Synthesis of Mo-based nanostructures from organic-inorganic hybrid with enhanced electrochemical for water splitting

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A simple method to fabricate Mo-based nanostructures were developed by the thermal decomposition of MoO₃-based organic-inorganic hybrid nanowires. Well-defined Mo-based nanostructures, including MoO₂ and MoO₃ nanowires, can be prepared by changing the hybrid precursor. More importantly, Mo₂C/MoO₂ heterostructures with porous structure were successfully synthesized under an inert atmosphere. The resultant Mo₂C/MoO₂ heterostructures show enhanced electrocatalytic activity and superior stability for electrochemical hydrogen evolution from water. The enhanced performance might be ascribed to the high electrical conductivity and porous structures with one-dimensional structure. Indeed, our result described here provides a new way to synthesize other Mo-based nanostructures for various applications.

INTRODUCTION

Transition metal compounds are receiving growing interest owing to their wide applications in catalysis, electrochemistry, optoelectronics and energy storage [1–7]. In particular, molybdenum oxides, including MoO₂ and MoO₃, have been regarded as promising materials in field effect transistors and energy storage. Recently, various molybdenum oxides have been prepared through different methods. Generally speaking, MoO₂ can be obtained via the reduction of MoO₃ under a H₂ atmosphere [8,9]. However, few reports focused on the preparation of molybdenum oxide nanostructures from organic-inorganic hybrids. Taking the diphasic structures into consideration, the well-defined organic-inorganic hybrid can be seen as an alternative for the design of novel functional materials.

Electrochemical water splitting to produce hydrogen has become a subject of interest to researchers because hydrogen is regarded as the next generation energy for replacing fossil fuels. High-efficiency electrocatalysts always require high current density at low overpotential [10–12]. Up to now, Pt-based metals are the best hydrogen evolution reaction (HER) catalysts [13,14]. While the

scarcity and high cost of Pt severely hinder their practical application. Recently, various molybdenum-based compounds, such as MoS₂, MoSe₂, Mo₂C, and MoP, are promising non-noble-metal candidates due to their comparable HER activity to Pt-based catalysts [15–17]. Among them, Mo₂C, as a typical interstitial alloys material, has similar metallic structures and possesses Pt-like catalytic behaviors. The traditional synthesis method usually involves the mix of metals with carbon and subsequent carbonization under high temperature to form Mo₂C structure, which results in serious aggregation and compromises their performance. Recently, various morphologies of Mo₂C nanostructure with excellent HER performance have been developed through various methods [18–23]. Sun and co-workers [24] synthesized closely interconnected network of molybdenum phosphide nanostructure with highly efficient electrocatalyst for HER. Tang's group reported that nanoporous Mo₂C can be obtained by thermal decomposition process under an inert atmosphere, which was used as a very effective electrocatalyst for generating hydrogen from water [25,26]. In addition, Sasaki's group demonstrated that small Mo₂C nanoparticles loaded on carbon nanotubes showed highly active and durable electrocatalyst for HER [27]. Evidently, these results suggest that Mo₂C can be used as an effective electrocatalyst for water splitting.

Recently, the formation of MoO₂ with carbon materials such as graphene was used to further improve the performance of MoO₂ [28–31]. For example, Mai's group [32] synthesized ultrathin MoO₂ nanosheets encapsulated carbon matrix with a facile thermal reduction method, which showed high specific capacities and enhanced cycling stability. Li and co-workers [33] fabricated flawed MoO₂ nanobelts on graphene with enhanced HER performance. However, few reports focus on constructing heterocomposite Mo₂C with MoO₂. Compared with those of the corresponding homogeneous materials, these heterostructured

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nanomaterials usually show enhanced performance, which can be attributed to their specific integrated multifunctionality between binary or ternary nanomaterials [34–39]. Moreover, Mo_2C possesses excellent structural stability and electronic conductivity because of its high specific conductance. For instance, Wang and co-workers [40] synthesized $\text{MoO}_2/\text{Mo}_2\text{C}$ heteronanotubes by using mesoporous carbon CMK-3 as both the template and the reactant. Owing to the high electronic conductivity and stability of Mo_2C , the obtained heteronanotubes exhibited high-performance in lithium-ion batteries. Therefore, it is necessary to develop novel Mo-based nanostructures and explore their application in energy storage and catalytic fields.

