXene in Fig. 6b. Meanwhile, the CoS₂@MXene shows a higher limited current density in all potential windows. The CoS₂@MXene exhibits a smaller Tafel slope than other samples in Fig. 6c, demonstrating more favorable electrocatalytic kinetics for ORR. For the further insight of ORR kinetics, the rotating disk electrode (RDE) measurements for CoS₂@MXene and other samples in different rotating speeds were also investigated in Fig. 6d and Fig. S20. The limited current density gra-

dually increases with the rotation speed due to the smaller oxygen diffusion layer on the electrode surface. The transfer electron number (*n*) calculated from the Koutecky-Levich (K-L) equation is about 4 for the CoS₂@MXene catalyst in Fig. 6e, suggesting apparent four-electron reduction mechanism, which could provide a high power density in metal air batteries. The current density slightly decays to 93.4% after 28,000-s continuous operation in the chronoamperometric measurement (Fig. 6f).

Inspired by the superior ORR/OER half-reaction activity, the quasi-solid-state zinc-air batteries based on CoS₂@MXene were assembled and measured under the practical condition for the demands of portable and flexible devices. As the typical sandwich structure, the zinc-air batteries were constructed with zinc foil anode, gel electrolyte and CoS₂@MXene-based air cathode. The open-circuit voltage for CoS₂@MXene achieves a high voltage of 1.46 V, which is comparable to that of Pt/C catalyst (1.45 V) in Fig. 7a. Polarization curves in Fig. 7b show smaller charge-discharge voltage gap for CoS₂@MXene. Zinc-air batteries based on CoS₂@MXene also exhibit a higher peak power density (29 mW cm⁻²) than that based on Pt/C (21 mW cm⁻²) (Fig. 7c). In the discharge performance test in Fig. 7d, the CoS₂@MXene is stable at 1.28 and 1.23 V with current densities of 1 and 3 mA cm⁻², respectively. Furthermore, under different current densities from 1 to 10 mA cm⁻², the CoS₂@

Figure 6 (a) CV curves in O₂- and N₂-saturated 0.1 mol L⁻¹ KOH solution at 50 mV s⁻¹. (b) LSV curves under 1600 rpm at 5 mV s⁻¹. (c) Tafel slopes of CoS₂, MXene, CoS₂@MXene, and Pt/C. (d) LSV curves of CoS₂@MXene at different rotating rates. (e) The corresponding transfer electron number (*n*) of CoS₂@MXene (inset shows the K-L plots at various potentials). (f) The stability tests of Pt/C and CoS₂@MXene.

MXene zinc-air batteries produce a small voltage decay with 1.13 V at 10 mA cm⁻², which demonstrates its superior current discharge capability (Fig. 7e). Two quasi-solid-state zinc-air batteries connected in series can light up an electronic watch (Fig. 7f). Interestingly, the overall water splitting system can be self-powered by two series zinc-air batteries based on CoS₂@MXene with obvious O₂ and H₂ bubbles in electrode (Fig. 4c). The stability test was conducted at 1 mA cm⁻² with the circle of 20 min in Fig. 7g. The zinc-air batteries based on CoS₂@MXene show a high discharge voltage (1.30 V) and low charge voltage (1.83 V) with a smaller voltage gap (0.53 V) and higher round-trip efficiency (71%) than those based on Pt/C+RuO₂ zinc batteries for voltage gap (0.76 V) and round-trip efficiency (62%). After 60 circles (20 h), the CoS₂@MXene-based air cathode displays significant long-time durability with a slight decay in voltage gap.

The desirable performance of CoS₂@MXene can be ascribed to these features. (i) The stronger electronegativity of MXene than CoS₂ may accelerate the charge transfer from CoS₂ to MXene to affect their surface electronic structure. (ii) Due to the high conductivity of MXene, the intimate contact within the composites can enhance the electrical conductivity. The electrostatic interaction within the composites would shorten the elec-

tron diffusion distance. (iii) The isolated 2D MXene with a large specific surface area can provide more anchored sites for active CoS₂. (iv) The hierarchical structure of CoS₂@MXene will protect the nanostructure from aggregation and therefore endow a long-time stability. (v) The unique structure with CoS₂ nanowires parallelly grown on MXene nanosheets will enhance the interfacial effect between the electrolyte and electrode, which provides rich reaction sites and promotes mass transport of reactants.

