Interface Engineering of Needle-Like P-Doped MoS_2/CoP Arrays as Highly Active and Durable Bifunctional Electrocatalyst for Overall Water Splitting

Yan Hu,[a] Hongbo Yu,[a] Luoluo Qi,[a] Jiaxin Dong,*[a] Puxuan Yan,[a] Tayirjan Taylor Isimjan,*[b] and Xiulin Yang*[a]

Developing a bifunctional water splitting catalyst with high efficiency and low cost are crucial in the electrolysis water industry. Here, we report a rational design and simple preparation method of MoS_2-based bifunctional electrocatalyst on carbon cloth (CC). The optimized P-doped MoS_2@CoP/CC catalyst presents low overpotentials for the hydrogen (HER) and oxygen evolution reactions (OER) of 64 and 282 mV in alkaline solution as well as 72 mV HER overpotential in H_2SO_4 at a current density of 10 mA cm^{-2}. Furthermore, P-MoS_2@CoP/CC as a bifunctional catalyst delivered relatively low cell voltages of 1.83 and 1.97 V at high current densities of 500 and mA cm^{-2} in 30% KOH. The two-electrode system showed a remarkable stability for 30 h, even outperformed the benchmark RuO_2 j j Pt/C catalyst. The excellent electrochemical performance can be credited to the unique microstructure, high surface area, and the synergy between metal species. This study presents a possible alternative for noble metal-based catalysts to overcome the challenges of industrial applications.

Introduction

At present, the energy depletion issue has aroused widespread concern and become an obstacle to economic development.[1] Developing a sustainable hydrogen economy has become a hot topic in the scientific world.[2] Electrocatalytic overall water splitting is considered as a sustainable approach of large-scale hydrogen generation hydrogen production from water. The two half reactions in the water splitting are hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).[3] The commercial water splitting systems are currently run at 1.8–2.4 V cell voltage and 200–400 mA cm^{-2} current density.[4] Therefore, anything higher than 200 mA cm^{-2} is considered high current density. Since the OER half-reaction is the rate-determining step, most of the electrolyzers are operated under alkaline conditions, where the HER kinetics is two orders of magnitude slower than in acidic conditions. Therefore, it is critical to develop low-overpotential HER catalysts in alkaline media. In addition, it is especially interesting if the HER catalyst also shows an excellent OER performance because the bifunctional catalyst will primarily simplify the production process and decrease the cost. To date, metal-based catalysts such as Pt-based materials and Ru oxides are still recognized as the most effective HER and OER catalysts, respectively.[5] However, their high cost and the inadequate resources of precious metals limit their extensive commercial applications. As a result, considerable attention has been devoted to developing earth-abundant transition metal-based HER and OER catalysts with performance comparable to these precious metal catalysts.[6]

Recently, transition metal-based electrocatalysts and their derivatives, including metal chalcogenides,[7] metal phosphides,[4a,8] and metal carbides[9] were reported as HER/OER bifunctional electrocatalysts. Still, they suffered from slow kinetics and low stability.[10] Among them, Mo-based catalysts revealed great potential. Density function theory (DFT) studies revealed that MoS_2 could exhibit excellent HER performance in acidic media due to the edge sites resulting in optimal hydrogen adsorption free energies (~ G& 0.08 eV).[11] However, the HER performance worsens in alkaline solutions because of surface-adsorbed hydroxyl species that hinder the water dissociation steps.[12] To address this problem, Hu et al.[13] proposed a combination of MoS_2 with layered double hydroxides (LDHs) materials, including Ni, Co, and Fe that are well-known OER catalysts. As a result, the HER kinetics of MoS_2-LDH catalysts were accelerated significantly due to the improved binding and dissociation kinetics of hydroxyl species. Besides, a MoO_2@Ni/carbon cloth (CC) heterostructure exhibited high hydrogen evolution performance over the entire pH range.[14] Similarly, an MoS_2@Co_2S electrocatalyst with rich structural defects has also shown high hydrogen evolution performance and outstanding durability.[15] The HER performance of Mo-based catalysts can be further improved by phosphorus doping.[16] Moreover, heterostructured MoS_2/NiS_2 revealed excellent HER and OER performance in alkaline electrolytes because of the synergy between Ni and Mo species and OER nature of the Ni-based catalysts.[17] Many studies have shown

