Tungsten-decorated MoP nanobelts for boosted hydrogen production

Dezhi Wang1,2, Yao Lu1, Kangyan Lv2,3 and Zhuangzhi Wu1,2*

1 School of Materials Science and Engineering, Central South University, Changsha 410083, People’s Republic of China
2 Key Laboratory of Ministry of Education for Non-ferrous Materials Science and Engineering, Changsha 410083, People’s Republic of China
3 The 92261th Unit of PLA, Haikou 570203, People’s Republic of China
E-mail: zwu2012@csu.edu.cn

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Abstract
To further improve the electrochemical catalytic performance of MoP for hydrogen generation, a tungsten decoration strategy is proposed in this work, and the effect of preparation temperature was also investigated. It is found that the decoration of W can significantly enhance the electron transfer ability and increase the amount of active sites, and the optimized catalyst can be obtained at 700 °C over the Mo-W-P-700 catalyst, which exhibits the best catalytic performance with a small Tafel slope of 53 mV dec⁻¹. This decoration strategy can be widely applied in other transition metal compounds to achieve further performance improvements.

1. Introduction
To produce new renewable energy to replace traditional fossil energy, hydrogen, as an ideal energy carrier, has attracted much attention in recent years [1]. And the hydrogen production by electrocatalytic water splitting has been widely studied due to the high efficiency and low cost [2]. However, the electrocatalytic hydrogen generation technique has not been widely adopted in the large-scale industrial applications, because currently the most efficient catalysts are Pt-based compounds, which are restricted by the high price and low abundance [3]. As a result, more other earth-abundant and cheap electrocatalysts for the hydrogen evolution reaction (HER) have been developed, containing transition metal dichalcogenides [4, 5], nitrides [6], phosphides [7, 8], carbides [9, 10], etc.

Because of a similar d-electron structure to Pt, MoP has been proposed as a potential candidate to replace the Pt-based electrocatalysts, and a lot of work has been done to improve the corresponding HER performances [7, 8, 11–13], which are generally according to the following strategies: exposing more active sites, increasing the intrinsic catalytic ability of each site and enhancing the charge transport ability. Although significant progress has been achieved, great efforts are still strongly demanded to further enhance the HER performances.

Herein, we proposed a tungsten decoration strategy to improve the HER activity of MoP nanobelts, in which a synergistic effect was demonstrated between single WP and MoP, leading to more exposed active sites, reduced charge transfer resistance and higher intrinsic activity of each active site.

2. Experimental
2.1. Materials
Molybdenum powder and hydrogen peroxide were purchased from Shanghai Wokai Biotechnology Co., Ltd and Shanghai Putian New Material Technology Co., Ltd, respectively. Sodium hypophosphite, tungsten chloride and absolute ethanol were bought from Aladdin Company of China.
2.2. Synthesis of W-decorated MoP nanobelts

The synthesis process of W-decorated MoP (donated as Mo-W-P) nanobelts is shown in scheme 1, and the details are described below:

2.2.1. Synthesis of the Mo–W–O precursor

Molybdenum powder (Mo, 0.53 g) was put into 10 ml of distilled water with magnetic stirring, and then 10 ml of refrigerated hydrogen peroxide (H₂O₂) was slowly dropped into the mixture. After being placed at room temperature for 30 min, a yellow sol solution can be obtained and subsequently placed into a polytetrafluoroethylene reactor, which was hold at 180 °C for 4 h in an oven. After being cooled to room temperature, the product was filtered and dried to obtain molybdenum trioxide (MoO₃). Next, 0.2 g of the gained MoO₃ was firstly mixed with 30 ml of distilled water, and then 0.1 g of tungsten chloride was slowly added with magnetic stirring. The mixture was kept at 60 °C for 2 h. After centrifugation, the Mo–W–O precursor can be collected.

2.2.2. Synthesis of Mo–W–P nanobelts

Typically, 0.05 g of the as-prepared Mo–W–O precursor and 3 g of sodium hypophosphite (NaH₂PO₂) were placed into porcelain arks in a tube furnace with the latter in the upstream of flow. Then, the furnace was calcined at different temperatures (600 °C, 700 °C and 800 °C) for 2 h in a flow of hydrogen. After being cooled to room temperature, the obtained black powder were collected and donated as Mo-W-P-X (X represents the calcination temperature). For comparison, pure MoP was prepared without the addition of tungsten chloride, and WP was synthesized in the absence of MoO₃ following the similar procedure.

