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Solvothermal access to rich nitrogen-doped molybdenum carbide nanowires as efficient electrocatalyst for hydrogen evolution reaction

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ABSTRACT

Rich N-doped molybdenum carbide (Mo_2C) nanowires for hydrogen evolution reaction (HER) have been prepared by a facile calcination-solvothermal treatment utilizing inorganic-organic hybrid MoO_x/aniline as precursor. Firstly, MoO_x/aniline nanowires provide one-dimensional nanostructure and N element for the synthesis of N-doped Mo_2C through calcination process. XRD and SEM show that uniform N-doped Mo_2C nanowires with ß-Mo_2C phase can be obtained after calcination of 750 °C. The electrocatalytic measurements show N-doped Mo_2C nanowires of 750 °C exhibit the better activity compared with other samples at 650 °C, 850 °C and 950 °C. Furtherly, ammonium-hydrazine solvothermal process has been used to optimize the N-doping degree of N-doped Mo_2C of 750 °C. XRD shows that rich N-doped Mo_2C nanowires contain the crystalline phase structure, which can be identified by HRTEM. XPS, EDX and elemental mapping data reveal the good distribution and valence of Mo, C and N. The electrocatalytic measurements confirm that rich N-doped Mo_2C possesses the lower overpotential, smaller Tafel slope, larger double-layer capacitances and excellent long-term stability after 5000 cycles than other samples, which may be attributed to ammonium-hydrazine solvothermal process. Therefore, Mo-based inorganic-organic hybrid nanostructure may be a promising precursor for excellent HER electrocatalysts through a facile calcination-solvothermal treatment.

1. Introduction

As the energy crisis and environmental problem become more severe, clean and sustainable energy sources have been widely explored. Hydrogen energy as a clean and renewable energy carrier has been considered to replace traditional fossil fuels [1–4]. In this regard, water splitting using electrochemistry into H_2 has been widely regarded as one of the most promising pathways for hydrogen evolution reaction (HER) [5–10]. Currently, noble metal Pt-based electrocatalysts are still the best electrocatalysts for HER due to its ideal hydrogen adsorption (ΔG_{H^*}) and low activation energy for H desorption from the surface of Pt [11–13]. However, the disadvantages of noble metals are the limited reserves, easy deactivation and high price which hamper their large-scale applications [14]. Thus, it is vital important to develop earth-abundant electrocatalysts with high HER activity.

Because of Pt-like electrochemical behaviors [15], Mo-based compounds, such as Mo_2C [16,17], MoN [18] and MoS_2 [19–23] have accumulated substantial interest as new noble-metal free electrocatalysts. Especially, Mo_2C has been found to exhibit electrocatalytic performances for HER due to the high conductivity, similar d-band electronic density-of-state to that of Pt and optimal hydrogen-adsorption energy [24]. For instance, Lan et al. reported Mo_2C supported on reduced graphene oxide with low onset overpotential for HER [25].

To maximum the activity of electrocatalysts for HER, two strategies including designing unique nanostructures [26] to expose more active sites or doping other element [27] to tailor the electronic structure usually have been applied. For elemental doping, nitrogen-doped materials have accumulated great attention as highly effective catalysts [12,28–31]. For instance, Xie et al. reported that N-doping can result in increased oxygen divacancies relative to synthesized materials without N-doping, which leads to

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much higher HER activity. In addition, density-functional calculations exhibited that the production of oxygen divacancies leads to improved states density near to the valence band edge, which favors for improved electronic conductivity [32]. Thus, it can be predicted that N-doping may be a promising strategy for achieving enhanced catalytic performances of Mo_2C-based catalysts. However, the systematic researches about N-doping of Mo_2C by facile solvothermal method have been seldom reported and it is still urgently needed to control morphology of N-doped Mo_2C in promoting HER using an effective method [33].

Herein, we reported a facile calcination-solvothermal process utilizing inorganic-organic hybrid MoO_x/aniline nanowires to synthesize rich N-doped Mo_2C for efficient HER (in Fig. 1). Firstly, calcination process has been used to synthesize N-doped Mo_2C nanowires using inorganic-organic hybrid MoO_x/aniline as precursor at different calcination temperature including 650 °C, 750 °C, 850 °C and 950 °C in Ar atmosphere. Secondly, the ammonium-hydrazine solvothermal method has been applied to convert N-doped Mo_2C of 750 °C into rich N-doped Mo_2C. The enhanced HER performances of rich N-doped Mo_2C are obtained with lower overpotential, smaller Tafel slope, lower charge-transfer resistance, larger double-layer capacitances, which may be attributed to the uniform nanowire structures and high conductivity derived from optimized N-doping. Therefore, designing uniform rich N-doped Mo_2C nanowires by facile solvothermal method provide a new way towards high-efficiency HER electrocatalysts.

2. Experimental

All of reagents were analytical grade and used without any further purification. The synthesis of $Mo_3O_{10}(C_6H_8N)_2{\cdot}2H_2O$ nanowires was carried out in the reaction where ammonium molybdate has been converted into anilinium molybdate by complex formation with aniline as reported earlier [34]. 2.48 g ammonium heptamolybdate and 3.34 g of aniline were dissolved in 40 mL distilled water. And then 1 M HCl aqueous solution was added dropwise with magnetic stirring until pH = 4. After a reaction at 50 °C for 2 h, the product was filtered and washed with deionized water and ethanol for several times, and then dried at 50 °C for 24 h in a vacuum oven.