In this paper, we present a simple strategy toward Mo-based nanostructures derived from organic-inorganic hybrid materials through a simple annealing method. The organic-inorganic hybrid precursor can be converted into various structures by thermal decomposition under different atmosphere. More importantly, a network of interconnected $\text{Mo}_2\text{C}/\text{MoO}_2$ heterostructures can be successfully synthesized through the same process. Benefiting from the enriched nanoporosity and large surface areas, the resultant $\text{Mo}_2\text{C}/\text{MoO}_2$ heterostructures shows enhanced electrocatalytic activity for HER. The performance might be ascribed to the high electrical conductivity and unique porous structures. Our results described here may provide a novel method to synthesize other functional Mo-based nanostructures for various applications.

EXPERIMENTAL METHODS

Synthesis

Chemicals

All chemicals were purchased from Sinopharm Chemical Reagent Beijing Company and were used as received without further purification. Deionized water was used throughout the experiment.

Synthesis of organic-inorganic hybrid nanowires

The MoO_x -based organic-inorganic hybrid nanowires were synthesized using a wet chemistry method described previously [41]. For the synthesis of $\text{Mo}_3\text{O}_{10}(\text{C}_2\text{H}_{10}\text{N}_2)$ nanowires, 1.24 g of ammonium heptamolybdate was dissolved in 15 mL of water, and then 0.8 g of ethylenediamine was added dropwise, with magnetic stirring at room temperature. A white precipitate was obtained at pH 4–5 under stirring for another 2 h. The product was filtered, washed with ethanol and then freeze-dried for next step. For $\text{Mo}_3\text{O}_{10}(\text{C}_6\text{H}_8\text{N})_2 \cdot 2\text{H}_2\text{O}$ nanowires, 1.24 g of ammonium heptamolybdate dissolved in 20 mL of water, and 1.67

g of aniline were used for the synthesis following the same procedure as above.

Preparation of MoO_2 nanowires

The as-synthesized $\text{Mo}_3\text{O}_{10}(\text{C}_2\text{H}_{10}\text{N}_2)$ nanowires were placed into a horizontal furnace and heated to 600°C for 2 h with a heat rate of 2.5°C min⁻¹ under Ar atmosphere, followed by cooling to room temperature.

Preparation of $\text{Mo}_2\text{C}/\text{MoO}_2$ heterostructures

$\text{Mo}_2\text{C}/\text{MoO}_2$ heterostructures were synthesized by the thermal decomposition of $\text{Mo}_3\text{O}_{10}(\text{C}_6\text{H}_8\text{N})_2 \cdot 2\text{H}_2\text{O}$ nanowires under N_2 atmosphere. The as-synthesized samples were placed into a horizontal furnace and heated to 750°C for 5 h with a heat rate of 2.5°C min⁻¹, followed by cooling to room temperature.

Preparation of MoO_3 nanowires

The as-synthesized $\text{Mo}_3\text{O}_{10}(\text{C}_6\text{H}_8\text{N})_2 \cdot 2\text{H}_2\text{O}$ nanowires were placed into a horizontal furnace and heated to 500°C in air for 2 h with a heat rate of 2.5°C min⁻¹, followed by cooling to room temperature.

Electrochemical measurements

The electrochemical measurements were conducted using an electrochemical workstation (CHI660E) in a typical three-electrode setup with an electrolyte solution of 0.5 mol L⁻¹ H_2SO_4 , graphite rod as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Typically, 5 mg of catalyst and 50 μL of Nafion solution (5 wt.%) were dispersed in 1 mL water-ethanol solution (1:3) by sonicating for 1 h to form a homogeneous ink. Then 10 μL of the catalyst ink was loaded onto a glassy carbon electrode of 5 mm in diameter. Linear sweep voltammetry (LS) was conducted in 0.5 mol L⁻¹ H_2SO_4 with a scan rate of 5 mV s⁻¹. Prior to the measurement, a resistance test was made and the iR compensation was applied by using the CHI software. Electrochemical impedance spectroscopy (EIS) measurements were also carried out in the frequency range of 100 kHz–0.1 Hz. In all measurements, the SCE reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). RHE calibration was performed according to reported method. In 0.5 mol L⁻¹ H_2SO_4 , $E(\text{RHE}) = E(\text{SCE}) + 0.281 \text{ V}$.

