Solid-state synthesis of MoS₂ nanorod from molybdenum-organic framework for efficient hydrogen evolution reaction

Jun-Dong Yi¹, Tao-Tao Liu^{1,2}, Yuan-Biao Huang^{1,2*} and Rong Cao^{1,2*}

ABSTRACT MoS₂ is a promising candidate for catalyzing hydrogen evolution reaction (HER) due to its low cost and high activity. However, the poor conductivity and the stack of active sites of bulk MoS₂ hinder its application. Herein, a new facile solid-state synthesis strategy was developed to fabricate MoS₂ nanorods by one-step pyrolysis of molybdenum-organic framework (Mo-MOF) in the presence of thiourea. The obtained MoS₂ keeps the Mo-MOF nanorod structure with more active sites, while the residual carbon left in the nanorod enhances the conductivity. The as-prepared MoS₂ nanorods exhibit superior stability and excellent activity towards HER with a small onset potential of 96 mV and a low Tafel slope of 93 mV decade⁻¹.

Keywords: metal-organic framework, MoS₂ nanorod, hydrogen evolution reaction

INTRODUCTION

Nowadays, most of the energy supply still comes from fossil fuels, which leads to environmental pollution and global warming problems. By contrast, hydrogen, as a clean and renewable energy, may replace fossil fuels in the future [1,2]. Electrochemical splitting of water has been regarded as a facile and effective method to produce hydrogen due to the environmentally friendly process and no emission of pollution species [3,4]. Although platinum-based catalysts show very high efficiency towards hydrogen evolution reaction (HER), the high cost and scarcity prevent their large-scale commercial application. Thus, extensive research efforts have been devoted to developing noble-metal-free catalysts and non-metallic carbon materials [5–14]. Since Hinnemann *et al.* [15] found that MoS₂ could promote HER, various

MoS₂-based catalysts have attracted considerable attention due to its abundance, low price and high activity [9,16–24]. However, the poor conductivity of MoS₂ obtained using solvothermal method or chemical vapor deposition (CVD) resulted in low activity for HER. Besides, the stack of MoS₂ layers causes the insufficient exposure of the active sites. Although different kinds of strategies have been developed to tackle these two obstacles, such as modification of the phase structure [25,26], elemental doping [27,28], and hybridization with conductive materials [39–31], the fabrication of highly efficient MoS₂ for HER to replace Pt-based catalysts is still a great challenge [32].

During the past two decades, metal-organic frameworks (MOFs) have been widely utilized in gas storage and separation, luminescence, drug delivery and catalysis due to their large surface areas, uniform pore sizes and tunable chemical structures [33–37]. However, most MOFs have poor conductivity, which hinders the electron transfer and limits their application in electrochemistry. Fortunately, the uniform distribution of metal nodes and heteroatoms in the highly ordered porous frameworks makes MOFs promising templates and/or precursors to fabricate functional heteroatom-doped carbon materials and metal-based compounds with superior conductivity for various applications such as supercapacitors, Li-ion batteries, and fuel cells [38–41]. However, to our knowledge, there was no report using MOF as precursor to prepare MoS₂.

Herein, for the first time, MoS₂ nanorods decorated with carbons were fabricated from a molybdenum-based MOF (Mo-MOF) *via* a solid-state synthesis method (Scheme 1). The Mo-MOF, [H₂im]₄[Mo₈O₂₆(Him)₂]

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Scheme 1 Schematic illustration of (a) the synthetic procedure of MoS₂ nanorod and (b) the relative location of the reactants inside the furnace.

(Him = imidazole), was transformed to MoS₂ nanorod in the atmosphere of H₂S *in situ* released from the decomposition of thiourea at high temperature. The obtained MoS₂ inherited the merits of MOF with nanorod shape and good crystallinity. Moreover, the residual carbons in the MoS₂ nanorod improve the conductivity of the composite, promoting the electrocatalytic activity of HER.

EXPERIMENTAL SECTION

Synthesis of molybdenum-based MOF

The Mo-MOF ([H₂im]₄[Mo₈O₂₆(Him)₂]) was synthesized according to the reported literature [42]. Typically, 1.4 g of MoO₃ and 0.664 g of imidazole were added into 100 mL deionized water and stirred uniformly. After the mixture was refluxed for 12 h at 110°C, the precipitate was collected by filtration, washed with deionized water for thrice and dried in vacuum at 70°C for 10 h. And then the Mo-MOF was obtained.

