



The Fe-promoted MoP catalyst with high activity for water splitting



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ABSTRACT

By the introduction of Fe element, a novel Fe-promoted MoP catalyst was proposed for the first time, which was prepared via a simple temperature-programmed reduction method. Benefitting from the promotion effect of Fe, the HER activity of the MoP catalyst is remarkably enhanced with smaller Tafel slope and much larger current density, which can be attributed to the reduced crystal size and smaller charge transfer resistances. However, it must be noted that the addition content of Fe must be accurately controlled, or the final HER activity will be deteriorated.

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1. Introduction

As a clean and renewable energy source, hydrogen is one of the promising alternatives to carbon-based fuels. And water splitting has attracted a great deal of attention to efficiently produce hydrogen, which requires active and economical catalysts [1]. Although Pt-based catalysts show the best HER activity up to now, their excessive price and lack of abundance limit the wide industrial applications [2]. Possible alternatives to replace Pt-based catalysts are molybdenum-based materials, including molybdenum disulfide [3], [4] and [5], molybdenum boride [6], molybdenum nitride [7], molybdenum carbide [8], [9] and [10], and molybdenum phosphide [11], [12], [13] and [14], etc. Among them, molybdenum phosphide is one of the best candidates to replace Pt because of its low cost, rich reserve, high activity and good stability.

In our previous work, we revealed that the MoP catalyst showed better HER activity than the counterpart of Ni₂P [11]. And more efforts have been made to further improve the HER activity over MoP-based catalysts. Both Xiao [12] and Xing [13] et al. adopted citric acid (CA) as the surfactant to increase the BET surface area, exposing more active sites, which greatly improved the final HER activity with a small Tafel slope of 54 mV dec⁻¹. McEnaney et al. even selected an oil bath method to prepare amorphous MoP nanoparticles, which was only about 4 nm in diameter, resulting in

more active sites and excellent HER activity with a small Tafel slope of 45 mV dec⁻¹ [14]. To reduce the charge transfer resistance, Cui [15] and Jyothirmayee [16] et al. adopted carbon flake and graphite as highly conductive supports, leading to a remarkable enhancement of the HER activity with Tafel slopes of 56.4 and 63 mV dec⁻¹, respectively. Despite of great efforts, more work is still strongly required to further improve the HER activity of MoP-based catalysts.

Herein, we describe a simple strategy of promotion with the Fe element, which leads to the great improvement of HER activity over the MoP catalyst with a small Tafel slope of 49 mV dec⁻¹. More importantly, the current density is also remarkably increased because of the promotion of Fe, which is about 137 mA cm⁻² at -400 mV with a small catalyst loading of 0.071 mg cm⁻², 6 times larger than that of the pure MoP catalyst.

2. Experimental

2.1. Catalyst preparation

Typically, certain amounts of FeCl₃·6H₂O, (NH₄)₆Mo₇O₂₄·4H₂O and (NH₄)₂HPO₄ with the Fe:Mo:P molar ratio of *x*:1:1.25 were dissolved into distilled water. The mixture solution was aged in a covered beaker held at 90 °C for 12 h in a water bath, dried in a furnace at 120 °C for 12 h, and calcined at 500 °C in air for 10 h to obtain the solid precursor. Finally, the active Fe-promoted MoP catalysts were obtained via temperature-programmed reduction (TPR) of the precursors by heating to 400 °C in 0.5 h and then from

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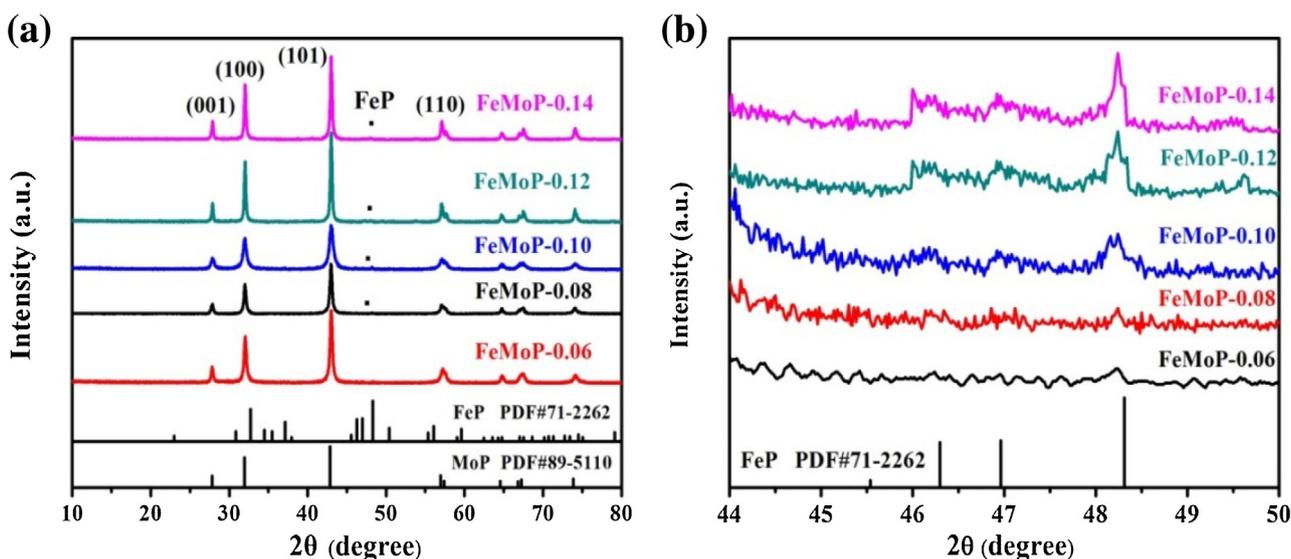


