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Influence of Mo/P Ratio on CoMoP nanoparticles as highly efficient HER catalysts

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ABSTRACT

Uniform unsupported Co-promoted MoP catalysts for the hydrogen evolution reaction (HER) were synthesized via a facile temperature-programmed reduction (TPR) of the corresponding metal phosphate salts, and the effect of Mo/P ratio was also investigated. It is found that the Mo/P ratio plays a crucial role in the final HER activity, and the CoMoP catalyst with a Mo/P molar ratio of 1:2 exhibits the best HER activity with a small Tafel slope of 50 mV per decade and a very low onset potential of -85 mV in 0.5 M H_2SO_4.

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1. Introduction

Hydrogen energy is a clean, abundant, renewable and high-combustion value resource as one of the most promising energy to replace fossil fuels in the future [1–3]. Electrolysis of water, especially by the solar cell, as a simple method for producing hydrogen requires the use of efficient electrocatalysts for the hydrogen evolution reaction (HER) to attain high current density at low overpotentials [4,5]. Pt-based group metals are currently used as the best HER catalysts, but the limited reserve and high price preserve the scalable applications [6,7]. To find an abundant, inexpensive, acid-stable HER catalyst would be desirable to facilitate the development of hydrogen energy technologies [8–10].

Transition metal phosphides (TMPs) are an important branch among series of exploring HER catalysts for the good electrical conductivity. Molybdenum phosphide (MoP) is endowed with high expectations for its active catalyzing hydrodesulfurization (HDS) reaction, as HDS and HER both rely on the reversible binding of the catalyst and hydrogen, with hydrogen dissociation to yield H_2S in the HDS, and protons bound to the catalyst to promote hydrogen formation in the HER [5,11–18]. However, only a few reports can be found over the MoP-based catalysts for the HER [19–23]. Xing et al. [19] prepared molybdenum phosphide with closely interconnected network by adding citric acid, exhibiting excellent HER activity with a Tafel slope of 54 mV/dec. Moreover, Cui et al. [23] explored a composite structure of MoP nanosheets supported on carbon flakes, which decides a Tafel slope of 56.4 mV/dec by improving the conductivity and enhancing the final activity. Despite great efforts, more work is still strongly required to further improve the final HER activity of MoP-based catalysts via much easier routes.

Generally, cobalt has been widely used as a promoter in the hydrotreating reactions [24–26], which can significantly enhance the intrinsic activity of each active site. Therefore, in this work, we described the Co-promoted MoP catalyst and discussed the effect of Mo/P ratio on the CoMoP nanoparticles as highly active HER catalysts for the first time. With a Mo/P molar ratio of 1:2, the CoMoP catalyst shows the best HER activity with a Tafel slope of 50 mV/dec, which is also amongst the most active and earth abundant HER catalysts reported to date.

2. Experimental

2.1. Materials

Ammonium molybdate tetrahydrate $((NH_4)_6Mo_7O_{24}\cdot4H_2O)$, ammonium monohydric phosphate $((NH_4)_2HPO_4)$ and cobaltous nitrate $(Co(NO_3)_2\cdot6H_2O)$ was purchased from Xilong Chemical Co., Ltd. (China). Nafion solution (5 wt%) was purchased from DuPont Company (USA). The commercial carbon black (Vulcan XC-72R) supported Pt (20 wt%) (Pt/C) was purchased from the Johnson Matthey company. All chemicals were used as received without

further purification. The water, used throughout all experiments, was distilled water.

2.2. Preparation of catalysts

The unsupported CoMoP catalysts were prepared by dissolving required amounts of $Co(NO_3)_2 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $(NH_4)_2HPO_4$ with different Co:Mo:P mole ratios in distilled water. The mixture solution was stirred for 0.5 h before aged in a water bath at 90 °C to remove moisture, then dried in constant-temperature drying oven at 120 °C for 12 h. Subsequently, the dried powder was calcined at 500 °C for 10 h, then cooled and ground to powders, collected as the catalyst precursor. The active metal phosphide was then obtained by temperature-programmed reduction (TPR) of the calcined precursor by heating to 400 °C for 0.5 h and then from 400 to 650 °C for 2.5 h at a heating rate of 1 °C/min in a hydrogen atmosphere (300 mL min^{-1}). To investigate the influence of Mo/P ratio, catalysts with different Co/Mo/P molar ratios of 0.05:1:1 (0.15 g:1.77 g:1.33 g), 0.05:1:2 (0.15 g:1.77 g:2.66 g) and 0.05:1:3 (0.15 g:1.77 g:3.99 g) were marked as CoMoP-1, CoMoP-2 and CoMoP-3, respectively.

2.3. Fabrication of the catalyst modified glassy carbon electrode (GCE)

In a typical procedure, 1 mg catalyst, and 80 μL Nafion solution (5 wt%) were dispersed in 1 mL solution composed of 200 μL ethanol and 800 μL distilled water. After sonication for 30 min, 5 μL of the catalyst slurry was dropped on the surface of a polished GCE (glassy carbon electrode) (3 mm in diameter). The GCE was then dried at room temperature to yield a catalyst loading of 71 μg cm^{-2}, 5 μg, namely.

