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Ultrafast Synthesis of Mo₂C-Based Catalyst by Joule Heating towards Electrocatalytic Hydrogen Evolution Reaction

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Abstract: Developing earth-abundant electrocatalysts useful for hydrogen evolution reactions (HER) is critical for electrocatalytic water splitting driven by renewable energy. Molybdenum carbide (Mo₂C) with the crystal structure of hexagonal symmetry has been identified to be an excellent HER catalyst due to its platinum-like electronic structure while the synthesis of Mo₂C is generally time consuming and energy intensive. Herein, we demonstrated the ultrafast synthesis of a Mo₂C-based electrocatalyst with Joule heating at 1473 K for only 6 s. Benefitting from several advantages including efficient catalytic kinetics, enhanced charge transport kinetics and high intrinsic activity, the as-prepared catalyst exhibited drastically enhanced HER performance compared with commercial Mo₂C. It showed an overpotential of 288 mV for achieving a current density of -50 mA cm^{-2} and good stability, which highlighted the feasibility of the Joule heating method towards preparing efficient electrocatalysts.

Keywords: Joule heating; molybdenum carbide; hydrogen evolution reaction; electrocatalytic water splitting



Citation: Zhang, H.; Qi, S.; Zhu, K.; Wang, H.; Zhang, G.; Ma, W.; Zong, X. Ultrafast Synthesis of Mo₂C-Based Catalyst by Joule Heating towards Electrocatalytic Hydrogen Evolution Reaction. *Symmetry* **2023**, *15*, 801. <https://doi.org/10.3390/sym15040801>

Academic Editors: László Hegedűs and György Keglevich

Received: 8 March 2023

Revised: 22 March 2023

Accepted: 24 March 2023

Published: 25 March 2023



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1. Introduction

The production of hydrogen (H₂) through electrocatalytic water splitting is a promising approach to convert renewable energy into storable chemical energy [1–6]. The hydrogen evolution reaction (HER) is critical in water electrolysis processes. However, because of the sluggish reaction kinetics of HER, a large overpotential must be overcome [7,8]. As a result, identifying efficient electrocatalysts to reduce the HER energy barrier is highly desirable [9,10]. Although noble metals such as Pt have been considered the benchmark catalysts for HER [11], their high costs and scarcity severely limit their large-scale applications [12,13]. Therefore, developing a high-performance electrocatalyst based on noble-metal-free materials is essential.

In the past few decades, a range of earth-abundant materials, including metal nitride [14,15], sulphide [16,17], phosphide [18,19], carbide [20,21], and alloys [22,23], have been identified as excellent catalysts for the HER process. Among all these materials, molybdenum carbide (Mo₂C) with hexagonal crystal symmetry has emerged as a strong contender due to its platinum-like electronic structure [24–26]. For example, Ma et al. demonstrated that Mo₂C nanoparticles coated with 1–3 graphene layers exhibited an excellent HER performance with an overpotential of 78 mV for achieving a current density of 10 mA cm^{-2} [27]. Cheng et al. fabricated an electrocatalyst with a ribbon-like nanostructure by embedding Mo₂C in nitrogen-doped carbon nanomesh [28]. This catalyst displayed superior HER activity comparable to commercial Pt/C in 0.5 M H₂SO₄. Up to now, several methods have been developed for the synthesis of Mo₂C catalyst, such as carbonization of metal complexes [29], chemical vapor deposition [30], and pyrolysis of metal precursors [31]. Different synthesis approaches affect the surface structure and therefore the HER performance of Mo₂C [24,32]. However, although these methods can successfully prepare Mo₂C, annealing at high temperatures and for long durations is inevitable because of the slow reaction kinetics between solid–solid interfaces [33–35].

Recently, Joule heating has emerged as an attractive method for synthesizing a variety of materials, such as graphene [36,37], high-entropy alloy nanoparticles [38,39], and single-atom catalysts [40,41]. In the process of Joule heating, a current pulse will flow through the precursor, thus allowing for the rapid heating of the precursor to the desired reaction temperature, followed by rapid cooling to room temperature [42], which demonstrates the possibility of using Joule heating to synthesize Mo_2C .

