

RESEARCH ARTICLE

Hydrogen evolution and pollutant purification over NiMoO₄/Twinned Mn_{0.5}Cd_{0.5}S mediated by ·OH radicals in alkaline media^①

Zhuonan Lei^a, Wenhua Xue^b, Haijiao Xie^c, Tao Sun^a, Enzhou Liu^{a,*}

a. School of Chemical Engineering/Shaanxi Key Laboratory for Carbon Neutral Technology, Northwest University, Xi'an 710069, P. R. China

b. Research Center for Eco-Environmental Engineering, Dongguan University of Technology, Dongguan, Guangdong 523808, China

c. Hangzhou Yanqu Information Technology Co., Ltd., Hangzhou 310003, China

ABSTRACT: Employing photocatalysis for water splitting to generate hydrogen (H₂) is regarded as a highly viable strategy for attaining green and efficient H₂ production. However, photocatalysis faces significant challenges in charge separation and instability. Notably, sulfide-based photocatalysts are often severely limited by photocorrosion issues. In this work, we employed a NiMoO₄/twinned Mn_{0.5}Cd_{0.5}S (NiMoO₄/T-MCS) heterojunction as a model catalyst. By modulating the alkalinity of the aqueous solution to promote rapid consumption of photogenerated holes (h⁺), the surface reaction kinetics was greatly enhanced, achieving an exceptional H₂ evolution rate (r_{H₂}) of 28.22 mmol·g⁻¹·h⁻¹ in 4 M NaOH solution. The external NaOH facilitates the water oxidation half-reaction, preferentially consuming photogenerated h⁺ to generate ·OH radicals. This process triggers surface hydroxylation, significantly boosting both catalytic activity and stability. Furthermore, the generated ·OH radicals effectively degrade methylene blue (MB). Critically, the substantially enhanced surface reaction efficiency—particularly the rapid consumption of photogenerated h⁺—dramatically improves the system's operational stability. This study demonstrates concurrent H₂ production and pollutant purification solely through solution modulation, alongside a significant enhancement in system efficiency.

KEYWORDS: Twinned Mn_{0.5}Cd_{0.5}S, Homo-heterojunctions, NiMoO₄, Double S-scheme, ·OH Radicals, Alkaline Media

Highlights

- [1]. Efficient photocatalytic H₂ evolution was achieved on NiMoO₄/T-MCS in NaOH solution.
- [2]. NaOH can facilitate the water oxidation half-reaction to generate ·OH for MB degradation.
- [3]. Surface hydroxylation can enhance the activity and stability of sulfide-based photocatalysts.
- [4]. Dual S-scheme NiMoO₄/T-MCS maximizes redox capacity and enhances charge utilization.

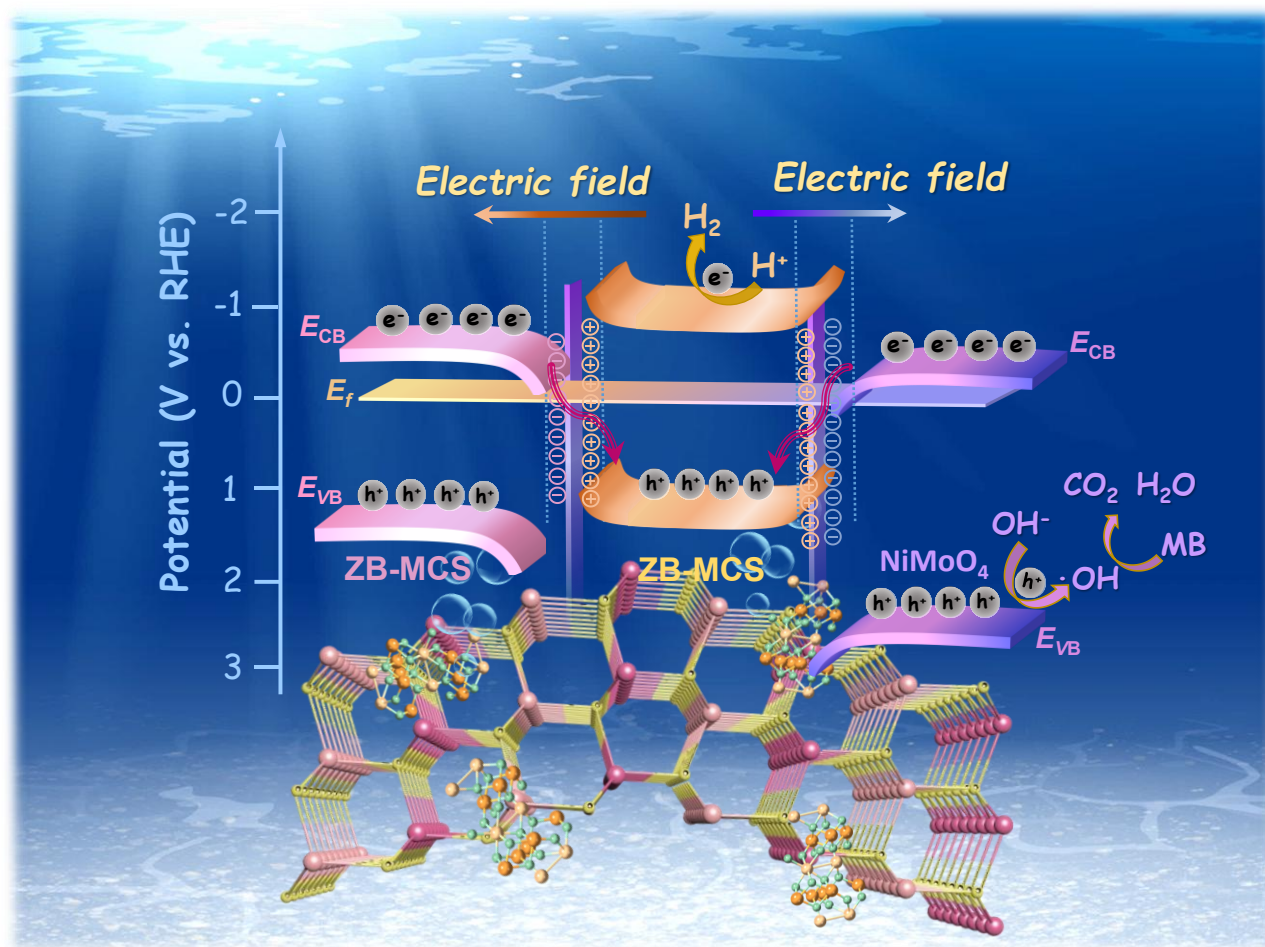
Received: April 19, 2026. Revised: July 5, 2026. Accepted: July 5, 2026. Available online: July 15, 2026

*Corresponding author: liuenzhou@nwu.edu.cn (Enzhou Liu)

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Graphical abstract



The NiMoO₄/T-Mn_{0.5}Cd_{0.5}S system demonstrates a double S-scheme charge transfer pathway, maximizing the redox capacity and facilitating the migration and utilization of charges.

1. Introduction

As a key component of the global energy transition, H₂ energy has gained widespread application across multiple domains, driven by its high energy density, carbon-free emission profile, and flexible energy storage capabilities [1-4]. It is anticipated to serve as the ultimate energy source for facilitating green and low-carbon transformation. Nevertheless, conventional industrial H₂ production methods fall short in achieving the desired level of carbon neutrality. In this context, powered by solar energy, the technology of photocatalytic water splitting presents a more practical solution to attain green and efficient H₂ production. Unfortunately, this process still faces two primary challenges: the high cost

and the sluggish surface reaction kinetics [5-8]. These two issues are intricately interconnected, thereby limiting the practicality of the H₂ production process.

Particularly, the current studies generally utilize Na₂S/Na₂SO₃ [9], organic alcohols [10], and lactic acid [11], etc. as sacrificial agents to consume h⁺ for simultaneously suppressing charge recombination and enhancing surface reaction. The continuous consumption of these reagents not only incurs considerable costs, but also the disposal of the by-products generated by the catalysts often leads to secondary environmental pollution [12-14]. Therefore, it is particularly significant to rationally design the reaction system to developing dual-functional systems for simultaneous H₂ evolution and other applications such

as pollutant purification.

