Triple Ni-Co-Mo metal sulfides with one-dimensional and hierarchical nanostructures towards highly efficient hydrogen evolution reaction

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ABSTRACT

Designing multi-transition metal-based sulfides holds promising in alkaline water electrolysis, whereas selecting proper candidates and facile building strategy remain challengeable. Herein, based on previous theory of combining 3d-transition metal (NiCo) with non-3d-transition metal (Mo) to lower hydrogen-adsorption energy barriers, we develop an indirect access to NiCoMo sulfides supported by nickel foam (CoMoO-S/NF) with one dimensional (1 D) and hierarchical nanostructures. In the first step, the metal oxides as precursor frameworks are designed as one-dimensional (1 D) nanostructures comprising interwoven nanosheets. The unique structure not only provides the large surface areas for exposing abundant active sites, but also improves the contact between catalyst/interface and facilitates the mass or charge transportation. Besides, the ternary metals are supposed to generate synergistic effect to boost hydrogen evolution reaction (HER) properties of CoMoO-S/NF via sulfurization in the second step. Furthermore, CoMoO-S/NF demonstrates high electrocatalytic performances with structural stability in long-term HER process. Therefore, the two-step building of ternary transition metal sulfides may be provide applications for various transition metal materials with unique architecture and high efficiency in alkaline HER.

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1. Introduction

Clean and sustainable hydrogen fuel is highly desired in worldwide energy supplying systems [1–3]. Water-alkali electrolysis is one of the promising pathways to achieve this goal, which is proceeded by cost-effective electrocatalyst materials [4–7]. So far, noble Pt-based catalysts show the best electrocatalytic performances for hydrogen evolution reaction (HER), whereas their high cost and scarcity impede the large-scale utilization [8–11]. Therefore, it is significant and urgent to research earth-abundant and active electrocatalysts to develop the hydrogen economy.

Prior to developing alternatives, it is essential and rational to understand HER kinetics in alkaline media for useful guidelines. The high kinetic energy barriers of the water dissociation step ($\Delta G(H_2O)$) in the first stage is rate limiting in contrast with that of acid HER [12,13]. The following step (Heyrovsky or Tafel) of combining hydrogen into molecular hydrogen is also crucial for HER. [12,14]. Therefore, non-noble metals are expected to contain efficient water dissociation centers to overcome the first step, and Ni has been proved as one of the satisfying candidates

[12,13,15–17]. In addition, Mo has shown superior hydrogen-adsorption property to generate H_2 molecule [18,19]. Recent researches have proposed that integrating 3d transition metals (such as Ni and Co) with non-3d transition metals (Mo, W) can effectively reduce the energy barriers in alkaline HER [20,21]. Many relevant practices have confirmed this theory with satisfying experimental results, such as Ni-Mo alloys [14,21–23], MoS_2/Ni_3S_2 heterostructures [24–26], NiS_2-MoS_2 hybrids [4,27], Ni-doped MoS_2 nanosheets [28], $CoMoS_x$ species [29–31] or chevrel phases of $M_xMo_6X_8$ (M = Co, Ni, etc.; X = S, Se, Te) [32–34]. These bimetallic complexes are supposed to provide rich active sites, intriguing the inert sites and improve the conductivity simultaneously [35–38]. Furthermore, multi-metallic composites, such as tri-metallic sulfides, have more potential to replace noble catalysts due to their better catalytic activities [39–41]. Very recently, Zhang's group has proved that ternary NiCoMo alloy may lower the hydrogen-adsorption energy barriers compared with binary metals [20]. However, the related sulfides remain seldom researched which inspire us to continue this study.

On the other hand, the electrocatalytic performances are largely determined by nanostructures and conductivity to optimize the water electrolysis efficiency. One sensible strategy is to design one-dimensional (1 D) nanostructures in-situ grown on conductive substrates [41]. The 1 D nanostructures contain open space for

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better dispersion of active sites and allow high utilization efficiency of active species [42,43]. The direct attachment to the conducting substrates as electron collectors can be efficient for charge transport superior to polymeric binder-dependent powder with decreased conductivity [44,45]. In addition, increasing surficial roughness in nanostructure is also beneficial for exposure of catalytic sites [43]. Therefore, building interwoven nanosheet structures to form hierarchically 1 D nanostructures may satisfy such proposal to enhance catalytic performances [4].

Herein, we have designed a two-step access to hierarchically 1 D nanostructure of tri-metallic Ni-Co-Mo sulfides on nickel foam (CoMoO-S/NF) to satisfy the above requirements, as illustrated in Fig. 1. Compared with $CoMoO_4$ nanorods derived from mere hydrothermal process of the first step, the adoption of nickel foam (NF) substrate induce formation of hierarchically 1 D nanostructure of $CoMoO_4$ comprising interwoven nanosheets. Such unique precursor frameworks may provide porous voids and large open space, thus ensuring uniform dispersion and exposing of active sites when transformed into metal sulfides in the second procedure. Besides, it is also advantageous for sufficient contact in electrolyte/catalysts interfaces and improves rapid mass or charge transportation. The as-prepared CoMoO-S/NF shows excellent HER performance with low overpotential (225 mV) to deliver 100 mA cm^{-2}, retaining high catalytic efficiency and structural stability in long-term HER process. The two-step transformation may provide facile strategy for multiple transition metal sulfides in delicate morphologies, and is promisingly applicable to other transition metals toward efficient catalysis of hydrogen production.

