PMo_{12} induced MoP as hydrogen evolution electrocatalysts

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Abstract. In recent years, electrolytic water has become the mainstream method of producing hydrogen energy, in which the development of efficient electrocatalysts is particularly important. Herein, MoP@C was synthesized by simple hydrothermal following one-step calcination process. MoP@C shows excellent catalytic activity in acidic environment, requiring only a small overpotential (196 mV) at the current density of 10 mA cm^{-2} and exhibiting a small Tafel slope (91 mV dec^{-1}). Meanwhile, MoP@C displays good stability within 24 hours. This work has a positive effect for the subsequent large-scale preparation of phosphides electrocatalysts.

1. Introduction

In the context of "dual carbon", environmentally friendly and reproducible hydrogen energy becomes the main choice [1]. Hydrogen production by electrolytic water, qua the opposite direction reaction of hydrogen burn, applys water as the only stuff and can realize the closed hydrogen circulate without contamination discharge, which is considered to be the lots of unpolluted and convenient device [2]. Current studies have shown that platinum (Pt) is the optimum products of electrolytic water, it has the highest hydrogen evolution activity and the fastest reaction kinetics [3]. However, high price and scarce resources limit the large-scale of Pt in hydrogen production process [4]. For this reason, the development of transition metal products, which can supersede the precious metals, has attracted extensive attention. Phosphides gradually comes into people's view due to the extensive structures and compositions, excellent electronic properties and conductivity [5]. Among them, molybdenum phosphide has been widely studied because of the similar electronic structure to Pt [6-7]. For example, Li et al. [8] used NaH_2PO_2 as phosphorus source to synthesize Ni-doped MoP/MoNiP@C for HER catalyst by one-pot method. In acidic media, the overpotential just entails lower overpotential (134 mV) to reach 10 mA cm^{-2}. As another example, Li et al. [9] used phytic acid (PA) as phosphorus source for the first time and successfully prepared two phosphates (MoP and CoP) through solution reaction and calcination process. Both catalysts exhibit outstanding hydrogen evolution effect in both sulfuric acid and potassium hydroxide solution.

In unison, Phosphomolybdate hydrate (PMo_{12}), a popular polyoxometalates (POMs), is often used as a metal source for hydrogen evolution catalysts due to its high Mo content and excellent reactivity. For example, Pnna et al. [3] firstly synthesized the precursors by hydrothermal method using cobalt chloride and PMo_{12} as metal sources, and then transferred the precursors to H_2(5%)/Ar atmosphere and pyrolytized them at 650 and 750 ° C, respectively, to obtain CoMoP and $CoMoP_2$ with outstanding catalytic effects. Li et al. [4] used PMo_{12} and nickel acetate as metal sources, polyaniline as carbon and nitrogen sources, and polyphosphoamine as phosphorus sources, and obtained a bimetallic catalyst by simple solution mixing and stirring, and calcined at 950 ℃. The catalyst showed excellent catalytic effect under acidic (98 mV) and alkaline (137 mV) environment.

Carbon sources rich in C and N elements are important factors for the preparation of super-duper hydrogen evolution catalysts. For example, Xu et al. [5] used chitosan as carbon source, PA as phosphorus source, nickel nitrate and ammonium molybdate as metal source to prepare gel precursors, and carbonized at high temperature (900 ℃) in N_2 atmosphere to obtain Ni_2P/MoP@NC catalyst. The catalyst is suitable for all pH environments. Pan et al. [10] obtained a bimetallic carbide catalyst using polyethylenimide as carbon source, PMo_{12} and nickel acetate as metal source by one-step carbonization, and proved the tip-top performance of the catalyst through theoretical calculation.

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On account of the above reference, an efficient catalyst was composed with flying colors by handy solution mixing and high temperature calcination. Polyethylenimide (PEI) was used as the carbon fountainhead, phytic acid (PA) as the phosphorus fountainhead and phosphomolybdic acid hydrate (PMo_{12}) as the metal fountainhead. According to studies, PEI can coordinate with positive charged metal ions in solution, thus preventing agglomeration [10]. Therefore, carbon layers coated molybdenum phosphide nanoparticles (MoP@C) was synthesized through the reaction of PMo_{12} and PA molecules on PEI. MoP@C exhibits terrific hydrogen evolution effect and outstanding corrosion resistance in 0.5 M Sulfuric acid.