Preparation of MoS₂ nanorod

The as-prepared Mo-MOF (100 mg) was placed at the hot center of the tube furnace, while 800 mg thiourea was placed at the upstream side of the furnace (Scheme 1b). The tube was firstly flushed with N₂ for 1 h to remove the residue oxygen in the tube. Then both of Mo-MOF and thiourea in the furnace were treated at a designated temperature (400, 600, 800, 900, 1,000°C) with a heating rate of 5°C min⁻¹ under a steam of N₂. After maintaining for 3 h, the sample in the tube furnace was cooled naturally. For comparison, the same amount of Mo-MOF and thiourea was physically mixed and then treated under the same conditions.

Physical and chemical characterization

Scanning electron microscopy (SEM) images were obtained using a JSM6700-F working at 10 kV. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were recorded by using an FEIT 20 working at 200 kV. Powder X-ray diffraction (PXRD) patterns were recorded on a Miniflex 600 diffractometer using Cu Kα radiation ($\lambda = 0.154$ nm). The Raman spectra were tested on a Labram HR800 Evolution over a range of 300–2,000 cm⁻¹. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere with a heating rate of 10°C min⁻¹ by using an SDT Q600 thermogravimetric analyser. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) using an Al Kα source (15 kV, 10 mA).

Electrochemical measurement

All the electrochemical experiments were performed on an IM6ex (Zahner, Germany) workstation. Firstly, 2 mg catalyst and 40 μL 5 wt% nafion were dispersed in 1 mL of 4:1 (v/v) water/ethanol mixed solvents, followed by ultrasonication for 2 h. Then 20 μL of the resulting ink was dropped onto the surface of glassy carbon electrode with the diameter of 5 mm and dried at room temperature. The loading of catalyst is 204 μg cm⁻². The electrochemical measurements were performed in a three-electrode cell with the use of an Ag/AgCl electrode as the reference electrode and a graphite rod as the counter electrode. Linear sweep voltammetry (LSV) at a scan rate of 10 mV s⁻¹ was conducted in 0.5 mol L⁻¹ H₂SO₄ at room temperature. The electrochemical impedance spectroscopy (EIS) measurement was conducted by applying AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz under open circuit potential condition. Before the electrochemical measurements, the electrolyte solution was purged with N₂ for 30 min to remove the oxygen completely, and polarization curves were recorded after 20 cycles.

All measured potentials were converted to reversible hydrogen electrode (RHE) scale using the following equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + 0.197 \text{ V}$.

RESULTS AND DISCUSSION

As illustrated in Scheme 1, a facile solid-state synthesis method involving the thermal annealing of Mo-MOF under an H₂S atmosphere *in situ* generated from the decomposition of thiourea was developed to fabricate MoS₂ nanorods. The Mo-MOF was selected due to its morphology and after pyrolysis the obtained sample may

maintain its rod shape [42]. Moreover, to avoid the use of dangerous and stinky H_2S gas, the cheap thiourea was used as the sulfide source, because it is easy to decompose at low temperature (Fig. S1, Equation (1)). During the solid-state synthesis process, the *in situ* released H_2S from thiourea placed in the upstream side of the furnace reacted with the pyrolytic product of Mo-MOF (Fig. S2) and generated MoS_2 decorated with residual of carbons [Equation (2)].

The obtained MoS_2 samples were denoted as $\text{MoS}_2/\text{C-X}$ ($X = 400, 600, 800, 900, 1,000$) based on the solid-state synthesis temperature.

In order to confirm the component and the crystalline of the products obtained at different temperatures, PXRD was conducted. As shown in Fig. 1a, no crystalline phase was generated at 400°C . When the temperature was increased to above 600°C , the peaks at 14° , 32° , 58° assigned to MoS_2 started to appear and became stronger and sharper with increasing temperature. Highly crystalline MoS_2 was obtained at 900 and $1,000^\circ\text{C}$, indicating that high temperature is beneficial to the growth of MoS_2 in the solid-state synthesis process.