2. Experimental section

All chemical reagents are of analytical grade without further purification. Nickel foam (NF) with thickness of 1.0 mm and surface density of 350 g m^{-2} was purchased from Shenzhen Poxon Machinery Technology Co., Ltd. Pt/C (10 wt%) was purchased from Alfa Aesar (China) Chemicals Co. Ltd. Nafion (5 wt%) was purchased from Sigma-Aldrich.

2.1. Synthesis of CoMoO and CoMoO-S

Typically, 30 mL of homogeneous solution of $Co(NO_3)_2 \cdot 6H_2O$ (1.5 mmol) was added by $Na_2MoO_4 \cdot 2H_2O$ (1.5 mmol), followed by transferring into autoclave (100 mL) at 150 °C for 6 h. Then the pink precipitation was annealed at 400 °C for 4 h in air to obtain CoMoO. The as-prepared CoMoO powder (0.1 g) was sulfurized in H_2S/N_2 gas (volume ratio of 1/9) at 300 °C for 2 h with heating rate of 3 °C/min to obtain CoMoO-S.

2.2. Synthesis of CoMoO/NF, CoMoO-S/NF and Ni$_3$S$_2$/NF

Prior to the synthesis, NF with area of 1×2 cm^2 was consecutively sonicated in acid, acetone and ethanol for 20 min. Then the clean NF was dried in vacuum at 60 °C for 6 h. The preparation of CoMoO/NF was similar with CoMoO, except for four pieces of as-cleaned NFs substrates were placed within autoclave. Typically, the preparation of CoMoO-S/NF was similar with CoMoO-S, except for CoMoO/NF as precursor to be sulfurized in H_2S/N_2 gas to obtain CoMoO-S/NF. Typically, the pristine NF was utilized as precursor to be sulfurized in H_2S/N_2 gas to obtain Ni$_3$S$_2$/NF, with similar sulfurization procedure as depicted before. The mass loadings of CoMoO/NF and CoMoO-S/NF were about and 2.8 and 4.3 mg cm^{-2}, respectively.

2.3. Characterizations

X-ray diffraction (XRD) patterns were collected on X'Pert PRO MPD diffractometer with Cu Kα irradiation. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were conducted on FEI Tecnai G2. X-ray fluorescence elemental analysis (EDX) was performed on representative areas of samples on the surface. X-ray photoelectron spectra (XPS) data were recorded on Thermo Fisher Scientific II spectrometer. The metal elemental analysis via inductively coupled plasma optical emission spectrometry (ICP-OES) for as-prepared samples have been performed on Shidmadzu ICPE-9000.

2.4. Electrochemical measurements

Electrocatalytic performances of all samples were measured in a three-electrode setup (Gamry Reference 600, USA) in 1.0 M KOH as electrolyte. Typically, all as-prepared NF-supported samples were used as the working electrode (2 cm^2) fixed by electrode clip, while a saturated calomel (SCE) electrode and a carbon rod were utilized as the counter and reference electrodes, respectively. For as-prepared powder catalysts such as CoMoO and CoMoO-S, as well as the commercial Pt/C (20 wt%), 4 mg of sample was
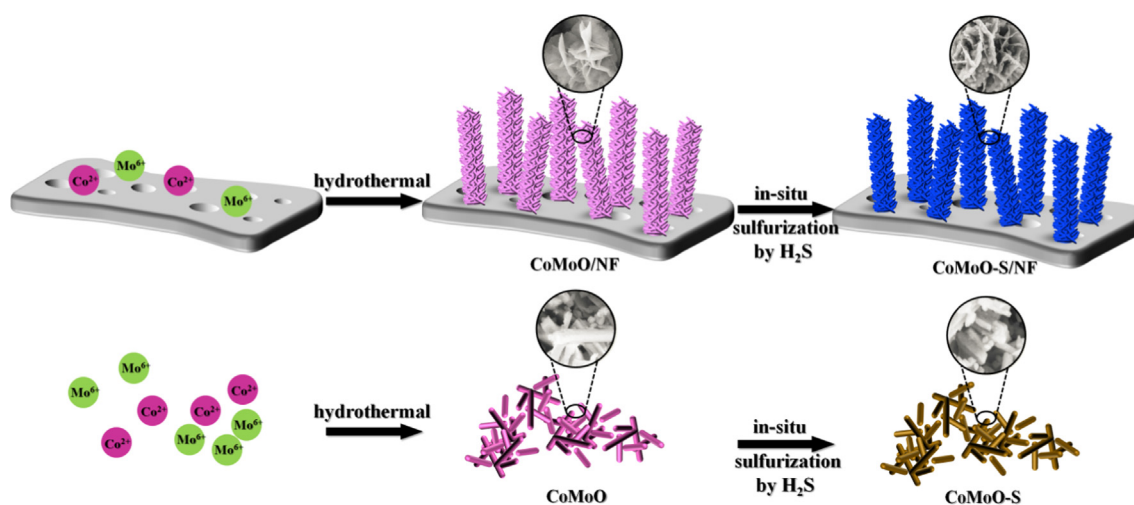

Fig. 1. Schematic illustration of two-step access to CoMoO-S/NF and CoMoO-S.