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Molybdenum carbide supported by N-doped carbon: Controlled synthesis and application in electrocatalytic hydrogen evolution reaction

Zhiwei Zhong [a], Ning Liu [a,c], Hongyu Chen [a], Xionghui Fu [a], Lichun Yang [b,*], Qingsheng Gao [a,*]

[a] *Department of Chemistry, Jinan University, No. 601 Huangpu Avenue West, 510632 Guangzhou, China*
[b] *School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, China*
[c] *Guangdong Provincial Key Laboratory of Emergency Test for Dangerous Chemicals, China National Analytical Center, Guangzhou 510070, China*

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ABSTRACT

Exploring noble-metal free electrocatalysts remains a great challenge for hydrogen evolution reaction (HER). Herein, we report the fabrication of molybdenum carbides supported by N-doped carbon (MoC_x/CN), employing glucose and melamine as precursors to generate conducting supports. The nanosized MoC_x, and its intimate contact with CN, favor the efficient HER. The optimal MoC_x/CN delivers an overpotential (η) of 220 mV to produce a current density (j) of 10 mA cm^{-2}, and a high j of 72 mA cm^{-2} at $\eta = 300$ mV in 0.5 M H_2SO_4.

1. Introduction

Hydrogen, a renewable and clean chemical fuel, is promising to replace fossil fuels in future [1]. To promote the sustainable H_2 production, electrochemical hydrogen evolution reaction (HER) from water has attracted much attention, requiring electrocatalysts being capable of reducing water rapidly at low overpotential [2]. Regarding the high cost and low abundance of platinum [3], noble-metal free electrocatalysts are desired [4–6]. Recently, remarkable progresses have been made in the use of metal carbides [3,4], such as Mo_2C, in which efforts focus on nanostructures with enriched active-sites [7–9]. However, the activity is still limited by its unsatisfied conductivity and the easy aggregation during high-temperature preparation. It's demanded to exploit well-dispersed Mo_2C on conducting supports, e.g. carbon matrix [10]. Noticeably, biomass-derived molecules with various functional groups provide a facile and low-cost way towards carbon-support Mo_2C with tailored composition and phase [11,12], which are important for HER.

Herein, we report the controlled synthesis of molybdenum-carbides (MoC_x) supported by N-doped carbon (CN) and their HER activity in acidic electrolytes. Employing glucose and melamine as precursors, ultrafine MoC_x nanoparticles (NPs) evenly integrated with CN are accomplished, which are denoted as MoC_x/CN-n, and n indicates the feeding ratio of melamine to glucose ($n_{M/G}$). With a suitable $n_{M/G}$ of 0.05, the MoC_x/CN presents a high activity with an overpotential (η_{10}) of 220 mV to produce a current density (j) of 10 mA cm^{-2}, and a high j of 72 mA cm^{-2} at $\eta = 300$ mV in 0.5 M H_2SO_4.

2. Experimental

Typically, 0.50 g of ammonium heptamolybdate tetrahydrate with varied glucose and melamine was dissolved in 15.0 mL of water (Table S1 in Supplementary material), and then turned to an autoclave, kept at 200 °C for 24 h. The MoC_x/CN was received after calcining the above solids at 800 °C for 5 h under Ar flow. Detail characterization and HER test were described in Supplementary material.

3. Results and discussion

As illustrated in Fig. 1a, melamine and glucose are polymerized

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* Corresponding authors.
E-mail addresses: mslcyang@scut.edu.cn (L. Yang), tqsgao@jnu.edu.cn (Q. Gao).

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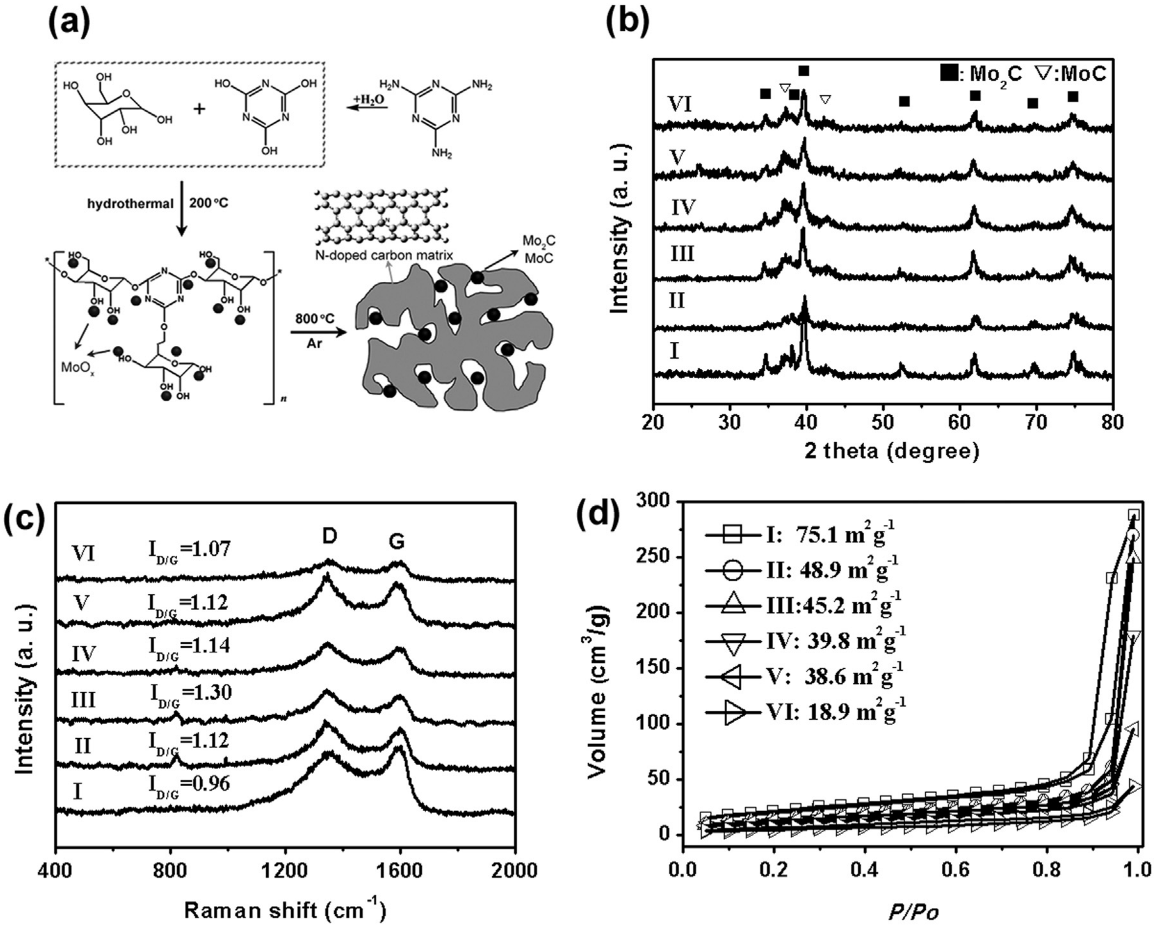