All the peaks of the samples matched well with the standard patterns of MoS_2 (JCPDS card No. 73-1508) and no other peak was observed, indicating that only MoS_2 formed during this solid-state synthesis process [43,44]. The strong peak at 14° corresponded to the distinctive diffraction of pure MoS_2 (002). The other three strong peaks of $\text{MoS}_2/\text{C-1000}$ at 32° , 39° , 58° can be assigned to the (100), (103) and (110) reflections of MoS_2 , respectively. When the synthesis temperature increased to above 900° , an additional peak at 49° appeared and corresponded to the (105) plane of MoS_2 . Raman

spectrum shows that $\text{MoS}_2/\text{C-1000}$ has two distinct peaks at the bands of 378 and 405 cm^{-1} (Fig. 1b), which were assigned to E_{2g}^1 vibration mode (the inplane displacement of Mo and S atoms) and A_{1g} vibration mode (out-of-plane symmetric displacements of S atoms along the c -axis), respectively [45,46].

XPS further confirms the existence of MoS_2 . As shown in Fig. 2a, the Mo, S, C, N and O can be clearly identified from the survey spectrum. Fig. 2b shows the C 1s characteristic peak at 284.5 eV , which is consistent with the sp^2 carbon of graphite. In Fig. 2c, the three characteristic peaks located at 232.3 , 229.2 and 226.4 eV are assigned to the binding energies of Mo $3d_{3/2}$, Mo $3d_{5/2}$ and S $2s$, respectively [47,48]. Notably, no other peak of Mo species was observed, indicating that molybdenum has been reduced to Mo^{4+} . In addition, the two characteristic peaks of S^{2-} appear at 162.0 and 163.2 eV (Fig. 2d) [47,48]. The atomic ratio of S to Mo was calculated to be 1.9:1, further indicating that ca. 95% Mo-MOF had been translated to MoS_2 during the solid-state synthesis process.

The morphologies of the original Mo-MOF and the derived $\text{MoS}_2/\text{C-X}$ catalysts were investigated using SEM and TEM. In Fig. 3a, the Mo-MOF nanorods have an average diameter of ca. 680 nm . After solid-state reaction with thiourea, the nanorod shape of the precursor Mo-MOF is maintained (Fig. 3c) even at $1,000^\circ\text{C}$ with an average diameter of 610 nm and the surface of the product $\text{MoS}_2/\text{C-1000}$ becomes rough, which could provide more active sites for catalysis. For comparison, we also conducted the control experiment by the physical mixture of Mo-MOF and thiourea (denoted as $\text{MoS}_2/\text{C-X-mixed}$, $X = 800, 1,000$). As shown in Fig. S3, the original rod shape of Mo-MOF disappeared at 800°C and irregular lumpy powder was produced at $1,000^\circ\text{C}$. The HRTEM image of $\text{MoS}_2/\text{C-1000}$ (Fig. 3f) shows that a

Figure 1 (a) PXRD patterns of $\text{MoS}_2/\text{C-X}$ ($X=400, 600, 800, 900, 1,000$) and standard patterns of MoS_2 (JCPDS card No. 73-1508). (b) Raman spectrum of $\text{MoS}_2/\text{C-1000}$.

Figure 2 (a) XPS survey spectrum of MoS₂/C-1000. High-resolution C 1s (b), Mo 3d (c), and S 2p spectra (d) of MoS₂/C-1000.

Figure 3 (a, b) SEM images of Mo-MOF. (c, d) SEM images of MoS₂/C-1000. (e) TEM and (f, g) HRTEM images of MoS₂/C-1000. (h) The high angle annular dark-field scanning TEM image of MoS₂/C-1000 and the corresponding elemental mapping of Mo, S and C, respectively. The scale bar in (h) is 100 nm.

typical interlayer spacing of 0.62 nm was observed, corresponding to the (002) plane of MoS₂ [18,20]. Furthermore, the specific lattice spacing of (002) facet of graphitic carbon (0.34 nm) at the surface of the MoS₂/C-1000 was observed (Fig. 3g), indicating that MoS₂ nanorods were coated with a few thin layers of carbons [49–51]. Meanwhile, the elemental mapping images from Fig. 3h show that the Mo, S, and C are distributed

uniformly in MoS₂/C-1000, which is consistent with the XPS analysis (Fig. 2). The residual graphitic carbon inside/at the surface of the catalyst is beneficial for enhancing the conductivity of the catalyst and expediting the transmission of electrons, thus improving the catalytic performance toward HER. EIS measurements were used to determine the electron transfer rate between the catalyst and reactant interfaces [20]. As shown in Fig. S4,