Characterizations

The morphology and size of the samples were characterized by a HITACHI H-7700 TEM with an accelerating voltage of 100 kV, and an FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscope (HRTEM)

equipped with energy dispersive spectrometer (EDS) analyses at 200 kV. The scanning electron microscope (SEM) was performed on an LEO 1530. The crystal structure was determined by X-ray diffraction (XRD) on a Rigaku D/max-2400 X-ray diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV voltage and a 40 mA current ranging from 10° to 80° . X-ray photoelectron spectroscopy (XPS) experiments were carried out on scanning X-ray microprobe (Quantera SXM, ULVAC-PHI. INC) operated at 250 kV, 55 eV with monochromated Al K α radiation. Brunauer-Emmett-Teller (BET) and pore size of the products were tested using a Quadrasorb SI-MP instrument.

RESULTS AND DISCUSSION

The synthesis of Mo-based nanostructures involves the synthesis of MoO $_x$ -based organic-inorganic hybrid nanowires, followed by annealing treatment of organic-inorganic hybrid precursor in an inert atmosphere. First, Mo $_3$ O $_{10}$ (C $_2$ H $_8$ N $_2$) nanowires were prepared by one-pot wet chemistry method reported in the literature [41]. The structure and morphology of the product were characterized by XRD and SEM (Supplementary information, Fig. S1). After freeze-dried, an annealing treatment at 600°C

in Ar atmosphere with a ramping rate of 2°C min^{-1} is utilized to convert the MoO $_x$ -based organic-inorganic hybrid nanowires into MoO $_2$ nanowires. As shown in Fig. 1a, all of the diffraction peaks can be well assigned to the monoclinic MoO $_2$ (JCPDS 32-0671, space group: $P2_1/n$). The morphology of the prepared MoO $_2$ nanowires was further examined by field-emission SEM (FESEM) and TEM, as shown in Figs 1b and c. Both SEM and TEM images show one-dimensional structure with several microns in length and 50–100 nm in width. A representative high-resolution HRTEM image is shown in Fig. 1d, and the (-111) lattice spacing (0.343 nm) of MoO $_2$ phase can be clearly observed.

More interestingly, other Mo-based nanostructures can also be obtained by changing the organic-inorganic hybrid precursors. For example, the as-prepared Mo $_3$ O $_{10}$ (C $_6$ H $_8$ N) $_2$ ·2H $_2$ O nanowires (Fig. S2) are transformed into Mo $_2$ C/MoO $_2$ heteronanowires by annealing in N $_2$. Mo $_3$ O $_{10}$ (C $_6$ H $_8$ N) $_2$ ·2H $_2$ O nanowires were obtained between ammonium heptamolybdate and aniline. Aniline was used as an intercalating molecule to form one-dimensional MoO $_x$ /amine hybrid structure. The as-synthesized product was characterized by XRD to identify the crystallographic structure and crystallinity, as shown in Fig. 2a. It is ob-

Figure 1 (a) XRD pattern of the MoO $_2$ nanowires. (b) SEM image of the MoO $_2$ nanowires. (c, d) TEM and HRTEM images of the MoO $_2$ nanowires.

