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$CoMo_2S_4/MoS_2$ Heterostructure with High Catalytic Performance for Overall Water Splitting in Alkaline Medium

Guo Peisheng[a], **Wang Chengxin**[b, *]

State Key Laboratory of Optoelectronic Materials and Technologies, School of Materials Science and Engineering, Sun Yat-Sen (Zhongshan) University, Guangzhou 510275, China

[a]e-mail: guopsh@mail2.sysu.edu.cn

[b, *]Corresponding author: Fax: +86-20-8411-3901; e-mail: wchengx@mail.sysu.edu.cn

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Abstract: Nowadays, exploring the non-noble bifuntional catalysts of high efficiency activity for both HER and OER in the alkaline media attracts great interest. Herein, the $CoMo_2S_4/MoS_2$ heterostructures were prepared by modified solid state method. Interestingly, the MoS_2 nano sheets exhibit good matching on the surface of $CoMo_2S_4$ nano/micro rods, which would form large semicoherent interfaces. For OER, the $CoMo_2S_4/MoS_2$ heterostructures exhibit higher activity than the noble metal oxides, RuO_2 delivers the current density of 10 $mAcm^{-2}$ at 1.52 V. Utilizing the $CoMo_2S_4/MoS_2$ as the bifuntional electracatalysts for overall water splitting, it just needs 1.65 V to achieve the current density of 10 mA cm^{-2}. It is believed that this research would attract more attention on the catalytic activity of $MoS_2/M\text{-}Mo_2S_4$, in particularly, the role of semicoherent interfaces plays in the catalytic process.

1. Introduction

To deal with the energy dilemma and environment pollutions resulted from the burning of fossil fuel, researchers spare no efforts to exploit high-efficiency, lost-cost and durable catalysts for clean and renewable energy generation, especially for electrochemical overall water-splitting. The electrochemical overall water-splitting can produce the clean hydrogen fuels (H_2) by hydrogen evolution reaction (HER) and oxygen (O_2) by oxygen evolution reaction (OER).[1] In this significant electrochemical water-splitting process, the key is to explore high-efficiency catalysts to minimize the overpotential to drive the hydrogen evolution reaction and oxygen evolution reaction, in particularly, the oxygen evolution reaction, which is more thermodynamically and kinetically challenging and has been considered as the bottleneck of electrochemical overall water-splitting.

In fact, overall water-splitting electrocatalysis in acid medium is hindered to commercial application due to the passable activity of scarce, noble and acid-insoluble OER catalysts. Hence, exploiting high-efficiency catalysts that can simultaneously drive the HER and OER with low overpotential in the alkaline media would boom the commercial application of alkaline water splitting. Recently, molybdenum sulfides are regarded as promising alternative catalysts for HER in acid. Lots of researches and DFT calculation indicated the efficient electrocatalytic HER performance depends on the edges sites of nanostructure MoS_2 in the acid media.[2-4] However, there is few reports focus on the electrocatalytic performance of MoS_2 in the alkaline media. In 2016, Zhang et al.[5] reported MoS_2/Ni_3S_2 heterostructures exhibit excellent catalytic performance for both HER and OER in the alkaline media. In 2017, Bai et al.[6] introduced $Co_9S_8@MoS_2$ heterostructures with excellent catalytic activity for overall water splitting. In 2018, Liu et al.[7] presented $Co_3O_4@MoS_2$ heterostructures for overall water splitting that exhibited high efficiency catalytic activity. These studies illustrated that MoS_2 and its hybrids possess outstanding electrocatalytic activity for both HER and OER, which would be promising catalysts for overall alkaline water splitting. What's more, Mo-based ternary metal sulfides possess high electronic conductivities due to the richer redox reactions from two metal ions. In 2016, Jiang et al.[8] reported the superior electrocatalytic performance of $NiMo_3S_4$ for HER in the alkaline media. In 2016, Yu et al.[9] introduced a general route to form hollow structures of M-MoS_3 (M = Co, Ni) and presented enhanced electrocatalytic activity for HER in acid media. Taking the synergistic effects into account, we surmised that the hybrids of MoS_2 and Mo-based ternary metal sulfides would be ideal catalysts for overall water splitting in the alkaline. As matter of facts, Zhang et al.[10] illustrated the robust electrocatalytic properties of hybrids of MoS_2 and $CoMo_2S_4$ for HER in acid media. However, the investigation of electrocatalytic performances of hybrids of MoS_2 and M-Mo_2S_4 is rare and designing the heterostructures of such hybrids for overall water splitting in alkaline medium with low overpotential and long-term stability is highly desirable but remain challenging.