2. Experimental

2.1 Preparation of MoP@C

Specifically, 500 mg PEI was scattered in 10 mL deionized water to attain liquid A, then 100 mg PMo_{12} and 800 mg PA were compounded and scattered in 10 mL deionized water to attain liquid B. Finally, liquid A and B were compounded and agitated vigorously about 1 h. Transfer the liquid to a crucible and vaporize to remove the solvent. The obtained solids were heated to 900 °C (5 °C min^{-1}) in N_2 atmosphere and persisted for 2 h.

3. Results and Discussion

3.1 Two - steps calcination synthesis MoP@C

The preparation transversion for MoP@C is shown in figure 1. PEI acts as a soft template, PMo_{12} and PA are evenly mixed, and after high temperature calcination, small sized MoP nanoparticles are obtained, which can be characterized in TEM images (figure 2b).

Figure 1. Schematic diagram of MoP@C composition.

3.2 Characterization of MoP@C

The structure and morphology of MoP@C are analyzed by PXRD and TEM. Figure 2a manifeasts the structure of the product, sharp diffraction peaks appear at 28.0°, 32.3°, 43.3°, 57.3°, 57.9°, 64.9°, 67.0°, 67.8°, 74.3°, and 85.6°, corresponding to (001), (100), (101), (110), (002), (111), (200), (102), (201) and (112) lattice planes of MoP(PDF#24-0771), respectively. Notably, broad peak belonging to graphitic carbons in the 20-30° (2θ) diffraction range are not very obvious, which may be attributed to MoP inhibition. Figure 2b and 2c show the TEM image of MoP@C. In figure 1c, MoP@C exhibits a lattice distance of 0.2nm, which is part of the (101) crystallographic plane for MoP (PDF#24-0771). Moreover, the mapping image (figure 2d-h) manifeasts that the various elements are uniform distribution in product. In the meantime, we also investigated the specific surface area of the product (MoP@C) and the structure of the control product (PC). The BET surface area of MoP@C is 14.18 m^2/g, the pore size is 1.5 nm, and the overall mesoporous distribution is shown (figure 3a). Figure 3b demonstrates the XRD pattern of the control product PC, and the only wide peak (20-30°) is the characteristic peak of carbon [11]. In the meantime, Raman spectra was used to analyze the degree of carbonization of all products (figure 4). Through calculation, the ratio of I_D and I_G was 0.92 and 0.85, respectively, indicating that the degree of carbonization was good and conducive to improving the catalytic effect.

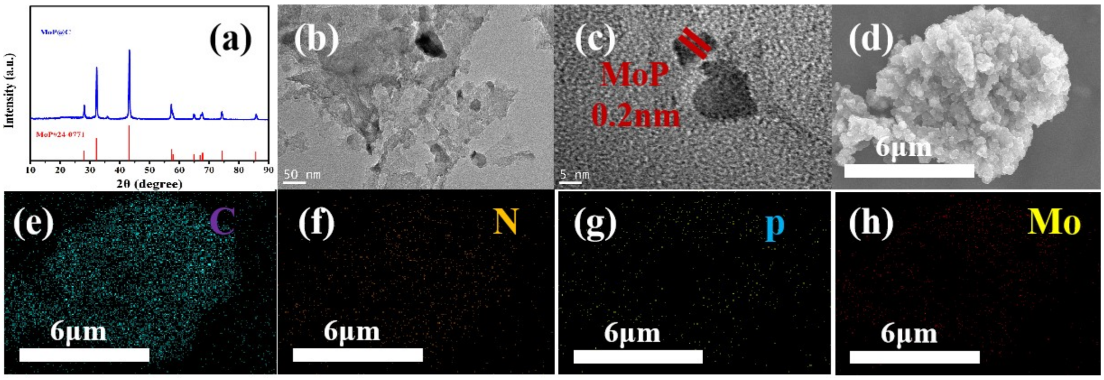

Figure 2. (a) The pattern of products structure (PXRD); (b) and (c) Product topography (TEM) and high resolution patterns (HRTEM); (d-h) Product element distribution and composition patterns (EDX).

