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A flower-like CoS₂/MoS₂ heteronanosheet array as an active and stable electrocatalyst toward the hydrogen evolution reaction in alkaline media†

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CoS₂/MoS₂ heteronanosheet arrays (HNSAs) with vertically aligned flower-like architectures are fabricated through *in situ* topotactic sulfurization of CoMoO₄ nanosheet array (NSA) precursors on conductive Ni foam. CoMoO₄ NSAs are prepared by a self-template hydrothermal method without using any hard template and surfactant. Benefiting from a 3D flower-like architecture constituted by ultrathin nanosheets with abundant exposed heterointerfaces as highly active sites and predesigned void spaces, the as-synthesized CoS₂/MoS₂ HNSAs exhibit an excellent hydrogen evolution reaction (HER) performance with a low overpotential of 50 mV at 10 mA cm⁻², and a small Tafel slope of 76 mV dec⁻¹ in 1.0 M KOH, which outperforms most previously reported CoS₂ and MoS₂ based electrocatalysts with compositional or morphological similarity. This work demonstrates the great potential in developing high-efficiency and earth-abundant electrocatalysts for alkaline HER through heterointerface engineering and morphological design by utilizing transition metal molybdate as a promising platform.

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1. Introduction

Water splitting has been widely regarded as a promising approach towards sustainable hydrogen generation from aqueous solution. Development of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) electrocatalysts with high-efficiency, long-term durability comparable to precious-metal based electrocatalysts is one of the key building blocks for any future renewable energy system.¹ However, electrochemical water splitting suffers severely from sluggish HER kinetics in high concentration alkaline solutions. Considering the high price and scarcity of Pt, a variety of transition metal based compounds and composites have been recently investigated for alkaline HER, including metal alloys,^{2,3} sulfides,^{4,5} carbides,^{6,7} nitrides^{8,9} and phosphides^{10,11} due to their abundance, high reactivity, electrochemical stability. In particular, transition metal sulfides are among the most investigated noble-metal-free candidates and have recently attracted substantial research interest as low-cost and active alternative

electrocatalysts for alkaline HER.^{12–14} The previous works revealed that both morphological control and interface engineering played indispensable roles in boosting the electrocatalytic performance of nanostructured transition metal dichalcogenide composites. Compared to mono-metal sulfides, such as NiS₂ and CoS₂, bi-metallic or mixed-metal sulfides (*e.g.*, Ni_{0.33}Co_{0.67}S₂ and NiCo₂S₄) demonstrated a higher HER electrocatalytic activity mainly due to the exposure of electrochemically active surface edge sites.^{15,16} Moreover, chemical doping and incorporation approaches played an essential role in boosting electrocatalytic performance through the modulation of intrinsic activity and electronic structures, such as N-doped Ni₃S₂ nanosheet arrays, Co-doped mesoporous MoS₂ foam and O-incorporated MoS₂ nanosheets.^{17–20} Transition metal dichalcogenide based nanocomposites were investigated as well, demonstrating enhanced electrocatalytic performance due to the heterointerfaces acting as accessible and stable active sites. For instance, various electrocatalysts with core/shell nanostructures have been recently investigated, such as CoS₂/MoS₂ nanowires, Ni₃S₂/MoS₂ nanorods, Ni₃S₂/MoS₂ nanoparticles and MoC/Mo₂C nanowires, *etc.*^{6,21–23} Those synergistically enhanced electrocatalytic performances of transition metal dichalcogenides or carbides could pave a pathway for achieving sustainable energy conversion.

The development of environmentally-friendly and facile synthetic routes for electrocatalysts with tunable morphology and composition to maximize the number of active surface sites still remains a challenging task. The fabrication of active electrocatalysts on a conductive substrate, such as Ni foam/foil,

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carbon fiber/cloth or Ti foil, could provide the efficient pathways for charge transport and open channels for rapid release of H₂ bubbles during HER process.²⁴ Among different approaches for synthesizing transition metal sulfides electrocatalysts, synergistic effects of morphological control and heterointerface engineering strongly significantly depend on the appropriate choice of precursors. Transition metal oxides and hydroxides with various nanostructures have been employed as precursors to synthesize transition metal sulfide based composites.^{21,25,26} A transformation process of transition metal oxides or hydroxides to transition metal sulfides would occur in a sulfur vapor atmosphere or ions solutions. According to previous works, metal molybdate (AMoO₄) comprising molybdenum and second transition metals (A = Fe, Co and Ni, *etc.*) could be prepared by several convenient synthetic approaches.²⁷ Although diverse metal molybdates have been reported to exhibit excellent performance in supercapacitor devices, those metal molybdates were found to be nearly inactive towards the HER.^{4,28–33} Recent studies shed light on the role of metal molybdates as potential precursors towards the rational design of transition metal dichalcogenides heterointerface through the simultaneous sulfurization of corresponding molybdenum and second transition metal. For instance, Yu *et al.* reported that NiMoO₄ nanowires were employed as the precursor for the preparation of bi-metal sulfide NiS₂/MoS₂ heteronanowires, which exhibiting an improved HER performance in comparison with NiS₂ and MoS₂.⁴ In order to further improve the electrocatalytic performance, great endeavors have been made to overcome the bottlenecks associated with the use of insulating binders and inactive conductive agent due to the serious concerns on the reduced number of exposed active edge sites and the increased resistance between the electrocatalyst and electrode.²⁴ It should be highlighted that some of metal molybdates can be directly grown on the conducting substrates through a facile one-step hydrothermal approach.^{32,34} Recently, Zheng *et al.* recently reported the synthesis of NiMoO₄ nanowire array on the Ti foil and the conversion to NiS₂/MoS₂ heteronanowire array with enhanced HER performance.³⁵ Due to their inherent characteristics, numerous molybdate compounds could be considered as prospective precursors for the synthesis of transition metal dichalcogenides, aiming at taking the advantages of synergistic effect through the optimization of precursor morphology and heterointerface engineering. In fact, the development of 3D integrated electrodes fabricated by electroactive nanomaterials are appealing not only in electrochemical water splitting but other electrochemical energy conversion and storage systems as well.

