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Polyoxometalrate Precursors for Precisely Controlling Synthesis of Bimetallic Sulfide Heterostructure through Nucleation-Doping Competition

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Molybdenum disulfide (MoS₂)-based bimetallic sulfides have drawn the increasing research attention because of the unique structures and properties. Herein, a one-pot hydrothermal synthesis method was proposed to grow a series of bimetallic sulfides on carbon cloth (M-Mo-S/CC, M = Co, Ni, Fe) using Anderson-type polyoxometalates (POMs) as bimetallic sources for the first time. The ideal model of M-Mo-S/CC was used to study the growth process through the nucleation-doping competition mechanism. It is firstly proved that M-Mo-S/CC possess certain compositions of bimetallic sulfides rather than metal doping into MoS₂ structures because the nucleation reaction plays a main role in the nucleation-doping competition. Moreover, the nucleation rates of different metals can be compared to study different morphologies of M-Mo-S/CC because Anderson-type POMs have fixed bimetal proportions and precise structures. Co-Mo-S and Ni-Mo-S show the spherical heterostructures with CoS₂ or NiS mainly inside and interconnected MoS₂ nanosheets outside, while Fe-Mo-S exhibits the uniform nanosheets morphology without stacking. As the electrodes for alkaline water electrolysis, M-Mo-S/CC with different compositions and morphologies exhibit distinguishing activities. Particularly, Co-Mo-S/CC achieves the best performance for hydrogen evolution reaction, oxygen evolution reaction and overall water splitting among all M-Mo-S/CC samples. This work presents a facile strategy using POMs as bimetallic precursors to study growth mechanism as well as water electrolysis performance of MoS₂-based bimetallic sulfides.

Introduction

Electrochemical water splitting for hydrogen (H₂) and oxygen (O₂) is one of the promising and environmental step in developing a possible hydrogen economy.¹ In general, overall water splitting (OWS), involving hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), is a thermodynamically unfavorable process, which requires highly-efficient electrocatalysts to reduce the overpotential and accelerates the reaction kinetics.²,³ So far, the benchmark electrocatalysts are the commercial platinum (Pt) for HER and iridium oxide (IrO₂) or ruthenium oxide (RuO₂) for OER.⁴ These noble metal-based catalysts have excellent activity but low natural abundance and high cost, which limiting the commercialization widely.⁵,⁶ Therefore, great efforts have been made to synthesize the non-noble metal-based electrocatalysts for water splitting, such as sulfides,⁷,⁸ carbides,⁹ phosphides,¹⁰,¹¹ oxides¹²,¹³ and carbon-based metal-free materials.¹⁴

Molybdenum disulfide (MoS₂), as a typical example of two-dimensional (2D) transition-metal dichalcogenides (TMDs) material, molybdenum disulfide (MoS₂) has received considerable research attention because of the high activity, tunable property and graphene-like structure. Introducing a secondary transition metal to form the MoS₂-based bimetallic sulfides can regulate morphologies and structures, thereby enhancing the electrochemical performance significantly. However, there are few reports to study the growth mechanisms of the bimetallic sulfides. Here, we have designed an ideal model of MoS₂-based bimetallic sulfides to study the growth process based on the nucleation-doping competition mechanism. Due to the different nucleation rates of transition metals, MoS₂-based bimetallic sulfides can be formed with unique heterostructures or uniform dispersed structures. Directly as the electrodes, bimetallic sulfides also achieve the enhanced performance for hydrogen evolution reaction, oxygen evolution reaction and overall water splitting.

Conceptual insights

As a typical two-dimensional transition-metal dichalcogenides (TMDs) material, molybdenum disulfide (MoS₂) has received considerable research attention because of the high activity, tunable property and graphene-like structure. Introducing a secondary transition metal to form the MoS₂-based bimetallic sulfides can regulate morphologies and structures, thereby enhancing the electrochemical performance significantly. However, there are few reports to study the growth mechanisms of the bimetallic sulfides. Here, we have designed an ideal model of MoS₂-based bimetallic sulfides to study the growth process based on the nucleation-doping competition mechanism. Due to the different nucleation rates of transition metals, MoS₂-based bimetallic sulfides can be formed with unique heterostructures or uniform dispersed structures. Directly as the electrodes, bimetallic sulfides also achieve the enhanced performance for hydrogen evolution reaction, oxygen evolution reaction and overall water splitting.

Published on 11 April 2018. Downloaded by Nanjing Normal University on 17/04/2018 12:59:41.
computational and experimental studies indicate that MoS$_2$ is a promising material for various applications, such as energy storage and conversion,\textsuperscript{17,19} sensing,\textsuperscript{20,21} and so on. Especially, MoS$_2$ has been traditionally found to be the excellent HER electrocatalysts in acidic electrolytes but seldom investigated in alkaline medium due to the poor stability and even no OER property. It is worth noting that hybridization of MoS$_2$ by introducing a secondary transition metal to form MoS$_2$-based bimetallic sulfide can regulate the morphology and structure thereby enhancing the relevant properties.\textsuperscript{22-24} So far, many ways have been reported to prepare MoS$_2$-based materials including exfoliation method, chemical vapor deposition (CVD) and wet chemical synthesis method.\textsuperscript{15,25} Wet chemical synthesis method can be divided into two types: one-pot hydrothermal synthesis and multiple step synthesis. Multiple step synthesis can be used to obtain metal sulfide/MoS$_2$ composite with certain composition and special morphology, such as nanosphere and nanosheet, which can improve OER and even OWS performance obviously.\textsuperscript{26-28} However, the synthesis of this kind of MoS$_2$-based bimetallic sulfides always need multi-step reaction, hash experimental condition and high energy cost, making the study of growth mechanism more complex and difficult.