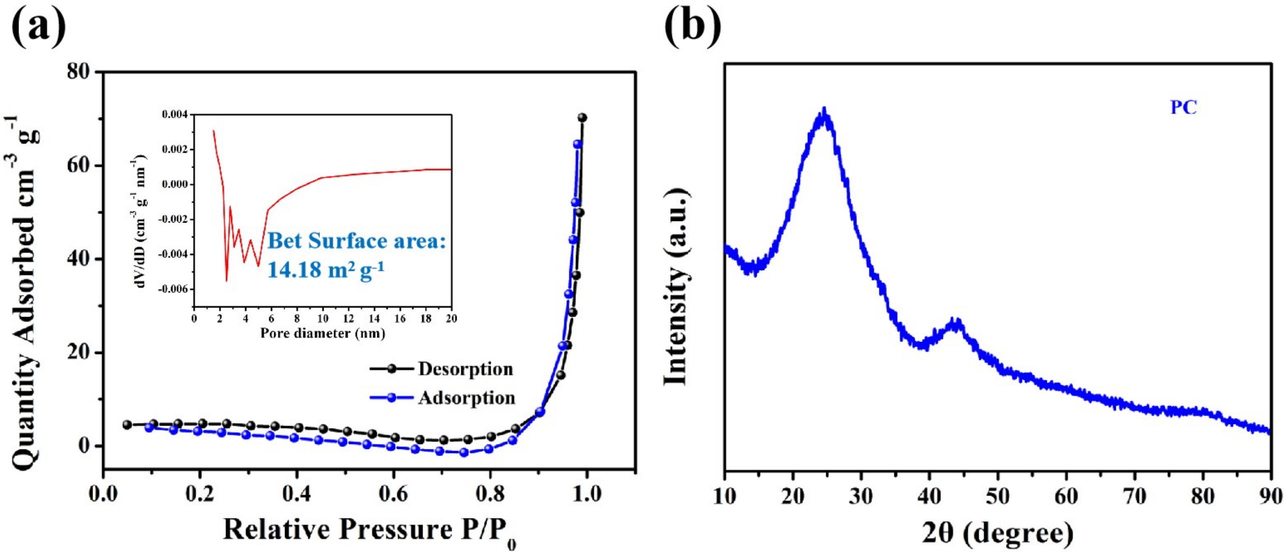

Figure 3. (a) N adsorption map of the product; (b) Compare the product PC XRD pattern

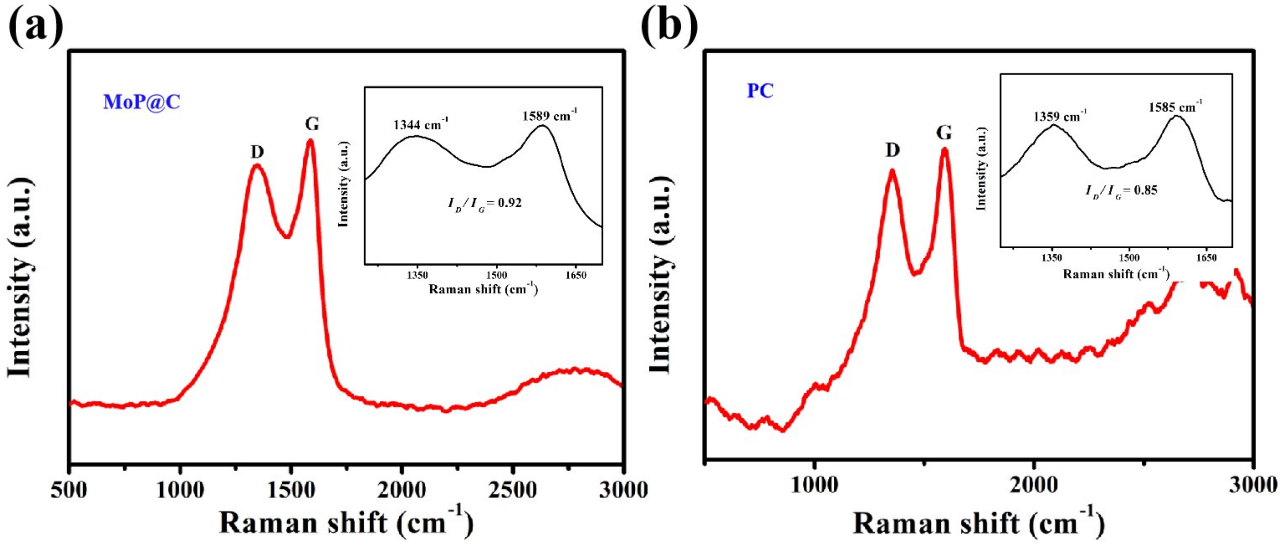

Figure 4. (a) Raman spectra of product MoP@C; (b) Raman spectra of product PC

3.3 Research on hydrogen evolution properties

The HER properties of MoP@C were measured in acid electrolyte using a three-electrode system. Figure 5a and 5b respectively manifeast the hydrogen evolution property of all products. MoP@C shows excellent catalytic effect. It only entails a 196 mV overpotential to achieve our desired target (10 mA cm^{-2} current density), and the product has relatively fast kinetics (Tafel slope is