Figure 4 Electrocatalytic HER performance of MoS₂/C-X (X = 400, 600, 800, 900, 1,000) and Pt/C in 0.5 mol L⁻¹ H₂SO₄. (a) LSV curves of MoS₂/C-1000 and MoS₂/C-1000-mixed. (b) LSV curves of MoS₂/C-X and Pt/C. (c) Overpotential at 10 mA cm⁻² and the onset potential of MoS₂/C-X. (d) The corresponding Tafel plots obtained from polarization curves. (e) Long-term cyclic voltammetry measurements of MoS₂/C-1000. (f) Chronoamperometry data of MoS₂/C-1000 and Pt/C conducted under η_{10} .

the radius of the semicircle in the Nyquist plots decreases with increasing temperature, suggesting that the samples obtained at higher temperature possess a smaller charge transfer resistance (R_{ct}) and a faster charge transfer rate during the HER process. As listed in Table S1, MoS₂/C-1000 shows the smallest charge transfer resistance (157 ohm), which may originate from the existence of residual carbon and high degree of graphitization at high temperature.

All the as-prepared samples for HER performances were performed in 0.5 mol L⁻¹ H₂SO₄ using a typical three-electrode system. Notably, the counter electrode was made of graphite rods instead of Pt foil to avoid any Pt electrodeposition [52]. Fig. 4a and b show the LSV curves of the samples. In Fig. 4a, MoS₂/C-1000 shows better activity than MoS₂/C-1000-Mixed. The reason may be that the irregular morphology and micrometer-level particle size (Fig. S3) reduced the active sites toward HER and decreased the HER activity. The result manifests that placing Mo-MOF and thiourea in the furnace separately is beneficial to the nanorod structure of MoS₂/C-1000. In Fig. 4b, the HER activity of MoS₂/C increases along with the increment of synthesis temperature, verified by the onset potential and the overpotential η_{10} (when $I = 10 \text{ mA cm}^{-2}$) in Fig. 4c. As we can see in Fig. 4c, MoS₂/C-400 has the poorest activity toward HER

with an onset potential of 248 mV and a η_{10} of 732 mV, which is due to the poor crystallinity of MoS₂ and the low conductivity at such low pyrolysis temperature. With the increasing temperature, the crystallinity of MoS₂ (Fig. 1a) and the conductivity of the composite are enhanced effectively (Fig. S4). Therefore, MoS₂/C-1000 exhibits the best HER activity with a small onset potential of 96 mV and η_{10} of 282 mV. The excellent HER performance of MoS₂/C-1000 is attributed to its high crystallinity, abundant exposed active sites and high conductivity. Furthermore, the smallest Tafel slope of 93 mV dec⁻¹ for MoS₂/C-1000 further verifies its superior activity (Fig. 4d), while the Tafel slopes of MoS₂/C-900, 800, 600, 400 are 150, 242, 260 and 320 mV dec⁻¹, respectively. The results indicate that there exist a faster increase of the HER rate along with the increasing potentials when using MoS₂/C-1000 as the catalyst.

Stability is another critical parameter in practical application. As depicted in Fig. 4e, the long-term cyclic voltammetry measurements reveal that only a slight current loss is observed for MoS₂/C-1000 after 3,000 cycles. In addition, in the chronoamperometry test, the current loss for MoS₂/C-1000 is only 14% after 5 h test, while the current of Pt/C decreases by 39% (Fig. 4f). The results indicate that MoS₂/C-1000 has excellent stability toward HER.

CONCLUSIONS

In summary, the Mo-MOF was used as the Mo source and template to fabricate MoS₂ nanorods through a one-step solid-state reaction for the first time. The crystallinity of MoS₂ increased with the increment of synthesis temperature and the resulting catalyst obtained at 1,000°C shows the best crystallinity and maintains the nanorod shape. MoS₂/C-1000 exhibits good HER activity and long-term durability, which is attributed to the high crystallinity, abundant active sites, and the high electrical conductivity. This work provides an effective solid-state synthesis strategy to fabricate MoS₂ from MOFs for electrocatalysis.