Herein, we developed a facile strategy to synthesize 3D flower-like CoS₂/MoS₂ heteronanosheet arrays (HNSAs) on conductive Ni foam by *in situ* topotactic conversion of CoMoO₄ nanosheet arrays (NSAs) precursor. The simultaneous sulfurization of Co and Mo in CoMoO₄ precursor led to the formation of CoS₂/MoS₂ nanocomposite while the structural and morphological characteristic of ultrathin nanosheets was well retained during the vapor phase sulfurization process. The as-prepared CoS₂/MoS₂ HNSAs demonstrated an excellent HER activity with a low overpotential of 50 mV at current density of

10 mA cm⁻² and a small Tafel slope of 76 mV dec⁻¹ in 1.0 KOH. The superior HER performance of CoS₂/MoS₂ HNSAs could be attributed to the following three aspects: (i) the abundant accessible CoS₂/MoS₂ heterointerface served as highly active catalytic sites after *in situ* topotactic sulfurization; (ii) 3D flower-like CoS₂/MoS₂ HNSAs integrating directly on the conductive Ni foam facilitated fast electron transport; (iii) the 3D network structure of CoS₂/MoS₂ HNSAs offered the internal void spaces between neighboring heteronanosheets, which were suitable for both the diffusion of electrolyte and release of gas bubble process. This work serves as a proof of concept for the heterointerface engineering of transition metal dichalcogenides nanocomposite as efficient electrocatalysts through rational compositional and morphological control.

2. Experimental section

2.1 Chemicals

All of the chemicals were purchased from Alfa Aesar and used as received without further purification, including sublimed S powder, Na₂MoO₄·2H₂O and Co(NO₃)₂·6H₂O. The porous Ni foams were obtained from Kunshan Company.

2.2 Materials synthesis

The Ni foams (1.0 cm × 1.5 cm) were cleaned in acetone, absolute ethanol, HCl solution for 30 min, respectively. The preparation of 3D flower-like CoMoO₄ NSAs was conducted as follow, 1.6 mM Na₂MoO₄·2H₂O and 1.6 mM Co(NO₃)₂·6H₂O was dissolved under continuous stirring in 20 mL deionized water. The pretreated Ni foams were then immersed into the mixed solution and kept at 90 °C in an electrical oven for 48 h. After cooling to the room temperature, the as-prepared CoMoO₄ NSAs on Ni foam were washed with the assistance of sonication to remove surface residues and then dried at 60 °C in a vacuum oven for overnight. The *in situ* topotactic sulfurization was conducted by a vapor phase sulfurization procedure. CoMoO₄ NSAs precursor was converted to CoS₂/MoS₂ HNSAs at 370 °C for 45 min. Mass loading of CoS₂/MoS₂ HNSAs on Ni foam was 0.9 mg cm⁻².

2.3 Materials characterization

The morphology of the as-prepared 3D flower-like CoMoO₄ NSAs and CoS₂/MoS₂ HNSAs were characterized by field emission scanning electron microscopy (SEM, SU8020, Hitachi), transmission electron microscopy (TEM, F20 and Talos F200S, FEI) with an energy-dispersive X-ray spectroscopy (EDS) detector. The crystal structure of all samples was characterized by X-ray diffraction (XRD, X'Pert³ Powder diffractometer, Cu K α radiation ($\lambda = 1.5418$ nm)). The chemical composition and valence state of CoMoO₄ NSAs and CoS₂/MoS₂ HNSAs was investigated by X-ray photoelectron spectroscopy (XPS, ThermoFisher Scientific ESCALAB 250Xi).

2.4 Electrochemical characterization

The electrochemical measurements of 3D flower-like CoS₂/MoS₂ HNSAs were conducted in a three-electrode system using a CHI

660E electrochemical workstation (CH Instruments, Shanghai, China). The 3D flower-like $\text{CoS}_2/\text{MoS}_2$ HNSAs were used as working electrode with a fixed geometric area of $1\text{ cm} \times 1\text{ cm}$, while $\text{Hg}|\text{HgO}$ and graphite rod was used as the reference electrode and counter electrode, respectively. In this work, the HER activity of 3D flower-like $\text{CoS}_2/\text{MoS}_2$ HNSAs was performed in 1.0 M KOH solution while all applied potentials were converted with respect to reversible hydrogen electrode (RHE). Linear sweep voltammetry (LSV) with a scan rate of 5 mV s^{-1} was conducted without iR compensation. The electrochemical double-layer capacitance (C_{dl}) was measured basing on the data of cyclic voltammetry (CV) at various scan rates (10, 20, 30, 40, 50 and 60 mV s^{-1}) in range between 0.1 and 0.2 V (*versus* RHE). The long-term stability was conducted by chronoamperometry and 2000 cycles continuously in 1.0 M KOH, respectively. Electrochemical impedance spectroscopy (EIS) measurements were carried out at an overpotential of 150 mV in a frequency range from 100 kHz to 0.01 Hz. The KOH solution was purged with high-purity N_2 to remove dissolved oxygen before each electrochemical measurement.