2.4. Characterizations

X-ray powder diffraction (XRD) patterns were recorded using a D/max-2500 system with Cu Kα radiation ($\lambda = 0.154$ nm). Microstructures were observed by the scanning electron microscopy (SEM, Quanta FEG 250) and transmission electron microscope (TEM, Tecnai G^{2}20) at an accelerating voltage of 200 kV with the sample supported on a copper grid. Specific surface areas (BET) were determined by N_2 adsorption at 77 K with BET method using a volumetric unit (Quadrasorb SI-3MP). X-ray photoelectron spectra (XPS, Escalab 250Xi) were conducted with a monochromatic Al Kα source and a charge neutralizer. The X-ray photoelectron spectra of all elements were referenced to the C 1s peak arising from adventitious carbon (its binding energy was set at 284.8 eV).

2.5. Electrochemical measurements

The electrochemical measurements were carried out in a standard three-electrode setup. The electrocatalytic activity was evaluated by linear sweep voltammetry (LSV) with a scan rate of 2 mV s^{-1} on CHI 660E (Chenhua, China) in 0.5 M H_2SO_4 at room temperature. A saturated calomel electrode (SCE) was used as the reference electrode and a glassy carbon electrode as the counter electrode. Electrode potentials were recorded as SCE reference electrode, which was calibrated with respect to reversible hydrogen electrode (RHE). All the potentials were calculated according to the following equation:

$$E(RHE) = E(SCE) + 0.273V$$

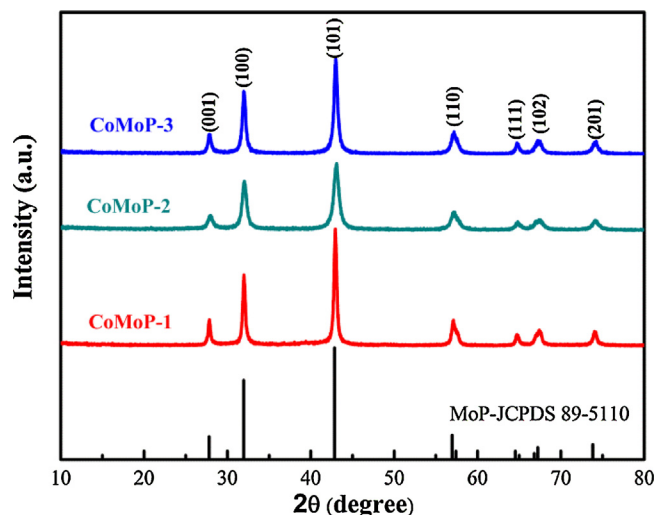The cyclic voltammetry scanning (CV) was performed with a scan speed of 50 mV s^{-1} from 0.1 V to −0.4 V for several times to activate the working electrode. Tafel plots are fitting into the Tafel equation ($\eta = b \log(j) + a$, where j is the current density and b is the Tafel slope). Durability test was also carried out in the range from 0.1 V to −0.4 V for 1000 cycles.

Fig. 1. XRD patterns of CoMoP catalysts.

3. Results and discussion

Fig. 1 presents the XRD crystallographic structure and the phase purity of the as-prepared CoMoP catalysts. It can be seen that all of them show sharp peaks, indicating good crystallinity, and match well with same characteristic peaks of (0 0 1), (1 0 0) and (1 0 1) of MoP (JCPDS 89-5110), respectively. In addition, the decrease of Mo/P ratio from 1:1 to 1:2 weakens the crystallinity and reduces the particle size, but a further decrease from 1:2 to 1:3 reverses the trend. It must be noted that the CoMoP-3 shows larger particle size than CoMoP-2, but still smaller than CoMoP-1, which is coincident with the diffraction peaks. However, Co is dissolved into the MoP matrix, and the existence of Co even cannot be detected by XRD due to the small amount and good dispersion. Moreover, the BET surface area of CoMoP-2 is about 16.5 m^2 g^{-1}, close to that of CoMoP-3 (15.9 m^2 g^{-1}), and much larger than that of CoMoP-1 (2.4 m^2 g^{-1}), demonstrating the influence of Mo/P ratio on the particle size and BET surface area which exposes more active sites. Furthermore, the electrocatalytic activity can be further improved by heteroatom doping [27]. When cobalt atoms are doped into MoP structures, they can increase the catalytic sites through inducing strain and defect sites [28]. Therefore, excellent HER activity can be expected due to the incorporation of Co promoter into the MoP catalyst.

The scanning electron microscopy (SEM) images of CoMoP-2 are shown in Fig. 2a and b. It can be clearly seen that CoMoP-2 shows fluffy honeycomb-like structure in good dispersion supplying an ideal specific area to act as an excellent catalyst. TEM observation was also conducted, as shown in Fig. 2c. CoMoP-2 nanoparticles are aggregated clusters with an average size about 13 nm, which is much smaller than that of pure MoP (50–60 nm) [21]. The interplanar distances are measured clearly at a higher magnification (Fig. 2d), revealing clear lattice fringes of 1.62 Å, 2.17 Å and 2.73 Å, corresponding to the (1 1 0), (1 0 1) and (1 0 0) crystal planes of MoP (JCPDS 89-5110), respectively.

XPS analysis was performed to characterize the chemical states of CoMoP in the composites. Fig. 3a–d presents the existence of Co, Mo and P elements and similar peak curves of same elements with slight peak position offset. Distinct peaks can be clearly seen in XPS