Recently, one-pot hydrothermal synthesis method has been largely applied to synthesize MoS$_2$-based bimetallic sulfides due to the advantages of low-cost, simple step and high yield. However, most reported products are transition metal doped MoS$_2$ materials. The existence and coordination forms of these doped transition metals into MoS$_2$ structures are still ambiguous, which often simulated and engineered by theoretical methods.\textsuperscript{29,30} Although the transition metal doped MoS$_2$ materials as water splitting electrocatalysts have been discussed in quantity, there is no report about the growth mechanism studies to clarify the formation reasons for their specific morphology and heterostructure. In addition, metal-doped MoS$_2$ materials usually have specific composition of MoS$_2$ through powder X-ray diffraction (PXRD) characterization but no other peak information for doping metals. If metal-doped MoS$_2$ materials show broad diffraction peaks for the low crystallized MoS$_2$ prepared at the relatively low hydrothermal temperature, it may cover up the peaks of other transition metal sulfides. Therefore, the exact compositions for MoS$_2$-based materials still remain controversial and lack the research of growth mechanism so far. In our view, MoS$_2$-based materials prepared by one-pot hydrothermal synthesis method not only have the existence of metal doped into MoS$_2$ structures but also can form the transition metal sulfides coupled with MoS$_2$. During the hydrothermal process, doping reaction and nucleation reaction must co-exist, which directly affect the final compositions due to the nucleation-doping competition. If the nucleation reaction dominates the hydrothermal process, metal sulfides/MoS$_2$ composite with certain compositions will be formed, otherwise it will be the metal doped MoS$_2$. Therefore, designing a suitable experimental platform to study the nucleation-doping competition of MoS$_2$-based materials by one-pot hydrothermal synthesis has great research significance.

Herein, we report a facile one-pot strategy to synthesize a new class of M-Mo-S nanosheets (M = Co, Ni, Fe) on carbon cloth without any binders (M-Mo-S/CC). The as-synthesized M-Mo-S contains two certain sulfides (MoS$_2$ and MS$_x$) when Anderson-type polyoxometalates (POMs) and thiourea (TU) are used as bimetallic and sulfur sources, respectively. POMs, in size of the nanometer scale, are a subset of early transition metal-oxygen clusters with unique physicochemical properties.\textsuperscript{31} Anderson-type POMs, represented by the formula of $[X\text{M}_x\text{O}_{24}\text{H}_4]^y$ ($X = \text{Zn}, \text{Cu}, \text{Co}, \text{Ni}, \text{Fe}$, etc., $M = \text{Mo}$), are a planar shaped structure formed by a metal-oxygen octahedral cavity at the center and six octahedral $\text{MO}_6$ in the peripheral.\textsuperscript{32} Anderson-type POMs not only possess precise structure, nanoscale size (<1 nm) and good water solubility but also can provide fixed proportions of bimetallic sources, which are the optimal precursors for the controlling synthesis of M-Mo-S/CC with special morphology and structure. Therefore, M-Mo-S/CC could be the ideal system to study the growth mechanism based on the nucleation-doping competition. Since the nucleation reaction takes a dominating role during the hydrothermal process, M-Mo-S/CC system show certain compositions but distinct morphologies because different transition metals have different nucleation rates. Besides, the water electrolysis properties of M-Mo-S/CC were discussed. In alkaline medium, Co-Mo-S/CC achieves the overpotential of 118 mV and 300 mV vs. RHE at the current density of 10 mA cm$^{-2}$ for HER and OER, respectively, which reveals the best performance among M-Mo-S/CC and is comparable to most of the reported MoS$_2$-based electrocatalysts. When applying in an advanced alkaline water electrolyzer, Co-Mo-S/CC electrodes as both anode and cathode only require a cell voltage of 1.80 V to deliver the high current density of 50 mA cm$^{-2}$.