3. Results and discussion

Inspired by recent studies of *in situ* synthesis of transition metal dichalcogenides based electrocatalysts on conductive substrate, the high density and uniformly distributed nanoarray architectures, such as 1D nanowire/rod and 2D nanosheet arrays, can significantly improve the HER catalytic activity and stability. The fabrication of 3D flower-like $\text{CoS}_2/\text{MoS}_2$ HNSAs on conductive Ni foam were facily conducted by a two-step procedure without using any surfactant and hard template. The synthetic process and composition evolution of $\text{CoS}_2/\text{MoS}_2$ HNSAs is schematically illustrated in Fig. 1.

The flower-like CoMoO_4 NSAs were synthesized on porous Ni foam *via* a self-template method (see Experimental section for more details).^{36,37} As shown in Fig. 2a and b, the low-magnification scanning electron microscopy (SEM) images

demonstrate that the 3D network structure of flower-like CoMoO_4 NSAs anchored on Ni foam. The self-assembled CoMoO_4 nanosheets with lateral sizes of about $2\text{ }\mu\text{m}$ were grown uniformly on Ni foam surface with a 3D flower-like micro/nanostructure (Fig. 2c). It can be explained by the large amount of nanosized CoMoO_4 nucleation clusters were formed in the solution for the self-assembly of 2D nanosheets, which further led to the formation of flower-like morphology. The high-magnification SEM image exhibits the as-synthesized CoMoO_4 nanosheets with thickness in the range of 10–20 nm are interconnected with each other (Fig. 2d), providing a large number of internal void spaces between adjacent nanosheets. It can be also observed some CoMoO_4 nanosheets with slightly curved surface and crumpled edges due to the larger lateral dimension than the thickness. Transmission electron microscopy (TEM) characterizations were conducted to investigate the structure of CoMoO_4 nanosheets. Fig. 2e and f presents that 3D flower-like CoMoO_4 micro/nanostructure is made up of interconnected nanosheets with a lateral size of several hundred nanometers. It is found that the CoMoO_4 nanosheets are slightly folded in some regions. For instance, the observation of dark strips resulted from the curled edges or wrinkles of the CoMoO_4 nanosheets which is consistent with the SEM observation. Fig. 2g shows the enlarged TEM image of CoMoO_4 nanosheet edge, revealing the existence of slight disorder. From high resolution TEM (HRTEM) image, the lattice spacing is 0.33 nm corresponding well to (002) plane of monoclinic CoMoO_4 (Fig. 2i).^{34,38} The high-angle annular dark-field scanning TEM (HAADF-STEM) and corresponding energy-dispersive X-ray spectroscopy (EDS) characterization (Fig. 2i-l) confirms the uniform distributions of Co, Mo and O elements throughout the 3D flower-like nanosheets. XRD pattern shows no obvious characteristic peak of the CoMoO_4 NSAs, indicating the polycrystalline nature of self-assembled nanosheets through the low temperature hydrothermal method.³²

Owing to the morphological features of ultrathin CoMoO_4 nanosheets, the *in situ* topotactic conversion to $\text{CoS}_2/\text{MoS}_2$

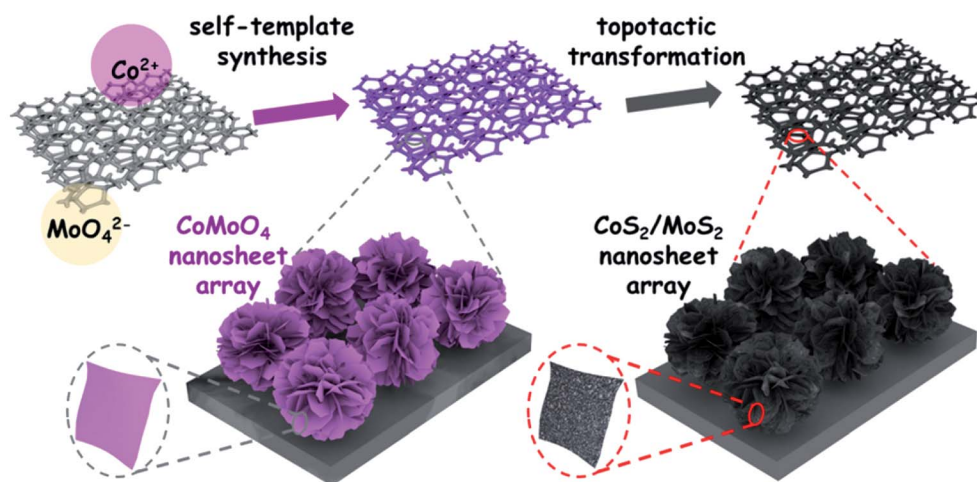


Fig. 1 Schematic illustration for the self-template synthesis of 3D flower-like CoMoO_4 NSAs and *in situ* topotactic sulfurization to $\text{CoS}_2/\text{MoS}_2$ HNSAs.