Figure 2 (a) XRD pattern of the porous $\text{Mo}_2\text{C}/\text{MoO}_2$ heteronanowires. (b–d) SEM images of the porous $\text{Mo}_2\text{C}/\text{MoO}_2$ heteronanowires. (e, f) TEM images of the porous $\text{Mo}_2\text{C}/\text{MoO}_2$ heterostructures.

served that all of the diffraction peaks can be assigned to the cubic Mo_2C (JCPDS 15-0457, space group: $Fm\bar{3}m$) and monoclinic MoO_2 (JCPDS 65-5758, space group: $P2_1/c$). The peaks located at 37.5° , 53.2° , 63.0° and 75.6° are ascribed to the (111), (200), (220) and (311) planes of Mo_2C , while the diffraction peaks located at 25.9° , 37.2° , and 53.4° can be assigned to the (011), (200), and ($\bar{3}11$) planes of the hexagonal MoO_2 . No MoO_3 or other impurities can be detected, indicating the high purity of the sample. FESEM

and TEM were used to examine the morphology of the prepared $\text{Mo}_2\text{C}/\text{MoO}_2$ heterostructures. As shown in Figs 2b and S3, the low-magnification FESEM image indicates that the obtained samples are highly uniform one-dimensional morphology with a diameter about 100 nm and a length of several micrometers. The magnified FESEM images (Figs 2c and d) reveal the resultant products are highly porous, which would facilitate the electron transfer and exchange during the catalytic reaction. It can be observed that such

nanostructure with porous network is composed of numerous irregular particles resulting from the thermal decomposition of organic-inorganic hybrid precursor. TEM further confirms the porous structure of the as-synthesized $\text{Mo}_2\text{C}/\text{MoO}_2$ heterostructures. As can be seen from Figs 2e, f and S4, the samples possess a well-defined porous structure, which are in good agreement with the SEM observation. During thermal decomposition under an inert atmosphere, amine molecules not only act as reducing agent, but also act as carbon resource. Therefore, the formation of porous structure may be associated with the shrinkage of the organic-inorganic hybrid precursor and the generation of Mo_2C structure. From representative HRTEM images shown in Figs 3a and b, highly crystalline feature can be clearly observed and the interplanar distance between lattice fringes is 0.207 nm, which is consistent with the (200) planes of the Mo_2C phase. Besides, the interplanar distance between lattice fringes of 0.243 nm is consistent with the (-112) plane of MoO_2 (Fig. 3b). The high-angle annular dark-field scanning TEM (HAADF-STEM) and the corre-

sponding energy-dispersive X-ray (EDX) mapping (Figs 3c and d) of $\text{Mo}_2\text{C}/\text{MoO}_2$ heterostructures show the uniform distribution of molybdenum, carbon and oxygen throughout the whole structure.

The composition and surface chemical state of $\text{Mo}_2\text{C}/\text{MoO}_2$ heterostructures were also investigated using XPS. The survey spectrum of the sample (Fig. S5a) shows several typical peaks of Mo 3d, Mo 3p_{3/2}, Mo 3p_{1/2}, C 1s, and O 1s. No peaks of other elements are observed on the survey spectrum. The corresponding high-resolution XPS spectra (Fig. S5b) show that the peaks at 227.87 and 231.17 eV can be assigned to Mo 3d_{5/2} and Mo 3d_{3/2} of MoO_2 , respectively [18,42]. While the peak located at 235.04 eV can be attributed to Mo 3d_{5/2} of MoO_3 , which might be ascribed to the surface oxidation of the sample [43]. Fig. S5d shows the XPS spectrum in the O 1s energy region, which indicates the presence of oxides. Moreover, the corresponding EDS spectrum (Fig. S6) confirms the presence of Mo, O, and C in the product, and the atom ratio of Mo to O is far above 1:2, indicating that the sample must contain other Mo-ba-

Figure 3 (a, b) HRTEM images of $\text{Mo}_2\text{C}/\text{MoO}_2$ heterostructures. (c, d) HAADF-STEM image and the corresponding EDS mapping images, indicating that molybdenum, sulphur, carbon and oxygen are distributed in this architecture.

sed structure. Based on the results mentioned above, the resulting product is composed of cubic Mo_2C and hexagonal MoO_2 .

