Direct synthesis of parallel doped N-MoP/N-CNT as highly active hydrogen evolution reaction catalyst

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ABSTRACT Doped phosphide is promising in earth-abundant element based catalysts for hydrogen evolution reaction (HER). Here we employ ammonium hypophosphite ($\text{NH}_4\text{H}_2\text{PO}_2$) to synthesize a novel parallel doped catalyst, nitrogen doped molybdenum phosphide nanoparticles (NPs) supported on nitrogen doped carbon nanotubes (N-MoP/N-CNTs). The $\text{NH}_4\text{H}_2\text{PO}_2$ as a bifunctional agent serves as both phosphidation agent and nitrogen source, which makes the synthetic route simple and efficient. The as-obtained parallel doped N-MoP/N-CNTs show an overpotential of 103 ± 5 mV at 10 mA cm^{-2} , which is 140 mV lower than that of MoP NPs. The enhanced HER performance is attributed to the electronic effect by doped MoP and CNTs supports. This work provides a facile route to synthesize doped phosphides for the potential applications in hydrogen energy.

Keywords: bifunctional precursor, ammonium hypophosphite, nitrogen-doped MoP, nitrogen-doped carbon nanotubes, hydrogen evolution reaction

INTRODUCTION

Hydrogen, with high energy density and zero polluted gas emission, has been considered as an ideal candidate for renewable, greenhouse-gas-free and sustainable energy [1,2–4]. Electrochemical water splitting coupled with renewable electricity is an ideal technique for sustainably realizing hydrogen production [5–7]. Pt-based electrocatalysts show the best electrocatalytic activity for hydrogen evolution reaction (HER) [8,9]. However, the high cost and scarcity of Pt limit their wide applications. Therefore, efficient noble-metal-free cathode materials for HER gained much attention in the past few years [10–16]. The pristine non-precious metals cannot survive in acidic environment, so the research mainly focuses on

their compounds. Transition metal phosphides are found promising for HER [12,14,17–21]. In particular, molybdenum phosphide (MoP), a recently discovered non-precious metal phosphide HER catalyst, has attracted intensive attention because of its good electrocatalytic activity and stability [22–26]. And their potential HER performance could be realized by fine tuning the structure of the catalysts.

Doping is considered as an effective way to improve the electrochemical activities [27–31]. Doping the MoP catalyst can tune the electronic structure of the active sites. Nitrogen doped [32], sulfur doped [33], or nitrogen and sulfur co-doped [34] MoP were reported to have better HER activities than the intrinsic MoP. Chan *et al.* [35] theoretically studied the doping effect of MoP, and they found that the hydrogen binding energy of MoP can be tuned by the dopant, leading to higher HER activity. Doping the support was also found to be beneficial for the electrocatalyst by the synergistic effect, because the commonly used carbon supports have strong interaction with the catalyst nanoparticles (NPs) [36–38]. Nitrogen-doped carbon supported MoP NPs enhanced HER performance [39,40]. Simultaneously doping both catalyst NPs and support might further improve the catalytic performance. However, the commonly used doping method is to introduce the doping agent in the synthesis, which makes the synthetic procedure complicated.

In this paper, we developed a novel bifunctional agent, ammonium hypophosphite ($\text{NH}_4\text{H}_2\text{PO}_2$), which can be used as both the phosphidation agent and also the nitrogen doping source in one reaction. Sodium hypophosphite [19,41] and ammonium phosphate [39] have been used previously. However, they can only be used as single functional agent. By annealing carbon

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nanotubes (CNT) supported molybdenum oxides (MoO_x/CNTs) precursor with $\text{NH}_4\text{H}_2\text{PO}_2$ in a sealed and evacuated tube, we successfully synthesized a novel parallel doped catalyst, N-doped MoP NPs supported on N-doped CNTs (N-MoP/N-CNTs). The as-obtained parallel doped N-MoP/N-CNTs catalyst has an overpotential of $103 \pm 5 \text{ mV}$ at 10 mA cm^{-2} , and a low Tafel slope of 42 mV dec^{-1} . The high HER activity is attributed to the tuned electronic structure by doping N in MoP NPs and the synergistic effect by coupling the NPs with N doped CNTs. This is a simple method to dope the catalyst and support with N *via* phosphidation, and the parallel doped N-MoP/N-CNTs electrocatalyst has a great potential to replace the noble catalyst for HER.