In this work, we reported the successful synthesis of a Mo_2C -based electrocatalyst using an ultrafast Joule heating method. The synthesis was time-saving, which can be completed in just 6 s at 1473 K. The as-prepared Mo_2C -based electrocatalyst exhibited an overpotential of 288 mV to yield a current density of -50 mA cm^{-2} for HER. Moreover, after 1000 cycles of cyclic voltammetry, the current density showed no apparent degradation. The good performance of the as-prepared catalyst was mainly attributed to the efficient catalytic kinetics, high intrinsic activity and reduced charge transfer resistance between the catalyst and electrolyte interface.

2. Materials and Methods

2.1. Reagents

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was bought from Aladdin Reagent Ltd. Carbon paper and carbon black were supplied by Gaosunion. Nafion (5 wt%) was purchased from Alfa Aesar. Ethanol was provided by Tianjin Damao Chemical Reagent Co., Ltd. All the chemicals in this study were purchased commercially and used without further purification. Deionized (DI) water from a Milli-Q purification system (resistivity $> 18 \text{ M}\Omega \text{ cm}$) was used to prepare solutions.

2.2. Preparation of the Mo_2C -Based Electrocatalyst

The Mo_2C -based electrocatalyst was synthesized by ultrafast Joule heating according to the reported method with some modifications [40]. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and carbon black (molar ratio $\text{Mo}:\text{C} = 1:10$) were mixed and ground by using a mortar and pestle. The mixture (20 mg) was loaded into a conductive carbon paper. The conductive carbon paper was then put onto a reaction platform. The reaction platform was placed into the chamber and connected to the Joule heating instrument (Eshock Co., Ltd. Changchun, China). When the system was evacuated to a pressure of 150 Pa, the reaction was carried out. The temperature quickly soared to 1473 K with a heating rate of $\text{ca. } 5000 \text{ K s}^{-1}$. After being heated for 6 s at 1473 K, the temperature rapidly dropped to room temperature at a rate of $\text{ca. } 1000 \text{ K s}^{-1}$.

2.3. Material Characterizations

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/Max-2500/PC powder diffractometer equipped with $\text{Cu K}\alpha$ radiation. The morphology was investigated by scanning electron microscopy (SEM, Quanta 200 FEG). High-resolution transmission electron microscopy (HRTEM) was conducted by a JEM-2100F. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCLAB 250Xi with a monochromatic $\text{Al K}\alpha$ X-ray source. The obtained XPS spectra were analyzed by XPSPEAK software.

2.4. Electrode Preparation

The carbon paper was cut into squares with an area of $0.5 \times 0.5 \text{ cm}^2$, and then washed by ultrasonication in ethanol and DI water for 20 min, respectively. Next, 1 mg of Mo_2C -based electrocatalyst was dispersed in a solution containing 50 μL DI water, 45 μL ethanol and 5 μL Nafion (5 wt%). The mixture was then sonicated for 20 min to form a catalyst ink. Afterwards, 35 μL of the ink was dropped onto the carbon paper and allowed to dry at room temperature.

2.5. Electrochemical Measurements

The electrochemical measurements were performed using a CHI 660E potentiostat in 0.5 M H₂SO₄. A three-electrode configuration was used with the drop-coated carbon paper electrode, a graphite plate and a saturated calomel electrode (SCE) as the working, counter and reference electrodes, respectively. Linear sweep voltammetry (LSV) curves were recorded at a scan rate of 10 mV s^{−1} without iR compensation. Cyclic voltammetry (CV) tests were conducted from −0.27 V to −0.53 V at a scan rate of 100 mV s^{−1}. Electrochemical impedance spectroscopy (EIS) was carried out at −0.48 V using an amplitude of 5 mV and a frequency range of 0.05 Hz to 100 kHz. The measured potentials versus SCE were transferred to the reversible hydrogen electrode (RHE) scale employing the following equation: $E_{\text{RHE}} = E_{\text{SCE}} + 0.2415 \text{ V} + 0.059 \times \text{pH}$.

3. Results and Discussion

Figure 1a shows the schematic procedure for the ultrafast preparation of a Mo₂C-based catalyst via the Joule heating method. A mixture of (NH₄)₆Mo₇O₂₄·4H₂O and carbon black (CB) was heated at 1473 K for 6 s under a pressure of 150 Pa. During the Joule heating process, bright light radiation was released (Figure 1b) because of high temperature produced by the current pulse. As a result, the Mo precursors quickly reacted with the CB, thus forming the Mo₂C-based catalysts.