Results and discussion

Synthesis and characterization of M-Mo-S/CC

The detailed synthesis process is illustrated in Scheme 1. A one-pot synthesis was applied to synthesize M-Mo-S/CC using POMs and TU as precursors. Firstly, the successful preparation of three Anderson-type POMs were proved by X-ray crystallographic data, fourier transform infrared spectroscopy (FT-IR) and PXRD characterizations (Fig. S1, S2 and Table S1, ESf†). Take Co-Mo-S/CC for example, $[\text{Ni}(\text{II})\text{Mo}_6\text{O}_{24}\text{H}_4]\cdot6\text{H}_2\text{O}$ POMs (CoMo$_6$) were selected as the bimetallic precursors and sonicated together with TU in water for 30 min. The above solution was transferred into the Teflon-lined stainless-steel autoclave by adding two pieces of CC (1×2 cm$^2$). After the hydrothermal reaction at 200 °C for 24 h, Co-Mo-S/CC can be obtained with Co-Mo-S nanospheres on CC uniformly (mass loading is ca. 1 mg cm$^{-2}$) (Fig. S3, ESf†). Besides, $[\text{Ni}(\text{II})\text{Mo}_6\text{O}_{24}\text{H}_4]\cdot4\text{H}_2\text{O}$ (NiMo$_6$) and $[\text{Ni}(\text{II})\text{Fe}(\text{III})\text{Mo}_6\text{O}_{24}\text{H}_4]\cdot6\text{H}_2\text{O}$ (FeMO$_6$) were chosen to prepare Ni-Mo-S/CC and Fe-Mo-S/CC, respectively. Ni-Mo-S exhibit the similar morphology to Co-Mo-S but covered on CC unevenly, while Fe-Mo-S nanosheets directly grow on CC without stacking. Sodium molybdate ($\text{Na}_2\text{MoO}_4$) instead of POMs as single Mo source was used to prepare MoS$_2$/CC for comparison. Energy dispersive X-ray spectrum (EDS) spectra (Fig. S4, ESf†) show the existence of M (Co, Ni, Fe), Mo and S elements, suggesting the successful synthesis of M-Mo-S/CC.

On the basis of inductively coupled plasma (ICP) and EDS
Different morphologies and structures of M-Mo-S/CC can be characterized by scanning electron microscopy (SEM). Firstly, pure CC (Fig. S5, ESI†) was observed with 3D carbon fiber network and fibrous morphology. After hydrothermal treatment, SEM image of Co-Mo-S/CC (Fig. 1a) presents that thin nanosheets are stacked into small-sized spheres and grown on CC uniformly and densely. To gain more details of the morphology, SEM images captured at different scales were also characterized. According to the magnified SEM image of Co-Mo-S/CC, the spheres stacked by nanosheets are uniform with a diameter of approximately 1 μm. In contrast, SEM image of Ni-Mo-S/CC (Fig. 1b) presents micro-sized crumpled particles on CC unevenly. The relevant low and high magnified SEM images are covered with thick Ni-Mo-S with different sizes. When FeMoO₄ is used to prepare Fe-Mo-S/CC, Fig. 1c displays the interconnected Fe-Mo-S nanosheets stacked directly on CC. SEM of MoS₂/CC (Fig. 1d) demonstrates that MoS₂ spheres with various sizes are grown on CC unevenly and unable to cover the surface of CC totally. TEM images of Mo-Mo-S/CC, the spheres stacked by nanosheets are also shown in Fig. S6, ESI† and in accord with SEM results. Moreover, PXRD was used to investigate the phase compositions of M-Mo-S. PXRD spectrum of Co-Mo-S/CC gives the corresponding diffraction patterns in accord with simulated MoS₂ (JCPDS 65-1941) and cobalt sulfide (CoS₂, JCPDS 65-3322) (Fig. S7a, ESI†). The sharp peaks of Ni-Mo-S are in agreement with simulated MoS₂ and nickel sulfide (NiS, JCPDS 75-613) (Fig. S7b, ESI†), while Fe-Mo-S is agreed with simulated MoS₂ and iron sulfide (FeS, JCPDS 65-9124) (Fig. S7c, ESI†). PXRD pattern of MoS₂ without metal doping (Fig. S7d, ESI†) exhibits the characteristic diffraction peaks assigned to the typical hexagonally symmetric structured MoS₂.³³ Raman spectrum (Fig. S8, ESI†) of M-Mo-S/CC and MoS₂/CC samples was used to prove the existence of pristine MoS₂ nanosheets, which show the typical in-plane E₂g and out-of-plane A₁₆ peaks for MoS₂. The specific surface area and porous property of M-Mo-S/CC were characterized by the N₂ adsorption-desorption isotherms and pore size distributions (Fig. S9, ESI†). In addition, X-ray photo-electron spectroscopy (XPS) analysis was used to study the composition and the surface chemical state (Fig. S10, ESI†). Co 2p spectrum of Co-Mo-S/CC (Fig. S11a, ESI†) presents four main peaks of Co²⁺ 2p₁/₂, Co³⁺ 2p₁/₂, Co²⁺ 2p₃/₂ and Co³⁺ 2p₃/₂ at 796.5, 793.9, 780.7 and 779.6 eV, respectively, with the satellites at the higher energy side, indicating the coexistence of Co²⁺ and Co³⁺ in Co-Mo-S/CC.³⁴ Three peaks of Mo 3d spectrum (Fig. S11b, ESI†) centered at 235.8, 232.4 and 228.8 eV are Mo⁶⁺ 3d₃/₂, Mo⁴⁺ 3d₃/₂ and Mo⁴⁺ 3d₅/₂, respectively, which are typical for MoS₂ and partial surface-oxidized MoO₃. The S 2s binding energy (225.8 eV) is also close to Mo 3d spectrum. S 2p spectrum (Fig. S11c, ESI†) can be deconvoluted into two component peaks of S 2p₁/₂ (162.8 eV) and S 2p₃/₂ (161.6 eV). The C 1s spectrum mainly derived from CC (Fig. S11d, ESI†) can be deconvoluted into two peaks of C-C/C=C bond (284.6 eV) and C-O bond (285.2 eV). The N 1s spectrum (Fig. S11e, ESI†) demonstrates two kinds of N species of graphitic N and pyridinic N, which are located at 398.3 eV and 401.1 eV, respectively. The intense peak at 394.6 eV is the Mo-N bond. O 1s spectrum in Fig. S11f, ESI† shows three peaks of C-OH (532.1 eV), O-C=O (531.2 eV) and Mo-O (530.4 eV) bonds, which are the oxygen-containing groups from Co-Mo-S/CC.³⁵ For comparison, XPS spectra of contrast samples are analyzed in Figs. S12-S14, ESI†.