EXPERIMENTAL SECTION

Materials

$\text{NH}_4\text{H}_2\text{PO}_2$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, ethylene glycol, NaNO_3 , NaH_2PO_2 , KMnO_4 were purchased from Sinopharm Chemical Reagent Beijing Ltd. H_2O_2 , HCl , H_2SO_4 (98%), were purchased from Beijing Chemical Factory. CNTs were purchased from Cnano Technology Ltd. Pt/C (20 wt%) and Nafion dispersion (5 wt%) was purchased from Alfa Aesar. All the chemicals were used as received without further purification. Deionized water ($18.2 \text{ M}\Omega \text{ cm}$) was used throughout all experiments.

Catalyst synthesis

Synthesis of MoO_x/CNTs

The CNTs were firstly oxidized through modified Hummer method [36]. 20 mg of oxidized CNTs were dissolved in 4 mL of deionized water and sonicated at least 30 min to form a homogeneous dispersion, and then 50 mg of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was added and sonicated for 10 min, followed by the addition of 16 mL of ethylene glycol and another 30 min of sonication. Then the dispersion was poured into a 40 mL Teflon-lined autoclave. The autoclave was sealed and placed in an oven for hydrothermal processing at 200°C for 24 h. After natural cooling to room temperature, the black precipitate was collected by centrifugation and washed three times with ethanol and deionized water, respectively. Then the product was frozen and lyophilized overnight for further experiments and characterizations.

Synthesis of N-MoP/N-CNTs

20 mg of MoO_x/CNTs and 1 g of $\text{NH}_4\text{H}_2\text{PO}_2$ were put into two ceramic boats respectively, and then transferred

into a quartz tube. The quartz tube was bubbled by N_2 , evacuated and finally sealed. Then, it was heated to 800°C with a slow heating rate of $2.5^\circ\text{C min}^{-1}$, and kept at this temperature for 2 h. The sample was collected after cooling to the ambient temperature.

Synthesis of the control samples

The control samples, including MoP/CNTs, MoP NPs and N-CNTs were synthesized according to the similar procedure to fabricate N-MoP/N-CNTs. MoP/CNTs were synthesized by replacing $\text{NH}_4\text{H}_2\text{PO}_2$ to NaH_2PO_2 . For MoP NPs, NaH_2PO_2 was used without CNTs. For N-CNTs, CNTs was heated with $\text{NH}_4\text{H}_2\text{PO}_2$.

Characterizations

The as-synthesized samples were characterized by X-ray powder diffraction (XRD) using a Bruker D8 diffractometer with Cu K α radiation ($\lambda=0.15406 \text{ nm}$). The morphology of the sample was investigated by a transmission electron microscope (TEM, FEI Quanta 250) operating at 200 kV. High resolution TEM (HRTEM) images and energy dispersive X-ray spectroscopy (EDX) elemental mapping profiles were obtained on Tecnai G2F20 S-TWIN electron microscope. The X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis Ultra DLD spectrometer using an Al K α monochromated ($h\nu=1486.6 \text{ eV}$, 150 W). Thermogravimetric analysis (TGA) was investigated on Mettler Toledo TGA1 connected to infrared (IR) analyzer (Thermo-Fisher 6700) to investigate the evolved gases.

The electrochemical performances were evaluated on CHI 660E electrochemical workstation using a standard three-electrode system. The HER tests were performed in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. Graphite rod was used as the counter electrode to avoid the Pt contamination and saturated calomel electrode was used as the reference electrode. The reference electrode was calibrated with respect to reversible hydrogen electrode (RHE) in this report and the zero point of RHE was calibrated using the equilibrium potential of HOR/HER of Pt catalyst in H_2 -saturated electrolyte. All the measurements reported in this paper were after *iR* correction. The catalyst deposited on the glassy carbon electrode was severed as the working electrode. The catalyst ink was made by dispersing 2 mg catalyst powder in 500 μL mixed solvent (380 μL H_2O , 100 μL ethanol and 20 μL Nafion dispersion (5 wt%)). Then the mixture was sonicated for at least 1 h to obtain homogeneous ink. 20 μL of the ink was transferred onto a polished glassy carbon electrode ($d=5 \text{ mm}$), resulting in a loading of 0.41 mg cm^{-2} . The HER performance was

Figure 1 The decomposition of $\text{NH}_4\text{H}_2\text{PO}_2$. (a) TGA curve of $\text{NH}_4\text{H}_2\text{PO}_2$ tested under N_2 atmosphere. (b) The corresponding IR spectra of the evolved gas during the TGA test.

Figure 2 The schematic of the formation of N-MoP/N-CNT.

measured by linear sweep voltammetry (LSV) at a sweep rate of 5 mV s^{-1} in H_2 saturated electrolyte. The electrochemical impedance spectroscopy (EIS) was carried out at the frequency from 0.1 Hz to 100 kHz.