2.3. Characterizations

The composition and phase were analyzed by a Rigaku D/Max 2500 x-ray diffractometer. The morphology was observed by a Quanta FEG 250 field emission scanning electron microscope (SEM), and the element surface distribution was further detected by an energy dispersive spectroscopy (EDX). The microstructure was further observed and analyzed by Tecnai G² 20 field emission transmission electron microscope (TEM). The surface valence and bonding state were analyzed by ESCALAB 250Xi photoelectron spectroscopy (XPS) manufactured by Thermo Fisher-VG Scientific. The thermal stability of catalysts was tested by the integrated thermal analysis system developed by SETARAM INSTRUMENTATION.

2.4. Electrochemical performance measurements

The electrochemical performance measurements were carried out on a CHI 660E electrochemical workstation produced by Shanghai Chenhua Company using a three-electrode system. The reference electrode, auxiliary electrode and working electrode were saturated calomel electrode, graphite rod electrode and modified glassy carbon electrode (GCE, diameter in 3 mm), respectively. Besides, other experimental details are described in the Supporting Information.

3. Results and discussions

The SEM image of the Mo–W–O precursor is shown in figure 1(a). We can see that the obtained samples are aggregated nanobelts, and their morphology is kept even after phosphorization, as revealed in figure 1(b). The TEM image in figure 1(c) further proves that the Mo-W-P-700 are nanobelts with a width about 100 nm, and a
corresponding enlarged selected region depicts the interplanar spacing of 3.19 Å, 2.79 Å and 3.11 Å, corresponding to the (001) and (100) crystal planes of MoP, and the (002) crystal plane of WP, indicating that the decorated W presents in the form of WP constructing an interface with MoP, as presented in figure 1(d). Moreover, to get a general view over the elemental distribution of Mo–W–P–700, the EDX elemental mapping was also conducted, demonstrating that all the elements are well dispersed, including W, Mo and P, as shown in figures 1(e)–(h).

Figure 2 shows the XRD patterns of the precursors. We can notice that all the diffraction peaks match well with the standard MoO₃ (JCPDS card No. 89-7112). With the decoration of W, there are no significant changes over the distribution of diffraction peaks, but their relative intensity is remarkably affected, which should be attributed to the incorporation of W. Due to a low content, the actual phase of W cannot be detected by the XRD. After phosphorization at 600 °C for 2 h, most of oxides are converted to form MoP (JCPDS card No. 65-6487), but a small part of PW₉O₄₆ (JCPDS card No. 50-0659) still can be found, which is revealed by the typical (200) peak located at 23.6°, and we do not find the diffraction peaks of WP, as described in figures 2(b) and S1 is available online at stacks.iop.org/MRX/7/015506/mmedia (a). However, when the phosphorization temperature is increased to 700 °C, the new peaks located at 31° and 44.5° can be found and assigned to the (011) and (211) crystal planes of WP (JCPDS card No. 29-1364), demonstrating a complete phosphorization. Up to 800 °C, all the diffraction peaks become sharper and stronger, but a new small typical peak is also detected at 40.2°, corresponding to the (110) crystal plane of W metal (JCPDS card No. 89-2767), indicating an excessive reduction with a loss of coordinative P, as demonstrated in figure S1(b). Evidently, we can conclude that the suitable reaction temperature is 700 °C, which can not only guarantee the complete phosphorization without the oxide residue but also avoid the excessive reduction to generate the W metal.

The composition and valence of Mo–W–P–700 were further analyzed by XPS. We can see that two characteristic peaks at 228.43 eV and 231.82 eV can be ascribed to Mo⁶⁺ (0 < δ ≤ 4) of Mo–P bond, as shown in figure 2(c). At the same time, two characteristic peaks at 32.12 eV and 34.23 eV in figure 2(d) represent the W 4f⁰/₂ and W 4f⁵/₂ electron orbits, corresponding to W⁶⁺ (0 < δ ≤ 4) of W–P bond. Similarly, in the XPS spectrum of P (figure 2(e)), the characteristic peaks at 129.65 eV and 130.56 eV should be ascribed to P 2p⁰/₂ and P 2p⁵/₂, which form chemical bonds with the Mo and W elements [14–16]. It should be noted that a strong peak at 134.2 eV corresponds to a P–O bond resulted from the surface oxidation. Due to the unavoidable surface oxidation by air contact, Mo–O and W–O bonds are also found at 233.11, 235.56, 229.02, 36.41, 38.58 eV, respectively. Accordingly, O-Mo or O-W bonds are also verified by the characteristic peak of O 1s at 531.1 eV, as depicted in figure 2(f).

