

Facile construction of Mo₂C-MoC heterojunction electrocatalysts for enhanced hydrogen evolution reaction

Xin Hao¹, Jianfeng Huang^{1*} , Liyun Cao^{1*} , Dewei Chu², Faliang Luo³, Haijun Ma³, Yijun Liu⁴, Dongping Wang¹ and Yongqiang Feng^{1*} 

Electrocatalytic decomposition of water represents a viable route for green hydrogen generation, where molybdenum carbide (Mo₂C) serves as a highly active catalytic material toward the cathodic proton reduction process. In this work, a Mo₂C-MoC/NC composite was synthesized via dicyandiamide dosage modulation and high-temperature calcination, with a detailed examination of the influence that dicyandiamide loading exerts upon its architecture and catalytic activity. Results show that the optimized Mo₂C-MoC/NC-0.3 catalyst possesses a loose, porous architecture, which markedly raising both active site population plus accessible interfacial region. Meanwhile, Mo²⁺ along with Mo³⁺ species adjust the electron configuration within this material while decreasing H binding strength, consequently greatly improving HER performance. Within a 1 molar KOH medium, this material demands merely 87 mV to reach 10 mA cm⁻², alongside a Tafel indicator equaling 54.80 mV dec⁻¹, and maintains stable performance over 100 h, demonstrating outstanding catalytic activity and durability. Our findings provide guidance for tuning the phase structure of Mo-based carbides to improve HER performance.

Hheavy reliance on traditional carbon-based energy sources now creates urgent worldwide problems such as climate change, environmental degradation, and the depletion of finite resources, making the transition to green renewable energy a scientific and societal imperative.^[1-3] Hydrogen energy, characterized by its high energy density and environmental compatibility, is emerging as one of the pivotal pathways in the global energy transition.^[4-5] Molecular hydrogen can be produced through a variety of routes including steam methane reforming,^[6] catalytic methane combustion,^[7] the iodine-sulfur thermochemical cycle,^[8] and photoelectrochemical water splitting.^[9,10] Among these, water electrolysis stands out as a green hydrogen-production technology that can be powered by renewable electricity generated from wind, solar, and other sustainable sources.^[11] To enhance energy efficiency and promote faster hydrogen evolution reaction (HER) kinetics, the choice of highly active electrocatalysts is crucial. The metals platinum, ruthenium, and also rhodium are widely re-

garded as top-performing electrocatalysts for HER, owing to their optimal hydrogen adsorption strength, near-zero onset overpotential, and outstanding catalytic activity.^[12-16] But the high expense and limited availability of this material have seriously blocked its commercial application on a large scale. Therefore, the development of alternative electrocatalysts with high activity, excellent stability, now stands as an investigative priority alongside crucial obstacle inside this area during preceding decades.

Molybdenum carbide (Mo_xC), a prototypical transition-metal carbide, has become an ideal alternative candidate for noble metal catalysts due to its electronic structure similar to that of Pt, wide pH tolerance, and exceptional electrical conductivity.^[17-19] However, the densely packed empty d-orbitals of Mo_xC^[20] severely hinder the desorption of the adsorbed hydrogen intermediate (H_{ads}),^[21] consequently resulting in an overly negative hydrogen adsorption free energy. To tackle this challenge, a variety of strategies, namely constructing heterogeneous synergy,^[22,23] introducing heteroatom doping,^[24,25] defect engineering,^[26,27] and morphology modulation,^[28-30] have been investigated in recent years to further improve electrocatalytic performance. There exist four major crystalline configurations for this carbide material, specifically the α -, β -, γ -, and η -polymorphs.^[31] As the most stable, commonly used, and relatively easy-to-synthesize hexagonal close-packed β -Mo₂C catalyst, it has been identified as one of the most electrocatalytically active materials for HER.^[32] Although the synthesis of metastable α -MoC demands more stringent conditions compared to the thermodynamically stable β -Mo₂C, α -MoC exhibits exceptional water-dissociation activity, enabling efficient activation of water molecules and

¹ School of Material Science and Engineering, International S & T Cooperation Foundation of Shaanxi Province, Shaanxi University of Science and Technology, Xi'an, 710021, China

² School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia

³ State Key Laboratory of High-efficiency Coal Utilization and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, 750021, China

⁴ Mona Lisa Group Co. Ltd., Foshan, Guangdong 528211, China

* Corresponding author, E-mail: huangjf@sust.edu.cn; caoliyun@sust.edu.cn; fengyq@sust.edu.cn

Received 3 May 2026; Accepted 10 June 2026; Published online 22 June 2026

the generation of abundant surface hydroxyl species in small-molecule conversion reactions. Hence, fabricating a junction amid α -MoC plus β -Mo₂C might harness mutual coupling benefits toward improved catalytic output for H₂ generation.

The construction of heterojunctions can substantially enhance HER performance by modulating the interfacial electronic structure, facilitating charge transport, and boosting the intrinsic activity of active sites. Nevertheless, studies have demonstrated that the HER performance of single-phase molybdenum carbide-based catalysts is usually constrained. Specifically, Mo₂C catalysts exhibit excessively strong Mo-H binding energy, whereas MoC catalysts possess relatively weak hydrogen binding energy (HBE), a Mo₂C-MoC heterojunction is expected to afford significantly enhanced HER performance. For instance, Hwang et al. fabricated a Mo₂C-MoC composite catalyst on nickel foam, which optimized the hydrogen binding energy to provide abundant active sites while offering a large surface area and high electrical conductivity. Its catalytic behavior rivaled that seen with Pt/C at the 10 mA·cm⁻².^[33] Ren et al. fabricated Mo/Mo₂C heterojunction nanosheets from bulk molybdenum disulfide through a molten salt-assisted strategy. In an alkaline electrolyte, the prepared junction material required merely 280 mV to achieve a large current reaching 500 mA·cm⁻², outperforming the benchmark commercial Pt/C electrode. Fundamental studies indicated a net displacement of negative charges away from Mo atoms heading into Mo₂C domains, plus gradual saturation of its empty antibonding molecular configurations, effectively weakens the M-H bond strength, facilitates H₂O adsorption/desorption processes, and optimizes hydrogen adsorption/desorption behaviors on the in-plane Mo/Mo₂C heterojunction nanosheets, thus accelerating the HER kinetics.^[34] Wang et al. prepared W-incorporated Mo₂C-MoC heterostructures through hydrothermal and annealing processes. The introduction of W increased the conversion of Mo₂C to MoC, resulting in more active sites and improved hydrogen adsorption/desorption properties, which contributed to excellent HER performance.^[35] Wu et al. reported a facile, scalable synthesis of flower-like heterostructures in which transition-metal-doped Mo₂C nanoparticles are anchored on nitrogen-doped carbon nanosheets. The resulting TM-Mo₂C/NC architectures exhibit bifunctional activity, delivering competitive performance for both hydrogen and oxygen evolution.^[36] Yao et al. fabricated Ru clusters combined with Ru single atoms supported on α -MoC_{1-x} encapsulated carbon nanospheres through pyrolysis. The synergistic electronic regulation weakens the Ru-H* binding and accelerates H₂ desorption, and the catalyst achieves a low overpotential of 9 mV at 10 mA cm⁻² for alkaline HER with high utilization of Ru sites.^[37] Tian et al. fabricated RuO_x-Mo₂C cluster-cluster heterostructures to trigger reverse hydrogen spillover via well-defined interfacial coupling, which accelerates alkaline HER kinetics by facilitating directional H* migration. The catalyst achieves 15 mV overpotential at 10 mA cm⁻², and the assembled electrolyzer requires 1.76 V at 1.0 A cm⁻² with superior durability exceeding 1500 h for industrial high-current operation.^[38] Bhattacharjee et al. revealed the structural evolution and surface oxidation behavior of pure Mo₂C and Mo/Mo₂C heterostructures under HER operating conditions. Moderate surface reconstruction optimizes hydrogen adsorp-