Among various materials, sulfides exhibit high application potential but face challenges of charge recombination and photocorrosion [15-18]. Recently, researchers have increasingly focused on promising sulfides solid-solution [19-21], for example, twinned $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ (T-ZCS) [22] and $\text{Mn}_{0.5}\text{Cd}_{0.5}\text{S}$ (T-MCS) [23] share a unique architecture, the Wurtzite (WZ) and Zinc blende (ZB) crystal planes are periodically arranged where the built-in electric field at the twin boundaries with interlaced energy band structures provides an effective driving force for the transfer of the bulk carriers, endowing them excellent activity comparing with other materials.

However, sulfides solid-solution catalysts still suffer from unresolved photocorrosion. To mitigate these issues, researchers have implemented several strategies, such as co-catalysts loading [24], doping [25], heterojunction constructing [26], recrystallization [27], and surface modification with protective layers [28], thereby enhancing both the activity and photostability of the photocatalysts. Notably, photocorrosion stems from the failure to promptly consume photogenerated h^+ migrating to the catalyst surface, indicating an intricate link between photocorrosion and surface reactions. Previous research has predominantly focused on surface charge separation, while strategies to facilitate rapid consumption of photogenerated h^+ have received comparatively less attention [29].

Interestingly, recent studies also demonstrated that the activity and photocorrosion behavior of photocatalysts are closely associated with the solution environment, including various electrolytes [30-31] and pH [32]. For example, Davis *et al.* explored how pH correlates with the photolytic oxidation and dissolution of CdS, tracking the concentration of Cd^{2+} ions in the solution throughout the process (as shown in the reaction: $\text{CdS} + 2\text{h}^+ \rightarrow \text{Cd}^{2+} + \text{S}$). At low pH values, the dissolution of CdS is at its maximum, resulting in a high concentration of Cd^{2+} in the solution. In contrast, the reaction solution at high pH values inhibits the corrosion of the photocatalyst and prevents the leaching of Cd^{2+} [33-34]. Further, our works have observed an effective hole's transfer powered by $\cdot\text{OH}/\text{OH}^-$ in an alkaline medium, this enhancement is primarily due to the mobility of the redox couple within the alkaline solution as well as the rapid water dissociation kinetics [35]. These previous reports motivate further construction of a dual-functional reaction system utilizing the $\cdot\text{OH}/\text{OH}^-$ redox couple for pollutant MB treatment. This approach offers multiple advantages: 1) elimination of costly sacrificial agents, reducing operational expenses; 2) simultaneous achievement of

efficient H_2 production and pollutant MB purification, enhancing practical applicability; 3) effective utilization of in-situ generated hydroxyl radicals, which accelerate surface reactions and enable photocorrosion inhibition.

However, how to further promote surface carrier separation still requires attention. Building on the above rationale, this work employed T-MCS as the substrate and further deposited NiMoO_4 to construct an S-scheme heterojunction that promotes surface-directed separation of photogenerated carriers. NiMoO_4 was chosen for its favorable band alignment with T-MCS to enable S-scheme charge separation, high HER activity to boost reaction kinetics, and good stability to suppress photocorrosion. Furthermore, NiMoO_4 is composed by a common edge-sharing connection between $[\text{NiO}_6]$ octahedron and $[\text{MoO}_4]$ tetrahedron, forming an open-framework architecture, which serves as a unique electronic structure and multiple active centers for H^+ adsorption [36-38].

By further introducing NaOH into the aqueous reaction system to modulate alkalinity, this work realizes concurrent high-efficiency photocatalytic H_2 production and methylene blue purification; compared with conventional $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ -based systems dependent on sacrificial hole scavengers, this alkalinity modulation strategy avoids extra hole-consuming additives and features low cost, zero secondary pollution and in-situ system self-purification, representing a promising bifunctional photocatalysis route aligned with the cutting-edge research trend of coupling multiple high-value reactions as reported by Chen *et al.*, who achieved efficient hydrogen peroxide photosynthesis and emerging contaminant removal through polymeric carbon nitride donor-acceptor regulation [39], which fully underscores the advanced design philosophy and practical application prospect of our research. Exogenous NaOH plays two core multifunctional roles: it accelerates water dissociation to boost surface reaction kinetics and reshapes water oxidation routes and products relying on the $\cdot\text{OH}/\text{OH}^-$ redox pair, and abundant in-situ generated $\cdot\text{OH}$ further drives pollutant degradation via radical-mediated pathways, delivering an outstanding H_2 evolution rate of $28.22 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ under 4 M NaOH accompanied by efficient MB removal. Comprehensive characterizations including XRD, TEM and XPS, combined with electrochemical tests, verify that NiMoO_4 greatly optimizes the photoelectric performance of composites and guarantees stable catalytic activity during synchronous H_2 generation and MB degradation, while ISI-XPS, band structure analysis, $\cdot\text{O}_2^-$ capture experiments, EPR and DFT calculations collectively clarify the internal dual S-scheme charge transfer mechanism of the catalyst

system.

2. Method

2.1 Preparation of T-MCS solid solution nanoparticles

A solvothermal synthesis process was employed to synthesize T-MCS nanoparticles, as described in **Fig. 1a**. Furthermore, the comprehensive experimental procedures and detailed materials specifications are provided in the supporting information.

2.2 Preparation of NiMoO₄ nanorods

Firstly, 30 mL of the pre-prepared 0.1 M Na₂MoO₄ solution was gradually combined with an equimolar NiCl₂ solution under continuous stirring (as shown in **Fig. 1a**). Subsequently, the solution was sealed to undergo solvothermal treatment at 180 °C for 15 h. Once the reaction was completed, the system was permitted to cool to ambient temperature in a natural manner. The resulting laurel-green precipitate was then harvested via centrifugation. Afterward, the product was dried at 60 °C. Finally, the sample underwent thermal treatment in a muffle furnace at 450 °C for a period of 2 h, yielding khaki-colored NiMoO₄ nanorods.

2.3 Preparation of NiMoO₄/T-MCS

A series of NiMoO₄/T-MCS composites were successfully prepared using a solution-based physical drying method (**Fig. 1a**). The detailed procedure was as follows: A predetermined amount of NiMoO₄ and T-MCS were separately introduced into 20 mL of ethanol solution and subsequently dispersed through ultrasonic treatment for 30 min to ensure complete dispersion of both components. Thereafter, followed by solvent evaporation under controlled conditions until dryness was achieved, resulting in a series of light yellow NiMoO₄/T-MCS. By systematically adjusting the content of NiMoO₄ in the composites, *x*% NiMoO₄/T-MCS photocatalysts were prepared. (Where *x*% denotes the mass ratio of NiMoO₄ to T-MCS, with *x* corresponding to 2, 6, 8, and 10, respectively.)

2.4 Characterization

The supplementary materials include a variety of in-depth analyses, including comprehensive physical and photoelectrochemical characterizations, detailed investigations into photocatalytic H₂ evolution, H₂ production coupled MB purification, active radical capture experiment, and DFT calculations.

3. Results and discussions

3.1 Material structure and chemical composition

The diffraction peaks of T-MCS patterns correspond to ZB-MCS (JCPDS 89-0440) and WZ-MCS (JCPDS 06-0314), respectively. As presented in **Fig. S1**, the peaks detected at 26.8°, 26.4° and 28.2° are attributed to the (111), (002) and (101) crystal planes of the WZ-MCS, respectively. Meanwhile, the characteristic peaks of ZB-MCS at 26.4° (111), 43.8° (220) and 51.9° (311) lattice plane are confirmed [40-41]. In addition, the peaks located at 14.3°, 25.3°, 28.2° and 43.9° are assigned to the (110), (112), (220) and (330) crystal faces of NiMoO₄ (JCPDS 33-0948), respectively (**Fig. 1b**) [42].

The above-mentioned diffraction peaks are also observable in the series of NiMoO₄/T-MCS composites, indicating that the incorporation of NiMoO₄ fails to impair the crystalline structure of T-MCS, which further verifies that the NiMoO₄/T-MCS composites have been successfully fabricated. As illustrated in **Fig. S2**, the determinations of Zeta potential reveal that 6% NiMoO₄/T-MCS (-16.7 mV) displays an electronegativity intermediate between NiMoO₄ (-11.1 mV) and T-MCS (-19.5 mV). This suggests a close interfacial contact between the components. Such negative charge characteristics facilitate effective electrostatic attraction with H⁺, thus furnishing beneficial proton source for the subsequent redox reaction process [43].