Here in, the MoS_2/$CoMo_2S_4$ hybrids were synthesized by modified solid state reaction. By controlling the temperature of post-annealing treatment, we can design the compositions of the hybrids. The hybrids exhibit superior electrocatalytic activity both for HER and OER in alkaline medium, and the hybrids annealed at 750 ^oC presents the highest catalytic activity because of the synergistic effects of $CoMo_2S_4$ and MoS_2. In particularly, the hybrids exhibit the higher catalytic activity than the commercial RuO_2 in the alkaline medium. Most notably, employing the MoS_2/$CoMo_2S_4$ hererostructures as the cathode and anode catalysts in the alkaline medium, the overall water splitting current of 10 $mAcm^{-2}$ can be achieved at a low potential of 1.65 V, and with remarkable durability. The applied potential to gain10 $mAcm^{-2}$ is only 85 mV higher than the noble metal Pt/C and RuO_2 electrocatalytic couple

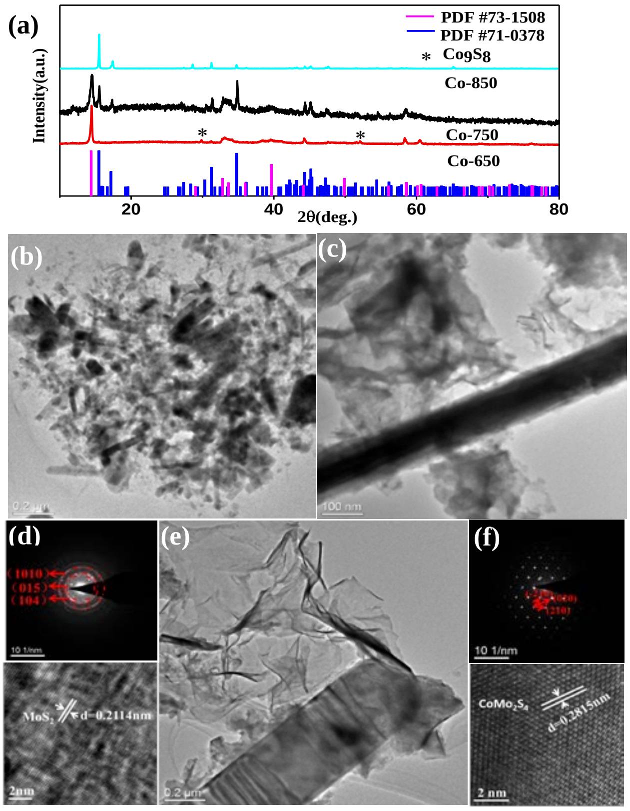
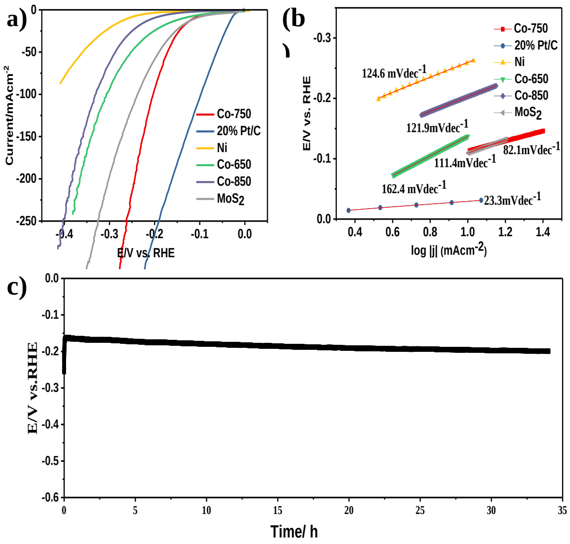


Figure 1 Structural characterization of as-synthesized hybrids of $CoMo_2S_4$ /MoS_2/C: (a) XRD patterns; (b), (c) and (e) TEM images at different magnifications, (d) and (f) are images of corresponding SAED pattern and HRTEM images of MoS_2 and $CoMo_2S_4$.