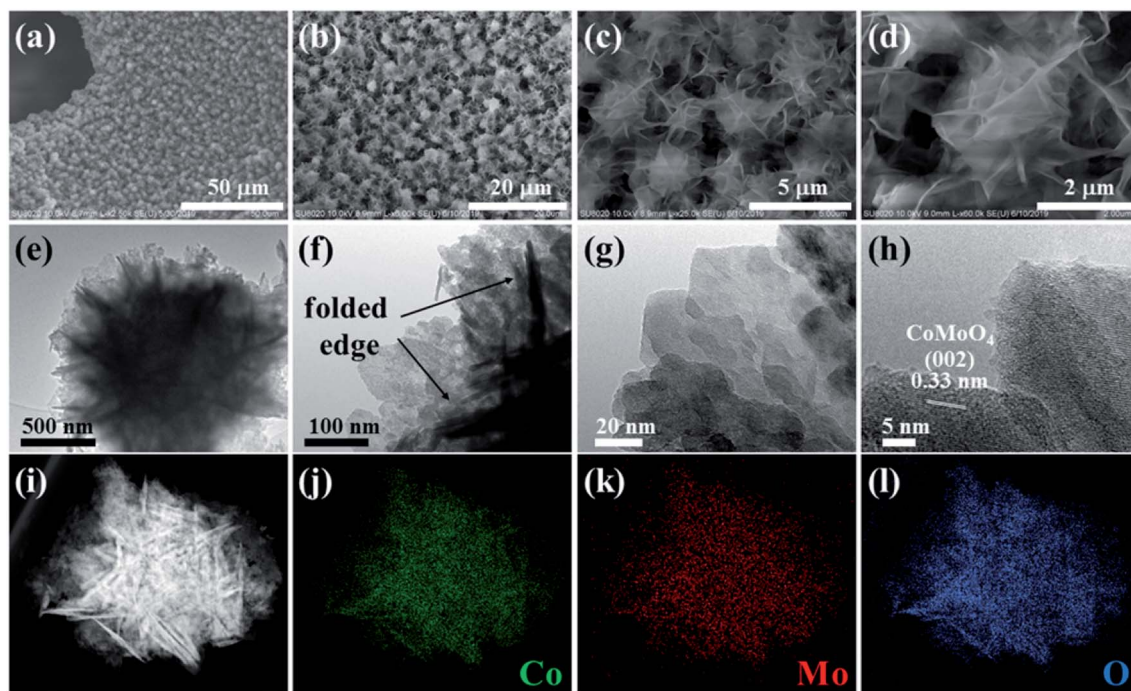


Fig. 2 (a–d) SEM images, (e–h) TEM images, (i) HAADF-STEM and (j–l) EDS mapping images of 3D flower-like CoMoO_4 nanosheets.

nanosheets was successfully achieved by the vapor phase sulfurization process. Fig. 3a–d demonstrates the dense and uniform coverage of flower-like $\text{CoS}_2/\text{MoS}_2$ HNSAs. Compared to CoMoO_4 nanosheets with a relative smooth surface, the high-magnification SEM image undoubtedly reveals that the coarse surface of $\text{CoS}_2/\text{MoS}_2$ heteronanosheets after sulfurization

(Fig. 3d). Basing on the morphology evolution, it can be seen that the flower-like CoMoO_4 NSAs acted as a self-template for the topotactic conversion to $\text{CoS}_2/\text{MoS}_2$ HNSAs. Similar to the case of CoMoO_4 nanosheets, $\text{CoS}_2/\text{MoS}_2$ heteronanosheets with transparent feature indicated the ultrathin nature was also retained after the *in situ* conversion (Fig. 3e and f). As shown in

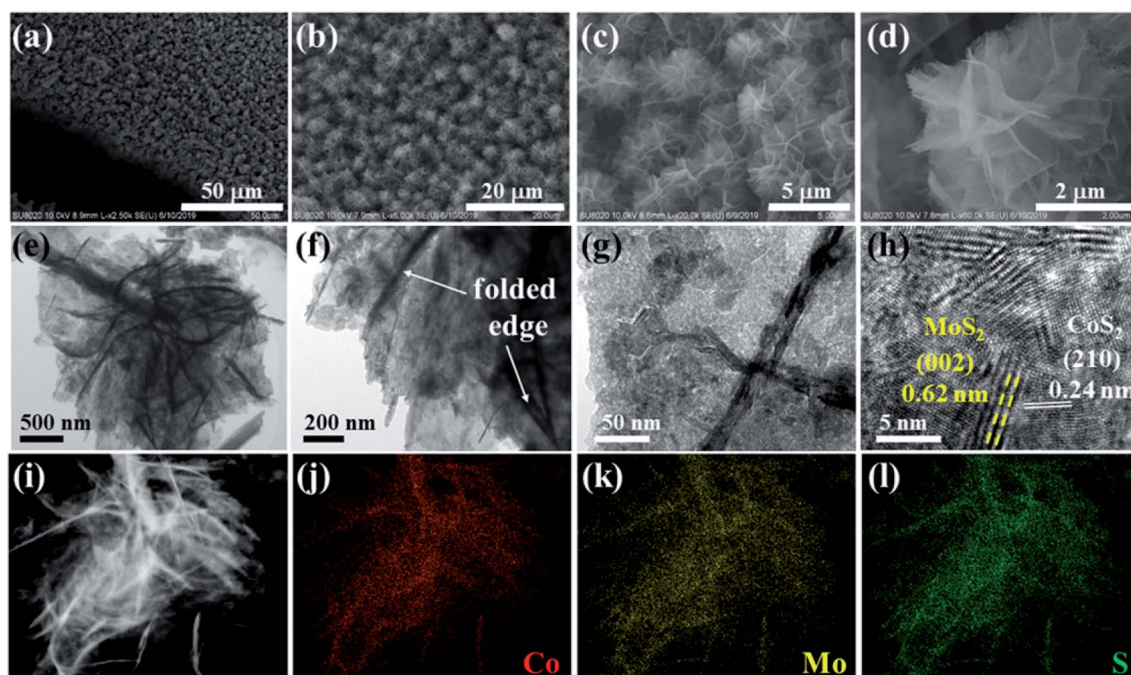


Fig. 3 (a–d) SEM images, (e–h) TEM images, (i) HAADF-STEM and (j–l) EDS mapping images of 3D flower-like $\text{CoS}_2/\text{MoS}_2$ nanosheets.