NiMoO₄ presents uniform, slender nanorods, where the average diameter is roughly 100 nm and the length is around 1 μm (**Fig. 1c-d**) [44]. In contrast, T-MCS consists of irregularly shaped nanoparticles with an average size distribution of 50±5 nm (**Fig. 1e-f**). The distinctive morphology not only facilitates the clear identification of NiMoO₄ in the SEM images of the 6% NiMoO₄/T-MCS composite (**Fig. 1g-h**) but also offers more active sites. Furthermore, the elemental mapping and EDS spectra (**Fig. 1i-j**) confirm that the sample is composed of Ni, Mo, Mn, Cd, O and S, further verifying the successful incorporation of NiMoO₄ into the composite.

As exhibited in **Fig. 1o**, NiMoO₄ nanorods and T-MCS nanoparticles are clearly observed to be fully and uniformly interwoven. The distinct morphologies of T-

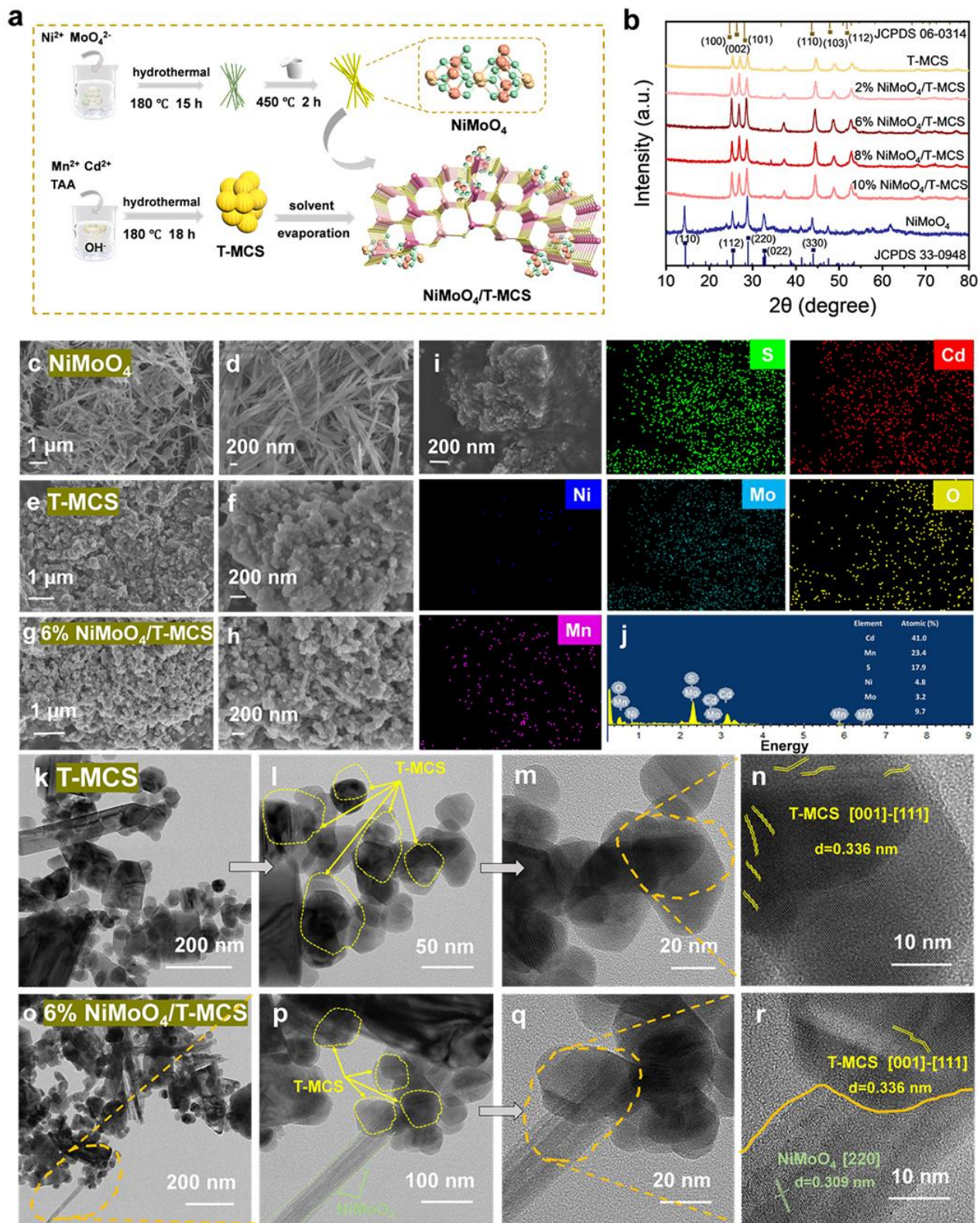


Fig. 1. (a) Diagram elucidating the formation process of NiMoO₄/T-MCS. (b) XRD patterns of the samples. SEM images of (c-d) NiMoO₄, (e-f) T-MCS, (g-h) 6% NiMoO₄/T-MCS. (i) Elemental mapping and (j) EDS spectrum of 6% NiMoO₄/T-MCS. TEM images of (k-n) T-MCS and (o-r) 6% NiMoO₄/T-MCS.

MCS and NiMoO₄ are respectively highlighted by yellow and green dotted lines (Fig. 1l, p). The HRTEM image (Fig. 1r) reveals jagged lattice fringes with a spacing of 0.336 nm, which are associated with the periodic structural changes resulting from the alternation of WZ and ZB-T-MCS along the (111-001) direction, which is consistent with observations in Fig. 1n [9, 40]. The lattice spacing of 0.309 nm marked by the green line corresponds to the (220) plane of NiMoO₄, aligning with the XRD diffraction peak at 28.2°. It is notable that the SEM and XRD analysis results corroborate the TEM findings, proving further evidence for the successful synthesis of the NiMoO₄/T-MCS composite.

The high-resolution ISI-XPS spectra of individual samples are displayed in Fig. 2. In the Cd 3*d* spectrum of T-MCS (Fig. 2a), the two characteristic peaks of Cd 3*d*_{3/2} and Cd 3*d*_{5/2} are located at 411.59 and 404.83 eV, respectively, with an energy difference of $\Delta E = 6.7$ eV. This result confirms that the Cd species is in the +2 valence state [45]. Similarly, for Mn 2*p*, the peaks detected at 639.80 and 652.23 eV are derived from the 2*p*_{3/2} and 2*p*_{1/2} orbitals of Mn in the Mn²⁺ state, respectively (Fig. 2b) [46]. As shown in Fig. 2c, the signal peaks at 161.27 and 162.48 eV are from S 2*p*_{3/2} and 2*p*_{1/2} of S²⁻ respectively, which precisely match the binding energies related to Mn-S and Cd-S interactions [47].

Regarding Ni 2*p* spectrum (Fig. 2d), the peaks at 855.88 eV for Ni 2*p*_{3/2} and 873.48 eV for Ni 2*p*_{1/2}, respectively [48]. As illustrated in Fig. 2e, signals at 235.54 and 232.41 eV are attributed to the Mo 3*d*_{3/2} and Mo 3*d*_{5/2}, respectively, with a peak separation of 3.1 eV, confirming the presence of Mo in the +6-valence state [37]. Additionally, the peaks identified at 532.45 eV (O II) and 530.57 eV (O I) are linked to the surface-adsorbed oxygen and lattice oxygen (M-O-M) in NiMoO₄, respectively [49]. It is notable that in 6% NiMoO₄/T-MCS, a minor positive shift can be detected in Mn 2*p*, Cd 3*d* and S 2*p* compared with pure T-MCS, indicating a reduction in electron (e⁻) density. Meanwhile, a shift of the Mo 3*d*, Ni 2*p*, and O 1*s* signals toward lower binding energy is observed relative to the NiMoO₄ monomer, indicating an enhancement in the e⁻ density of the system.