2. Result and discussion

The XRD patterns of hybrids of $CoMo_2S_4$/MoS_2/C annealed at different temperature were shown in Fig. 1 (a). When annealed at 650 ^oC, the phase can be ascribed to MoS_2 (JCPDS, PDF #73-1508), and small peaks assigned to Co_9S_8 can be found also. While annealed at 850 ^oC, the phase can be ascribed to $CoMo_2S_4$ (JCPDS PDF #71-0378). And annealed at 750 ^oC, the hybrids are composed of $CoMo_2S_4$ and MoS_2, which can be proved by the XRD pattern. Fig. 1 (b) and (c) present the typical morphologies of hybrids of $CoMo_2S_4/MoS_2/C$. The hybrids consist of $CoMo_2S_4$ nano/micro rods and MoS_2 nanosheets. What's more, the HRTEM images and SAED patterns of $CoMo_2S_4$ nano/micro rods and MoS_2 nanosheets. Fig, 1d exhibits an interlayer distance of 0.2114 nm, which can be indexed to the (0 1 5) lattice fringe of 2H-MoS_2 and the MoS_2 sheets show the amounts of edge sites, indicating the excellent catalytic activities both for HER and OER. What's more, the corresponding SAED pattern (Fig. 1 (d)) revealed the polycrystalline feature of MoS_2. And the three diffraction rings could be indexed to the (104), (015), (1010) planes of MoS_2. The HRTEM image of $CoMo_2S_4$ nano/micro rods exhibits 0.2815 nm, which can be corresponding to the (-2 1 0) plane of monoclinic $CoMo_2S_4$. Meanwhile, the corresponding SAED pattern indicates the single phase of monoclinic $CoMo_2S_4$, and the corresponding planes were marked by red arrows (Fig. 1(f).

HER activity of transition-metal dichalcogenides, such as, MoS_2 is sensitive to the valence state and coordination environment of both metal and chalcogen edges. Therefore, the XPS spectrums were applied to confirm the chemical composition and oxidation state. As shown in Fig. 2 (a), the Co 2p spectrum exhibits four peaks, and the peaks located at 780.3 eV and 796.7 eV could be resulted from the $2p_{3/2}$ and $2p_{1/2}$ of Co^{2+} ions. What's more, the satellite peaks lied at 786.0 eV and 802.0 eV also proved that the oxidation state of Co ion is +2. The Mo 3d spectrum (Fig. 2(b)) can be deconvoluted into five peaks. The peaks located at 229.7 and 232.7 eV could be ascribed to the Mo^{4+} of MoS_2, and the peaks located at 235.5 and 231.6 eV could be caused by the oxidization of surface Mo ion to form Mo^{6+}. What's more, the peak located at 228.7 eV could be assigned to the Mo ion of $CoMo_2S_4$, which is similar to the NIST XPS database. The S 2p spectrum was shown in Fig. 2(c), the peaks lied at 161.5 eV and 162.6 eV is corresponding to the S $2p_{3/2}$ and S $2p_{1/2}$, indicating the existence of S^{2-} ions, which are HER activity. And the peak at 168.8 eV could be attributed to the satellite peak of S, which is similar to previous works. The C 1s spectrum was presented in Fig. 2(d). The component peak deconvoluted by Gaussian fitting method at 284.7 eV could be attributed to the C=C/C-C bond, while the peak at 285.6 eV could be assigned to C-S bond.