Fig. 1. XRD patterns of the as-obtained samples (a) and the enlarged figure from 44 to 50° (b).

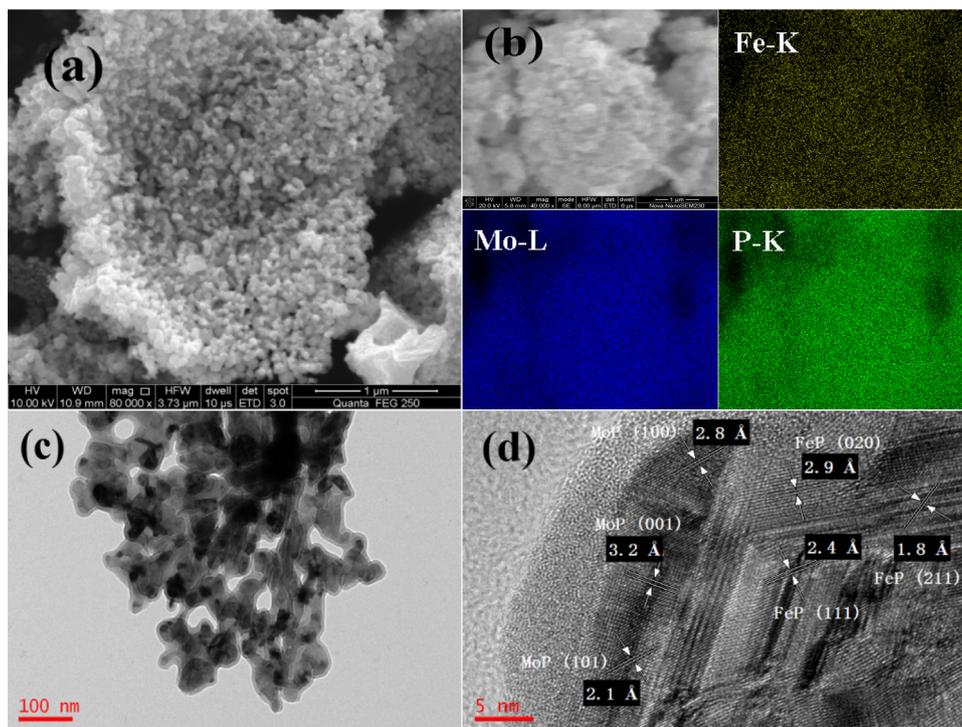


Fig. 2. SEM image (a), EDX-mapping (b), TEM (c) and HRTEM images (d) of the FeMoP-0.10 catalyst.

400 to 650 °C for 2.5 h at a heating rate of 1 °C/min in a hydrogen atmosphere (300 mL min⁻¹), represented by FeMoP-x.

2.2. Characterizations

X-ray powder diffraction (XRD) patterns were recorded using a D/max-2500 system with a Cu K α radiation ($\lambda=0.154$ nm). The microstructures were observed using the scanning electron microscopy (SEM, Quanta FEG 250) and transmission electron microscopy (TEM, JEOL 2100) at an accelerating voltage of 200 kV with the sample supported on copper grids. X-ray photoelectron spectra (XPS, Escalab 250Xi) were conducted using a monochromatic Al K α source and a charge neutralizer. All the analysis of XPS

data were referenced to the C 1s peak arising from adventitious carbon (its binding energy was set at 284.8 eV).

2.3. Preparation of electrodes and electrochemical measurements

In a typical procedure, 1 mg of catalyst and 80 μ L of a 5 wt% Nafion solution were dispersed in 1 mL of a solution of deionized water and ethanol (4:1 in volume). After the mixture had been stirred by ultrasonication for 30 min, 5 μ L of the catalyst slurry was dropped onto smooth glassy carbon electrodes (GCEs) with a diameter of 3 mm and dried at room temperature. The mass loading was about 0.071 mg cm⁻².

The electrochemical measurements were carried out in a standard three-electrode setup at a CHI 660E electrochemical station.

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