Under light conditions, it is notable that all the binding energy peaks of the Mn 2*p*, Cd 3*d* and S 2*p* in the 6% NiMoO₄/T-MCS composite display a negative shift, while the Mo 3*d*, Ni 2*p* and O 1*s* exhibit a slight positive shift. This indicates that there is a

photogenerated e⁻ transfer from NiMoO₄ to T-MCS contrary to the behavior in the dark state. These phenomena confirm that the formation of the heterojunction triggers the initial migration of e⁻ from T-MCS to NiMoO₄ until the Fermi level (E_F) is balanced at the interface, thereby establishing a built-in electric field at the interface. After light excitation, driven by built-in electric field, the photogenerated e⁻ subsequently transfer from NiMoO₄ to T-MCS in the reverse direction, which is highly consistent with the typical S-scheme charge transfer mechanism [50]. Furthermore, the above-mentioned signal peaks (Cd 3*d*, Mn 2*p*, S 2*p*, Ni 2*p*, Mo 3*d*, O 1*s*) are all observed in the full XPS spectrum of NiMoO₄/T-MCS (Fig. S3), which aligns well with the results of SEM mapping analysis.

3.2 Photocatalytic activity evaluation

Without adding any cocatalysts, the H₂ evolution activity of the samples was evaluated in different concentrations of NaOH solution (c_{NaOH}) under a 300 W Xe-lamp. Notably, as exhibited in Fig. 3a, the activity of each sample increases with increasing c_{NaOH} concentration. Specifically, when c_{NaOH} increases from 1 M to 4 M, the r_{H_2} of T-MCS increases from 2.68 to 9.17 mmol·g⁻¹·h⁻¹, representing an approximate 2.4-fold increase. However, the H₂ evolution reaction (HER) ability of NiMoO₄ nanorods is relatively weak, with r_{H_2} reaching only 0.24 mmol·g⁻¹·h⁻¹, which is much lower than the activity of T-MCS.

When NiMoO₄ is loaded onto T-MCS, in a 1 M NaOH environment, the r_{H_2} of NiMoO₄/T-MCS increases significantly with the increase of NiMoO₄ content. The 6% NiMoO₄/T-MCS exhibits satisfactory performance, reaching a maximum r_{H_2} of 16.07 mmol·g⁻¹·h⁻¹, which is 4.9 and 106.1 times higher than that of the pure T-MCS (2.68 mmol·g⁻¹·h⁻¹) and NiMoO₄ (0.15 mmol·g⁻¹·h⁻¹), respectively. When the loading content exceeds 6%, the activity of NiMoO₄/T-MCS decreased, primarily as a result of the shielding effect caused by excessive NiMoO₄ loading and unbalanced charge migration [51]. Notably, the r_{H_2} of each NiMoO₄/T-MCS sample increases with the increase in c_{NaOH} , reaching a maximum of 28.22 mmol·g⁻¹·h⁻¹. This value is 2.1 times higher than that of T-MCS (9.17 mmol·g⁻¹·h⁻¹) and 116.6 times higher than that of NiMoO₄ (0.24 mmol·g⁻¹·h⁻¹) under the same concentration. In summary, this phenomenon can be characterized as a “photocatalyst-electrolyte” effect. It demonstrates that the r_{H_2} of T-MCS-based catalysts can be effectively enhanced by adjusting the alkalinity of the reaction solution.

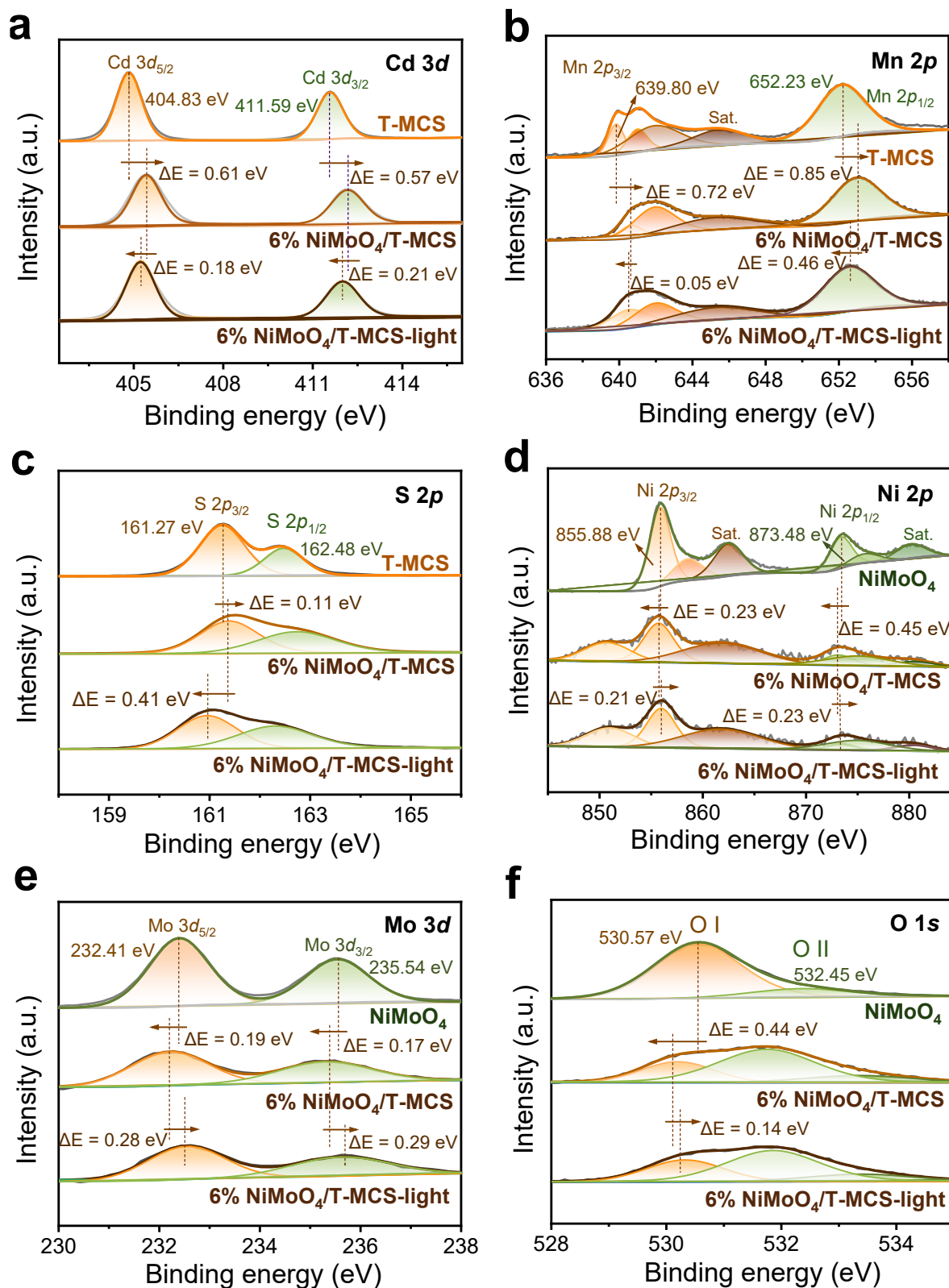


Fig. 2. High-resolution XPS spectra (a) Cd 3d, (b) Mn 2p, (c) S 2p, (d) Ni 2p, (e) Mo 3d and (f) O 1s respectively in T-MCS, NiMoO₄ and 6% NiMoO₄/T-MCS.