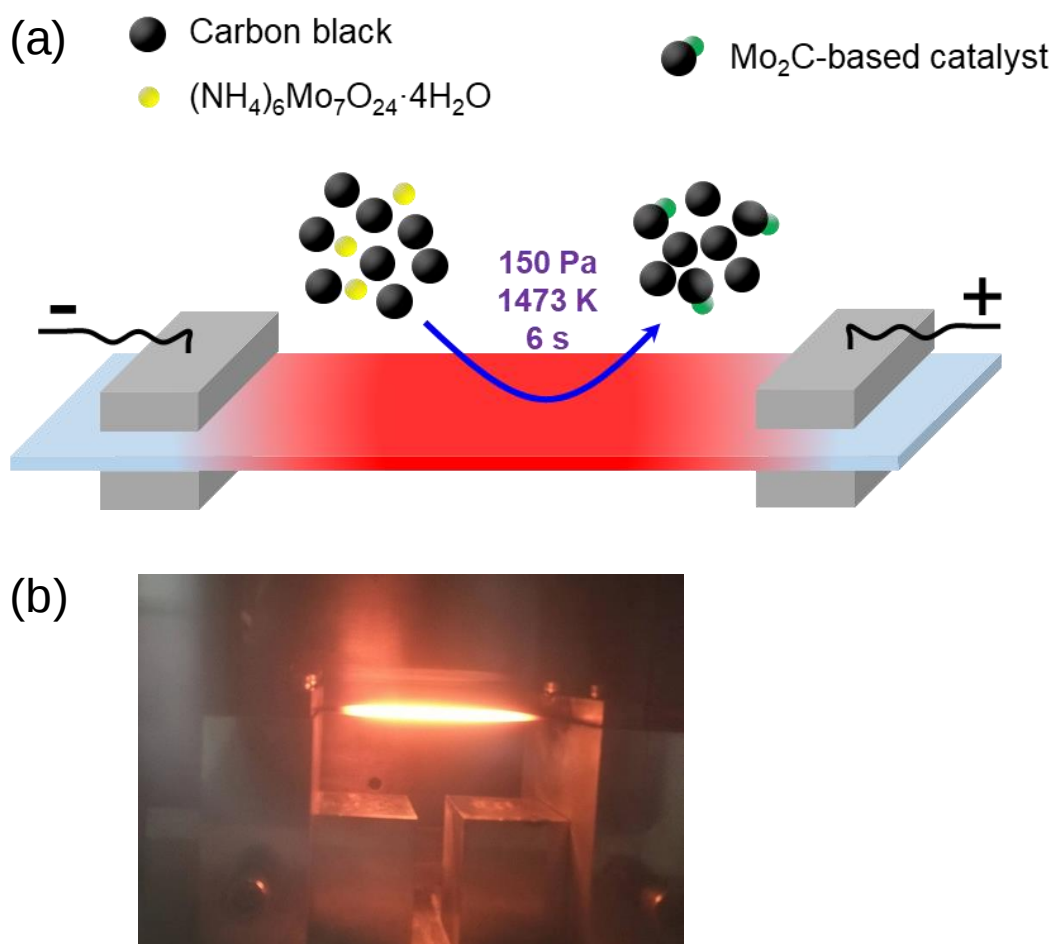


Figure 1. (a) The schematic illustration of the synthesis of the Mo₂C-based catalyst with Joule heating. (b) The picture of the Joule heating system during synthesis.

The crystal structure of the catalyst was analyzed by XRD. As shown in Figure 2a, the XRD pattern of the as-prepared sample displayed a set of diffraction peaks. The broad diffraction peak located at 21° was assigned to CB according to the literature [43]. Other

distinctive diffraction peaks can be well indexed to Mo_2C and Mo, respectively. Therefore, a composite catalyst of Mo_2C and Mo anchored on CB was obtained (denoted as $\text{Mo}_2\text{C-Mo/CB}$). The morphology of the $\text{Mo}_2\text{C-Mo/CB}$ electrocatalyst was investigated by SEM. Figure 2b,c demonstrated that the sample exhibited a nanoparticle morphology with no obvious agglomeration.