N-doped Mo_2C nanowires was prepared through carbonization process under a flow of ultrapure argon atmosphere at 750 °C for 3 h at a heating rate of 5 °C min^{-1}. To explore the performance of $Mo_3O_{10}(C_6H_8N)_2{\cdot}2H_2O$ nanowires heated with different temperatures, the obtained $Mo_3O_{10}(C_6H_8N)_2{\cdot}2H_2O$ nanowires was calcinated at 650 °C, 850 °C and 950 °C keeping other conditions unchanged, respectively.

For the synthesis of rich N-doped Mo_2C, 20 mL distilled water containing mixture of obtained N-doped Mo_2C nanowires (750 °C), 5 mL ammonium hydroxide solution and 2 mL hydrazine hydrate solution were added into the 100 mL Teflon-lined autoclave and then was sealed and experienced a hydrothermal treatment at 150 °C for 6 h. The final product was collected by centrifugation at 4000 r.p.m. for 10min, and then filtered with water and dried in oven at 50 °C.

Structure of all the samples were characterized by X-ray powder diffraction (XRD, X'Pert PRO MPD, Cu KR) with the range of 2θ from 10° to 70°. X-ray photoelectron spectra (XPS) were performed on a Thermo Fisher Scientific II spectrometer using an Al Ka photon source to study the valence state of all obtained samples. The morphology of the samples was investigated by scanning electron microscopy (SEM, Hitachi, S-4800). Transmission electron microscopy (TEM, FEI Tecnai G2) and high-resolution TEM (HR-TEM) were used to investigate the crystal structure of rich N-doped Mo_2C nanowires. Mapping and EDX were used to identify the main elements of the representative surface area of samples.

HER electrochemical measurements have been carried out using a standard three-electrode system in solution of 0.5 M H_2SO_4 (purging N_2 for 30 min in advance to saturate the electrolyte) on the electrochemical workstation (Gamry Reference 600 Instruments, USA). Ag/AgCl (3 M KCl) and Pt foil were used as reference and counter electrodes respectively. The working electrode was prepared on glassy carbon electrode (GCE), which was polished with alumina slurry then ultrasonicated in water. 5 mg of as-obtained sample was dispersed in 1 mL water-ethanol solution with volume ratio of 1:1 containing 20 μL Nafion solution (5 wt %) by sonicating for 1 h to form a homogeneous ink. Then 5 μL of the dispersion was loaded onto the GCE with the geometric area of 0.1256 cm^2. Linear sweep voltammetry (LSV) plots were used to investigate the HER activity of samples from 0 V to −0.7 V (vs. Ag/AgCl) with a scan rate of 10 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were recorded at an overpotential of −0.42 V (vs. Ag/AgCl) with a frequency range from 10^5 Hz to 0.1 Hz. Cyclic voltammograms (CV) were used to evaluate the long-term stability of samples from −0.35 V to −0.45 V (vs. Ag/AgCl) at a scan rate of 100 mV s^{-1} for 5000 cycles.

3. Results and discussion

XRD of obtained $Mo_3O_{10}(C_6H_8N)_2{\cdot}2H_2O$ nanowires is displayed in Fig. 2a. Fig. 2a shows that the peaks of the sample are highly consistent with the standard card (PDF No. 00-050-2402) of

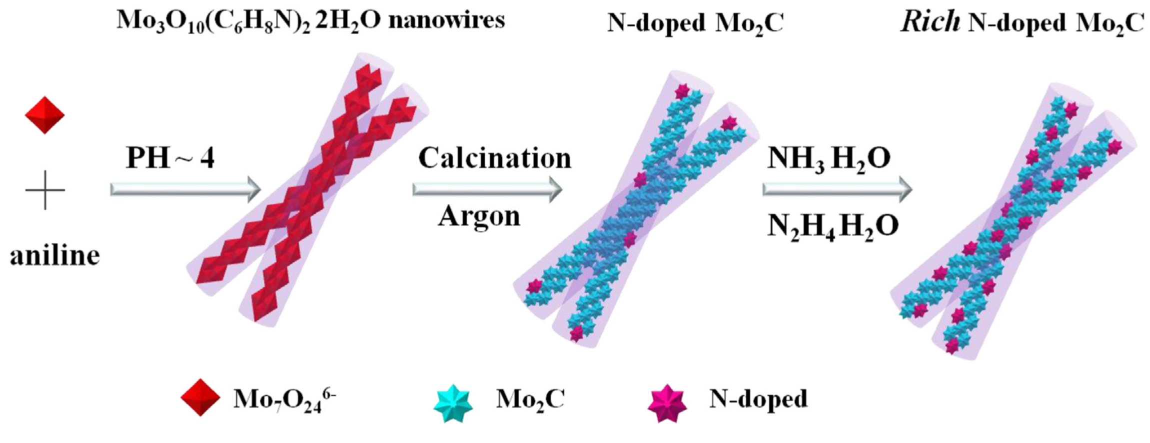

Fig. 1. Schematic illustration of the synthesis process for rich N-doped Mo_2C.