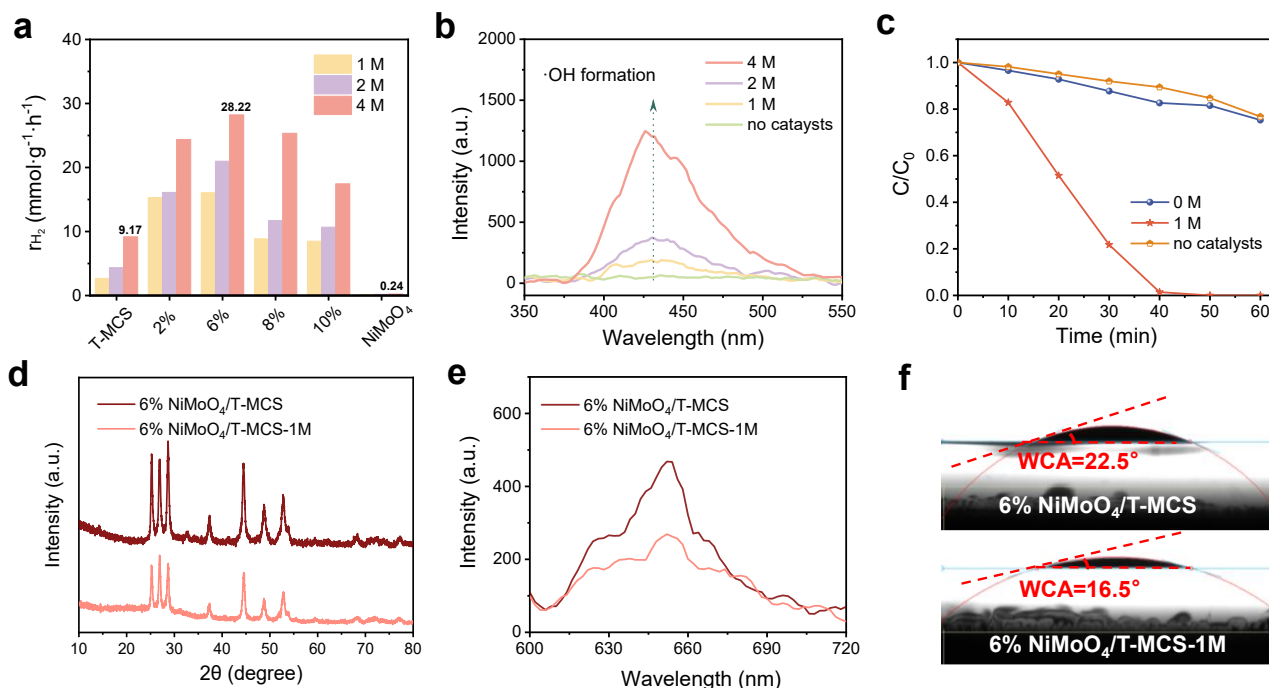
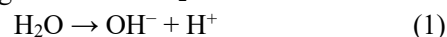


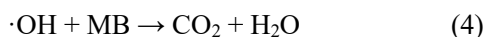
Fig. 3. (a) Photocatalytic H₂ production rates of the different materials under different c_{NaOH} . (b) $\cdot\text{OH}$ formation after H₂ production. (c) MB purification rate. (d) XRD patterns and (e) PL spectra of 6% NiMoO₄/T-MCS and 6% NiMoO₄/T-MCS-1M. Water contact angle test (f) 6% NiMoO₄/T-MCS-1M.

Furthermore, to elucidate the reaction mechanism more comprehensively, radical trapping experiments were conducted on the solution after reaction. As displayed in **Fig. 3b**, a substantial quantity of $\cdot\text{OH}$ is detected via fluorescence spectroscopy. The concentration of $\cdot\text{OH}$ exhibits a positive correlation with c_{NaOH} (1 M–4 M), which is consistent with the aforementioned experimental trends. This observation indicates that $\cdot\text{OH}$ radicals are generated through the one- e^- oxidation pathway ($\text{OH}^- + h\nu \rightarrow \cdot\text{OH}$) during the oxidative half-reaction of water. Kinetically, this single- e^- transfer pathway is more favorable compared to the conventional multi- e^- water oxidation mechanism under neutral conditions. To make the H₂ production process sustainable, it is necessary to rapidly consume a large quantity of $\cdot\text{OH}$ radicals generated in the reaction solution. Herein, the H₂ evolution coupled MB purification was employed to consume $\cdot\text{OH}$. Studies have found that an alkaline environment can not only promote the r_{H_2} but also increase the purification rate (**Fig. S4a-c**). As displayed in **Fig. S5b**, after the addition of 1 M NaOH, the purification rate of MB can reach 98.57 % within 40 min, and the complete purification of MB can be achieved within 50 min, which has obvious advantages compared with the direct purification of MB

without NaOH. To further investigate the relationship between $\cdot\text{OH}$ production and MB degradation, pseudo-first-order kinetic analysis was performed. The rate constants (k) were calculated as 0.0047 min^{-1} for the reaction without NaOH and 0.0984 min^{-1} for the reaction in 1 M NaOH solution. The ~21-fold increase in the degradation rate constant with NaOH addition is consistent with the enhanced $\cdot\text{OH}$ fluorescence intensity under alkaline conditions, confirming that $\cdot\text{OH}$ radicals play a dominant role in MB degradation.

The detailed reaction equations over the photocatalytic water splitting in this highly alkaline environment reaction system are listed in **Equations (1)–(4)** below. It is evident that this represents a cascade reaction mechanism. During the HER, water molecules are decomposed into H₂ and OH⁻ by the photoexcited e^- generated by the catalyst. Simultaneously, the photogenerated h^+ oxidizes the introduced OH⁻ to generate $\cdot\text{OH}$, which can participate in the purification of MB to generate CO₂ and H₂O subsequently. Furthermore, the consumed OH⁻ can be supplemented by means of water dissociation, which in turn supports the continuous generation of H₂ [35].





Notably, our catalyst achieves an outstanding HER rate of $28.22 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, which is significantly higher than most sulfide-based systems under similar conditions, including the redox dual-cocatalyst-modified ZnIn_2S_4 hollow spheres reported by Liu et al., which realize efficient coupling of hydrogen evolution and benzyl alcohol oxidation with a rate of 6.29 and $5.26 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ [52-55]. It is worth emphasizing that this excellent performance is achieved in the $\text{Mn}_{0.5}\text{Cd}_{0.5}\text{S}$ -based system, which is more prone to photocorrosion in alkaline environments, yet the present strategy only involves simple NiMoO_4 heterojunction construction and solution alkalinity modulation, without complex structural design or noble metal cocatalysts. Meanwhile, the $\text{NiMoO}_4/\text{T-MCS}$ catalyst also simultaneously accomplishes efficient methylene blue degradation, demonstrating its inherent bifunctional advantages over conventional single-function sulfide-based photocatalysts. These comparisons fully confirm the efficiency, innovation, and practical application potential of the strategy proposed in this work.

To further explore the influence of OH^- on the reaction, we systematically analyzed the samples collected after the reaction in 1 M NaOH, which were designated as 6% $\text{NiMoO}_4/\text{T-MCS-1M}$. As illustrated in **Fig. 3d** and **Fig. S6**, no notable changes are found in morphologies or the positions of the XRD diffraction peaks prior to and after the reaction, indicating that the crystal structure remains intact after alkali treatment. The PL spectra indicate that the intensity of 6% $\text{NiMoO}_4/\text{T-MCS-1M}$ has slightly decreased compared to that prior to the reaction (**Fig. 3e**). This reduction is likely attributed to the surface hydroxylation induced by the introduction of OH^- , which facilitates carrier migration [56]. In addition, the water contact angle (WCA) of the catalyst was measured to investigate the surface hydrophilicity of the sample. As displayed in **Fig. S7** and **Fig. 3f**, the WCA of pure T-MCS, NiMoO_4 and $\text{NiMoO}_4/\text{T-MCS}$ are 54.6° , 9.0° and 22.5° , respectively. These results indicate that all three materials exhibit excellent surface hydrophilicity, which facilitates the extraction of H^+ from water and enhances the generation of H_2 . Notably, the WCA of 6% $\text{NiMoO}_4/\text{T-MCS-1M}$ decreases significantly (**Fig. 3f**) under strongly alkaline conditions (16.5°), indicating an enhanced hydrophilicity in such environments. This phenomenon may be due to the promotion of OH^- adsorption on the sample surface by

the highly alkaline solution, thereby improving water molecule adsorption. Additionally, the reaction-induced formation of abundant $\cdot\text{OH}$ groups on the sample surface plays a critical role in enhancing its hydrophilic properties.

3.3 Photoelectrochemical properties

To clarify the effect of NiMoO_4 on the activity of T-MCS, the photoelectrochemical properties of the catalyst were conducted from the perspective of carrier separation kinetics, as illustrated in **Fig. 4**. **Fig. 4a-b** display the characteristic periodic transient photocurrent responses (I-t) and electrochemical impedance spectra (EIS) of the samples. In agreement with the H_2 production results, a relatively weak photocurrent density ($1.6 \mu\text{A} \cdot \text{cm}^{-2}$) is observed for NiMoO_4 , whereas T-MCS exhibits superior activity with a photocurrent density reaching $28.2 \mu\text{A} \cdot \text{cm}^{-2}$. However, monomer retains only a limited number of photogenerated carriers. Further analysis reveals that both NiMoO_4 and T-MCS exhibit large semicircular radii in their EIS plots, indicating relatively high charge transfer resistances.