tion, yet severe oxidation degrades catalytic activity, demonstrating that self-limited surface oxidation governs the intrinsic HER performance of molybdenum carbide.^[39] These studies together show that tailored molybdenum carbide-based composite structures enable high-performance HER electrocatalysts.

Therefore, the core focus of this work is to synthesize molybdenum carbide-based catalysts with Mo₂C-MoC/NC composite phases via a straightforward one-step calcination approach. By tailoring the dosage of dicyandiamide to modulate the carbon content, the described pathway substantially reduces fusion of molybdenum-based carbide entities under sintering conditions and concurrently accelerates their evolution into an alternative phase arrangement. Experimental results demonstrate that the Mo₂C-MoC/NC-0.3 catalyst, fabricated with 0.3 g of dicyandiamide, exhibits the optimal HER performance. Within a 1 molar KOH medium, this material demands merely 87 mV to reach 10 mA cm⁻², alongside a Tafel indicator equaling 54.80 mV dec⁻¹, while maintaining long-term stability for at least 100 hours. The highly porous framework of this composite yields a sizable accessible surface domain and dense active center distribution, consequently greatly improving the electrochemical conversion efficiency. This work is anticipated to offer fresh perspectives on logically constructing active, durable catalysts for the hydrogen evolution process.

Experimental section

Materials

Molybdenum trioxide (MoO₃), melamine (C₃H₆N₆), dicyandiamide (DCD, C₂H₄N₄), and ethanol (EtOH, CH₃CH₂OH) were all purchased from Guoxun Chemical Reagent Co., Ltd. The 5% Nafion solution was obtained from Sigma-Aldrich. Commercial-grade platinum carbon (20% Pt/C) and potassium hydroxide (KOH, ≥ 85%) were purchased from Shanghai Heshen Electrical Co, Ltd. Throughout the experiment, deionized water with a resistance of 18.25 MΩ·cm was utilized. The chemicals used in this study were all of analytical grade and were applied without further purification, exactly as obtained.

Synthesis of Mo₂C

Firstly, 0.72 g of molybdenum trioxide (MoO₃) and 1.00 g of melamine were weighed and placed in a porcelain mortar for 5 minutes of grinding to ensure complete mixing. Then, the mixed powder was transferred to porcelain and placed in a tube furnace. A homogeneous powder was obtained after thorough grinding of the mixture. Subsequently, this powder was then put into a porcelain boat, heated under Ar to 800 °C at 10 °C·min⁻¹, and held for 2 h at that point for carbonization at high temperature. Upon completion of the reaction, the obtained dark gray product was gathered, namely the carbonized molybdenum (Mo₂C) powder.

Synthesis of Mo₂C-MoC

The Mo₂C-MoC/NC catalysts were prepared via a similar procedure to that of Mo₂C. Briefly, 0.72 g of MoO₃ (5 mmol) and 1.00 g of melamine were weighed, and 0.1 g, 0.3 g, 0.5 g, and 1.0 g of DCD were added as additional carbon sources, respectively. The mixture was thoroughly ground to form a homogeneous powder. The obtained mixture was then

placed in a porcelain boat, heated to 800 °C at a heating rate of 10 °C·min⁻¹ under an Ar atmosphere, and held at this temperature for 2 hours for high-temperature carbonization. After the reaction, the system was naturally cooled to room temperature, and the product was collected and ground into a fine powdered catalyst. According to the added amount of DCD, the as-prepared catalysts were denoted as Mo₂C-MoC/NC-0.1, Mo₂C-MoC/NC-0.3, Mo₂C-MoC/NC-0.5, and Mo₂C-MoC/NC-1.0, respectively.

Material characterization

X-ray diffraction (XRD) patterns were collected using a Rigaku D/max-2500PC diffractometer (Japan) with Cu K α radiation ($\lambda = 1.5418$ Å), and the intensity data were recorded at a scanning rate of 15° min⁻¹. A field-emission scanning electron microscope (FE-SEM, Hitachi S-4800) was used to observe the morphology of the samples. The microstructure and elemental distribution were investigated via transmission electron microscopy (TEM) on an FEI Tecnai G2 F20 S-TWIN microscope equipped with energy-dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific ESCA Lab 250Xi spectrometer using monochromated Al K α radiation (200 W) to determine the chemical and electronic states of the elements.