**Growth mechanism study of M-Mo-S/CC**

In order to understand the morphology and composition evolution process, M-Mo-S/CC-t samples (t = 3 h, 6 h, 10 h and 24 h) obtained at different time intervals were observed by SEM and PXRD. Take Co-Mo-S/CC for example, firstly reacting
at 200 °C for 3 h, SEM image of Co-Mo-S/CC-3h shows irregular structures coated on CC entirely (Fig. 2a). When the reaction time is extending to 6 h, a number of nanosheets start to grow epitaxially at the outer irregular surface according to SEM image in Fig. 2b. Further increasing the hydrothermal time to 10 h, uniform-sized spheres stacked by nanosheets begin growing on CC (Fig. 2c). Both of the number and the thickness of these pellets would continue to increase and arrange on CC tightly and regularly as hydrothermal reaction processed up to 24 h. PXRD patterns (Fig. 2d) are also in accord with SEM images. In the first three hours, there are only two characteristic broad peaks for Co-Mo-S/CC-3h at 26.5 ° and 43.3 ° assigning to CC substrate. When reacting for 6 h, all the weak diffraction peaks in PXRD pattern of Co-Mo-S/CC-6h are matched well with CoS$_2$ phase. Notably, there is a new peak at 14.4 ° for (002) plane of MoS$_2$ accompanied with the intensity increase of CoS$_2$ peaks until the hydrothermal reaction carried for 10 h. After 24 h hydrothermal reaction, PXRD pattern of Co-Mo-S/CC-24h shows the emerging peaks at 14.4 °, 33.6 °, 39.5 ° and 59.1 °, which are assigned to the (002), (100), (103), and (110) planes of hexagonally symmetric structured MoS$_2$. Additionally, the peak intensity of CoS$_2$ is enhanced gradually with the increase of the reaction time (Fig. 2d), suggesting that some CoS$_2$ still can be nucleated even when the MoS$_2$ nanosheets starting to form outside the particles. Consequently, early formed CoS$_2$ on CC can serve as the structural backbones to provide active sites for further growth of MoS$_2$ to form the Co-Mo-S heterostructures with CoS$_2$ nanospheres mainly inside and MoS$_2$ nanosheets intercrossed outside. In order to clearly describe the growth process, the simulated morphologies of individual Co-Mo-S particle obtained at different time interval were presented in Fig. 2e. What’s more, aberration-corrected high-angle annular dark field (HAADF) image and EDS elemental mappings and overlay image of Co-Mo-S obtained at 24 h (Fig. 2f) demonstrate that the homogenous distribution of Mo but the central aggregate distribution of Co, further implying the heterostructure with CoS$_2$ particles coated by MoS$_2$ nanosheets. The growth process of Ni-Mo-S/CC is similar to Co-Mo-S/CC (Fig. S15, ESI†). NiS can be formed at the early stage of 3 h and served as the substrates for the growth of MoS$_2$. When the reaction time reach to 6 h, MoS$_2$ aggregates with diverse sizes start to grow outside NiS particles randomly to form Ni-Mo-S heterostructures, which are in consistent with the element mappings. In contrast, Fe-Mo-S/CC shows totally different growth process. Fe-Mo-S can be synthesized at the early stage of 3 h with FeS and MoS$_2$ nanosheets grown on CC simultaneously without aggregates (Fig. S16, ESI†). When the reaction time increasing, the morphology and composition of Fe-Mo-S keep unchanged. Fe-Mo-S nanosheets only grow thicker and the intensity of peaks become higher according to
It seems that Anderson-type POMs as bimetallic sources have a direct effect on the formation of M-Mo-S/CC with different morphology and structure, which can be explained by the nucleation-doping competition mechanism below. In M-Mo-S/CC system, the nucleation rates are much faster than the doping rates thus producing the bimetallic sulfides with certain compositions. Although M-Mo-S contain similar compositions of $\text{MS}_x/\text{MoS}_2$, they show totally different structures and morphologies due to their different nucleation rates. In Co-Mo-S, $S^{2-}$ ions can be released from TU quickly during the hydrothermal process and preferentially react with Co$^{2+}$ ions to nucleate CoS$_2$ particles on rough CC via van der Walls interaction. Then excess $S^{2-}$ ions continuously react with Mo$^{6+}$ from CoMo$_6$ that distributed around CoS$_2$ particles, leading to the continued epitaxial nucleation of MoS$_2$ nanosheets outside CoS$_2$. Because of the existence of excess S sources, Co and Mo ions would prefer to nucleate and grow into the Co-Mo-S nanospheres. In addition, the ionic radius of Co$^{2+}$ (74 pm) is larger than Mo$^{6+}$ (62 pm) so that the outward diffusion rate of Co$^{2+}$ is much slower than Mo$^{6+}$. Although the Co/Mo molar ratio is 1:6 in CoMo$_6$ precursors, the nucleation reaction to form CoS$_2$ still takes advantage during the nucleation-doping competition. Moreover, from the thermodynamics perspective, the smaller the solubility product constant ($K_{sp}$), the better the stability of the sulfides. Compared with CoS$_2$ ($3 \times 10^{-26}$), the smaller $K_{sp}$ of MoS$_2$ ($2.2 \times 10^{-56}$) confirms its good stability. Therefore, Co-Mo-S with heterostructures of CoS$_2$ mainly inside and MoS$_2$ outside prefers to be formed due to the higher thermodynamical stability of MoS$_2$ than CoS$_2$.