Upon the formation of the 6% $\text{NiMoO}_4/\text{T-MCS}$, the material manifests a markedly increased photocurrent density reaching $59.2 \mu\text{A} \cdot \text{cm}^{-2}$ and a reduced charge transfer resistance. This improvement can be ascribed to the established interfacial electric field within the 6% $\text{NiMoO}_4/\text{T-MCS}$ heterojunction, which effectively accelerates charge transfer and promotes carriers transfer kinetics [57]. To further explore how NiMoO_4 affects H_2 evolution kinetics, LSV curves were obtained in the range of -2 to 0 V (**Fig. 4c**). When the current density reaches $-2 \text{ mA} \cdot \text{cm}^{-2}$, the H_2 evolution overpotential of 6% $\text{NiMoO}_4/\text{T-MCS}$ (-1.58 V vs. SCE) is smaller than that of T-MCS (-1.65 V vs. SCE), which suggests that the introduction of NiMoO_4 improves the H_2 evolution kinetics [58].

Through the analysis of photoluminescence (PL) and time-resolved photoluminescence spectra (TRPL) of the samples, the influence of NiMoO_4 on carrier recombination and migration was systematically explored. As depicted in **Fig. 4d**, all samples exhibit prominent fluorescence emission peaks around 640-650 nm. Notably, the PL intensity of 6% $\text{NiMoO}_4/\text{T-MCS}$ is significantly lower than that of T-MCS, suggesting that the incorporation of NiMoO_4 effectively suppresses the recombination of e^- - h^+ pairs [59]. The

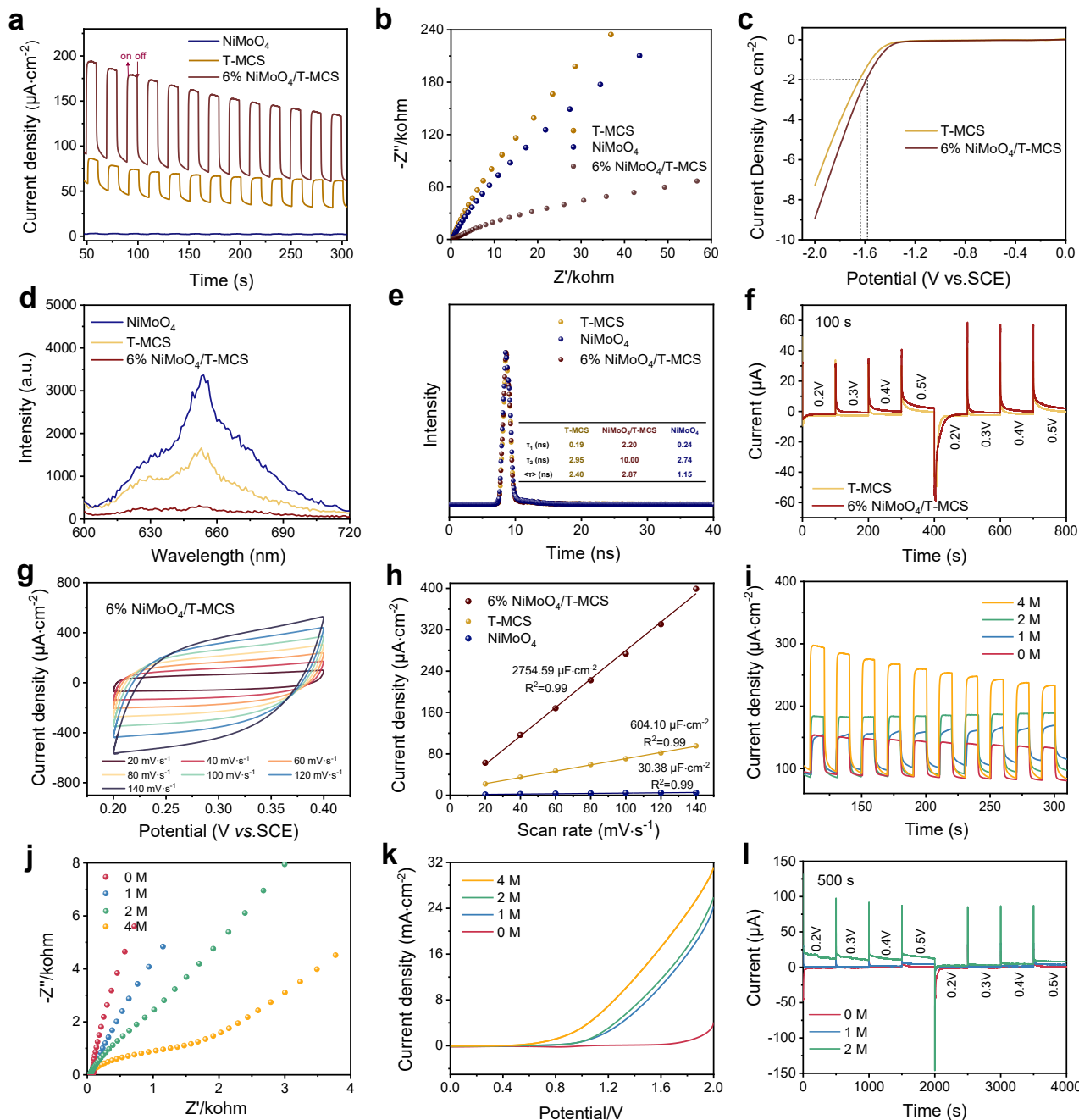


Fig. 4. (a) I-t curves, (b) EIS plots, (c) LSV curves, (d) PL spectra and (e) TRPL spectra, (f) multi-potential steps I-t plots of the materials. (g) CV curves of 6% NiMoO₄/T-MCS obtained at various scan rates and (h) the correlation between current density and corresponding scan rates for different samples. (i) I-t curves, (j) EIS plots, (k) LSV curves and (l) multi-potential steps I-t plots of 6% NiMoO₄/T-MCS under different C_{NaOH} .

TRPL spectra of the samples also lead to similar conclusions (**Fig. 4e**) [60]. In this context, τ_1 , τ_2 , and τ represent spontaneous emission, non-radiative transitions and the average excited-state e^- lifetime,

respectively. The τ of 6% NiMoO₄/T-MCS (2.87 ns) compared to pure T-MCS (2.40 ns) highlights the role of the heterojunction in enhancing charge utilization efficiency. Furthermore, the electrochemical

performance and stability of the samples were evaluated using multi-potential steps I-t curves, as displayed in **Fig. 4f** [51]. Upon increasing the applied voltage, all samples demonstrate a current peak at 0.5 V. Specifically, 6% NiMoO₄/T-MCS exhibits a significantly higher current at 0.5 V relative to T-MCS. Additionally, long-term cyclic voltammetry tests demonstrate its excellent stability.

In addition, the electrochemical double-layer capacitance (C_{dl}), derived from the CV curves, was used to evaluate the electrochemical active surface area (ECSA) [48]. **Fig. 4g** and **Fig. S8** record the CV curves of various samples under different scan rates. The C_{dl} can be evaluated by the slope presented in **Fig. 4h**, with the following ranking: 6% NiMoO₄/T-MCS ($2754.6 \mu\text{F}\cdot\text{cm}^{-2}$) > T-MCS ($604.1 \mu\text{F}\cdot\text{cm}^{-2}$) > NiMoO₄ ($30.4 \mu\text{F}\cdot\text{cm}^{-2}$). These results indicate that the introduction of NiMoO₄ effectively increases the ECSA of the catalyst, thereby promoting the contact between reaction molecules and active sites, and accelerating the surface mass transfer and diffusion process. Therefore, based on the above-mentioned analysis, the construction of NiMoO₄/T-MCS heterojunction not only optimizes the separation and transport of photogenerated e^- - h^+ but also prolongs the carrier lifetime, accelerates surface reaction kinetics, and provides additional active sites, ultimately enhancing the H₂ evolution performance of the system.