Fig. 3g, the enlarged TEM image demonstrates that heteronanosheet integrated with CoS₂ and MoS₂ species after sulfurization. The HRTEM image reveals lattice fringes of 0.62 and 0.24 nm, corresponding to the (002) plane of MoS₂ and (210) plane of CoS₂, respectively (Fig. 3h). The observation of lattice discontinuities in CoS₂/MoS₂ heteronanosheet indicates the existence of the slight disordered structure. On the one hand, a large number of heterointerface forming between CoS₂ and MoS₂ can be undoubtedly identified. On the other hand, the intimate contact of CoS₂ and MoS₂ can be ascribed to the simultaneous sulfurization of Co and Mo in CoMoO₄ precursor. It should be noted that the as-obtained heteronanosheets demonstrated a relatively uniform distribution of CoS₂ and MoS₂ species. Furthermore, the elemental distributions of 3D flower-like CoS₂/MoS₂ nanosheets were characterized by HAADF-STEM and the corresponding EDS characterizations, revealing the homogeneous distribution of Co, Mo and S throughout the whole heteronanosheets (Fig. 3i–l). As shown in Fig. S1 (ESI[†]), the EDS spectra analysis further confirmed CoMoO₄ NSAs were transformed to CoS₂/MoS₂ HNSAs after *in situ* topotactic sulfurization due to the disappearance of O signal and appearance of S signal. The overlapping Co, Mo and S signals indicates the uniform formation of CoS₂ and MoS₂ nanocomposites while the predesigned void spaces can still be observed between neighboring heteronanosheets. Attributed to the good preservation of 3D network structure of CoMoO₄ precursor after *in situ* topotactic conversion, 3D flower-like CoS₂/MoS₂ HNSAs exhibit porous structures which is essential to increase the accessible surface areas and facilitate the effective contact between electrocatalyst and electrolyte ions.

To confirm the composition and valence states of the as-prepared flower-like CoMoO₄ NSAs and CoS₂/MoS₂ HNSAs, X-ray photoelectron spectroscopy (XPS) characterization were conducted. For the CoMoO₄ NSAs, the Co 2p spectrum exhibits two main peaks at 780.8 and 797.1 eV (Fig. 4a), corresponding to the low energy band of Co 2p_{3/2} and high energy band of Co 2p_{1/2},

respectively, as well as their satellite peaks (denoted as “sat.”).³⁹ In the Mo 3d spectrum of CoMoO₄ precursor, two significant peaks at 232.1 and 235.3 eV are associated with Mo 3d_{5/2} and Mo 3d_{3/2} electronic configurations, respectively, indicating a +6 oxidation state of Mo in the CoMoO₄ NSAs (Fig. 4b). As shown in Fig. 4c, the O 1s spectrum of CoMoO₄ precursor can be deconvoluted into four peaks at 530.2, 530.9, 531.8 and 533.0 eV, corresponding to the Co–O bonds, hydroxyl groups in the hydrated sample, oxygen ions in low coordination and physis- and/or chemisorbed water, respectively.⁴⁰ After sulfurization, the XPS spectrum of Co 2p_{3/2} and Co 2p_{1/2} signals are found to be 778.9 and 793.9 eV, respectively. The obvious shifts of Co 2p_{3/2} and Co 2p_{1/2} binding energy indicate the formation of CoS₂ after *in situ* sulfurization because sulfur has a lower electronegativity than oxygen (see Fig. 4d). As shown in Fig. 4e, two characteristic peaks at the binding energies of 228.8 and 232.0 eV are ascribed to Mo 3d_{5/2} and Mo 3d_{3/2}, indicating a +4 oxidation state of Mo and therefore confirming the conversion of MoS₂ after *in situ* topotactic sulfurization.²¹ It should be noted the observation of broad S 2s peaks around 226.0 eV suggests the formation of Co–S and Mo–S bonding. The analysis of the S 2p spectrum reveals the characteristic peaks at 161.6 and 162.6 eV are assigned to S 2p_{3/2} due to the formation of Co–S and Mo–S bonding while the broad peak around 163.2 and 164.2 eV is attributed to bridging S₂²⁻ between CoS₂ and MoS₂ (Fig. 4f), which were identified as active HER sites.^{41–43} Therefore, it can be concluded that the formation of CoS₂/MoS₂ nanocomposite *via in situ* topotactic conversion.