CONCLUSIONS

In this study, the composites of CoS₂ nanowires anchored on electronegative surfaces of exfoliated MXene nanosheets were prepared *via* a hydrothermal reaction followed by sulfurization. The coupling interaction accelerates the electron transfer from CoS₂ to MXene matrix and tailors the electron structure, due to the stronger electronegativity of MXene than that of CoS₂. Besides, the CoS₂ nanowires can protect the MXene nanosheets from aggregation resulting in an open architecture which can promote the mass transport of reactants. Benefitting from the combined features, the CoS₂@MXene composite achieves superior trifunctional electrocatalyst with a lower overpotential for ORR, OER

Figure 7 (a) Open-circuit voltages; (b) charge and discharge polarization curves; (c) power density curves of CoS₂@MXene and Pt/C. (d) Discharge curves at 1, 3 and 5 mA cm⁻²; (e) rate capability measurement of CoS₂@MXene. (f) An electronic watch powered by CoS₂@MXene-based zinc-air batteries. (g) The stability of zinc-air batteries based on CoS₂@MXene and Pt/C for 20 h.

and HER in alkaline solutions, better than the individual components of CoS₂ and MXene. As expected, only 1.63 V is needed to achieve 10 mA cm⁻² for water splitting. Furthermore, the quasi-solid zinc batteries based on CoS₂@MXene show small voltage gap and long-time durability. Therefore, the multi-dimensional engineering of 1D CoS₂ nanowires and 2D MXene substrate drives new insight to design efficient noble metal-free catalysts for energy conversion systems.

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

Silin Han is currently a MSc candidate in physical chemistry under the supervision of Prof. Shengjie Peng at Nanjing University of Aeronautics and Astronautics. His research focuses on developing excellent catalyst materials of energy storage.

Feng Hu received his PhD degree in chemistry from the University of Chinese Academy of Sciences (UCAS) in 2017. He is currently an associate professor at the College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics. His current research interests focus on the design of functional nanomaterials for electrocatalysis.

Shengjie Peng received his PhD degree in Nanjing University in 2010. Following postdoctoral fellow with Prof. Qingyu Yan and Prof. Seeram Ramakrishna at Nanyang Technological University and National University of Singapore, he is now working as a full professor at Nanjing University of Aeronautics and Astronautics. He has co-authored over 120 peer-reviewed publications. His current research interests focus on functional nanomaterials in electrochemical catalysis and storage.

多维分层 CoS_2 @MXene作为三功能电催化剂应用于锌-空气电池和水分解

韩四林¹, 陈宇¹, 郝亚楠¹, 谢耀毅¹, 谢登裕¹, 陈影¹, 熊一星¹, 何铮瑶¹, 胡峰^{1*}, 李林林¹, 朱纪欣², 彭生杰^{1*}

摘要 设计高效的非贵金属催化剂对于电催化能量转化过程, 比如 ORR, OER和HER至关重要. 多功能的催化剂需要复杂且耗时的材料设计, 本文通过简单水热生长和硫化结合的策略构建了MXene基底结合 CoS_2 活性位点的高效催化界面. 由一维 CoS_2 纳米线和二维MXene纳米片组成的多维 CoS_2 @MXene电催化剂, 具有分层结构(大的比表面积和丰富的活性位点), 优化的空间电子结构(高本征活性)和高结合强度(优异的稳定性). 因此, 在ORR, OER和HER催化过程中都展示了优异的电催化活性, ORR的半波电位是0.80 V, OER和HER达到 10 mA cm^{-2} 的过电位分别为270和175 mV. 对于电催化水分解, CoS_2 @MXene需要1.63 V就能达到 10 mA cm^{-2} . 以 CoS_2 @MXene为空气电极组装的固态锌空气电池也展示了低充放电电压差(在 1 mA cm^{-2} 为0.53 V)和高稳定性(能循环60圈, 20 h), 且两节串联的固态锌空气电池即可驱动水分解. 因此, 这项工作为多功能催化剂的设计和应用提供了新思路.