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- Dresselhaus MS, Thomas IL. Alternative energy technologies. *Nature*, 2001, 414: 332–337
- Chu S, Majumdar A. Opportunities and challenges for a sustainable energy future. *Nature*, 2012, 488: 294–303
- Turner JA. Sustainable hydrogen production. *Science*, 2004, 305: 972–974
- Mallouk TE. Water electrolysis: divide and conquer. *Nat Chem*, 2013, 5: 362–363
- Zou X, Zhang Y. Noble metal-free hydrogen evolution catalysts for water splitting. *Chem Soc Rev*, 2015, 44: 5148–5180
- Morales-Guio CG, Stern LA, Hu X. Nanostructured hydrotreating catalysts for electrochemical hydrogen evolution. *Chem Soc Rev*, 2014, 43: 6555
- Li P, Yang Z, Shen J, *et al.* Subnanometer molybdenum sulfide on carbon nanotubes as a highly active and stable electrocatalyst for hydrogen evolution reaction. *ACS Appl Mater Interfaces*, 2016, 8: 3543–3550
- Zhu B, Zou R, Xu Q. Metal-organic framework based catalysts for hydrogen evolution. *Adv Energy Mater*, 2018, 8: 1801193
- Tabassum H, Guo W, Meng W, *et al.* Metal-organic frameworks derived cobalt phosphide architecture encapsulated into B/N co-doped graphene nanotubes for all pH value electrochemical hydrogen evolution. *Adv Energy Mater*, 2017, 7: 1601671
- Yan H, Xie Y, Jiao Y, *et al.* Holey reduced graphene oxide coupled with an Mo₂N-Mo₂C heterojunction for efficient hydrogen evolution. *Adv Mater*, 2017, 30: 1704156
- Wu A, Xie Y, Ma H, *et al.* Integrating the active OER and HER components as the heterostructures for the efficient overall water splitting. *Nano Energy*, 2018, 44: 353–363
- Chen W, Pei J, He CT, *et al.* Rational design of single molybdenum atoms anchored on N-doped carbon for effective hydrogen evolution reaction. *Angew Chem Int Ed*, 2017, 56: 16086–16090
- Wang H, Min S, Wang Q, *et al.* Nitrogen-doped nanoporous carbon membranes with Co/CoP Janus-type nanocrystals as hydrogen evolution electrode in both acidic and alkaline environments. *ACS Nano*, 2017, 11: 4358–4364
- Zhang FS, Wang JW, Luo J, *et al.* Extraction of nickel from NiFe-LDH into Ni₂P@NiFe hydroxide as a bifunctional electrocatalyst for efficient overall water splitting. *Chem Sci*, 2018, 9: 1375–1384
- Hinnemann B, Moses PG, Bonde J, *et al.* Biomimetic hydrogen evolution: MoS₂ nanoparticles as catalyst for hydrogen evolution. *J Am Chem Soc*, 2005, 127: 5308–5309
- Xie J, Zhang H, Li S, *et al.* Defect-rich MoS₂ ultrathin nanosheets with additional active edge sites for enhanced electrocatalytic hydrogen evolution. *Adv Mater*, 2013, 25: 5807–5813
- Guo Y, Tang J, Qian H, *et al.* One-pot synthesis of zeolitic imidazolate framework 67-derived hollow Co₃S₄@MoS₂ heterostructures as efficient bifunctional catalysts. *Chem Mater*, 2017, 29: 5566–5573