To evaluate the electrocatalytic activity for HER, 3D flower-like CoS₂/MoS₂ HNSAs was tested in a 1.0 M KOH solution using a typical three-electrode configuration. Fig. 5a demonstrates the polarization curves without *iR* correction. The overpotential for 3D flower-like CoS₂/MoS₂ HNSAs to achieve a current density of 10 mA cm⁻² (η_{10}) is 50 mV (*vs.* RHE) while the conductive Ni foam demonstrated negligible HER activity. In comparison with the previously reported transition metal sulfides based electrocatalysts (Table S1 in ESI[†]), the η_{10} of 3D

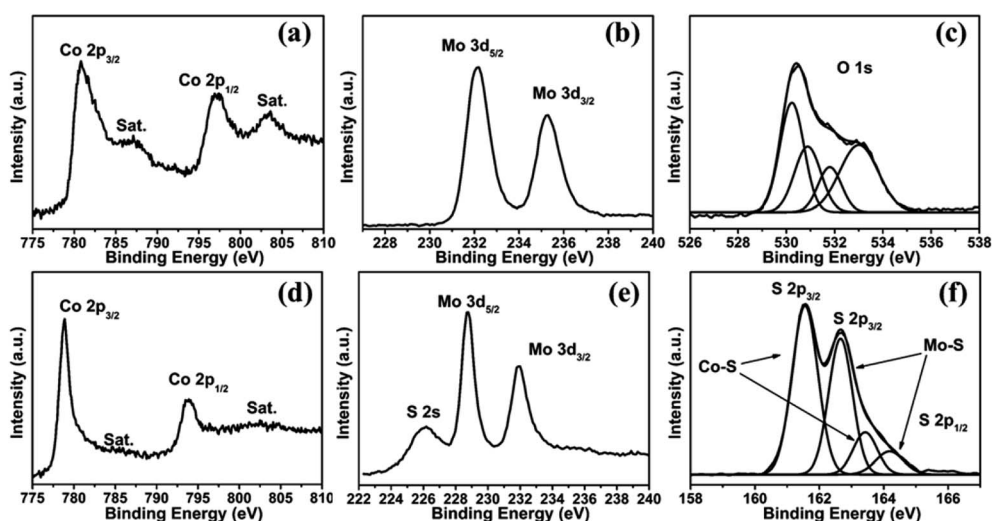


Fig. 4 High-resolution XPS profiles of (a) Co 2p, (b) Mo 3d and (c) O 1s in CoMoO₄ NSAs; (d) Co 2p, (e) Mo 3d and S 2s, and (f) S 2p in CoS₂/MoS₂ HNSAs.

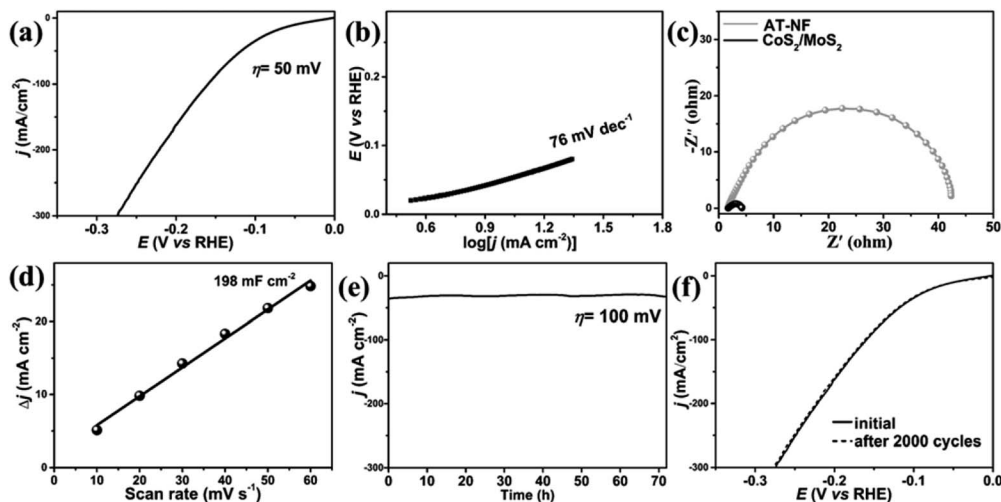
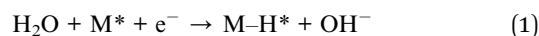


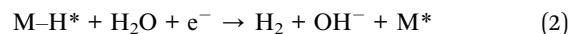
Fig. 5 (a) Polarization curves and (b) Tafel plots of as-synthesized 3D flower-like $\text{CoS}_2/\text{MoS}_2$ HNSAs, (c) Nyquist plots of acid-treated Ni foam and 3D flower-like $\text{CoS}_2/\text{MoS}_2$ HNSAs in 1.0 M KOH at $\eta = 150$ mV, (d) the differences in the current density (Δj) at 0.15 V vs. RHE plotted against scan rate fitted to a linear region for the calculation of C_{dl} , (e) the long-term durability test of $\text{CoS}_2/\text{MoS}_2$ HNSAs at $\eta = 100$ mV, (f) stability for $\text{CoS}_2/\text{MoS}_2$ NSAs with initial polarization curve and after 2000 cycles.