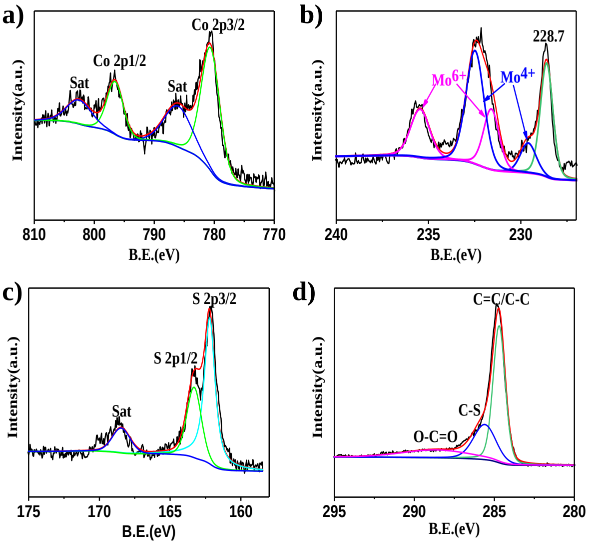


Figure 2 XPS spectrum of hybrids of $CoMo_2S_4/MoS_2/C$: (a) Co 2p; (b) Mo 3d; (c) S 2p; (d) C 1s.

Fig. 3 exhibits the HER performance tested in 1 M KOH solution at room temperature. As shown in Fig. 3 (a), polarization curves of the hybrids annealed at different temperature, and the pure MoS_2, bare Ni foam and 20% Pt/C were examined for comparison. Among them, the hybrids annealed at 750 °C exhibit the excellent catalytic activity for HER in alkaline media. The $CoMo_2S_4/MoS_2$ heterostructure (Co-750) catalysts present the onset potential of ~ 76 mV. To achieve the current density of 10 mA cm^{-2} and 20 mA cm^{-2}, the overpotential is 112 mV and 136 mV, respectively. Fig. 3 (b) presents the Tafel slopes corresponding to the polarization curves shown in Fig. 3 (a). The Tafel slope of $CoMo_2S_4/MoS_2$ heterostructure (Co-750) is 82.1 mV dec^{-1}, indicates the $CoMo_2S_4/MoS_2$ heterostructures activate water-oxidation reaction kinetics. To evaluate the catalytic durability of $CoMo_2S_4/MoS_2$ heterostructure, the potential–time curves under constant current (50 mA cm^{-2}) was tested for more than 30 hours, as shown in Fig. 3 (c). The result indicates $CoMo_2S_4/MoS_2$ could maintain the steady catalytic activity of OER and only slightly increases potential augment can be observed.

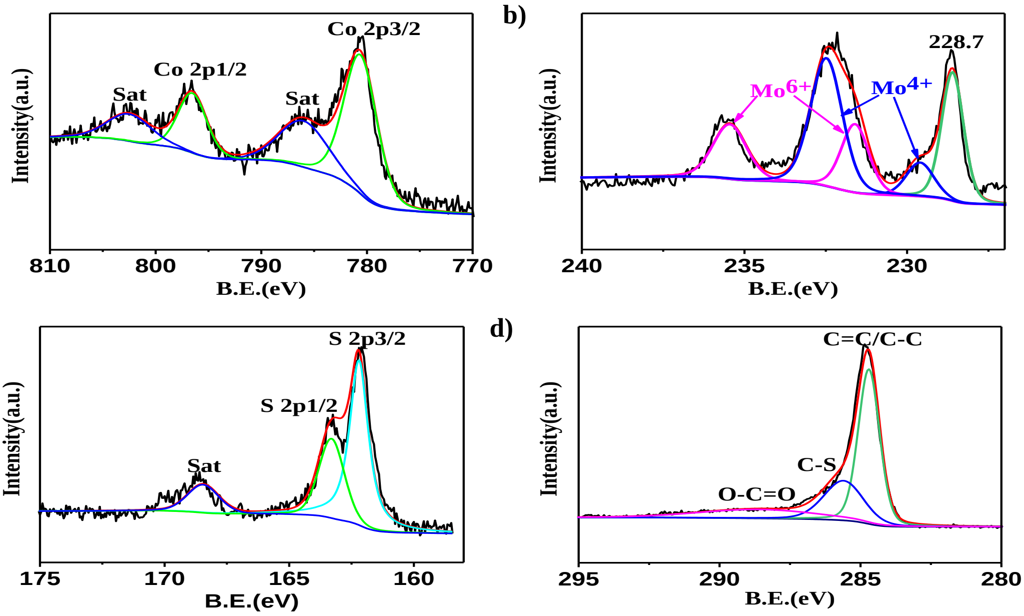


Figure 3 (a and b) Polarization curves and Tafel plots of Ni foam, commercial Pt/C, MoS_2 and hybrids of $CoMo_2S_4/MoS_2/C$ at 650 ^{o}C,750 ^{o}C and 850 ^{o}C in 1 M KOH for HER. (c) The time dependent potential curves of hybrids of $CoMo_2S_4/MoS_2/C$ annealed at 750 ^{o}C under a steady-state current density of 50 mA cm^{-2} for 30 h. All of the potentials and voltages are iR corrected.