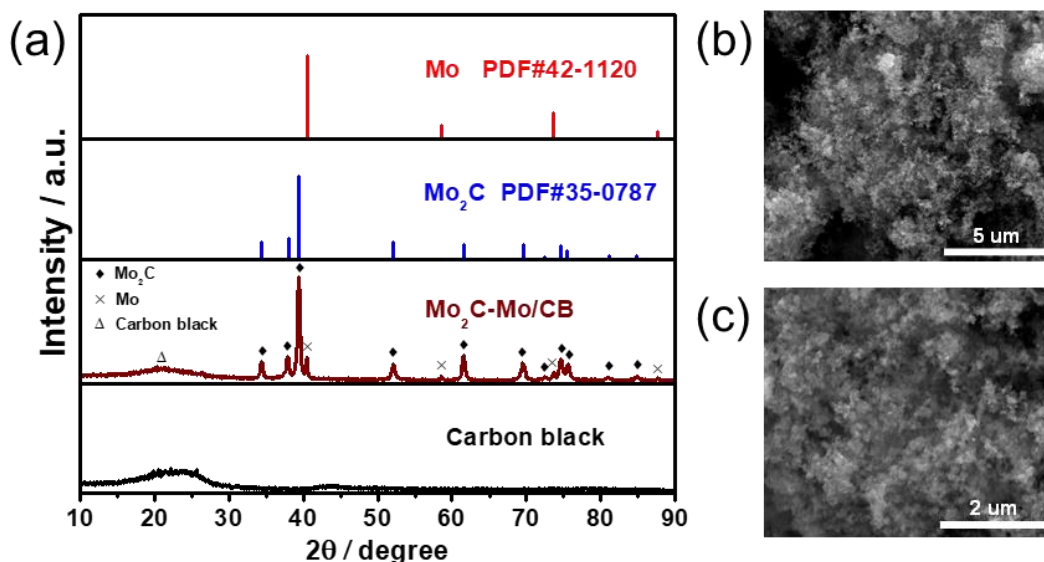


Figure 2. (a) XRD patterns of $\text{Mo}_2\text{C-Mo/CB}$ and carbon black; (b) and (c) SEM images of $\text{Mo}_2\text{C-Mo/CB}$ with different scale bars.

The structures of $\text{Mo}_2\text{C-Mo/CB}$ were further characterized by HRTEM. Figure 3a showed that the $\text{Mo}_2\text{C-Mo}$ nanoparticles were evenly and intimately anchored on the CB surface. Figure 3b exhibited that the average particle size of the $\text{Mo}_2\text{C-Mo}$ nanoparticle was 12 nm. The small particle size indicated rapid nucleation kinetics because of the high temperature provided instantaneously by the Joule heating method [44–46]. As shown in Figure 3c, lattice fringes with an interspace of 0.22 nm and 0.23 nm were observed in the HRTEM image, corresponding to the (110) lattice plane of metallic Mo and the (101) lattice plane of Mo_2C , respectively. Moreover, energy-dispersive spectroscopy (EDS) mapping images revealed the distribution of elemental Mo and C. Figure 3d showed that the Mo and C elements were uniformly distributed over the catalyst particles.

XPS was used to investigate the chemical compositions of the $\text{Mo}_2\text{C-Mo/CB}$. As shown in Figure 4a, there were four chemical states for the Mo, including Mo^{6+} , Mo^{4+} , Mo^{2+} and Mo^0 . Peaks at 228.6 and 231.8 eV can be assigned to the $3d_{5/2}$ and $3d_{3/2}$ of Mo^0 , respectively [47,48]. Peaks located at 228.8 and 232.2 eV can be assigned to the $3d_{5/2}$ and $3d_{3/2}$ of Mo^{2+} , respectively [47,48]. Other peaks can be attributed to Mo^{6+} and Mo^{4+} , respectively [48,49]. As for C, peaks at 284.2 eV (C 1s) and 284.8 eV (C 1s) can be assigned to carbon species of C-Mo and C-C, respectively (Figure 4b) [50,51]. Other peaks can be indexed to carbon species of C-O and O=C-O, respectively [50,51]. According to previous studies [48,52], the presence of higher-valence Mo and C species such as Mo^{6+} , Mo^{4+} , C-O and O=C-O was ascribed to superficial oxidation upon exposure to air. Therefore, these results indicated that the $\text{Mo}_2\text{C-Mo/CB}$ catalyst was successfully synthesized via the present Joule heating method.