flower-like $\text{CoS}_2/\text{MoS}_2$ HNSAs is much lower than those of the reported NiCo_2S_4 nanowire arrays (210 mV),¹⁵ $\text{Ni}_{0.33}\text{Co}_{0.67}\text{S}_2$ nanowire arrays (88 mV),¹⁶ Ni–Mo–S nanowire networks (210 mV),⁴⁴ MoS_2 nanosheet arrays (200 mV),⁴⁵ Ni_3S_2 nanosheet arrays (223 mV),⁴⁶ CoS_2 nanosheet arrays (192 mV),⁴⁷ FeS_2 mesoporous nanoparticles (96 mV),⁴⁸ Ni_3S_2 nanorod arrays (200 mV),⁴⁹ Na-doped 1T- MoS_2 nanosheets (183 mV)⁵⁰ and 1T- MoSe_2 nanosheets (152 mV).⁵¹ In particular, the electrocatalytic performance of 3D flower-like $\text{CoS}_2/\text{MoS}_2$ HNSAs is also comparable to the noble metal doped or decorated transition metal sulfides, such as Pt- MoS_2 nanosheet clusters (60 mV),⁵² Pt- MoS_2 nanoparticles (58 mV)⁵³ and Rh- MoS_2 nanosheets (47 mV).⁵⁴ Via further comparison with other Co-, Mo- and Ni-based heterostructured electrocatalysts (Table S1, ESI†), the electroactivity of 3D flower-like $\text{CoS}_2/\text{MoS}_2$ HNSAs is better than those of $\text{CoS}_2/\text{MoS}_2$ nanosheet composites (154 mV),⁵⁵ $\text{MoS}_2/\text{CoS}_2$ nanowire arrays (87 mV),²¹ $\text{NiS}_2/\text{CoS}_2/\text{C}$ carnation-like nanosheets (165 mV),⁵⁶ $\text{Co}_9\text{S}_8/\text{MoS}_2$ core/shell nanocrystals (97 mV),⁵⁷ $\text{MoS}_2/\text{NiS}/\text{MoO}_3$ nanowire arrays (90 mV),⁵⁸ $\text{NiS}_2/\text{MoS}_2$ nanowires (204 mV),⁴ $\text{MoS}_2/\text{Ni}_3\text{S}_2$ nanorod arrays (98 mV),²² $\text{CoS}_2@-\text{MoS}_2/\text{RGO}$ composites (98 mV),⁵⁹ $\text{MoS}_2/\text{Ni}_3\text{S}_2$ nanosheets/particles (110 mV),²³ oxygenated- $\text{CoS}_2/\text{MoS}_2$ nanosheet arrays (97 mV),⁶⁰ $\text{CoS}_2/\text{MoS}_2$ nanowire arrays (97 mV)⁶¹ $\text{CoS}_2-\text{C}@-\text{MoS}_2$ nanofibers (173 mV)⁶² and $\text{Ag}_2\text{S}/\text{MoS}_2/\text{RGO}$ composites (190 mV).⁶³ In particular, previous report demonstrated $\text{CoS}_2/\text{MoS}_2$ nanosheet composites were synthesized through a one-step hydrothermal method.⁵⁵ However, the $\text{CoS}_2/\text{MoS}_2$ HNSAs demonstrated a remarkable alkaline HER activity, which can be attributed to the formation of heteronanosheet-based flower-like microarchitecture anchored on the Ni foam. It should be highlighted that the Ni foam with porous and conductive characteristics played essential roles in providing more pathways for charge transport and offering open channels for the release of gas bubbles.

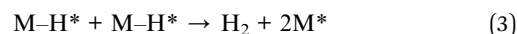
Volmer reaction



Heyrovsky reaction



Tafel reaction



According to the previous reports, three principal steps were proposed for hydrogen evolution: (1) Volmer reaction with a Tafel slope of ~ 120 mV dec^{-1} , (2) Heyrovsky reaction with a Tafel slope of ~ 40 mV dec^{-1} , and (3) Tafel reaction with a Tafel slope of ~ 30 mV dec^{-1} . It should be noted that the asterisk indicates the active site for HER while $\text{M}-\text{H}^*$ represents the hydrogen atom bound to the active site on electrocatalyst. In fact, the determination of the specific mechanism cannot be achieved by the direct evaluation of the Tafel slope for most of electrocatalysts. As shown in Fig. 5b, the relatively small slope of 3D flower-like $\text{CoS}_2/\text{MoS}_2$ HNSAs (76 mV dec^{-1}) falls within the range of 40–120 mV dec^{-1} , which is comparable to those of abovementioned composites, such as $\text{CoS}_2/\text{MoS}_2$ nanosheets (61 mV dec^{-1}),⁵⁵ $\text{MoS}_2/\text{CoS}_2$ nanowire array (73.4 mV dec^{-1}),²¹ and $\text{Co}_9\text{S}_8/\text{MoS}_2$ core/shell nanocrystals (71 mV dec^{-1}),⁵⁷ $\text{Co}_9\text{S}_8@-\text{MoS}_2$ nanoparticles (110 mV dec^{-1}),⁴³ $\text{NiS}_2/\text{MoS}_2$ nanowires (65 mV dec^{-1}),⁴ $\text{MoS}_2/\text{Ni}_3\text{S}_2$ nanorod arrays (61 mV dec^{-1}),²² $\text{MoS}_2/\text{Ni}_3\text{S}_2$ nanosheets/particles (88 mV dec^{-1}),²³ oxygenated- $\text{CoS}_2/\text{MoS}_2$ nanosheet arrays (83.1 mV dec^{-1}),⁶⁰ $\text{CoS}_2/\text{MoS}_2$ nanowire arrays (78.7 mV dec^{-1})⁶¹ and $\text{CoS}_2-\text{C}@-\text{MoS}_2$ nanofibers (61 mV dec^{-1}).⁶² The small Tafel slope of 3D flower-like $\text{CoS}_2/\text{MoS}_2$ HNSAs unveils a fast increase of hydrogen generation rate with increasing applied overpotential. It can be concluded that the considerably promoted Volmer step in HER kinetics indicates that the Heyrovsky mechanism is dominant for