[a] Y. Hu, H. Yu, L. Qi, J. Dong, P. Yan, Prof. Dr. X. Yang
Guangxi Key Laboratory of Low Carbon Energy Materials
School of Chemistry and Pharmaceutical Sciences
Guangxi Normal University
Guilin 541004 (P. R. China)
E-mail: chemdjx@gxnu.edu.cn
xlyang@gxnu.edu.cn
[b] Dr. T. Taylor Isimjan
Saudi Arabia Basic Industries Corporation (SABIC) at King Abdullah University of Science and Technology (KAUST)
Thuwal 23955-6900 (Saudi Arabia)
E-mail: isimjant@sabic.com

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that as a promising OER catalyst,[18] introducing cobalt-based phosphide into HER catalyst can improve its performance.[19] As a result, MoS_2 is coupled with cobalt-based phosphides and phosphorous doping to enhance HER performance in alkaline media further. It was envisioned that Mo-based materials facilitate HER/OER kinetics in alkaline media by facilitating binding and dissociation kinetics of the hydroxyl species. As compared to the commonly available methods in the literature,[20] including high-temperature annealing of metal-organic framework (MOF) precursors, we used a moderate temperature in situ thermal growth followed by drip-coating and PH_3 chemical vapor deposition approach that results in needle-like nanoarrays on the CC support. The prepared P-MoS_2@CoP/CC materials can be directly used as a self-supported electrode, which is easier to scale up than the traditional powder system.

Here, we developed a facile and controllable method to construct P-doped MoS_2@CoP/CC heterostructure catalyst. Three steps of the catalyst preparation are: 1) growing Co(OH)F nanowire arrays on CC, 2) quantitatively pipetting ammonium thiomolybdate (3 wt% of $(NH_4)_2MoS_4$ in DMF), and 3) phosphorization treatment. The microstructure, crystallinity, and chemical state of the resulting P-MoS_2@CoP/CC were characterized and analyzed in detail. Electrochemical studies showed that the optimized catalyst show low overpotentials of 64 mV (HER, Figure S1 in the Supporting Information) and 282 mV (OER) at 10 mA cm^{-2} in 1.0 M aqueous KOH. Furthermore, the catalyst exhibits two-electrode cell voltages of 1.83 and 1.97 V at 500 and 1000 mA cm^{-2} as well as long-term stability for overall water splitting in 30% alkaline solution, implying a potential commercial application.

Results and Discussion

Synthesis strategy and structural analysis

The synthetic processes of the P-MoS_2@CoP/CC are illustrated in Figure 1, and photographs of different samples are shown in Figure S2. The hydrothermal deposition procedure was used to prepare Co(OH)F array in situ grown on CC, and the corresponding crystal structure was confirmed as orthorhombic Co(OH)F (JCPDS 50-0827) by X-ray diffraction (XRD; Figure S3). Then, ammonium thiomolybdate (3 wt% of $(NH_4)_2MoS_4$ in DMF) was used to prepare the support's surface with different loadings. Finally, a series of hybrid precursors are phosphated to P-doped MoS_2@CoP/CC via PH_3 gas produced by NaH_2PO_2 pyrolysis. The inductively coupled plasma (ICP) results (Table S1) indicate that the maximum MoS_2 loading was around 70 wt%. TEM elemental mappings revealed that MoS_2 was well dispersed on the surface of the CoP nanowire arrays. XRD crystal phase analysis shows that the diffraction peaks of the obtained P-MoS_2@CoP/CC can be well indexed to the standard diffraction patterns of CoP (JCPDS 29-0497) and MoS_2 (JCPDS 37-1492),[19c,21] respectively (Figure 2a). The strong diffraction peak at ~25° belongs to the (002) lattice plane of graphitic carbon.[22] Notably, the XRD patterns of CoP/CC and P-MoS_2/CC are very similar to these of P-MoS_2@CoP/CC (Figure S4).