Electrochemical measurement

Using a CHI660E electrochemical workstation (Chenhua, Shanghai, China) at room temperature, all electrochemical measurements were conducted with a typical three-electrode system. A homogeneous ink was obtained by dispersing 5 mg of catalyst powder into a solution containing 150 μ L of isopropanol and 6 μ L of 5 wt% Nafion, after which ultrasonication was applied for 1 hour. Then 4 μ L of this ink was drop-cast onto a clean glassy carbon electrode (3 mm diameter) and air-dried at room temperature to form the working electrode. In 1 mol/L KOH alkaline electrolyte, the counter electrode was a graphite rod and the reference electrode was a Hg/HgO electrode. Potential conversion to RHE followed $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.059\text{pH}$.^[40] To obtain polarization curves, linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV·s⁻¹, giving the HER performance of the catalysts. All LSV curves and corresponding overpotential data were collected without iR compensation. Electrochemical impedance spectroscopy (EIS) was carried out at the potential giving 10 mA·cm⁻², across a frequency range of 0.1 Hz to 100 kHz. To estimate the electrochemical active surface area (ECSA), cyclic voltammetry (CV) scans were conducted in 1 M KOH within the non-Faradaic region at scan rates of 20, 40, 60, 80, 100, 120 and 140 mV·s⁻¹. The double-layer capacitance (C_{dl}) was extracted from the linear slope of capacitive current as a function of scan rate. The calculation of ECSA followed the formula $\text{ECSA} = C_{\text{dl}}/C_s \cdot S$, wherein S denotes the geometric area of the working electrode, and the standard specific capacitance C_s of 40 $\mu\text{F cm}^{-2}$ was utilized in alkaline media.^[41] Stability evaluation of the catalyst involved 1000 successive CV scans at 100 mV·s⁻¹ combined with simultaneous chronoamperometric recording over an extended period.

Results and discussion

The Mo₂C-MoC/NC composite phase catalyst was success-

fully synthesized via a one-step grinding and sintering method, utilizing DCD as a nitrogen-carbon source and MoO₃ as the molybdenum precursor. An illustrated summary outlining the fabrication steps appears in Fig. 1a. X-ray diffraction measurements served to determine how varying DCD amounts influence the final crystal phase composition within the obtained materials. The structural evolution from single-phase Mo₂C to dual-phase Mo₂C-MoC composites was monitored across a series of Mo₂C-MoC/NC- x materials ($x = 0.1, 0.3, 0.5, 1.0$) with systematically varied DCD concentrations. The XRD pattern of the pure Mo₂C sample is shown in Fig. 1b. The recorded diffractogram displayed nine prominent peaks positioned at 34.4°, 38.0°, 39.4°, 52.1°, 61.5°, 69.6°, 72.4°, 74.6°, and 75.5° on the 2θ axis. These features index perfectly to the (100), (002), (101), (102), (110), (103), (200), (112), together with (201) planes of hexagonal β -Mo₂C, consistent with database entry JCPDS 35-0787.^[33] Examining the XRD profile of Mo₂C-MoC/NC-0.3 revealed that, beyond those reflections assigned to β -Mo₂C, five further peaks were detected at 2θ values equaling 36.4°, 42.3°, 61.3°, 73.4°, along with 77.3°, which match respectively the (111), (200), (220), (311), and (222) crystallographic orientations characteristic of MoC phase, as referenced in standard card JCPDS 65-0280,^[42] confirming the successful formation of the Mo₂C-MoC composite phase. As the amount of DCD added was increased, the phase composition of the molybdenum carbide exhibited a systematic evolution (Fig. 1c-d). For the Mo₂C-MoC/NC-0.1 sample, the pattern was still dominated by the characteristic peaks of Mo₂C; however, weak diffraction peaks corresponding to MoC emerged, indicating the initial formation of the MoC phase. When the DCD addition was increased to 0.5 g (Mo₂C-MoC/NC-0.5), the intensity of the MoC diffraction peak at 36.4° increased significantly, suggesting that MoC gradually became the predominant crystalline phase. Upon a further increase in DCD to 1.0 g (Mo₂C-MoC/NC-1.0), a complete transformation from the Mo₂C phase to the MoC phase was observed. This result indicates that a higher carbon content promotes the complete formation of MoC.

SEM along with TEM imaging served to investigate both surface texture and internal structural details of the prepared catalytic materials. Compared with the Mo₂C, Mo₂C-MoC/NC-0.1, and Mo₂C-MoC/NC-0.5 (Figure S1), Mo₂C-MoC/NC-0.3 delivered a small flower-like multilayer stacked structure (Fig. 2a). The resulting loose and porous structure is expected to enhance HER performance by increasing the specific surface area, improving electrolyte contact, and exposing a greater number of active sites. Furthermore, observation of the microscopic morphology of Mo₂C-MoC/NC-0.3 at different magnifications using TEM revealed that the sample is uniformly dispersed and exhibits a thin sheet-like morphology (Fig. 2b-c), which is advantageous for electrolyte mass transport. HRTEM analysis of the material (Fig. 2d-h) provided direct evidence for its defect structure and phase composition. Fringe separation distances observed within the carbide phase registered at 0.256, 0.234, and 0.227 nm, attributable sequentially to those (100), (002), as well as (101) crystallographic orientations documented for the β -Mo₂C polymorph,^[33] respectively. At the same time, an interplanar distance measuring 0.244 nm appeared in the image, which matches the (111) facet belonging to cubic MoC phase.^[43]