alkaline HER on 3D flower-like CoS₂/MoS₂ HNSAs.⁶⁴ Furthermore, the electrochemical impedance spectroscopy (EIS) measurements were conducted to investigate the electrochemical behavior during the HER process (Fig. 5c). The Nyquist plot of 3D flower-like CoS₂/MoS₂ HNSAs demonstrates the low charge transfer resistance, indicating the fast electron transfer at the solution electrode interfaces. We further investigate the double-layer capacitance (C_{dl}) of as-fabricated 3D flower-like CoS₂/MoS₂ HNSAs, which is known to be proportional to the electrochemical surface area (Fig. S2, ESI†). Fig. 5d plots the capacitive current densities of CoS₂/MoS₂ HNSAs ($\Delta j = j_a - j_b$, where j_a and j_b denotes current densities in CV at 0.15 V (vs. RHE)), the C_{dl} value is estimated to be 198 mF cm⁻², which is comparable to the previously reported transition metal based electrocatalysts.²⁶ The large C_{dl} value indicates the enriched active sites for alkaline HER, resulting from a large number of heterointerfaces between CoS₂ and MoS₂ after *in situ* sulfurization. The long-term stability in high concentration alkaline solutions is an essential issue for transition metal dichalcogenides electrocatalysts to be practically applicable.⁶⁵ As presented in Fig. 5e, the stability test was conducted for 70 h, there was no apparent change in the current density at $\eta = 100$ mV. As demonstrated in Fig. 5f, the stability test of 3D flower-like CoS₂/MoS₂ HNSAs was also conducted for 2000 CV cycles, indicating the good durability in alkaline media. In comparison with previously reported alkaline HER electrocatalysts, the considerable enhancement in alkaline HER performance of 3D flower-like CoS₂/MoS₂ HNSAs will be discussed in more details below. Basing on the morphological evolution, flower-like CoMoO₄ NSAs were employed as precursor for the topotactic conversion of CoS₂/MoS₂ HNSAs with well retained 3D network structure. After sulfurization, the coarse nanosheets surface indicated the homogeneous distribution of CoS₂ and MoS₂ species through the whole nanosheets as well as abundant heterointerfaces. On the one hand, the high conductivity of porous Ni foam enabled the efficient electron transport to 3D flower-like heteronanosheets. On the other hand, the intimate integration of CoS₂ and MoS₂ play a key role in facilitating the faster charge transport through the whole heteronanosheets and then promoted the hydrogen generation. The formation of 3D flower-like heteronanosheet array morphology significantly increased the electroactive surface areas through the exposed active sites and well-exposed heterointerface not only from the nanosheet edges but also the nanosheet surfaces, which considerably facilitated efficient electron and ion transportation as well as the release of as-produced H₂ gas bubbles during the HER process. According to previous studies, multi-layered MoS₂ have rarely shown superior HER performance without surface modification and/or heterointerface engineering because the highly active sites of multilayer MoS₂ are mainly located on the exposed edges instead of the basal plane.⁵ The heterointerface between CoS₂ and MoS₂ facilitated electron transfer between Co and Mo through bridging S₂²⁻ species which simultaneously bonding to Co and Mo atoms, leading to the creation of latent active sites.⁴³ Theoretical studies also indicated that H* preferably adsorbs on these transition metal-site at the localized heterointerface region due to a lower chemisorption free

energy, therefore resulting in the remarkably enhanced HER performance.⁴ For these reasons, 2D ultrathin heteronanosheets composed of interconnected CoS₂ and MoS₂ species would be highly advantageous. Previous studies unveiled that the well-exposed transition metal related active sites could act as an exceptional H₂O dissociation center while the Mo-related active sites demonstrate superior adsorption capability toward H.^{4,13,57,66} The formation of well-exposed CoS₂/MoS₂ heterointerfaces may simultaneously promote the adsorption towards H in alkaline media and strengthen the dissociation of H₂O molecules, which require further theoretical investigation.^{67,68}

4. Conclusion

In summary, 3D flower-like CoS₂/MoS₂ heteronanosheets array was fabricated on conductive Ni foam through a self-template hydrothermal synthesis and subsequent *in situ* topotactic sulfurization. The morphological design of CoMoO₄ nanosheet array as precursor allow the well-retained 3D network structure with large exposed surface areas after sulfurization. CoS₂/MoS₂ heteronanosheet array as efficient electrocatalyst for alkaline HER with a low overpotential of 50 mV at current density of 10 mA cm⁻² and small Tafel slope of 76 mV dec⁻¹, which is comparable to those of benchmark transition metal based electrocatalysts. Basing on our experimental characterizations, we demonstrated that the enhanced electrocatalytic performance can be mainly attributed to the synergistic effect of rational morphological design of 3D interconnected network structure and the formation of abundant well-exposed CoS₂/MoS₂ heterointerfaces. Our synthetic strategy can possibly be extended to the preparation of other traditional metal dichalcogenide nanocomposite by the rational design of metal molybdate precursor, including substituting Co with other transition metal (such as Fe, Ni or Cu) or tuning their morphology from 2D heteronanosheet to 1D heteronanowire arrays. Further improvement in electrochemical energy conversion and storage systems basing on low-cost and earth-abundant transition metal dichalcogenides can be expected by utilizing the various molybdate precursors to increase the intrinsic activity of non-precious electrocatalysts *via* morphological control and heterointerface engineering.

Conflicts of interest

There are no conflicts of interest to declare.

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