The surface morphologies of the materials were characterized by scanning electron microscopy (SEM). Figure S5a shows a smooth CC surface before the in situ growth of Co(OH)F species. A thin layer of a needle-like nanoarray structure was formed (Figure S5b) after Co(OH)F deposition. Furthermore, the CoP/CC morphology remained the same during the phosphorizing treatment (Figure S5c). After P-doped MoS_2 decoration, a thin layer of P-doped MoS_2 was formed on the CoP nanoneedles surface (Figure 2b,c). As the concentration of the Mo precursor increases, the surface coverage of the CoP nanoneedles becomes denser (Figure S5d,e). Notably, the surface of P-MoS_2-modified CC shows severe aggregation without a Co(OH)F buffer layer (Figure S5f).

Transmission electron microscopy (TEM) was used to further study the microstructure features of the P-MoS_2@CoP/CC. Figure 2d shows that the thickness of the P-MoS_2 species modified on the surface of the CoP nanoarray is about 95 nm. The high-resolution (HR)-TEM image shows two types of lattice fringes (Figure 2e) that correspond to the lattice spacing of 0.162 nm (301) and 0.245 nm (102) of the orthorhombic CoP crystal planes. The other set corresponds to the (105) and (106) crystal planes of hexagonal MoS_2 with lattice spacings of 0.183 and 0.164 nm.[23] The formed heterostructure was also confirmed by selected area electron diffraction (SAED; Figure 2f). The TEM images show the diffraction spots of (200) and (211) corresponding to CoP and (106) for MoS_2.[19c,24] Moreover, the high-angle annular dark field (HAADF) TEM elemental mappings suggest that Co, Mo, P, and S are distributed uniformly in P-MoS_2@CoP/CC (Figure 2g).

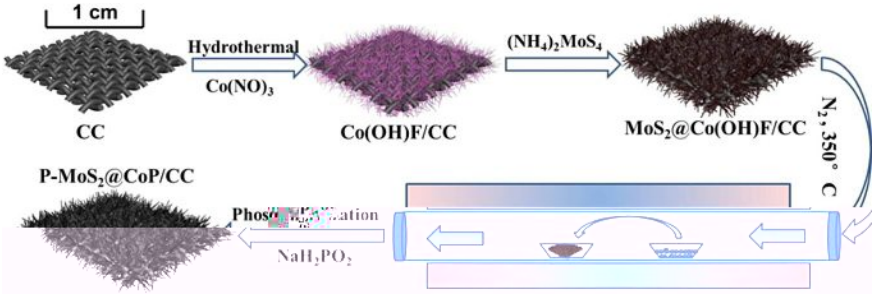

Figure 1. Schematic illustration of the synthesis of P-MoS_2@CoP/CC.

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that as a promising OER catalyst,[18] introducing cobalt-based phosphide into HER catalyst can improve its performance.[19] As a result, MoS_2 is coupled with cobalt-based phosphides and phosphorous doping to enhance HER performance in alkaline media further. It was envisioned that Mo-based materials facilitate HER/OER kinetics in alkaline media by facilitating binding and dissociation kinetics of the hydroxyl species. As compared to the commonly available methods in the literature,[20] including high-temperature annealing of metal-organic framework (MOF) precursors, we used a moderate temperature in situ thermal growth followed by drip-coating and PH_3 chemical vapor deposition approach that results in needle-like nanoarrays on the CC support. The prepared P-MoS_2@CoP/CC materials can be directly used as a self-supported electrode, which is easier to scale up than the traditional powder system.

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