The HER performances of the $\text{Mo}_2\text{C-Mo/CB}$ electrocatalyst were evaluated in 0.5 M H_2SO_4 with a three-electrode system. For comparison, the HER performances of bare carbon paper and commercial Mo_2C were also investigated. As shown in Figure 5a, the bare carbon paper demonstrated a negligible cathodic current density. Meanwhile, commercial Mo_2C showed an overpotential of 300 mV to achieve a current density of -8 mA cm^{-2} . In contrast, the $\text{Mo}_2\text{C-Mo/CB}$ exhibited significantly enhanced HER activity, requiring an overpotential of 180 mV to yield a current density of -8 mA cm^{-2} .

Additionally, an impressive current density of $-50 \text{ mA} \cdot \text{cm}^{-2}$ was achieved for the $\text{Mo}_2\text{C-Mo/CB}$ electrocatalyst at an overpotential of 288 mV. The Tafel slope can be calculated from the linear sweep voltammetry curve, which reflects the reaction kinetics [53,54]. As shown in Figure 5b, $\text{Mo}_2\text{C-Mo/CB}$ displayed a smaller Tafel slope (125 mV dec^{-1}) than that of commercial Mo_2C (458 mV dec^{-1}), demonstrating more efficient HER catalytic kinetics of $\text{Mo}_2\text{C-Mo/CB}$. Moreover, the $\text{Mo}_2\text{C-Mo/CB}$ exhibited good stability for HER. After 1000 cycles of cyclic voltammetry, no obvious decrease in current density was observed (Figure 5c). The good stability of $\text{Mo}_2\text{C-Mo/CB}$ was ascribed to the immobilization of the $\text{Mo}_2\text{C-Mo}$ nanoparticle on CB, which can avoid the detachment of the $\text{Mo}_2\text{C-Mo}$ nanoparticle in the HER process. Furthermore, The EIS analysis was employed to investigate the change in charge transfer resistance between the catalyst and electrolyte interface [55,56]. As shown in Figure 5d, the charge transfer resistance of $\text{Mo}_2\text{C-Mo/CB}$ was lower than that of commercial Mo_2C , which indicated that the $\text{Mo}_2\text{C-Mo/CB}$ could act as a facilitator to drastically enhance charge transport kinetics. The lower charge transfer resistance may be attributed to the formation of an efficient charge transfer channel in the $\text{Mo}_2\text{C-Mo/CB}$ electrocatalyst.