It should be emphasized that the ventilation of N_2 flow in advance shows great influences on the final structure and morphology. Fig. S7 shows the XRD patterns of the sample obtained by annealing treatment after expelling air with different time. All of them can be assigned to cubic Mo_2C and hexagonal MoO_2 . It is worth noting that increasing the ventilation time with N_2 flow leads to an increased intensity for Mo_2C structure. The corresponding TEM images of the sample were examined in Fig. S8. A lot of nanoparticles can be seen without expelling air. After expelling air by N_2 flow for 6 h, we found that these nanoparticles disappeared and porous heterostructures can be obtained. Therefore, ventilation of N_2 flow in advance benefits the formation of porous heterostructures. In addition, we also annealed $\text{Mo}_3\text{O}_{10}(\text{C}_6\text{H}_8\text{N})_2 \cdot 2\text{H}_2\text{O}$ hybrid nanowires under Ar-H_2 flow, and the corresponding XRD result (Fig. S9) shows that the hexagonal phase Mo_2C nanowires can be obtained. This is in accordance with the previous reports [24,25]. These results suggest that the structure and morphology of the final sample have a close relationship with the pretreatment of calcination and annealing atmosphere.

Moreover, we found that ultra-long MoO_3 nanowires can be obtained after annealing treatment at 500°C in air. The crystallographic structure of the sample is examined by XRD (Fig. 4a). All of the diffraction peaks can be perfectly assigned to orthorhombic MoO_3 (JCPDS 35-0609, space group: $Pbnm$ (62)). No other possible impurities such as MoO_2 are detected. As shown in Figs 4b and c, it is obvious that the products exhibit intact one-dimensional shape with a diameter of about 200 nm and a length of several micrometers. In agreement with the SEM image, the nanowires structure can be observed from the low-magnification TEM image. The HRTEM image (Fig. 4d) shows that the obvious interplanar distance between lattice fringes is 0.380 nm, which is consistent with the (110) planes of the MoO_3 phase. Apparently, this result shows that various Mo-based nanostructures can be obtained by thermal decomposition of organic-inorganic hybrid.

The electrocatalytic activity for HER of the obtained porous $\text{Mo}_2\text{C}/\text{MoO}_2$ sample was further studied by electrochemical measurements in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ using a rotating disc electrode (RDE) in a typical three-electrode setup on a glassy carbon electrode. For comparison, the HER catalytic activity of the commercial Mo_2C , the as-obtained MoO_2 nanowires, MoO_3 nanowires and Pt-C was also in-

Figure 4 (a) XRD pattern of the MoO_3 nanowires. (b, c) SEM and TEM images of the MoO_3 nanowires. (d) HRTEM image of the MoO_3 nanowires.

vestigated. As shown in Fig. 5a, the polarization curves of porous Mo₂C/MoO₂ heteronanowires (*I*-*V* plot, *iR* corrected) exhibit a small overpotential of -0.19 V. And the overpotential is about 315 mV *vs.* RHE at an HER current of 10 mA cm⁻². In sharp contrast, the commercial Mo₂C, MoO₂ nanowires and MoO₃ nanowires exhibit poor HER activity, and no reduction current can be seen until the electrode potential over -0.4 V.

The Tafel slopes were further evaluated the intrinsic activity of all samples. It is generally acknowledged that three principle steps for the conversion of H⁺ to H₂ have been suggested for the HER in acidic media as below [24]:

Volmer step: H⁺ + e⁻ → H_{ads}, (Tafel slope: ~120 mV)

Heyrovsky step: H_{ads} + H⁺ + e⁻ → H₂, (Tafel slope: ~40 mV)

Tafel step: H_{ads} + H_{ads} → H₂, (Tafel slope: ~30 mV)

The linear portions of the Tafel plots (Fig. 5b) were fit to the Tafel equation ($\eta = b \log j + a$, where *b* is the Tafel slope) [44,45]. And the corresponding Tafel slopes are ~30, ~94 and ~329 mV for Pt-C, as-obtained Mo₂C/MoO₂ heteronanowires and commercial Mo₂C, respectively. Such Tafel slope of