- Meng C, Liu Z, Zhang T, *et al.* Layered MoS₂ nanoparticles on TiO₂ nanotubes by a photocatalytic strategy for use as high-performance electrocatalysts in hydrogen evolution reactions. *Green Chem*, 2015, 17: 2764–2768
- Zhao Z, Qin F, Kasiraju S, *et al.* Vertically aligned MoS₂/Mo₂C hybrid nanosheets grown on carbon paper for efficient electrocatalytic hydrogen evolution. *ACS Catal*, 2017, 7: 7312–7318
- Zheng X, Xu J, Yan K, *et al.* Space-confined growth of MoS₂ nanosheets within graphite: the layered hybrid of MoS₂ and graphene as an active catalyst for hydrogen evolution reaction. *Chem Mater*, 2014, 26: 2344–2353
- Hu WH, Han GQ, Dai FN, *et al.* Effect of pH on the growth of MoS₂ (002) plane and electrocatalytic activity for HER. *Int J Hydrogen Energy*, 2016, 41: 294–299
- Shang X, Hu WH, Li X, *et al.* Oriented stacking along vertical (002) planes of MoS₂: a novel assembling style to enhance activity for hydrogen evolution. *Electrochim Acta*, 2017, 224: 25–31
- Hu WH, Shang X, Xue J, *et al.* Activating MoS₂/CNs by tuning (001) plane as efficient electrocatalysts for hydrogen evolution reaction. *Int J Hydrogen Energy*, 2017, 42: 2088–2095
- Liu Y, Zhou X, Ding T, *et al.* 3D architecture constructed via the confined growth of MoS₂ nanosheets in nanoporous carbon derived from metal-organic frameworks for efficient hydrogen production. *Nanoscale*, 2015, 7: 18004–18009
- Voiry D, Salehi M, Silva R, *et al.* Conducting MoS₂ nanosheets as catalysts for hydrogen evolution reaction. *Nano Lett*, 2013, 13: 6222–6227
- Toh RJ, Sofer Z, Luxa J, *et al.* 3R phase of MoS₂ and WS₂ outperforms the corresponding 2H phase for hydrogen evolution. *Chem Commun*, 2017, 53: 3054–3057
- Ren X, Ma Q, Fan H, *et al.* A Se-doped MoS₂ nanosheet for improved hydrogen evolution reaction. *Chem Commun*, 2015, 51: 15997–16000
- Wang H, Tsai C, Kong D, *et al.* Transition-metal doped edge sites in vertically aligned MoS₂ catalysts for enhanced hydrogen evolution. *Nano Res*, 2015, 8: 566–575
- Li Y, Wang H, Xie L, *et al.* MoS₂ nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction. *J Am Chem Soc*, 2011, 133: 7296–7299
- Zhou W, Zhou K, Hou D, *et al.* Three-dimensional hierarchical frameworks based on MoS₂ nanosheets self-assembled on graphene oxide for efficient electrocatalytic hydrogen evolution. *ACS Appl Mater Interfaces*, 2014, 6: 21534–21540
- Zhu H, Du ML, Zhang M, *et al.* S-rich single-layered MoS₂ nanoplates embedded in N-doped carbon nanofibers: efficient co-electrocatalysts for the hydrogen evolution reaction. *Chem Commun*, 2014, 50: 15435–15438
- Zhang G, Liu H, Qu J, *et al.* Two-dimensional layered MoS₂: rational design, properties and electrochemical applications. *Energy Environ Sci*, 2016, 9: 1190–1209
- Zhou HC, Long JR, Yaghi OM. Introduction to metal-organic