91 mV dec^{-1}). PC shows scarcely any HER activity. The double-layer capacitor (C_{dl}) is manifeasted in figure 3c and 5d, and the C_{dl} of MoP@C is 9.31 mF cm^{-2}. Furthermore, the electrochemical impedance spectroscopy (EIS) of MoP@C was determined at an overpotential of 200 mV (figure 5e). The outcomes manifeast that the impedance of PC is much larger than that of MoP@C, indicating that MoP@C has better hydrogen evolution capability than PC. Finally, the constancy of MoP@C was determined by cyclic voltammetry (CV) and chronoamperometry method (figure 5f). After 24h, MoP@C still maintained a high activity, indicating good stability of the catalyst.

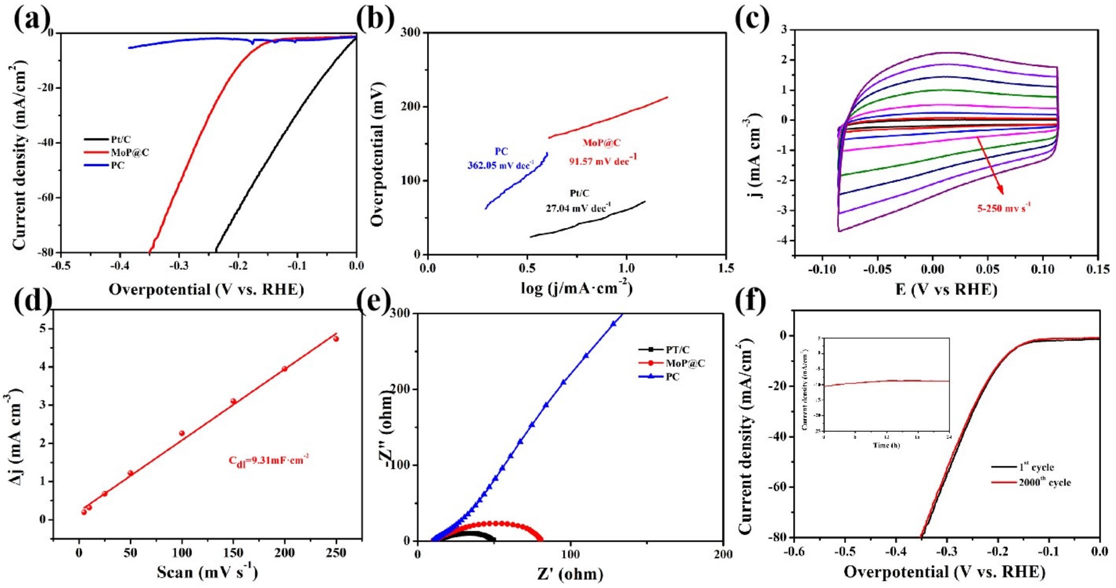

Figure 5. (a) Hydrogen evolution properties (LSV) of all products in acidic solutions; (b) hydrogen evolution kinetics of all products (Tafel); (c) and (d) The active area (CV) and C_{dl} for MoP@C were obtained at different scanning rates (50 - 250 mV s^{-1}), (e) the EIS pattern of all products; (f) MoP@C's LSV after 2000 cycles in an acidic medium (The illustration shows the current density change of the products at high voltage for 24 h.)

4. Conclusion

To sum up, we conflated MoP@C by simple hydrothermal method and high temperature calcination process. Hydrogen evolution performance tests unfold that MoP@C has a good catalytic effect in acidic electrolyte, the product has a low overpotential (196 mV), faster catalytic kinetics (91.57 mV dec^{-1}), large active area (9.31 mF cm^{-2}) and outstanding corrosion resistance. These outcomes declare that our work furnishes a reference about using PEI as carbon fountainhead for batch preparation of single metal phosphide catalyst for HER.

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