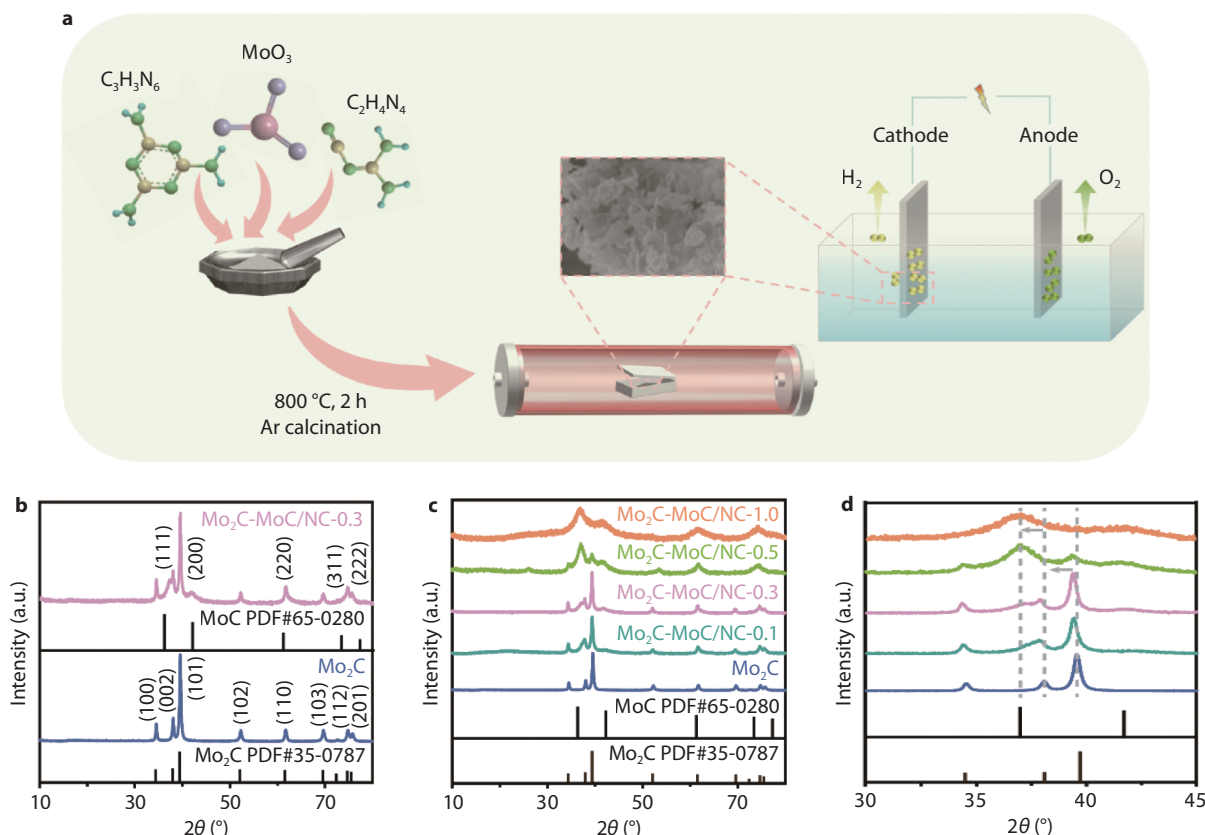


Fig. 1 **a** Schematic illustration of the synthesis process. **b-d** XRD patterns of Mo₂C, Mo₂C-MoC/NC-0.1, Mo₂C-MoC/NC-0.3, Mo₂C-MoC/NC-0.5, Mo₂C-MoC/NC-1.0.

This result directly confirmed the coexistence of Mo₂C and MoC phases in the material, which was mutually corroborated by the XRD analysis results. It can be found in Fig. 2d that there are discontinuous regions in the lattice fringes, indicating the formation of Mo or C vacancy defects. Such defects can increase the density of active sites, regulate the surface charge distribution, and potentially enhance HER performance by optimizing the hydrogen adsorption free energy.^[44,45] Acquired SAED results (provided in Fig. 2i) revealed distinct polycrystalline ring features, readily indexed to the (101) crystallographic orientation of molybdenum carbide (β -Mo₂C) plus the (111) plane of cubic MoC, thus offering supplementary evidence for the coexistence of both phases. Compositional maps derived from EDS mapping (Fig. 2j) verify the even spatial dispersion of C, N, O, and Mo atoms across the entire Mo₂C-MoC/NC-0.3 architecture. Each element was uniformly distributed throughout the sample, with mass fractions of 0.42 wt%, 0.21 wt%, 2.14 wt%, and 97.24 wt%, respectively (Figure S2 and Table S1). Collectively, these results confirm the successful preparation of the Mo₂C-MoC/NC-0.3 catalyst. Its unique porous structure, mixed crystal phase, and defect characteristics provide a robust structural foundation for its electrocatalytic performance.

Employing XPS, a systematic investigation was performed on surface chemical states, elemental composition, and inter-component interactions of the catalysts. Survey spectra displayed in Fig. 3a verify Mo, C, and O are present in both Mo₂C-

MoC/NC-0.3 and Mo₂C, consistent with EDS results. From the high-resolution C 1s spectrum (Fig. 3b), binding energies of 284.8, 285.8, 288.7, and 283.9 eV are characteristic peaks representing C-C/C=C, C-O, O-C=O, and C-Mo bonds, in order. In Fig. 3c, the high-resolution Mo 3d XPS spectrum of Mo₂C shows fitted peaks indicating Mo²⁺, Mo⁴⁺, and Mo⁶⁺ species. The Mo²⁺ species shows characteristic peaks at 228.1 and 231.0 eV (3d_{5/2} and 3d_{3/2}), confirming the existence of the Mo₂C phase.^[46] Meanwhile, peaks at 229.0 and 232.1 eV belong to Mo⁴⁺ and Mo⁶⁺, which is typically due to the partial surface oxidation.^[47] For Mo₂C-MoC/NC-0.3, deconvolution of the Mo 3d spectrum gives four components, including the newly emerged Mo³⁺ species (228.6 eV and 231.4 eV).^[48] This provides direct evidence for the existence of MoC and collectively confirms the formation of the Mo₂C-MoC composite structure. According to the literature, both Mo²⁺ and Mo³⁺ can serve as active centers for electrocatalytic HER. The concentration ratio of these two species can modulate the hydrogen-catalyst interaction; A suitable balance yields moderate surface charge on the catalyst, facilitating adsorbed hydrogen (H*) dissociation and boosting HER kinetics.^[49] Furthermore, compared with Mo₂C, the characteristic peak binding energies of Mo²⁺ (227.3 eV and 230.6 eV), Mo⁴⁺ (228.9 eV and 233.3 eV), and Mo⁶⁺ (231.9 eV and 234.7 eV) in Mo₂C-MoC/NC-0.3 exhibit a significant negative shift. This phenomenon indicates an increased electron density around Mo atoms, leading to a rearrangement of surface charge distribution and op-