- frameworks. *Chem Rev*, 2012, 112: 673–674
- 34 Zhou HC, Kitagawa S. Metal-organic frameworks (MOFs). *Chem Soc Rev*, 2014, 43: 5415–5418
- 35 Zhu QL, Xu Q. Metal-organic framework composites. *Chem Soc Rev*, 2014, 43: 5468–5512
- 36 Cook TR, Zheng YR, Stang PJ. Metal-organic frameworks and self-assembled supramolecular coordination complexes: comparing and contrasting the design, synthesis, and functionality of metal-organic materials. *Chem Rev*, 2012, 113: 734–777
- 37 Fang Z, Bueken B, De Vos DE, *et al.* Defect-engineered metal-organic frameworks. *Angew Chem Int Ed*, 2015, 54: 7234–7254
- 38 Xia W, Mahmood A, Zou R, *et al.* Metal-organic frameworks and their derived nanostructures for electrochemical energy storage and conversion. *Energy Environ Sci*, 2015, 8: 1837–1866
- 39 Mahmood A, Guo W, Tabassum H, *et al.* Metal-organic framework-based nanomaterials for electrocatalysis. *Adv Energy Mater*, 2016, 6: 1600423
- 40 Liang Z, Qu C, Guo W, *et al.* Pristine metal-organic frameworks and their composites for energy storage and conversion. *Adv Mater*, 2018, 30: 1702891
- 41 Zhang H, Osgood H, Xie X, *et al.* Engineering nanostructures of PGM-free oxygen-reduction catalysts using metal-organic frameworks. *Nano Energy*, 2017, 31: 331–350
- 42 Cao X, Zheng B, Shi W, *et al.* Reduced graphene oxide-wrapped MoO₃ composites prepared by using metal-organic frameworks as precursor for all-solid-state flexible supercapacitors. *Adv Mater*, 2015, 27: 4695–4701
- 43 Zhao X, Zhu H, Yang X. Amorphous carbon supported MoS₂ nanosheets as effective catalysts for electrocatalytic hydrogen evolution. *Nanoscale*, 2014, 6: 10680–10685
- 44 Srivastava SK, Kartick B, Choudhury S, *et al.* Thermally fabricated MoS₂-graphene hybrids as high performance anode in lithium ion battery. *Mater Chem Phys*, 2016, 183: 383–391
- 45 Wan Z, Shao J, Yun J, *et al.* Core-shell structure of hierarchical quasi-hollow MoS₂ microspheres encapsulated porous carbon as stable anode for Li-ion batteries. *Small*, 2014, 10: 4975–4981
- 46 Yi JD, Shi PC, Liang J, *et al.* Porous hollow MoS₂ microspheres derived from core-shell sulfonated polystyrene microspheres@MoS₂ nanosheets for efficient electrocatalytic hydrogen evolution. *Inorg Chem Front*, 2017, 4: 741–747
- 47 Bian H, Ji Y, Yan J, *et al.* *In situ* synthesis of few-layered g-C₃N₄ with vertically aligned MoS₂ loading for boosting solar-to-hydrogen generation. *Small*, 2018, 14: 1703003
- 48 Wang H, Lu Z, Kong D, *et al.* Electrochemical tuning of MoS₂ nanoparticles on three-dimensional substrate for efficient hydrogen evolution. *ACS Nano*, 2014, 8: 4940–4947
- 49 Zhang Z, Li W, Yuen MF, *et al.* Hierarchical composite structure of few-layers MoS₂ nanosheets supported by vertical graphene on carbon cloth for high-performance hydrogen evolution reaction. *Nano Energy*, 2015, 18: 196–204
- 50 Khalid M, Honorato AMB, Varela H, *et al.* Multifunctional electrocatalysts derived from conducting polymer and metal organic framework complexes. *Nano Energy*, 2018, 45: 127–135
- 51 Xia BY, Yan Y, Li N, *et al.* A metal-organic framework-derived bifunctional oxygen electrocatalyst. *Nat Energy*, 2016, 1: 15006
- 52 Chen R, Yang C, Cai W, *et al.* Use of platinum as the counter electrode to study the activity of nonprecious metal catalysts for the hydrogen evolution reaction. *ACS Energy Lett*, 2017, 2: 1070–1075
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- Author contributions** Cao R and Huang YB conceived and designed the experiments. Yi JD performed the catalyst preparation, characterizations, and wrote the paper. Liu TT helped with the sample characterization. All authors contributed to the general discussion.
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- Supplementary information** Supporting data are available in the online version of the paper.

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钼基金属有机框架为模板合成二硫化钼纳米棒用于高效电解水产氢

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摘要 在电解水产氢反应(HER)中, 为了替代传统使用的价格高昂的铂基催化剂, 开发含量丰富、高效的非贵金属催化剂是近年来的研究热点. 其中, 二硫化钼(MoS_2)由于其低廉的成本和良好的活性受到了广泛的关注. 目前, 大多数报导均使用水热法合成 MoS_2 , 很少使用固相法. 本文, 我们使用一种钼基金属有机框架作为牺牲模板, 通过一步高温固相合成得到尺寸均匀的 MoS_2 纳米棒. 所得棒状形貌能够有效暴露 MoS_2 边缘活性位点, 提升HER活性. 同时, 固相合成后, 材料中仍有少量碳残留, 这些残余的碳提升了催化剂的导电性, 加速了HER过程中的电子转移, 提升了催化剂的反应活性. 因此我们合成的 MoS_2 纳米棒表现出优异的HER性能, 拥有很小的起始电位(96 mV)以及很低的塔菲尔斜率(93 mV dec^{-1}). 本工作为固相合成基于 MoS_2 的复合材料提供了一种新的思路.