RESULTS AND DISCUSSION

$\text{NH}_4\text{H}_2\text{PO}_2$ is the key agent for the phosphidation and the nitrogen doping. $\text{NH}_4\text{H}_2\text{PO}_2$ decomposes upon heating to disproportionally generate PH_3 which works as the phosphidation agent. NH_3 was also released, which served as the nitrogen doping agent. Fig. 1a shows the TGA curve of $\text{NH}_4\text{H}_2\text{PO}_2$ under N_2 flow, and the evolved gases were tested by Fourier transform infrared spectrometer (FTIR, Fig. 1b). $\text{NH}_4\text{H}_2\text{PO}_2$ started to decompose at around 160°C and released ammonia confirmed by the typical N-H vibration located at $3,330$, $1,625$, 970 and 933 cm^{-1} [42]. When the temperature increased to 225°C , PH_3 was detected, indicated by P-H vibration located at $2,320$ and $1,125 \text{ cm}^{-1}$ [43]. PH_3 came from the disproportionation of hypophosphite, with phosphoric acid generated at the same time. Phosphoric acid is

unstable upon heating, and it condensed to form polyphosphoric acids, followed by the gradual evaporation, which was demonstrated by the gradual weight loss and the P-O vibration located at $1,236 \text{ cm}^{-1}$ in the evolved gas [43]. Thus, $\text{NH}_4\text{H}_2\text{PO}_2$ decomposes as Equations (1–3):

NH_3 and PH_3 are both generated by heating $\text{NH}_4\text{H}_2\text{PO}_2$, so it is a bifunctional agent that can be used as both phosphidation agent and nitrogen doping agent.

N-MoP/N-CNT was synthesized by incorporation of $\text{NH}_4\text{H}_2\text{PO}_2$ through a simple two step route. As shown in Fig. 2, MoO_x was first coated onto CNTs *via* solvothermal method by using ammonium molybdate $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O})$ as the Mo source and water and ethylene glycol mixture as the solvent. Then the precursor was heated with $\text{NH}_4\text{H}_2\text{PO}_2$ in a sealed tube which was

Figure 3 Characterization of the as-obtained N-MoP/N-CNTs. (a) XRD patterns of MoO_x/CNTs and N-MoP/N-CNTs. (b, c) TEM images of MoO_x/CNTs and N-MoP/N-CNTs; inset: HRTEM image of N-MoP/N-CNTs, (d) STEM images and EDX mapping of Mo, P and N of N-MoP/N-CNTs.

previously evacuated. By using this bifunctional agent, the coated MoO_x transformed into MoP NPs supported on CNTs, and MoP and CNTs were doped with N at the same time.

Fig. 3a shows the XRD patterns of the MoO_x/CNTs precursor and N-MoP/N-CNTs catalyst. Only one major peak assigned to CNTs was shown for the MoO_x/CNTs precursor, indicating the existence of the amorphous structure of the coated MoO_x. After the phosphidation process, additional reflection peaks assigned to MoP (JCPDS card No. 65-6487) revealed the successful conversion of MoO_x to MoP. The TEM image (Fig. S1) indicates the obtained oxidized nanotubes are highly dispersed with a diameter of about 20 nm. After reacting with ammonium molybdate, the obtained MoO_x/CNTs precursor shows a rough tubular surface (Fig. 3b), which is considered as the coated amorphous MoO_x. After the phosphidation process at high temperature, MoO_x layers transform into MoP NPs to form N-MoP/N-CNTs, as

shown in Fig. 3c. The CNTs maintain the structure after the high temperature treatment, and the MoP NPs, with diameter of 8–15 nm, distributed on the CNTs uniformly. The HRTEM image (inset of Fig. 3c) further reveals the lattice fringe with spacing of 0.27 nm, which corresponds to the (100) plane of MoP. The EDX mapping profiles for N-MoP/N-CNTs show that the Mo, N and P are distributed in CNTs uniformly in Fig. 3d.

We also investigated the effect of the amount of Mo source used in the synthesis on the morphologies of N-MoP/N-CNTs. As shown in Fig. S2, with the amount of the Mo source increasing, more MoP NPs formed on the CNTs. However, too much Mo source used in the synthesis resulted in large particle size of the MoP on CNTs. Thus the optimal amount of the Mo source was identified. MoP NPs and MoP/CNTs are also synthesized for comparison, and their XRD patterns and TEM images are shown in Figs S3 and S4.