The growth mechanism of Ni-Mo-S could be explained similarly to Co-Mo-S system because of the approximative ionic radius of Ni$^{2+}$ (72 pm) to Co$^{2+}$ and the larger $K_{sp}$ of NiS ($3.2 \times 10^{-19}$) than MoS$_2$. However, Fe-Mo-S with homogeneous nanosheet structures exhibits different growth mechanism because Fe$^{3+}$ and Mo$^{6+}$ both give the same nucleation rates with $S^{2-}$ ions. Similar ionic radius of Fe$^{3+}$ (64 pm) and Mo$^{6+}$ (62 pm) also accelerate the nucleation reaction, making FeS and MoS$_2$ nanosheets grown on CC simultaneously. The $K_{sp}$ of FeS is $6.3 \times 10^{-15}$, which is also much larger than MoS$_2$. Although FeS and MoS$_2$ show the same nucleation rates, the contents of

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**Fig. 2.** (a-c) SEM images of Co-Mo-S/CC-t (t = 3 h, 6 h and 10 h) obtained at different hydrothermal time. (d) PXRD spectrum of Co-Mo-S/CC-t obtained at different hydrothermal time (● represents the peaks of CoS$_2$). (f) Aberration-corrected HAADF image and corresponding elemental mappings of Co-Mo-S and overlay image of Co and Mo elements. Mo is shown in green and Co is shown in red.
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MoS$_2$ are higher than FeS, suggesting that Fe-Mo-S nanosheets still have a relatively stable structure. In contrast, the size of MoS$_2$ spheres on CC are various because the different epitaxial nucleation rates are happened at different sites on rough CC using Na$_2$MoO$_4$ as the single Mo sources. The CC surface exhibits allocated striations randomly which hinders the growth of MoS$_2$ sheets epitaxially and leads to winkles and stacked pellets with irregular sizes to some extent. Therefore, nucleation-doping competition mechanism plays an important role in synthesizing M-Mo-S with different morphologies and structures.

Co-Mo-S was then characterized by high-resolution TEM (HRTEM). The evident lattice fringe with the interlayer spacing of 0.62 nm (Fig. 3a) is directly indexed to the (002) plane of the typical 2H-MoS$_2$. In Fig. 3b, the lattice fringe of 0.273 nm demonstrates that the (100) and (010) planes of MoS$_2$ are exposed with active Mo and S edges. Another kind of lattice fringe with the lattice spacing of 0.276 nm corresponds to the (200) plane of CoS$_2$, suggesting the successful hybridization of MoS$_2$ and CoS$_2$ for Co-Mo-S.$^{30}$ HRTEM image of Ni-Mo-S (Fig. 3c) reveals that the lattice spacing of 0.296 nm is in accord with the (100) plane of NiS. And the lattice spacing of 0.273 nm under NiS nanosheets is assigned to the (100) and (010) planes of MoS$_2$, further proving the heterostructure of Ni-Mo-S. HRTEM image of Fe-Mo-S (Fig. 3d) displays the lattice fringes of 0.62 nm and 0.284 nm corresponding to (002) plane of MoS$_2$ and (002) plane of FeS, respectively. Pure MoS$_2$ nanosheets was also characterized by HRTEM and mappings for comparison (Fig. S17, ESI†).