94 mV per decade means that the porous Mo₂C/MoO₂ heteronanowires follow a mechanism of Volmer-Heyrovsky combination process, and desorption step is the rate-determining step for HER [46]. While the Pt-C electrode with a small Tafel slope of 30 mV per decade belongs to Tafel step and the chemical recombination of H_{ads} is the rate-determining step [45,47]. In addition, EIS was also used to characterize the interfacial reactions and electron-transfer kinetics in HER. Fig. 5c shows the representative Nyquist plots of all samples. The Mo₂C/MoO₂ heteronanowires exhibited much lower charge transfer impedance of ~270 Ω than commercial Mo₂C (~850 Ω) and MoO₃ (~900 Ω), indicating faster interfacial reactions during HER process, which is consistent with the polarization measurements. The stability of the Mo₂C/MoO₂ heterostructures were further evaluated through the accelerated durability tests by cycling the electrode at a scan rate of 100 mV s⁻¹. As shown in Fig. 5d, the performance of the Mo₂C/MoO₂ heterostructures after 4000 cycles showed no degradation compared with the fresh electrode. The performance of Mo₂C/MoO₂ heterostructures displays an increasing trend.

Figure 5 (a) Polarization curves and (b) corresponding Tafel plots of the Mo₂C/MoO₂ heteronanowires along with the as-obtained MoO₂ nanowires, MoO₃ nanowires, commercial Mo₂C and Pt/C for comparison. (c) Nyquist plots of the Mo₂C/MoO₂ heteronanowires, the as-obtained MoO₂ nanowires, MoO₃ nanowires, commercial Mo₂C and Pt/C. (d) Durability test for the Mo₂C/MoO₂ heteronanowires after 4000 CV cycles at a scan rate of 100 mV s⁻¹ between -0.6 and -0.2 V *vs.* SCE.

This increase is likely associated with a gradual activation of the electrode materials. In addition, the electrochemical inactive Mo₂C nanostructure is also responsible for the structural stability, leading to a good cycling performance in acidic media.

The improved HER performance of the porous Mo₂C/MoO₂ heterostructures might be mainly ascribed to their unique structure. First, enriched porous structure would effectively facilitate the transport of electrons or protons during the catalytic reaction. As determined by nitrogen adsorption-desorption isotherms (Fig. S10), such a unique structure gives rise to BET surface area of 55.26 m² g⁻¹ and a relatively high pore volume of 0.249 cm³ g⁻¹. Second, the existence of Mo₂C with a high electrical conductivity not only decreases the resistance of the sample, but also improves the structural stability of the heteronanowires. It is believed that the HER activity of such porous Mo₂C/MoO₂ heterostructures could be further improved by decorating with graphene. As a result, the porous Mo₂C/MoO₂ heteronanowires can be used as a promising material for HER catalyst.

CONCLUSION

In summary, we have demonstrated a facile strategy to synthesize Mo-based nanostructures through calcination treatment of MoO_x-based organic-inorganic hybrid precursor. Well-defined Mo-based nanostructures, including one-dimensional MoO₂ and MoO₃ nanowires, can be prepared in large quantities by changing the hybrid precursor under an inert atmosphere. What is more, a network of interconnected Mo₂C/MoO₂ heterostructures was successfully synthesized after thermal decomposition. The resultant Mo₂C/MoO₂ heteronanowires possess highly crystalline, enriched porous structure and large surface areas. When evaluated as a catalyst towards HER, the resultant material shows good active and stable catalysts in acidic electrolytes. The improved HER catalytic effects of porous Mo₂C/MoO₂ heterostructures can be ascribed to the high electrical conductivity of Mo₂C and porous structures. Taking the facile fabrication method and excellent electrochemical performance into consideration, it is believed that the present work described here presents a way to fabricate other Mo-based nanostructures for various applications.

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Conflict of interest The authors declare that they have no conflict of interest.

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

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中文摘要 钼基纳米材料因其特殊的结构和良好的化学性质被广泛应用于传感器和催化领域. 其中, 碳化钼具有类似贵金属的电子结构和催化特性, 受到了越来越多的关注. 在本研究工作中, 通过对有机-无机复合材料在惰性气氛下进行热处理, 制备了不同的一维钼氧化物纳米材料以及碳化钼/氧化钼多孔异质纳米材料. 析氢电催化性能表明碳化钼/氧化钼多孔异质材料显示出优异的析氢性能和循环稳定性. 此方法制备过程简单有效且适合大量制备, 同时为制备新型钼基纳米材料提供了新的思路.