The electrocatalytic activity of $CoMo_2S_4/MoS_2$ heterostructure toward the OER was tested in 1 M KOH solution by linear scan voltammetry (LSV). Fig. 4 (a) presents the polarization curves of hybrids annealed at different temperature and pure MoS_2, bare Ni foam, RuO_2 for comparison. The results illustrate that the $CoMo_2S_4/MoS_2$ heterostructure (Co-750) exhibits the highest catalytic efficiency for OER in the alkaline media. The $CoMo_2S_4/MoS_2$ heterostructure presents a low onset potential of 1.48 V. what's more, to achieve the current density of 10 mA cm^{-2} and 20 mA cm^{-2}, the needed potential is 1.52 V and 1.53 V, respectively. Fig. 4 (b) shows the Tafel slopes corresponding to the polarization curves in Fig. 4 (a). The Tafel slope of $CoMo_2S_4/MoS_2$ heterostructure (Co-750) is 85.8 mV dec^{-1}., outperform the commercial noble metal oxides RuO_2 (131.2 mV dec^{-1}), indicating a rapid OER rate for $CoMo_2S_4/MoS_2$ heterostructure. Except for the catalytic activity, long-term stability is a significant property to determine the application of electrocatalysts into practice. Hence, the potential–time curves under constant current were applied to evaluate the durability of electrocatalysts. Fig. 4 (c) exhibits the potential-time curve under the current of 50 mA cm^{-1} for almost 60 hours. As time goes on, the potential presents negligible increase, indicating the good durability of $CoMo_2S_4/MoS_2$ heterostructure for OER. The $CoMo_2S_4/MoS_2$ heterostructures were applied as a bifunctional electrocatalyst for overall water splitting in a two electrode system in 1m KOH solution. Fig. 5 (a) shows the polarization curves of $CoMo_2S_4$/ MoS_2 heterostructure and Pt/C- RuO_2 couple. An overall water splitting current density of 10 mA cm^{-2} can be achieved at the low potential of 1.65 V. The applied potential is just 85 mV higher than the Pt/C-RuO_2 couple. The stability of this system for overall water splitting was tested for 24 hours in 1.0 M KOH solution. As shown in Fig. 5 (b), the potential applied to achieved the current density of 10 mA cm^{-2} is slightly increase, indicating the long-term stability of the $CoMo_2S_4/MoS_2$ heterostructure as bifuntional electrocatalyst for overall water splitting.

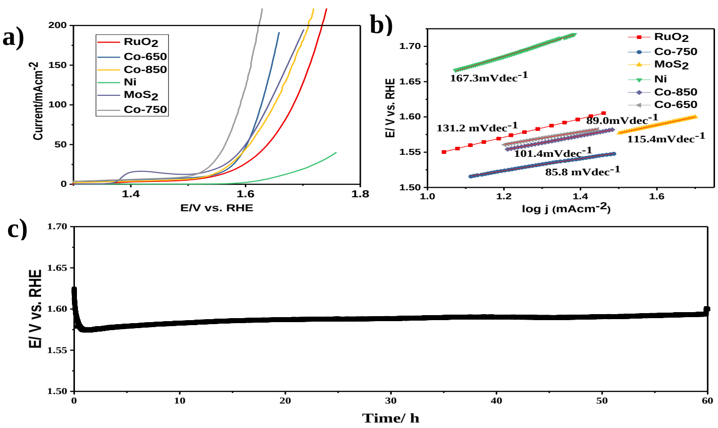


Figure 4. (a and b) Polarization curves and Tafel plots of Ni foam, commercial Pt/C, MoS_2 and hybrids of $CoMo_2S_4/MoS_2/C$ at 650 °C,750 °C and 850 °C in 1 M KOH for OER. (c) The time dependent potential curves of hybrids of $CoMo_2S_4/MoS_2/C$ annealed at 750 °C under a steady-state current density of 50 mA cm^{-2} for 60 h. All of the potentials and voltages are iR corrected.