**Electrocatalytic HER and OER performance of M-Mo-S/CC**

The HER performance was firstly investigated in N$_2$-saturated 1 M KOH electrolyte using M-Mo-S/CC as the direct working electrodes. For comparison, the linear sweep voltammogram (LSV) curves of Co-Mo-S/CC, Ni-Mo-S/CC, Fe-Mo-S/CC, MoS$_2$/CC as well as the commercial 20% Pt/C were studied with 85% $iR$-compensation. Bare CC electrode was tested with poor HER and OER performance (Fig. S18, ESI†). In Fig. 4a, Co-Mo-S/CC affords an onset overpotential of ca. 60 mV vs. RHE approaching the commercial 20% Pt/C catalyst, which is more positive than those of Ni-Mo-S/CC (78 mV), Fe-Mo-S/CC (170 mV), MoS$_2$/CC (126 mV). Tafel slope is a well-known parameter to represent the reaction kinetics for water electrolysis. Except for 20% Pt/C (48 mV $\text{dec}^{-1}$), Co-Mo-S/CC exhibits an enhanced HER electrocatalytic activity, yielding a small Tafel slope of 84 mV $\text{dec}^{-1}$, which is much better than Ni-Mo-S/CC (90 mV $\text{dec}^{-1}$), Fe-Mo-S/CC (108 mV $\text{dec}^{-1}$) and MoS$_2$/CC (97 mV $\text{dec}^{-1}$) (Fig. 4b). Moreover, OER performance was measured under the same alkaline condition. Especially, Co-Mo-S/CC (Fig. 4c) delivers the smallest onset overpotential and the vertical rising oxygen-evolving current among all contrast samples. The Tafel slope of Co-Mo-S/CC (Fig. 4d) is 78
mV dec$^{-1}$, which is the smallest among the values of 90 mV dec$^{-1}$ for Ni-Mo-S/CC, 86 mV dec$^{-1}$ for Fe-Mo-S/CC, 88 mV dec$^{-1}$ for MoS$_2$/CC and 86 mV dec$^{-1}$ for commercial IrO$_2$. Such good HER and OER performance of Co-Mo-S/CC largely depends on the active Co$_2$S$_2$ and Mo$_2$S$_2$ species, unique heterostructures and fast electron transfer abilities in alkaline electrolyte.

The overpotential at the current density of 10 mA cm$^{-2}$ ($\eta_{10}$) is an important parameter for both HER and OER, which is a metric benchmark to solar fuel synthesis.$^7$ According to the LSV curves, $\eta_{10}$ of Co-Mo-S/CC for HER is only 118 mV vs. RHE for HER and 300 mV vs. RHE for HER. In Fig. 4a, except for commercial 20% Pt/C catalyst (20 mV), $\eta_{10}$ of Co-Mo-S/CC for HER is smaller than the samples including Ni-Mo-S/CC (140 mV), Fe-Mo-S/CC (267 mV) and MoS$_2$/CC (193 mV). For OER, $\eta_{10}$ of Co-Mo-S/CC is the smallest among all the contrast samples including Ni-Mo-S/CC (370 mV), Fe-Mo-S/CC (500 mV), MoS$_2$/CC (380 mV) and even commercial IrO$_2$ catalyst (330 mV). Such low $\eta_{10}$ values of Co-Mo-S/CC are comparable to the most of the reported sulfides-based materials and other non-noble-metal-based catalysts for both HER (Table S2) and OER (Table S3), such as Co/Co$_2$S$_2$@SNGS,$^{39}$ Ni$_2$S$_3$/NF,$^{40}$ CoMoS$_2$$^{31}$ and Co$_2$S$_2$.$^{41}$ Additionally, LSV curves and the calculated Tafel slopes of Co-Mo-S/CC and the contrast samples measured in 0.5 M H$_2$SO$_4$ were shown and analysed in Fig. 5S, ESI†.

Stability was tested to reflect the durable operation of electrocatalyst for water electrolysis. Firstly, LSV curves before and after 1000 cyclic voltammetry (CV) cycles were used to examine the stability in alkaline medium. Inset Fig. 4f is the LSV curves of Co-Mo-S/CC before and after 1000 CV cycles, which exhibit almost no deactivation for both HER and OER. Moreover, chronoamperometry (CA) of Co-Mo-S/CC shows no current loss for HER and only about 4.0 % drop in current density for OER, which is reacted at the constant overpotential of 120 and 300 mV vs. RHE over 14 h, respectively (Fig. 4f). The stability of other three samples were also measured and shown in Fig. 5S, ESI†. LSV curves of Ni-Mo-S/CC, Fe-Mo-S/CC and MoS$_2$/CC before and after 1000 CV cycles exhibit a slight deactivation for HER but obvious decrease for OER. In addition, CA tests of contrast samples for HER have almost no degradation after 14 h operation. However, for OER stability performance, MoS$_2$/CC lose more than 30.8 % of its initial current density, while 90.5 % current density retention of Ni-Mo-S/CC and even 22.3 % increase in current density of Fe-Mo-S/CC were observed (Table S4). Thus, different morphologies and structures of M-Mo-S/CC have a great effect on their stability performance. These results all indicate that the nucleation reaction to form the MoS$_2$-based bimetallic sulfides, especially Co-Mo-S, can improve the activity and stability for electrochemical water splitting.

To get further insight into the activity, we conducted the electrochemical impedance spectroscopy (EIS) measurements at the overpotential of 150 mV for HER and 300 mV for OER in 1 M KOH.$^{42}$ The nyquist plots (Fig. S21, ESI†) all show the obvious semicircles referring to the charge transfer resistance ($R_q$). $R_q$ value of Co-Mo-S is only 9.3 $\Omega$ for HER and 4.9 $\Omega$ for OER via the circuit simulation, smaller than that of Ni-Mo-S/CC, Fe-Mo-S/CC and MoS$_2$/CC (Table S5). More importantly, the electrolychemically active surface area (ECSA) was evaluated by the electrochemical double-layer capacitance (C$_{dl}$) (Fig. S22, ESI†).$^{44}$ The C$_{dl}$ value of Co-Mo-S/CC is 50.6 mF cm$^{-2}$, which is higher than that of Ni-Mo-S/CC (35.7 mF cm$^{-2}$), Fe-Mo-S/CC (15.1 mF cm$^{-2}$) and MoS$_2$/CC (4.6 mF cm$^{-2}$), respectively. Such low $R_q$ and high C$_{dl}$ values of Co-Mo-S/CC should be benefit from the active heterostructures with easily accessible active sites.