In addition, to explore the surface reaction process in a highly alkaline environment, 6% NiMoO₄/T-MCS, which exhibits optimal photoelectric properties, was studied under varying C_{NaOH} (electrolytes composed of 0.1 M Na₂SO₄ and 1, 2, and 4 M NaOH). As depicted in **Fig. 4i-j**, as C_{NaOH} increases, the photocurrent density of the sample gradually rises, reaching $207.5 \mu\text{A cm}^{-2}$ at 4 M NaOH, which is approximately 3.5 times that without NaOH ($59.2 \mu\text{A}\cdot\text{cm}^{-2}$). Concurrently, the diameter of the EIS curves decreases with increasing C_{NaOH} , representing a lowering of the charge transfer resistance in the system.

Furthermore, the LSV curve reveals that at a same voltage, increasing the alkaline strength of the electrolyte leads to a gradual increase in the current density of the sample, which aligns with the previously observed trend in H₂ production performance. As displayed in **Fig. 4l**, the current density exhibits a positively correlation with C_{NaOH} and reaches its maximum at a voltage of 0.5 V. A long-term cyclic voltammetry test lasting 500 seconds demonstrates that the material maintains excellent activity and stability under highly alkaline conditions. This finding highlights the material's robust electrochemical durability and consistent functionality in alkaline environments, which

is crucial for practical applications in photocatalytic H₂ evolution systems. In conclusion, the presence of NaOH not only promotes rapid charge migration within the system and enhances the kinetics of water splitting but also ensures to the stability of the system.

In addition, femtosecond transient absorption spectroscopy (fs-TAS) was utilized to investigate the photoinduced charge carrier dynamics of as-prepared samples, which can visually reveal ultrafast carrier migration, separation and recombination behaviors at the microscopic level. As displayed in **Fig. 5a-c**, T-MCS shows strong excited-state absorption (ESA) signals in the 450-580 nm region, with the peak centered at 550 nm. The kinetic trace at 550 nm (**Fig. 5c**) is fitted by a biexponential decay model, affording fast component $\tau_1=193.24$ ps, slow component $\tau_2=938.55$ ps, and an average carrier lifetime (τ_{Ave}) of 801.34 ps. The short-lived decay component corresponds to rapid non-radiative recombination of photogenerated carriers inside pure T-MCS, which restricts the utilization efficiency of excited carriers. For pure NiMoO₄ (**Fig. 5d-f**), ESA signals concentrate in the short-wavelength visible region, and the kinetic curve at 430 nm exhibits an ultrafast decay component of 3.25 ps, resulting in a short τ_{Ave} of 123.96 ps, which demonstrates severe rapid charge recombination and poor intrinsic carrier separation ability.

Impressively, the T-MCS/NiMoO₄ composite (**Fig. 5g-i**) shows greatly prolonged ESA duration and suppressed decay rate. The kinetic trace at 550 nm is fitted via a triexponential model, delivering $\tau_1=110.75$ ps, $\tau_2=318.19$ ps, $\tau_3=1831.42$ ps, and a high τ_{Ave} of 1414.88 ps. The newly emerged long-lived decay component fully proves the existence of efficient interfacial charge transfer pathway between two components. These results verify that the constructed heterojunction interface significantly accelerates spatial charge separation, effectively inhibits bulk and interfacial charge recombination, and thus generates abundant long-lived charge carriers to sufficiently participate in subsequent photocatalytic redox reactions.

3.4 Analysis of photocatalytic mechanism

To achieve a more profound understanding of the activity enhancement mechanism in this system, it is imperative to explore the light absorption properties and band structures of the two semiconductors. As depicted in **Fig. 6a**, NiMoO₄ demonstrates significantly stronger light absorption than T-MCS within the 200-400 nm wavelength range. Moreover, the light-harvesting efficiency of the NiMoO₄/T-MCS heterojunctions increases significantly with

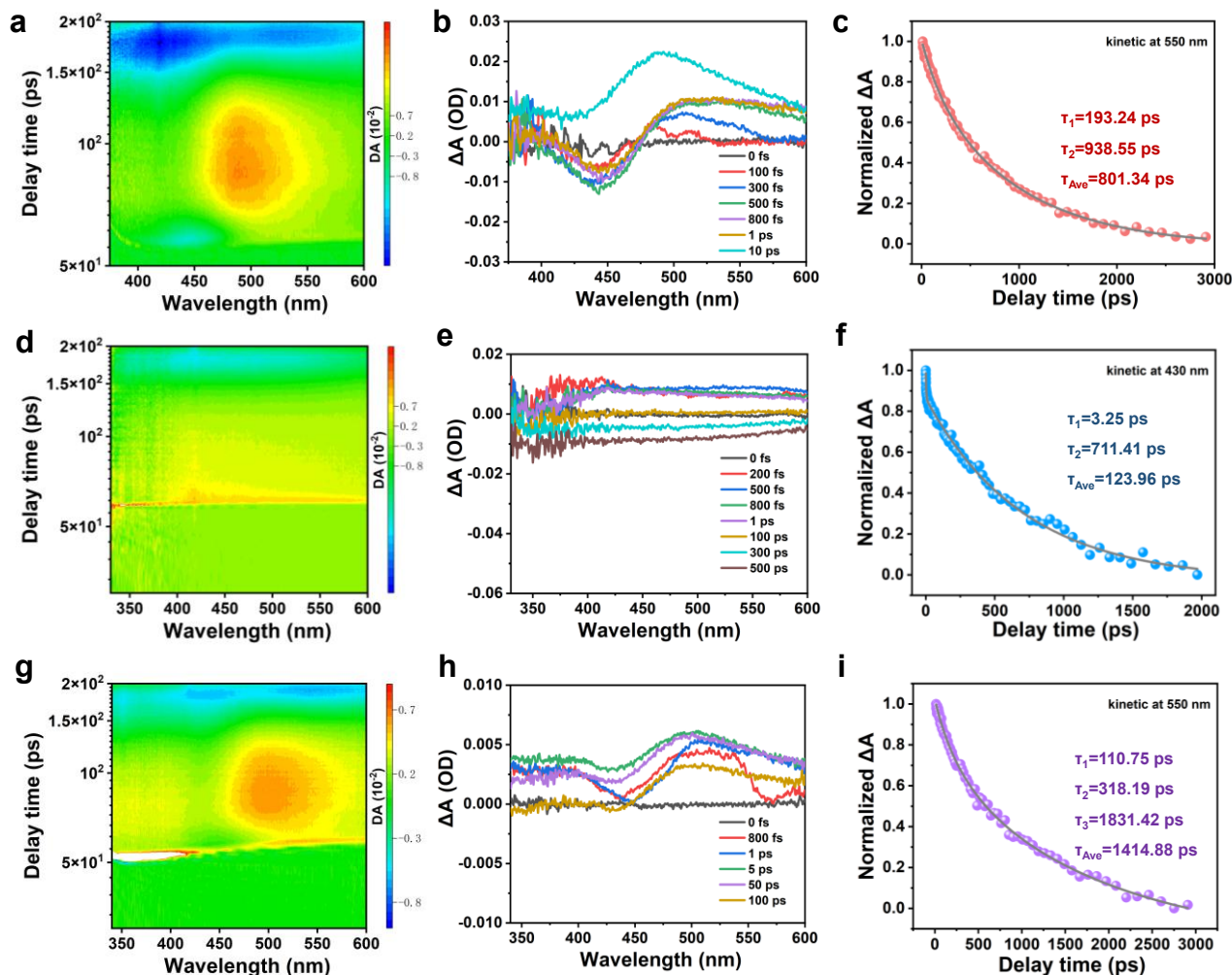


Fig. 5. 2D color contour map of fs-TAS for (a) T-MCS, (d) NiMoO₄ and (g) T-MCS/NiMoO₄. fs-TAS spectra of (b) T-MCS, (e) NiMoO₄ and (h) T-MCS/NiMoO₄ at selected delay times. Normalized kinetic decay trace of (c) T-MCS at 550 nm, (f) NiMoO₄ at 430 nm with biexponential fitting and (i) Normalized kinetic decay trace of T-MCS/NiMoO₄ at 550 nm with triexponential fitting.

increasing NiMoO₄ loading, thereby facilitating the generation of a greater number of photogenerated carriers for redox reactions. By employing the Kubelka-Munk formula and analyzing Tauc plots [61], the band gaps (E_g) of the individual components are determined: 2.48 (Fig. 6b) and 3.03 eV (Fig. 6d). Additionally, Fig. 6c not only illustrates the UV spectra of the WZ-MCS, ZB-MCS, and T-MCS crystal phases, emphasizing their respective absorption edges at 570, 580 and 550 nm, but also provides the corresponding band E_g for the two crystal phases, thus providing a comprehensive overview of their optical properties.