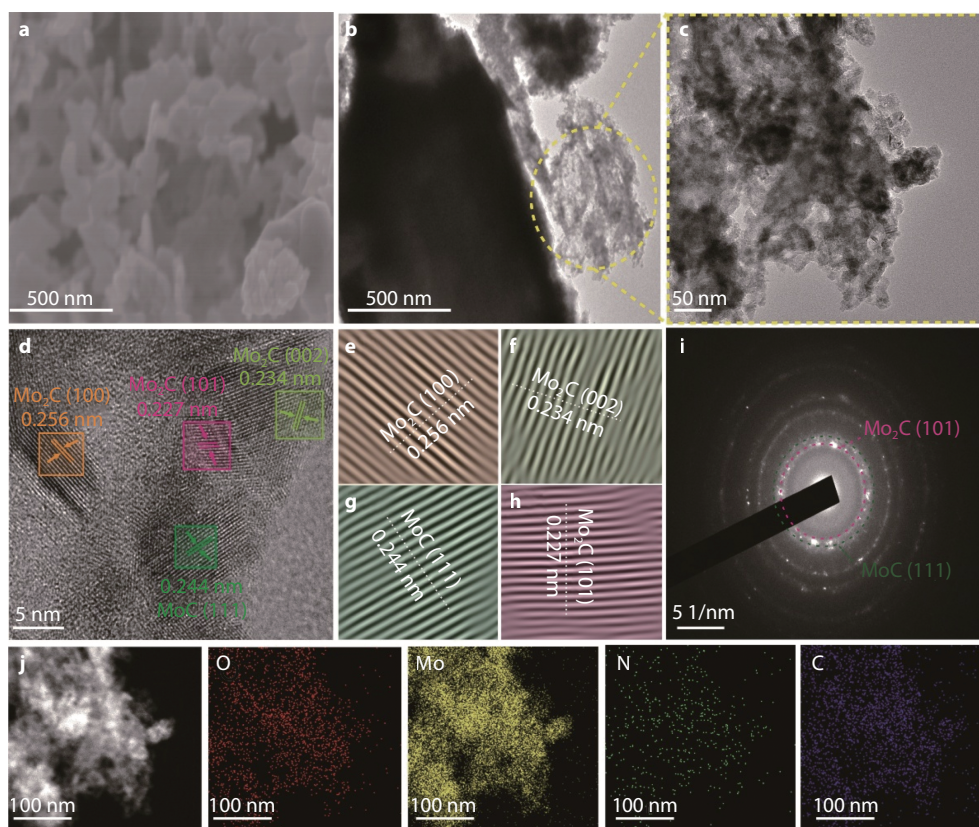


Fig. 2 **a** SEM, **b, c** TEM, **d-i** HRTEM and the corresponding SAED pattern, and **j** TEM image and the corresponding EDS elemental mapping of the synthesized Mo₂C-MoC/NC-0.3.

timization of the electronic configuration. Such efficient electron transfer enhances the synergistic effect between Mo₂C and MoC, thereby facilitating the desorption of adsorbed H* during the HER and accelerating the reaction kinetics. The O 1s XPS spectrum (Fig. 3d) shows that the binding energies at 531.0 eV and 532.5 eV respectively belong to the Mo₂Co_x and Mo₂C(OH)_x species, which are the C-O/C=O bonds and the O-H bonds in the physical or chemical adsorbed water near the surface.^[50,51] In the Mo₂C-MoC/NC-0.3 sample, the binding energies of the two characteristic peaks are 530.1 eV and 531.6 eV, with negative shifts relative to Mo₂C. Combined with TEM and XRD characterization, it is confirmed that a unique composite structure has formed between Mo₂C and MoC, which provides abundant active sites and a synergistic electron effect, jointly endowing the material with excellent HER performance.

Fig. 4a shows that different catalysts' HER performance was measured in 1 M KOH with a conventional three-electrode system. A more intuitive presentation of the 10 mA cm⁻² overpotentials for various samples is provided by the bar graph in Fig. 4b. Mo₂C-MoC/NC-0.3 needed a mere 87 mV for 10 mA cm⁻² relative to all examined samples. Far below the values for Mo₂C-MoC/NC-0.1 (137 mV), Mo₂C-MoC/NC-0.5 (125 mV), and pristine Mo₂C (151 mV), this figure is nevertheless above that recorded for commercial 20% Pt/C (40 mV). The results emphasize the crucial role of DCD in optimizing catalytic performance. Tafel analysis provided further insight into the reaction mechanism (Fig. 4c). The Tafel slope for

Mo₂C-MoC/NC-0.3 was calculated to be 54.80 mV dec⁻¹. Meanwhile, Mo₂C, Mo₂C-MoC/NC-0.1, Mo₂C-MoC/NC-0.5, and 20% Pt/C gave slopes of 103.78, 82.22, 73.56, and 40.66 mV dec⁻¹ in order. It is known from prior work that slopes of roughly 30, 40, and 120 mV dec⁻¹ are indicative of the Tafel, Heyrovsky, and Volmer mechanisms when each acts as the HER's rate-determining step.^[52] Based on the obtained value suggests Mo₂C-MoC/NC-0.3 operates through a Volmer-Heyrovsky route for HER. This catalyst has a reduced Tafel slope versus other molybdenum carbide systems, suggesting quicker reaction rates. As shown in Fig. 4d, EIS and equivalent circuit fitting results indicated Mo₂C-MoC/NC-0.3 achieved the minimal R_{ct} (43.74 Ω), which was significantly lower than that of Mo₂C (153.7 Ω), Mo₂C-MoC/NC-0.1 (111.1 Ω), and Mo₂C-MoC/NC-0.5 (80.27 Ω), but higher than that of commercial 20% Pt/C (19.64 Ω). This result confirms that the Mo₂C-MoC/NC composite structure effectively reduces the interfacial charge transfer resistance, thereby enhancing electron transport capability and HER kinetics. Using CV in the non-Faradaic region (Figure S3), the C_{dl} was measured to estimate the electrochemical active surface area. As illustrated in Fig. 4e, Mo₂C-MoC/NC-0.3 showed the largest C_{dl} of 71.71 mF cm⁻², far exceeding Mo₂C (5.17 mF cm⁻²), Mo₂C-MoC/NC-0.1 (28.27 mF cm⁻²), Mo₂C-MoC/NC-0.5 (51.54 mF cm⁻²), and commercial 20% Pt/C (51.74 mF cm⁻²). Chronoamperometric measurements were used to evaluate the operational durability of Mo₂C-MoC/NC-0.3 under 1 M KOH conditions. To separate the influences of accessible active site quantity and