XPS was adopted to explore the surface composition

Figure 4 High resolution core level XPS spectra. (a) Mo 3d spectra of N-MoP/N-CNTs and MoP/CNTs. (b) N 1s spectra of N-MoP/N-CNTs, N-CNTs and MoP/CNTs.

and valence states of the N-MoP/N-CNTs. The survey of N-MoP/N-CNTs (Fig. S5a) confirms the existence of Mo, P, and N. Fig. 4a shows the Mo 3d core level spectra of N-MoP/N-CNTs. The peaks at 228.5 and 231.8 eV are assigned to the Mo(δ^+) 3d_{5/2} and 3d_{3/2} of MoP, respectively [44]. Compared with the Mo(δ^+) 3d_{5/2} peak of MoP/CNT (228.3 eV), there is a positive shift of 0.2 eV for the N-MoP/N-CNTs, which is ascribed to the high electronegativity of doped N. And other two peaks at 236.7 and 233.5 eV are assigned to Mo⁶⁺ due to the surface oxidation [25]. For the P 2p core level spectra (Fig. S5b), two peaks at 129.3 and 130.7 eV can be assigned to P–Mo species in N-MoP/N-CNTs at 2p_{3/2} and 2p_{1/2}, and the peak at 134.0 eV can be assigned to the oxidized species (PO₄³⁻ or P₂O₅) owing to exposure to the air [45]. Fig. 4b shows the N 1s core level spectra of MoP/CNTs, N-CNTs and N-MoP/N-CNTs. No N signal was observed for MoP/CNTs. For N-CNTs, a broad peak in the range of 395–405 eV was observed, which can be deconvoluted into three peaks at 398.9, 399.7 and 401.6 eV, corresponding to pyridinic, pyrrolic and graphitic N, respectively, confirming that the N atoms were doped into the CNTs. For N-MoP/N-CNTs, similar N species from N-CNT was observed, and the doping level was calculated as 8.3 at% according to the XPS results. In addition, there are two peaks at 397.5 and 394.6 eV assigned to the N–Mo species in N-MoP/N-CNTs [34,46], which confirms the successful doping of nitrogen into MoP. For the C 1s core level spectra (Fig. S5c), there are two peaks at 284.8 and 286.0 eV which are ascribed to C–C(C=C) and C–N(C=N) [47], respectively, also suggesting the successful incorporation

of N into the CNTs.

The electrochemical activity of the as-synthesized N-MoP/N-CNTs catalyst towards HER was investigated in H₂-saturated 0.5 mol L⁻¹ H₂SO₄ using a standard three-electrode system. MoP/CNTs, MoP NPs, N-CNTs and CNTs were also studied under the same conditions. All the potentials reported in this paper are *versus* RHE with the *iR* compensation. The catalyst loadings on the glassy carbon electrode were controlled at 0.41 mg cm⁻². Fig. 5a shows the polarization curves of as-prepared samples with a sweep rate of 5 mV s⁻¹. The CNTs and N-CNTs show poor HER performance. The MoP NPs can be used as HER catalyst, but with low activity. When MoP is supported on CNTs, the HER performance is promoted. MoP/CNTs show an overpotential of 129 mV at 10 mA cm⁻², which is lower than that of MoP NPs (243 mV). The promoted HER activity is attributed to uniform dispersion of the MoP NPs on CNTs and also the good electronic conductivity of CNTs. When parallel doped the MoP NPs and CNTs with N, the HER performance was further improved. N-MoP/N-CNTs only needs an overpotential of 103±5 mV (the error is the standard deviation obtained at five independent experiments) at 10 mA cm⁻², which is 26 and 140 mV smaller than MoP/CNTs and MoP NPs, respectively. The HER performance of all the catalysts are summarized in Table 1. It demonstrates that doping with N, both in the CNTs substrate and the MoP NPs, is beneficial to HER. These parallel doped N-MoP/N-CNTs also show good HER performance compared with the reported MoP-based HER catalysts (Table S1). It was found that 800°C was the optimal temperature for the synthesis of the

Figure 5 (a) Polarization curves for CNTs, N-CNTs, MoP NPs, MoP/CNTs, N-MoP/N-CNTs and Pt/C in 0.5 mol L⁻¹ H₂SO₄ at a scan rate of 5 mV s⁻¹. (b) Tafel plots for MoP NPs, MoP/CNTs, N-MoP/N-CNTs. (c) Nyquist plots for MoP NPs, MoP/CNTs, and N-MoP/N-CNTs at an overpotential of 150 mV. The inset is the equivalent electrical circuit. (d) LSV polarization curves of N-MoP/N-CNTs initially and after 1,000 CV cycles at a scan rate of 100 mV s⁻¹ between 0 and -176 mV, respectively.