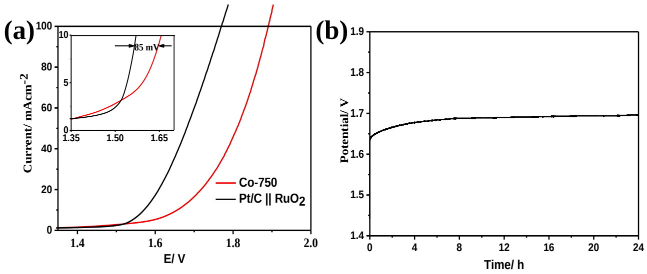


Figure 5 (a) Polarization curves of $CoMo_2S_4/MoS_2/C$ at 750 °C and Pt/C-RuO_2 couple. (b) Durability of $CoMo_2S_4/MoS_2/C$ at 750 °C in a two electrode system. All of the potentials and voltages are iR corrected.

In contrast, the $CoMo_2S_4/MoS_2$ heterostructure presents much higher efficient catalytic activity than MoS_2 and $CoMo_2S_4$ both for HER and OER. The superior catalytic activity would be resulted from the following factors: i) the MoS_2 and $CoMo_2S_4$ intrinsically possess the active site for both OER and HER. ii) The high electronic conductivities of $CoMo_2S_4$ and the large active area of MoS_2 would facilitate the catalytic process. iii) The MoS_2 sheets adhere to the surface of $CoMo_2S_4$ nano/micro rods, which would result in unique interface that enhance the catalytic activity. More experiments and calculations should be done to explain the excellent activity.

3. Conclusions

In summary, we prepared the $CoMo_2S_4/MoS_2$ heterostructure by modified solid state method. We also show that the $CoMo_2S_4/MoS_2$ heterostructure exhibits the excellent activity both for HER and OER in the alkaline meida. What's more, as advanced bifuntional catalysts for overall water splitting, the $CoMo_2S_4/MoS_2$ heterostructure can achieve the 10 mA cm^{-2} at the potential of 1.65 V and with long-tern stability. This work would bring a new way to explore the application of $MoS_2/M\text{-}Mo_2S_4$ hybrids materials for overall water splitting.

4. Experiments

Sample preparation: 4 m mol (184 mg) Li_2S and 200 mg glucose were added in 20 mL ethylene glycol and stirring for 1h to dissolve. Then, 2 m mol (500 mg) cobalt(II) acetate tetrahydrate and 2m mol (546 mg) Molybdenum(V) chloride were transported in the solution and stirring for another hour. After that, 10 mL black solution was transferred in the oven that have preheated to 300 °C and maintain 5~10 min to evaporate the solvent. Following, the black powders were transported into the tube furnace and calcined with the temperature of 650 ^oC (Co-650), 750 ^oC (Co-750) and 850 ^oC (Co-850) for 2 h in the vacuum. Finally, the powders were washed by ultrasonic with de-ion water and alcohol for more than three time, collected by centrifugation and dried at 80 ^oC in the air.

Characterization: XRD pattern collected by Rigaku SmartLab to analyze the phase of the hybrids. The transmission electron microscope (FEI Tecnai G2 F30) was applied to evaluate the morphology and structure. The oxidation state of elements was analyzed by X-ray photoelectron spectroscopy (ESCALAB 250). The HER and OER electrochemical properties were tested by utilizing a three-electrode setup. The Hg/HgO electrode was used as the reference electrode and the graphite rod is the counter electrode. The overall water splitting is measured with a two-electrode system. The polarization curves were recorded with the scan rate of 2 mV s^{-1} in 1M KOH solution at room temperature. The catalysts were dispersed in the 0.5% Nafion solution under ultrasonic condition to form uniform ink and loaded in the Ni foam. And the loading is about 4~6 mg cm^{-2}.

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