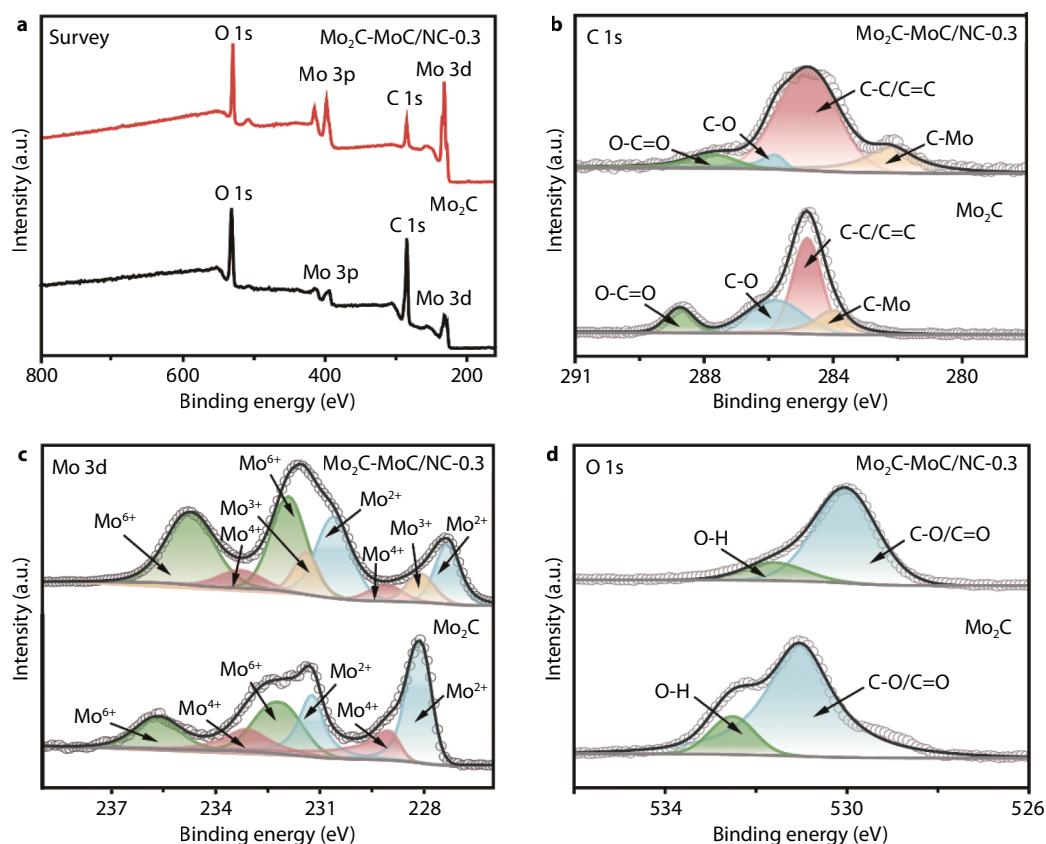


Fig. 3 a Experimental XPS spectrum of Mo₂C-MoC/NC-0.3. High-resolution XPS profiles of b C 1s c Mo 3d and d O 1s for Mo₂C-MoC/NC-0.3.

single-site intrinsic activity on hydrogen evolution performance, electrochemical active surface area (ECSA) for all catalysts is calculated using double-layer capacitance (C_{dl}). Subsequent ECSA normalization of LSV curves is implemented for intrinsic activity evaluation. As presented in Figure S4(a), the Mo₂C-MoC/NC-0.3 catalyst displays the largest ECSA of 128.00 cm², substantially surpassing those of the reference samples, which unambiguously indicates its most abundant accessible catalytic sites. After ECSA normalization (Figure S4(b)), the variation in site density is effectively excluded, and the normalized polarization curves follow the same trend as Fig. 4a, confirming the remarkably high intrinsic activity of each active site in the optimized catalyst. As shown in Fig. 4f, a constant current was maintained by the catalyst for 100 h at 25 mA cm⁻², where only slight deterioration appeared over the prolonged period. Its long-term electrochemical stability was further corroborated by cyclic voltammetry. Figure S5 reveals that comparing the curves before and after 1000 CV cycles yielded no notable decay in catalytic activity. To gain deeper insight into its robustness, post-stability characterizations were performed using SEM, TEM, and XPS (Figures S6 and S7). These analyses collectively confirmed that the structural integrity and morphology of Mo₂C-MoC/NC-0.3 were well-preserved after prolonged electrolysis. To fully gauge how well Mo₂C-MoC/NC-0.3 catalyzes, it was benchmarked with other previously reported ones. As shown in Fig. 4g and Table S2, Mo₂C-MoC/NC-0.3 exhibits significant performance advantages. These results firmly establish Mo₂C-MoC/NC-0.3 as a

highly promising candidate for practical alkaline water electrolysis.

Conclusions

In summary, this study successfully constructed a Mo₂C-MoC/NC composite electrocatalyst by introducing dicyandiamide as the carbon and nitrogen source combined with high-temperature sintering. This strategy effectively inhibits particle agglomeration during the carbonization process, yields a loose and porous morphology, and induces the formation of a new crystalline phase. The synergistic effect between the two phases significantly enhances the material's electrocatalytic performance. In 1 M KOH electrolyte, the optimized Mo₂C-MoC/NC-0.3 catalyst only requires an overpotential of 87 mV to achieve a current density of 10 mA cm⁻², with a Tafel slope of 54.80 mV dec⁻¹. Furthermore, it exhibits excellent stability during a 100 h continuous operation test, and its comprehensive performance is superior to that of other comparative samples. The findings here offer useful guidance for creating high-activity, high-stability Mo-based carbide HER electrocatalysts via phase structure engineering.

■ ASSOCIATED CONTENT

The following files are available free of charge.

Additional SEM, TEM, LSV, CV, XPS profiles are shown in electronic Supporting Information(PDF).