Table 1 Comparison of catalytic performance of different HER electrocatalysts in 0.5 mol L⁻¹ H₂SO₄

Electrocatalyst	@10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)
20% Pt/C	21	30
N-MoP/N-CNTs	103	42
MoP/CNTs	129	59
MoP NPs	243	95
N-CNTs	493	300

parallel doped N-MoP/N-CNTs with the highest HER performance (Fig. S6). Lower temperature is not enough for the phosphidation of MoO₃, while higher temperature leads to the aggradation of the MoP NPs.

The hydrogen binding energy is essential for the HER performance. Doped N atoms modulate the electronic structure of MoP. Doping CNTs with N, the synergistic effect between the NPs and the substrate also adjusts the

electronic structure of MoP. The XPS results confirm the positive shift of the Mo 3d peaks.

Fig. 5b shows the Tafel plots of the catalysts. The Tafel slope, an inherent property of catalyst, was fitted to the Tafel equation (Equation (4))

$$\eta = b \log j + a, \quad (4)$$

where j is the current density and b is the Tafel slope. The Tafel slope of N-MoP/N-CNTs is 42 mV dec⁻¹, which is lower than that of MoP/CNTs (59 mV dec⁻¹) and MoP NPs (95 mV dec⁻¹), suggesting that N-MoP/N-CNTs has an effective facilitation on the HER process.

EIS was also conducted to characterize the electrochemical activity. Fig. 5c shows the EIS spectra of N-MoP/N-CNTs, MoP/CNTs and MoP NPs conducted at an overpotential of 150 mV, and the equivalent electrical circuit is shown in the inset of Fig. 5c, where R_s , R_{ct} and CPE represent the solution resistance, charge transfer resistance and constant phase element, respectively. The R_s of N-MoP/N-CNTs, MoP/CNTs and MoP NPs are 5 Ω

owing to the same electrolyte. The R_{ct} for N-MoP/N-CNTs is $7\ \Omega$, which is lower than that of MoP/CNTs ($16\ \Omega$) and MoP NPs ($120\ \Omega$), suggesting that N-MoP/N-CNTs have faster charge transfer in hydrogen evolution process. For the stability of the as-obtained N-MoP/N-CNTs, we conducted 1,000 continuous cyclic voltammograms (CV) between 0 and $-176\ \text{mV}$ with a scan rate of $0.1\ \text{V s}^{-1}$. As shown in Fig. 5d, little activity loss after 1,000 CV cycles indicates the high stability of N-MoP/N-CNTs in acid environment.

All the above results suggest the parallel doping of nitrogen leads to the high HER activity and stability of N-MoP/N-CNTs. In our method, benefiting from the bifunctional phosphidation agent $\text{NH}_4\text{H}_2\text{PO}_2$, the MoP NPs and CNTs are doped with N at the same time in the phosphidation. This is a general strategy which can be used to synthesize other doped phosphides.

CONCLUSIONS

In summary, $\text{NH}_4\text{H}_2\text{PO}_2$ was developed as a bifunctional agent for both phosphidation and nitrogen doping, with which parallel doped N-MoP/N-CNTs were synthesized through a simple process. N doped MoP NPs and CNTs exhibited excellent HER performance in the acid electrolyte. This work developed a facile method to synthesize doped phosphides with promoted HER performance, which sheds light on the design and synthesis of doped catalysts.

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Supplementary information Supporting data are available in the online version of the paper.

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直接合成双掺杂N-MoP/N-CNT及其高效析氢催化性能

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摘要 清洁氢能源是未来发展的重要方向, 因此开发高效廉价的析氢材料尤为重要. 掺杂的磷化物作为一种优异的析氢材料得到了广泛的关注. 本文提出了一种将氮原子同时掺杂在磷化物催化剂和载体上的新的合成方法. 在热处理的过程中, 利用次磷酸铵($\text{NH}_4\text{H}_2\text{PO}_2$)分解产生的氨和磷化氢气体与前驱体进行反应, 一步得到双掺杂的氮掺杂碳纳米管负载氮掺杂磷化钼催化剂(N-MoP/N-CNT). 该催化剂展现出了良好的析氢反应活性, 当电流密度为 10 mA cm^{-2} 时, 过电势只有 $103 \pm 5 \text{ mV}$, 明显低于MoP纳米颗粒的过电势(243 mV). 催化活性的提升主要来自掺氮带来的电子效应以及协同效应. 该催化剂在电解水产氢方面具有应用前景.