The HER performances were measured on the electrochemical station in 0.5 M H₂SO₄, and the obtained polarization curves are shown in figure 3(a). A commercial available Pt/C electrocatalyst (20 wt%, Johnson Matthey Corp.) was also compared to give a reference. It can be seen that the Pt/C catalyst still shows the best HER activity with the smallest overpotential of −150 mV to achieve 50 mA cm⁻². And the as-prepared Mo–W–P–700 catalyst requires a little larger overpotential of −220 mV, much smaller than those of pure MoP (−300 mV) and WP (−320 mV), demonstrating a possible synergistic effect between MoP and WP. Moreover, the Mo-
W-P-700 catalyst exhibits a Tafel slope of 53 mV dec\(^{-1}\), much smaller than those of MoP and WP (64 and 65 mV dec\(^{-1}\)), which is also among the best records of MoP and WP-based catalysts, as depicted in figure 3(b) and table S1.

To gain deep insights over the activity improvement mechanism, the electrochemical impedance spectroscopy (EIS) was also collected, and the corresponding Nyquist plots are depicted in figure 3(c). We can see that the decoration of W significantly reduces the charge transfer resistance of MoP, resulting in the smallest resistance value of 24.5 Ω over the Mo-W-P-700 catalyst associated with the best electron transfer ability. To evaluate the amount of active sites, the electrochemical active area (ECSA) were obtained by the electrochemical capacitance plots (figure 3(d)), and the ECSA value of Mo-W-P-700 is about 219.8 cm\(^2\), much larger than those of MoP (79.3 cm\(^2\)) and WP (79.8 cm\(^2\)). Accordingly, the turnover frequency (TOF) plots were also drawn to give a direct comparison over the intrinsic activity, as shown in figure 3(e). We can notice that although the Mo-W-P-700 catalyst exhibits the largest TOF value over all the overpotential range, its intrinsic activity is close to those of other counterparts without remarkable improvement. Generally, the HER activity is decided by the following three factors: the amount of exposed active sites, intrinsic activity of active sites (TOF value) and charge transport ability. Considering the similarity of intrinsic activity, the enhanced HER activity of the Mo-W-P-700 catalyst

Figure 2. XRD patterns of the (a) precursor and (b) Mo-W-P-X; XPS spectra of Mo-W-P-700: (c) Mo 3d, (d) W 4f, (e) P 2p and (f) O1s.
should be mainly attributed to the smallest charge resistance and the largest ECSA value, guaranteeing the highest electron transfer efficiency and strongest mass transport ability, respectively.

Durability is another important criterion to evaluate a HER catalyst, which was performed by long-term cycling and i-t tests, as depicted in figure 3(f). It can be seen that only a little loss of current density is found after running for 1000 cycles, and the degradation under continuous operation for 10 h is also acceptable, demonstrating a good stability, which is consistent with previous reports \[7, 8\]. To further demonstrate the stability of Mo-W-P-700, the XRD patterns and SEM images of Mo-W-P-700 after cycling 1000 cycles were collected, as shown in figures S3 and S4. We can notice that there are no remarkable changes over morphology and component after the long-term stability test in acidic media. Besides, the thermogravimetric of Mo-W-P-700 was also conducted, demonstrating a good thermal stability, as revealed in figure S5.

4. Conclusion

The W decorated MoP nanobelts have been successfully prepared, which exhibit outstanding HER performances with a small Tafel slope of 53 mV dec\(^{-1}\) and a good stability. With the decoration of W, the charge
transfer resistance of MoP is significantly reduced and the amount of active sites is greatly increased, leading to a remarkable improvement of the HER activity. The optimal synthesis temperature is 700 °C, which can guarantee the complete phosphorization without the oxide residue and avoid the excessive reduction to generate the W metal. This work paves a facile way to further improve HER performances by tungsten decoration, and can be adopted in other transition metal compounds.

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ORCID iDs

Dezhi Wang © https://orcid.org/0000-0003-3453-7677
Zhuangzhi Wu © https://orcid.org/0000-0002-2365-9196

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