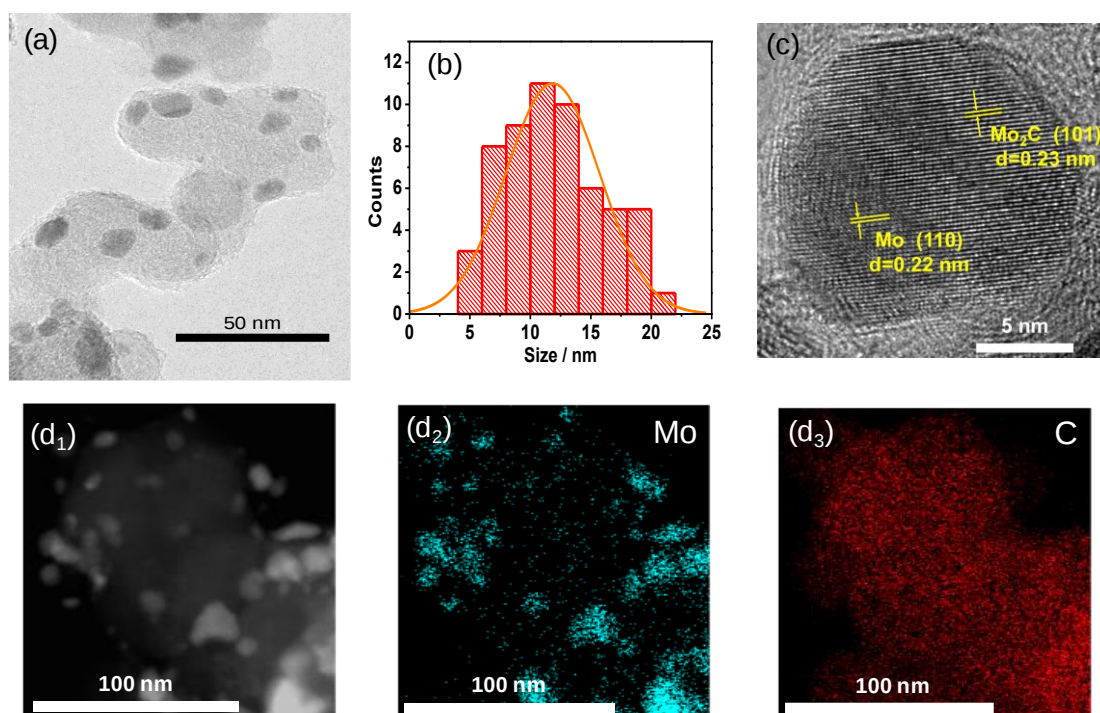


Figure 3. (a) TEM image of the $\text{Mo}_2\text{C-Mo/CB}$ catalyst. (b) The statistics of $\text{Mo}_2\text{C-Mo/CB}$ particle size distribution. (c) HRTEM image of the interface between $\text{Mo}_2\text{C (101)}$ and Mo (110) in $\text{Mo}_2\text{C-Mo/CB}$. (d) EDS mapping of Mo and C elements in $\text{Mo}_2\text{C-Mo/CB}$.

In addition, the double-layer capacitance (C_{dl}) of the electrocatalyst was measured. The electrochemically active surface area (ECSA) is usually related to C_{dl} [57,58]. Figure 6a showed that the capacitance of $\text{Mo}_2\text{C-Mo/CB}$ (49.7 mF cm^{-2}) was higher than that of commercial Mo_2C (9.5 mF cm^{-2}), which indicated that $\text{Mo}_2\text{C-Mo/CB}$ possessed increased ECSA and catalytic active sites for HER. This may be because of the smaller $\text{Mo}_2\text{C-Mo}$ particle size in $\text{Mo}_2\text{C-Mo/CB}$. Furthermore, Figure 6b presents the normalization of the geometric current density with active site concentration at an overpotential of 300 mV. Because of the unknown capacitive behavior (C_s) of the Mo_2C , active site activity* C_s (ASA* C_s) was employed to compare the intrinsic activity [59,60]. The ASA* C_s of $\text{Mo}_2\text{C-Mo/CB}$ was 1.18 mA cm^{-2} , which was larger than that of commercial Mo_2C (0.83 mA cm^{-2}). Therefore, it is reasonable to demonstrate that the good performance of $\text{Mo}_2\text{C-Mo/CB}$ catalyst

is attributed to efficient catalytic kinetics, enhanced charge transport kinetics and high intrinsic activity.