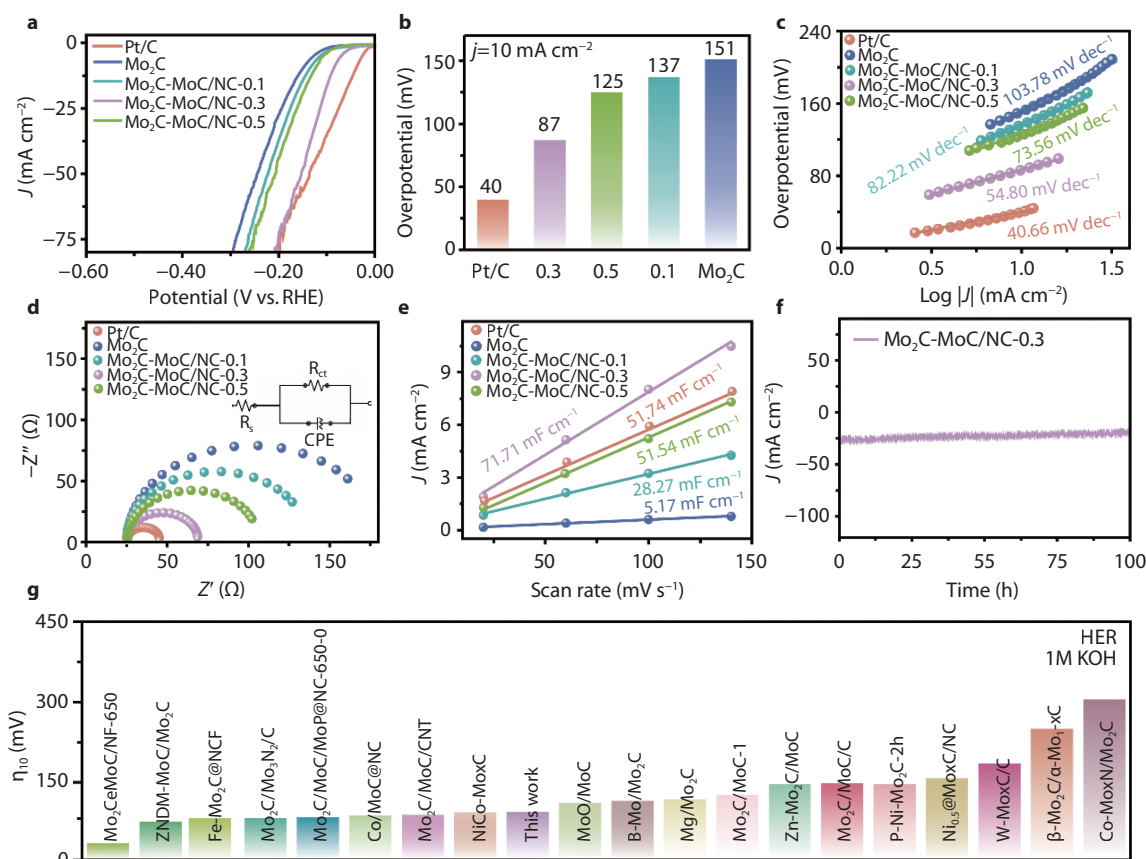


Fig. 4 a LSV curves, b Overpotential, c Tafel plots, d Nyquist plots of Mo₂C, Mo₂C-MoC/NC-0.1, Mo₂C-MoC/NC-0.3, Mo₂C-MoC/NC-0.5, and Pt/C, the inset in e showing the corresponding equivalent circuit diagrams (R_s: electrolyte resistance, R_{ct}: charge transfer resistance, CPE: constant-phase element), e Current density difference against scan rate, and f i - t curve of as-prepared Mo₂C-MoC/NC-0.3 at 25 mA cm⁻² in 1 M KOH. g Comparison of η_{10} for Mo₂C-MoC/NC-0.3 with the recently reported Mo₂C-based HER electrocatalysts.

AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

NOTES

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No. 52572110, U22A20144, 52572048), International S&T Cooperation Foundation of Shaanxi Province (2025GH-GHJD-002), Open Foundation of Guangdong Province Key Laboratory for Large-sized Ceramic Tile (kFkT2026001), Scientific Research Innovation Capability Support Project for Young Faculty (SRICSPYF-BS2025053).

REFERENCES

1. A. Kazemi, F. Manteghi, Z. Tehrani, *ACS omega*, 2024, 9, 7310-7335
2. Y. Q. Dou, A. J. Wang, L. Zhao, X. Yang, Q. Wang, M. S. Sudi, W. H.

- Zhu, D. H. Shang, *J. Colloid Interface Sci.*, 2023, 650, 943-950
3. Y. Chen, X. Q. Chen, M. P. Chen, H. C. Sun, T. W. He, D. Q. Li, G. H. Na, Y. W. Wu, G. Y. Qiu, T. Zhou, *Chin. Chem. Lett.*, 2025, 1, 111813
4. Q. Zhang, P. C. Liu, W. X. Liu, Z. W. Wang, J. He, G. Z. Hu, X. J. Liu, *Energy Lab*, 2025, 3, 250009
5. J. Chi, H. M. Yu, *Chin. J. Catal.*, 2018, 39, 390-394
6. A. Alipour-Dehkordi, S. J. Neek, A. Shahnazar, *J. Ind. Eng. Chem.*, 2022, 113, 264-274
7. T. Uehara, M. Asahara, T. Miyasaka, *Energies*, 2024, 17, 367
8. M. Y. Zhao, Z. Ying, Y. B. Chen, X. Xie, X. Y. Zheng, *J. Environ. Chem. Eng.*, 2025, 1, 118754
9. J. Mohammed, E. R. Elsharkawy, S. M. El-Bahy, H. Y. Hafeez, R. Musa, S. Idris, S. Maikudi, Z. M. El-Bahy, *Mater. Today Sustain.*, 2025, 1, 101227
10. Y. R. Qi, J. F. Huang, L. Y. Cao, X. G. Kong, L. L. Feng, H. J. Ma, F. L. Luo, Q. Q. Liu, Y. Wang, W. C. Li, *J. Power Sources*, 2026, 666, 239176
11. X. R. Zhao, M. Q. Che, Y. Q. Gong, *Sustain. Mater. Technol.*, 2025, 43, e01302
12. Q. Li, W. Y. Cheng, C. Zeng, X. F. Zheng, L. M. Sun, Q. Jiang, Y. You, *Int. J. Hydrogen Energy*, 2022, 47, 7504-7510
13. M. Y. Ma, W. Xia, X. Y. Guo, W. H. Liu, D. Cao, D. J. Cheng, *Small Struct.*, 2024, 5, 2300284
14. X. Xie, Y. X. Fan, W. Y. Tian, M. Zhang, J. Cai, X. G. Zhang, J. Ding, Y. S. Liu, S. Y. Lu, *J. Energy Chem.*, 2023, 83, 150-157
15. S. L. Liu, S. L. Yin, L. Cui, H. J. Yu, K. Deng, Z. Q. Wang, Y. Xu, L. Wang, H. J. Wang, *Energy Lab*, 2023, 1, 220005