Motivated by the active HER and OER performance in alkaline electrolyte, Co-Mo-S/CC was evaluated in a two-electrode water splitting electrolyzer as both anode and cathode (Fig. 5a). Co-Mo-S/CC || Co-Mo-S/CC exhibits a small onset potential and quickly increased current density to release bubbles of H$_2$ and O$_2$ simultaneously (Video S1). In particular, Co-Mo-S/CC || Co-Mo-S/CC requires the potential of only 1.80 V to achieve the high current density of 50 mA cm$^{-2}$, which is even better than the commercial 20% Pt/C || IrO$_2$ (Fig. 5b). The overpotential (570 mV vs. RHE) of overall water splitting is also very close to the voltage difference ($\Delta V$) between HER and OER of Co-Mo-S/CC at 50 mA cm$^{-2}$ (565 mV). For comparison of the same electrode used as both anode and cathode, IrO$_2$ || IrO$_2$ requires the large potential of 2.07 V to afford 50 mA cm$^{-2}$ and 20% Pt/C || 20% Pt/C gives the potential of 2.16 V at 50 mA cm$^{-2}$. Moreover, Ni-Mo-S/CC as both cathode and anode requires the potential of 1.89 V to reach the current density of 50 mA cm$^{-2}$, while Fe-Mo-S/CC electrode needs the potential of 2.09 V to get to 50 mA cm$^{-2}$ (Fig. S23, ESI†). The overall water splitting performance of M-Mo-S/CC is in accord with their relevant HER and OER properties. Therefore, the overall water splitting performance of Co-Mo-S/CC || Co-Mo-S/CC is much better than these contrast samples and is superior to most of the reported sulfides-based and other non-noble metal-based materials (Table S6).

**Conclusions**
In summary, MoS$_2$-based bimetallic sulfides including Co-Mo-S/CC, Ni-Mo-S/CC and Fe-Mo-S/CC were synthesized by a one-pot hydrothermal method using Anderson-type POMs as the bimetallic sources. M-Mo-S/CC with unique morphology and structure was an ideal model to study the growth mechanism for MoS$_2$-based bimetallic sulfides through the nucleation-doping competition. Co-Mo-S and Ni-Mo-S nanospheres have the heterostructures with Co$_2$S$_3$ or NIS mainly inside and MoS$_2$ nanosheets outside due to the fast nucleation rate of transition metal sulfides than MoS$_2$. The same nucleation rate of FeS and MoS$_2$ in Fe-Mo-S can be explained to form the uniform structure without stacking into spheres. Besides, M-Mo-S/CC exhibit excellent electrocatalytic performance for water splitting in alkaline electrolyte. Especially, Co-Mo-S/CC shows the low $\eta_{10}$ of 118 and 300 mV vs. RHE and enhanced stability for HER and OER, respectively. The two-electrode electrolyzer using Co-Mo-S/CC as both anode and cathode obtains the current density of 50 mA cm$^{-2}$ at the potential of 1.80 V. The outstanding electrocatalytic performance of Co-Mo-S/CC can be attributed to the following aspects: (1) the homogeneous Co-Mo-S particles grown on CC increase the surface area and expose the active sites to facilitate the electrocatalytic reaction in harsh electrolyte; (2) the hybridization of Co$_2$S$_3$ inside and MoS$_2$ outside to form the stable Co-Mo-S heterostructure ensure to improve the activity and stability for both HER and OER dramatically; (3) CC substrate possesses woven networks and good electrical conductivity, making it an favorable platform to grow sulfides uniformly and transfer electrons easily. In brief, together with the facile one-pot hydrothermal method, bimetallic sulfides can be synthesized using POMs precursors with fixed metal sources to study the growth mechanism and energy conversion and storage property prospectively.

**Experimental**

**Synthesis of M-Mo-S/CC**

Carbon cloth was firstly treated with water, ethanol and concentrated nitric acid for 30 min respectively to remove the residual organic species. CoMo$_6$ (0.12 g, 0.1 mmol) and thiourea (0.18 g, 2.4 mmol) were dissolved in 35 mL water by sonication for 30 min to form a homogenous solution. Then the solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave with two pieces of treated 1 x 2 cm$^2$ CC added. The reaction was kept at 200 °C for 24 h. The resultant Co-Mo-S/CC was washed and sonicated using water for several time, followed by drying at 60 °C overnight. The mass loading of Co-Mo-S on CC was ~ 1 mg cm$^{-2}$. The preparation process of Ni-Mo-S/CC, Fe-Mo-S/CC and MoS$_2$/CC is similar to Co-Mo-S/CC, except that NiMo$_6$ (0.12g, 0.1 mmol), FeMo$_6$ (0.12g, 0.1 mmol) and Na$_3$MoO$_4$·2H$_2$O (0.145g, 0.6 mmol) were used as the metal precursors, respectively.