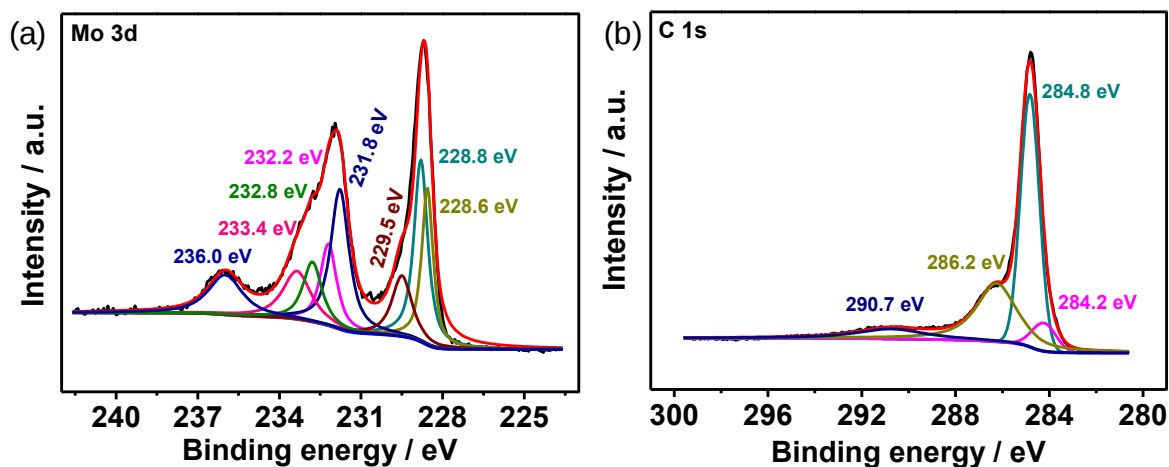


Figure 4. XPS spectra of Mo₂C-Mo/CB. (a) Mo 3d region and (b) C 1s region.

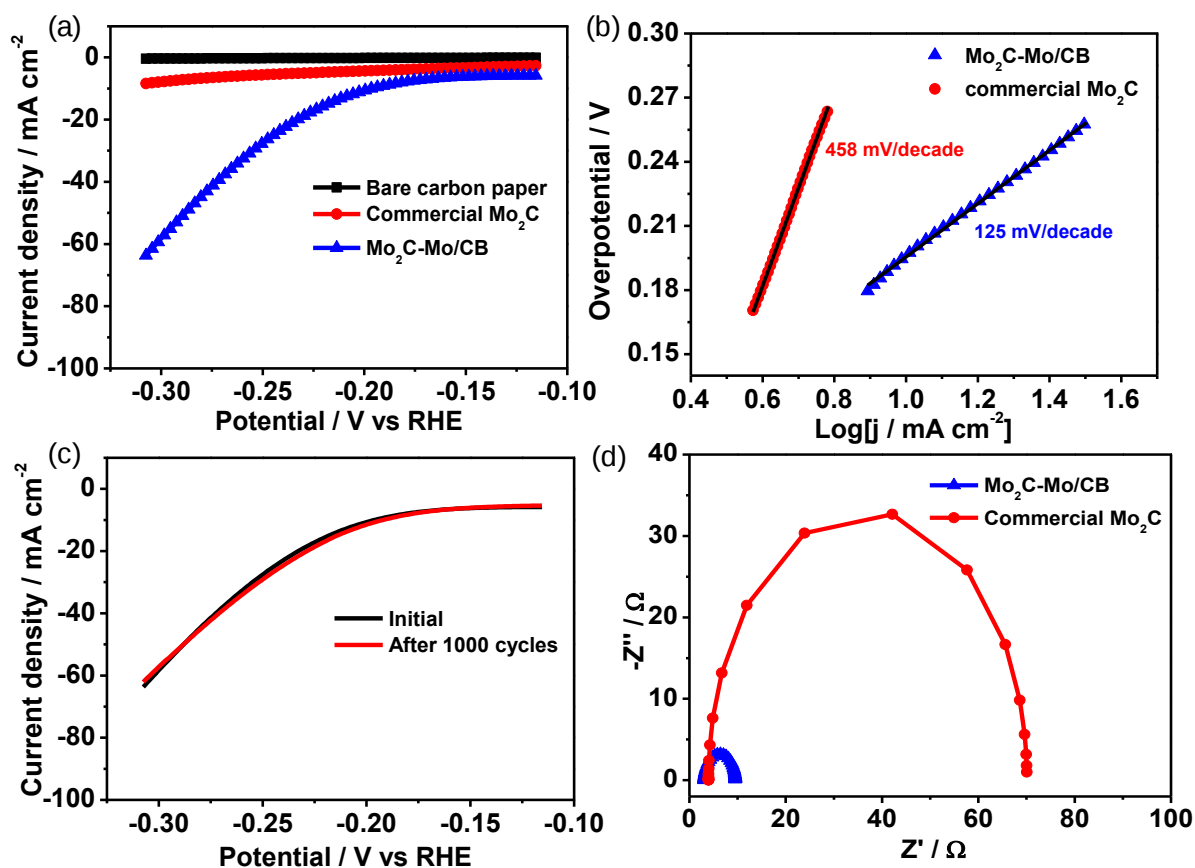


Figure 5. (a) Linear sweep voltammetry curves of bare carbon paper, commercial Mo₂C and Mo₂C-Mo/CB in 0.5 M H₂SO₄ without iR compensation. (b) Tafel plots of commercial Mo₂C and Mo₂C-Mo/CB. (c) Linear sweep voltammetry curves of Mo₂C-Mo/CB before and after 1000 cycles of cyclic voltammetry in 0.5 M H₂SO₄ without iR compensation. (d) Nyquist plots of commercial Mo₂C and Mo₂C-Mo/CB recorded at −0.24 V vs RHE in 0.5 M H₂SO₄.