Fig. 1. (a) Illustration for fabricating MoC_x/CN, and their (b) XRD patterns, (c) Raman spectra and (d) N_2 sorption isotherms with a varied $n_{M/G}$ of (I) 0, (II) 0.03, (III) 0.05, (IV) 0.07, (V) 0.10 and (VI) 0.20.

during hydrothermal processes, resulting in a matrix with abundant hydrophilic groups for loading Mo species. Afterwards, such matrix not only serves as carbon source for generating MoC_x, but also converts to a conducting support during calcination. With an increased $n_{M/G}$ from 0 to 0.2, the N content in the MoC_x/CN increases accordingly (Table S2 in Supplementary material). Their crystalline is investigated by X-ray diffraction (XRD, Fig. 1b). The diffraction peaks at 34.4°, 38.0°, 39.4°, 52.1°, 61.5°, and 69.6°, are assigned to the (100), (002), (101), (102), (110), and (103) of Mo_2C (JCPDS No. 35-0787), respectively. And those at 36.8°, 39.3° and 42.6° correspond to the (006), (103) and (104) of MoC (JCPDS No. 08-0384). Meanwhile, the Raman spectra (Fig. 1c) displays the characteristic D and G bands of carbon at 1347 and 1590 cm^{-1}, respectively, identifying the presence of carbon matrix. It's found that the value of D/G bands increases with the increasing $n_{M/G}$ from 0 to 0.05, indicating the reduced graphitization by N-doping. However, as the excessive N-doping is adopted, such value decreases. Accordingly, the above products show a surface area in the range of 18.9–75.1 $m^2\ g^{-1}$ (Fig. 1d), which decreases with the increasing $n_{M/G}$.

Taking MoC_x/CN-0.05 for example, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) were further conducted. SEM image shows the morphology of NPs (Fig. 2a), analogous to others received with different $n_{M/G}$ (Fig. S1 in Supplementary material). However, as the $n_{M/G}$ is increased to 0.1, the aggregation is visible, consistent with the N_2 sorption isothermals showing the decreasing surface area (Fig. 1d). The TEM image of MoC_x/CN-0.05 (inset of Fig. 2b) shows that Mo_2C NPs (10∼20 nm) are well dispersed on amorphous carbon. And, the lattice fringes on a single NP can be assigned to the (101) and (01$\bar{1}$) of Mo_2C (Fig. 2b).

Furthermore, the presence of Mo, C, N and O is identified in MoC_x/CN-0.05 by the XPS survey (Fig. S2 in Supplementary material). In the profile of Mo 3d (Fig. 2c), the peak fitting suggests that there are two states for Mo (+2 and +6). Mo^{6+}results from inactive MoO_3 [13], which usually contaminate Mo_2C surface as exposed to air. The peaks at 228.4 and 231.6 eV are attributed to Mo $3d_{3/2}$ and $3d_{5/2}$ of Mo^{2+}in Mo_2C, respectively, which are believed as the active sites for HER [9]. They are slightly higher than the reported values [13], probably associated with the doping of N and MoC. Meanwhile, for N 1 s (Fig. 2d), the peak at 397.1 eV is ascribed to the N species bonding with Mo [14], and those at 398.3 and 399.4, and 401.2 eV are assigned to pyridinic, pyrrolic and quaternary-type nitrogen, respectively [15]. Obviously, the N-doping is in both Mo_2C and carbon matrix.

Fig. 3a displays the polarization curves of various MoC_x/CN with iR-drop corrections. The bare Mo_2C fabricated via a urea-glass route delivers a poor HER activity because of its bulky dimension and insufficient active-sites (Fig. S3 in Supplementary material). Integrated with carbon matrix, MoC_x/CN presents the obviously improved activity. Particularly, a highest activity featured by a low η_{10} of 220 mV is achieved on MoC_x/CN-0.05. At $\eta=300$ mV, a j of 72 mA cm^{-2} is further delivered, higher than that of other MoC_x/CN. Such high activity also performs among the recently reported noble-metal free catalysts, e.g., carbides, nitrides and phosphide (Table S3 in Supplementary material). Accordingly, the Tafel plots display the consistent order (Fig. 3b), and MoC_x/CN-0.05 shows the lowest η_{onset} (180 mV) and slope (80.4 mV dec^{-1}), which indicates