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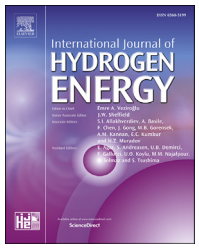

Short Communication

N-doped MoP nanoparticles for improved hydrogen evolution

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ABSTRACT

It is still strongly required to explore non-noble catalysts with excellent performances for hydrogen generation. MoP-based catalysts are demonstrated as good candidates and further improvements are highly encouraged. Herein, a novel strategy of N-doping has been proposed to increase the HER performance over the MoP-based catalysts, in which nitrilotriacetic acid ($N(CH_2COOH)_3$, NTA) is selected to provide the doping element of N. With the addition of NTA, the N-doped MoP catalysts with good distribution have been successfully prepared, showing smaller particle size, reduced electrical resistance, increased amount and better quality of active sites, resulting in much better performances compared to pure MoP. This strategy can also be extended to other counterparts for the further improvement of HER activity by N-doping.

Introduction

With the consumption of fossil fuels and the increased environment problems, renewable clean energy is strongly desired [1]. As one of the most promising candidates, hydrogen has received much attention because of its renewability, carbon-free and sustainability [2]. Generally, hydrogen can be produced by the electrolysis of water, which consumes a great lot of energy. To reduce the energy consumption of water splitting, an electrocatalytic hydrogen evolution reaction (HER) is highlighted and widely explored in recent years [3]. Nowadays, Pt-based compounds are still considered as the best catalysts for HER. However, due to high cost and poor reserve, the wide applications of Pt-based catalysts are remarkably limited [4,5]. Therefore, it is extremely important to explore alternative earth-abundant and highly active materials to replace Pt-based catalysts [6].

Over the past few years, molybdenum-based compounds have been taken as the best non-Pt HER catalysts, including molybdenum sulfide (MoS_2) [7–11], molybdenum phosphide (MoP) [12–14] and molybdenum carbide (Mo_2C) [15,16]. Among them, MoP has received a lot of attentions due to the low cost, high activity, excellent durability and rich reserve [13,17]. To improve the HER performances, many efforts have been made to optimize the microstructures and components over MoP-

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based catalysts. Sun et al. [18] reported novel interconnected MoP nanoparticles by adding citric acid, showing outstanding HER performances with a small onset overpotential. McEnaney et al. [19] introduced a simple solvothermal method to synthesize MoP nanoparticles, which were about 4 nm in diameter and demonstrated as highly active HER catalysts. Moreover, Wu et al. [20] designed hierarchical MoS_2@MoP core–shell nanostructures as highly efficient electrocatalysts for HER. Although some great achievements have been obtained, the catalytic performance is still unsatisfactory, and more work is still required to explore new strategies to further improve it.

Nitrilotriacetic acid (NTA) can provide four coordinate bonds for metallic ions with a small molecular weight and could be a good complexing agent. In this work, for the first time, we adopted NTA as the chelant to prepare the N-doped MoP nanoparticles through a simple temperature-programmed reduction (TPR) method, which exhibits outstanding HER performances due to the optimized microstructures and components.

Experiments

Materials

Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), ammonium monohydric phosphate ($(NH_4)_2HPO_4$) and nitrilotriacetic acid ($N(CH_2COOH)_3$) were bought from Xilong Chemical Company. The Pt catalyst and Nafion solution (5 wt %) were obtained from the Johnson Matthey and DuPont Company, respectively.

Preparation of catalysts

The synthesis of the N-doped MoP catalysts follows the same strategy of our previous report [21]. Briefly, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$,$(NH_4)_2HPO_4$ and NTA with a certain Mo:P:NTA mole ratio (1:1:2) were dissolved into 50 mL deionized water with stirring for 0.5 h, and subsequently kept at 120 °C to eliminate moisture. The collected sample was dried at 60 °C for 24 h, and then annealed at 500 °C for 10 h. Next, the obtained precursor was heated to 400 °C within 50 min, then up to 650 °C at 2 °C min^{-1} in H_2, and hold for another 2.5 h. Finally, the catalysts could be collected and retained for use after being cooled, marked as MoP-NTA. Following the same procedure, the pure MoP nanoparticles were also synthesized in the absence of NTA.

Preparation of working electrodes

Typically, the catalyst (1 mg) and Nafion solution (5 wt %, 80 μL) were mixed with ethanol (200 μL) and deionized water (800 μL) to form a well dispersed slurry. After sonication for 0.5 h, a few slurry (5 μL) was painted onto the exposed surface of a glassy carbon electrode (GCE, 3 mm in diameter). At last, after being dried for 12 h at room temperature, the catalyst modified GCE could be obtained (71 μg cm^{-2}).

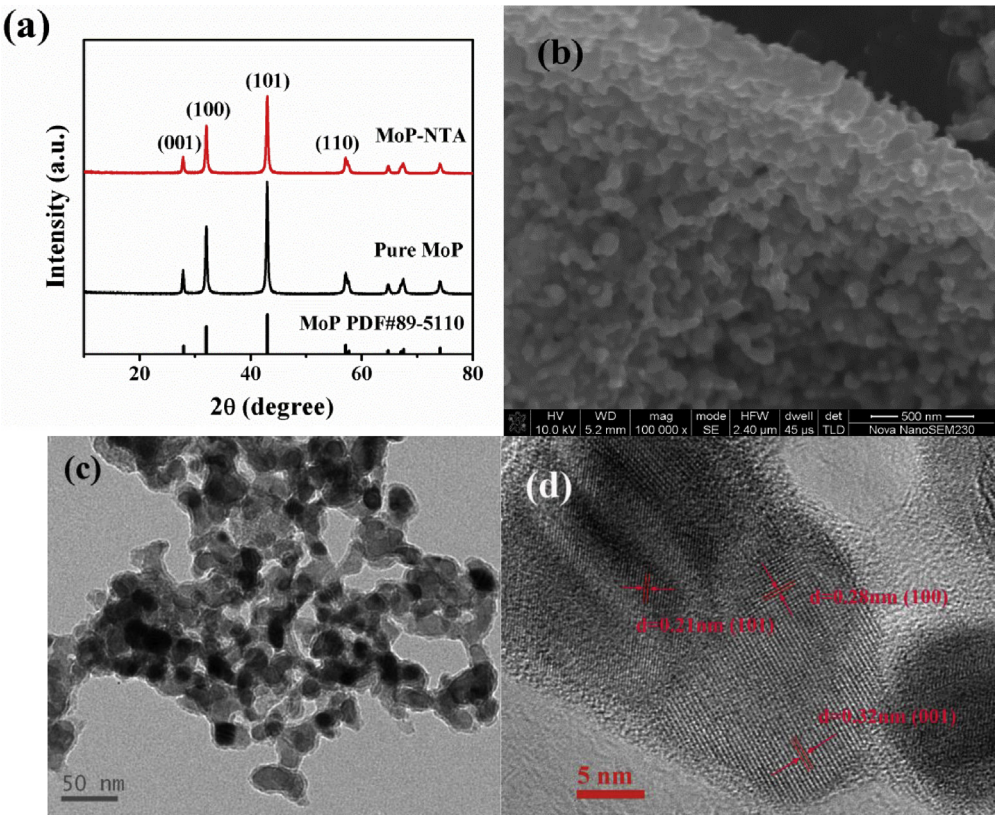

Fig. 1 – (a) XRD patterns of pure MoP and MoP-NTA, (b) SEM and (c and d) TEM images of MoP-NTA.

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