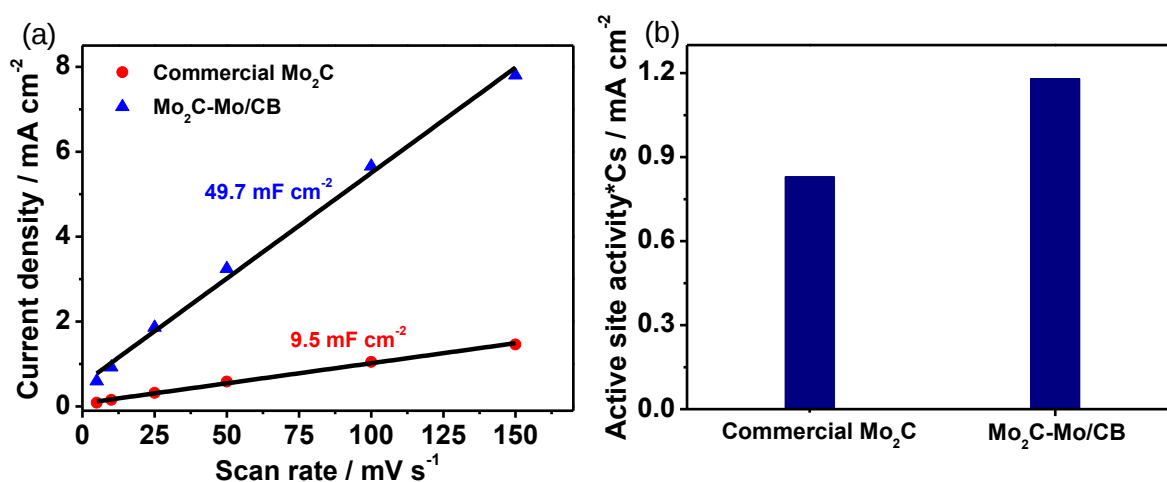


Figure 6. (a) Capacitive current densities of commercial Mo₂C and Mo₂C-Mo/CB plotted against scan rates. (b) Normalization of the geometric current density with active site concentration at an overpotential of 300 mV. Because of the unknown capacitive behavior (Cs) of the Mo₂C, active site activity*Cs was employed to compare the intrinsic activity.

4. Conclusions

In conclusion, we employed an ultrafast Joule heating method to prepare a Mo₂C-Mo/CB electrocatalyst for HER. The reaction was conducted at 1473 K for only 6 s. The Mo₂C-Mo/CB electrocatalyst showed an overpotential of 288 mV to achieve a current density of -50 mA cm^{-2} . Furthermore, after 1000 cycles of cyclic voltammetry, no obvious decrease in current density was observed. The good activity and durability of the Mo₂C-Mo/CB electrocatalyst was due to the favourable catalytic kinetics, decreased charge transport resistance and high intrinsic activity. The earth-abundant nature and good electrochemical performance of Mo₂C-Mo/CB will enable it to be a promising candidate for future electrocatalytic hydrogen evolution driven by renewable energy.

Author Contributions: Conceptualization, X.Z. and W.M.; data curation, H.Z. and S.Q.; investigation, H.Z. and K.Z.; methodology, G.Z.; resources, H.W.; validation, S.Q. and K.Z.; supervision, X.Z. and W.M.; writing—original draft preparation, H.Z. and X.Z.; writing—review and editing, X.Z. and W.M. All authors have read and agreed to the published version of the manuscript.

Funding: This work was Funded by China Postdoctoral Science Foundation (grant number 2021M700651), the Fundamental Research Funds for the Central Universities (grant number 3132022216 and 3132022217).

Data Availability Statement: The data presented in this study are available on request from the corresponding authors.

Conflicts of Interest: The authors declare no conflict of interest.

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