16. J. R. Kitchin, J. K. Nørskov, M. A. Barteau, J. G. Chen, *Catal. Today*, 2005, 105, 66-73
17. J. W. Ma, T. A. Zhang, F. S. Yin, J. Wang, Z. J. Zhang, C. W. Sun, *J. Colloid Interface Sci.*, 2023, 650, 506-514
18. K. Chen, Y. X. Zhu, Z. J. Huang, B. Han, Q. C. Xu, X. L. Fang, J. Xu, *ACS nano*, 2024, 18, 34791-34802
19. T. T. Gu, R. J. Sa, L. J. Zhang, F. Zhou, R. H. Wang, X. J. Li, *J. Mater. Chem.*, 2020, 8, 20429-20435
20. P. Guo, M. H. Wang, Y. Z. Zhang, Y. J. Wang, X. Xin, R. L. Wang, W. J. Huang, X. H. Li, *Appl. Surf. Sci.*, 2023, 625, 157169
21. S. S. Yuan, M. S. Xia, Z. P. Liu, K. W. Wang, L. J. Xiang, G. Q. Huang, J. Y. Zhang, N. Li, *Chem. Eng. J.*, 2022, 430, 132697
22. H. Q. Chang, G. H. Zhang, K. C. Chou, *Electrochim. Acta*, 2021, 394, 139119
23. J. C. Li, R. Y. Ge, P. P. Lan, J. Yang, J. Feng, Y. Li, S. Li, B. Liu, W. X. Li, *J. Mater. Chem. A*, 2022, 10, 10493-10502
24. L. T. Li, Z. Y. Chen, J. J. Zheng, F. M. Zhao, Y. H. Zhu, H. J. Zheng, Y. Q. Chu, *J. Power Sources*, 2025, 643, 237030
25. Y. F. Ma, M. Chen, H. B. Geng, H. F. Dong, P. Wu, X. M. Li, G. Q. Guan, T. J. Wang, *Adv. Funct. Mater.*, 2020, 30, 2000561
26. X. Y. Zhang, T. T. Zhao, L. K. Yan, Z. M. Su, *Phys. Chem. Chem. Phys.*, 2023, 25, 12371-12378
27. Q. Q. Jing, J. H. Zhu, X. R. Wei, Y. Q. Lin, X. N. Wang, Z. X. Wu, *J. Colloid Interface Sci.*, 2021, 602, 520-533
28. X. Yang, J. Cheng, X. Yang, Y. Xu, W. F. Sun, J. H. Zhou, *Chem. Eng. J.*, 2023, 451, 138977
29. H. Wang, F. S. Xiao, *Joule*, 2025, 9, 101918
30. C. Wan, Y. N. Regmi, B. M. Leonard, *Angew. Chem. Int. Ed.*, 2014, 126, 6525-6528
31. P. Chithaiah, C. Rao, *Chem. Mater.*, 2025, 37, 8252-8260
32. N. Wazzan, *Polyhedron*, 2025, 275, 117522
33. J. Y. Hwang, J. Y. Kim, D. H. Youn, *Int. J. Hydrogen Energy*, 2024, 49, 58-66
34. Y. L. Ren, R. Huo, X. L. Li, H. Song, X. M. Zhang, B. Gao, P. K. Chu, K. F. Huo, *J. Colloid Interface Sci.*, 2025, 691, 137400
35. Q. T. Wang, F. F. Mi, J. Li, Y. X. Wu, X. Z. Zhou, G. F. Ma, S. F. Ren, *Electrochim. Acta*, 2021, 370, 137796
36. F. Wu, F. Zhong, W. L. Kong, L. Zou, F. Q. Yu, *J. Power Sources*, 2025, 660, 238506
37. J. X. Yao, J. Wang, W. Wang, H. F. Xu, D. M. Chen, G. Li, Z. Jin, *Adv. Mater.*, 2025, 38, 19840
38. D. Tian, J. Yan, L. Yang, T. Liu, Z. Ni, S. Sun, A. Chen, H. Zhang, *Adv. Energy Mater.*, 2026, 16, 71275
39. P. J. Gogoi, C. Alex, S. Ram, N. N. Rao, M. S. N. Kovilakath, S. -C. Lee, S. Bhattacharjee, N. S. John, *Mater. Horiz.*, 2026, 13, 4643
40. X. M. Huo, J. F. Huang, M. T. Gao, W. J. Zhu, W. W. Liu, Q. Q. Liu, L. Y. Cao, K. Kajiyoshi, Y. Zhao, Y. J. Liu, *ACS Appl. Energy Mater.*, 2024, 7, 2862-2871
41. L. Wu, J. P. Hofmann, *ACS Energy Lett.*, 2021, 6, 2619-2625
42. R. A. Mir, S. Upadhyay, N. Kaur, O. P. Pandey, *J. Phys. : Conf. Ser.*, 2022, 2267, 012118
43. Y. X. Ji, W. Y. Zhang, J. R. Xue, J. Y. Zhang, Y. P. Ge, N. Zhu, R. B. Jiang, Z. B. Lei, Z. H. Liu, J. Sun, *New Carbon Mater.*, 2026, 41, 109-125
44. C. Huang, X. W. Miao, C. R. Pi, B. Gao, X. Zhang, P. Qin, K. F. Huo, X. Peng, P. K. Chu, *Nano Energy*, 2019, 60, 520-526
45. F. Li, X. L. Zhao, J. Mahmood, M. S. Okyay, S. M. Jung, I. Ahmad, S. J. Kim, G. F. Han, N. Park, J. B. Baek, *ACS nano*, 2017, 11, 7527-7533
46. J. T. Ren, L. Chen, D. D. Yang, Z. Y. Yuan, *Appl. Catal. B-Environ.*, 2020, 263, 118352
47. J. Wan, J. B. Wu, X. Gao, T. Q. Li, Z. M. Hu, H. M. Yu, L. Huang, *Adv. Funct. Mater.*, 2017, 27, 1703933
48. Y. L. Liu, X. H. Luo, C. L. Zhou, S. Du, D. S. Zhen, B. Chen, J. Li, Q. Wu, Y. Iru, D. C. Chen, *Appl. Catal. B-Environ.*, 2020, 260, 118197
49. X. Zou, H. T. Tang, J. Z. Li, G. C. Gao, Z. B. Geng, L. P. Li, G. S. Li, *Int. J. Hydrogen Energy*, 2024, 79, 525-536
50. M. X. Li, Y. Zhu, H. Y. Wang, C. Wang, N. Pinna, X. F. Lu, *Adv. Energy Mater.*, 2019, 9, 1803185
51. Z. K. Kou, L. Zhang, Y. Y. Ma, X. M. Liu, W. J. Zang, J. Zhang, S. Z. Huang, Y. H. Du, A. K. Cheetham, J. Wang, *Appl. Catal. B-Environ.*, 2019, 243, 678-685
52. W. Xu, X. Q. Tang, Z. Zhang, Y. R. Wang, J. L. Luo, I. Bulugu, W. J. Yin, X. Tang, Y. Shen, *Fuel*, 2024, 358, 130174



©2026 The Authors. *Energy Lab* is published by Lab Academic Press. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.