**Physicochemical characterization**

Powder X-Ray diffraction (PXRD) patterns were recorded on a D/max 2500VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu Kα radiation ($\lambda$ = 1.54060 Å). Corresponding work voltage and current is 40 kV and 100 mA, respectively. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were carried out on JEOL-2100F apparatus at an accelerating voltage of 200 kV. Morphology and microstructure analysis was conducted using a scanning electron microscope (SEM, JSM-7600F) at an acceleration voltage of 10 kV. Energy dispersive X-ray spectroscopy (EDS) was performed with JSM-5160LV-Vantage type energy spectrometer. The metal molar ratio was determined by inductively coupled plasma atomic emission spectrometry (ICP, Prodigy). HADDF image and element mappings were carried out using an image aberration-corrected TEM (Titan3 G2 60-300) at an acceleration voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) was collected on scanning X-ray microprobe (PHI 5000 Verasa, ULAC-PHI, Inc.) using Al kα radiation and the C 1s peak at 284.8 eV as internal standard. Raman spectra of powder samples were obtained on Lab-RAM HR800 with a laser excitation wavelength of 532 nm. Fourier transform infrared spectroscopy (FT-IR) was collected on a Nexus 670 spectrometer. Nitrogen adsorption-desorption isotherms were collected at 77 K on a Quantachrome Instruments Autosorb AS-6B.

**Electrochemical measurements**

Both HER and OER tests were performed in a three-electrode system on the electrochemical station (Bio-Logic SP-150) using SCE and graphite rod (Sigma-Aldrich, 99.995% trace metals basis) as the reference and counter electrode, respectively. M-Mo-S/CC and MoS$_2$/CC were directly used as the working electrode with the geometric surface area of 1 cm$^2$. Commercial 20% Pt/C or IrO$_2$ were firstly sonicated in ethanol solution mixed with 0.5 wt% Nafion to obtain the concentration of 10 mg mL$^{-1}$. Then 100 µL dispersion was drop-casted on CC with the mass loading of 1 mg cm$^{-2}$ (the coating area is about 1 cm$^2$). All LSV curves were measured at the scan rate of 5 mV s$^{-1}$ in N$_2$-saturated 1 M KOH and corrected for the 85% IR-compensation. Tafel slope was calculated according to the Tafel equation ($\eta = b \log i + a$, where $\eta$ is the overpotential, $j$ is the current density and b is the Tafel slope). For LSV stability tests, CV were carried out from 0 to -0.2 V vs. RHE for HER and from 1.3 to 1.5 V vs. RHE for OER at the scan rate of 100 mV s$^{-1}$. EIS measurements were performed at the overpotential of 150 mV vs. RHE for HER and 300 mV vs. RHE for OER from 10 mHz to 1000 kHz with an AC voltage of 10 mV. To estimate ECSA, CV was tested at the potential from -0.2 to -0.1 V vs. RHE with different scan rates (10, 20, 40, 60 and 100 mV s$^{-1}$). For overall water splitting electrolysis, Co-Mo-S/CC was directly used as both cathode and anode in 1 M KOH. The LSV curves were recorded at the scan rate of 5 mV s$^{-1}$. RHE calibration was converted via the Nernst equation: $E_{\text{RHE}} = E_{\text{SCE}} + 0.059pH + E_\theta^0$. In 0.5 M H$_2$SO$_4$, $E_{\text{RHE}} = E_{\text{SCE}} + 0.245$ V. In 1 M KOH, $E_{\text{RHE}} = E_{\text{SCE}} + 1.07$ V. In 0.5 M PBS, $E_{\text{RHE}} = E_{\text{SCE}} + 0.65$ V.

**Conflicts of interest**
There are no conflicts to declare.

Acknowledgements

This work was financially supported by NSFC (No. 21622104, 21471080 and 2170010097), the NSF of Jiangsu Province of China (No. BK2017040708), the Natural Science Research of Jiangsu Higher Education Institutions of China (No. 17KJB150025), Priority Academic Program Development of Jiangsu Higher Education Institutions and the Foundation of Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, the Postgraduate Research & Practice Innovation Program of Jiangsu Province (No. KYCX17_1060).

Notes and references

23 H. Wang, C. Tsai, D. Kong, K. Chan, F. Abdil-Pedersen, J. K. Nørskov and Y. Cui, Nano Research, 2015, 8, 566-575.
Graphical Abstract

Polyoxometalate Precursors for Precisely Controlling Synthesis of Bimetallic Sulfide Heterostructure through Nucleation-Doping Competition

A one-pot hydrothermal synthesis method was proposed to grow a series of bimetallic sulfides containing MoS$_2$ and another transition metal sulfide on carbon cloth (M-Mo-S/CC, M = Co, Ni, Fe) using Anderson-type polyoxometalates (POMs) as bimetallic sources. The ideal model of M-Mo-S/CC was used to study the growth process by the nucleation-doping competition mechanism. We have firstly proved that M-Mo-S possesses certain bimetallic sulfides compositions rather than metal doping into MoS$_2$ structures because the nucleation reaction plays a main role in the nucleation-doping competition. Due to the different nucleation rates of three transition metals, M-Mo-S exhibit different morphologies. As the electrodes for alkaline water electrolysis, Co-Mo-S/CC achieves the best performance for hydrogen evolution reaction, oxygen evolution reaction and overall water splitting among all M-Mo-S/CC samples.