Furthermore, the tests conducted using MS curves at three distinct frequencies confirm that both samples

display typical N-type semiconductor properties. According to the horizontal intercept in Fig. 6e-f, the E_{fb} of NiMoO₄ and T-MCS can be determined, respectively. Utilizing the equations ($E_{RHE} = E_{Hg/HgCl_2} + 0.059 \times pH + E_{Hg/HgCl_2}$ and $E_{VB} = E_g - E_{CB}$), it is calculated that the CB for NiMoO₄ and T-MCS are 0.01 and -0.76 V, while the VB are 3.02 and 1.72 V, respectively [62]. These results indicate that NiMoO₄ and T-MCS can form a heterojunction with interlaced energy bands, which has the potential to effectively enhance charge separation efficiency and utilization.

Building upon the previously discussed band structure analyses, the CB of NiMoO₄ exhibits a more positive potential compared to the reduction potential of -0.33 V

for the $O_2 / \cdot O_2^-$ redox couple [63]. As a result, $NiMoO_4$ lacks the thermodynamic driving force

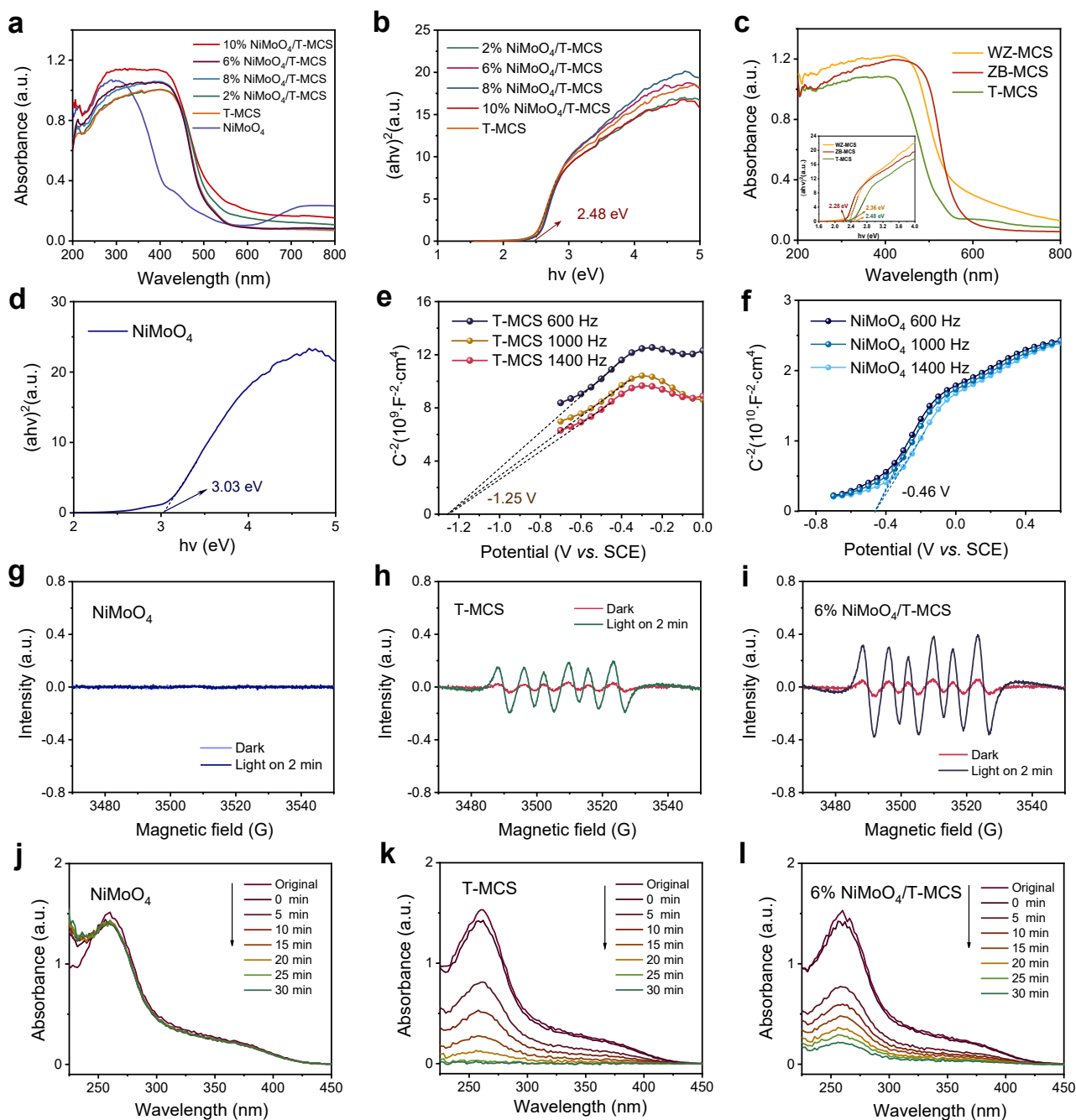


Fig. 6. (a, c) UV-Vis spectra and (b, d) Tauc plots of the samples. MS plots of (e) T-MCS and (f) $NiMoO_4$. EPR of (g-i) T-MCS, $NiMoO_4$ and 6% $NiMoO_4$ /T-MCS. NBT trapping of (j) T-MCS, (k) $NiMoO_4$ and (l) 6% $NiMoO_4$ /T-MCS.

required to generate $\cdot O_2^-$ radicals under theoretical considerations. Conversely, the CB of T-MCS possesses a more negative potential, which endows it with the ability to produce $\cdot O_2^-$ species. This theoretical prediction has been experimentally validated through

subsequent electron paramagnetic resonance (EPR) spectroscopy and radical trapping experiments (Fig. 6g-l).

Notably, an even stronger $\cdot O_2^-$ signal is detected in the solution containing the $NiMoO_4$ /T-MCS

heterojunction (**Fig. 6i**). This finding suggests that the formation of the heterojunction enhances its reducing capacity, thereby facilitating the generation of a greater number of reductive e^- on the surface. Such an increase in reductive e^- can be attributed to the synergistic effects within the heterojunction structure, which facilitates efficient charge separation and transfer, thus favoring the production of $\cdot O_2^-$ radicals.

Furthermore, nitrotriazolium chloride (NBT) was employed as a trapping agent for $\cdot O_2^-$, and the generation of $\cdot O_2^-$ was quantified by detection the UV absorption [64]. Following 30 min of illumination with a 300 W Xe-lamp, the UV absorption peaks of T-MCS and 6% NiMoO₄/T-MCS composite are almost entirely quenched (**Fig. 6l**), whereas those of NiMoO₄ remain largely unchanged (**Fig. 6j**). These results strongly suggest that the improved activity of the NiMoO₄/T-MCS composite stems from its capacity to sustain a robust reducing ability. Specifically, e^- are retained on the CB of T-MCS, while h^+ are maintained on the VB of NiMoO₄.

Subsequently, the work functions (Φ) of NiMoO₄ and

T-MCS were analyzed by DFT theory to further explore the charge transfer mechanism within the system. Based on the (002) crystal plane of T-MCS and the (110) crystal face of NiMoO₄, the structural model was computationally optimized, as depicted in **Fig. 7a-b**. The calculated Φ values are 4.75 and 5.43 eV, respectively. The physical meaning of Φ lies in its representation of the difference between the vacuum energy (E_{vac}) and E_F ($\Phi = E_{vac} - E_F$) [65]. Consequently, the E_F of NiMoO₄ is lower than that of T-MCS, which aligns well with the experimental results mentioned above.

According to the above experiments and theoretical analyses, a schematic diagram illustrating the charge transfer within the system is developed, as displayed in **Fig. 7c-e**. Upon intimate contact between the two materials, the difference in E_F induces the spontaneous flow of e^- from T-MCS to NiMoO₄ nanorods until the E_F reaches equilibrium. This process results in the formation of an e^- accumulation layer at the heterojunction interface. Meanwhile, edge bending and an internal electric field are established at the contact interface, thereby enhancing the separation and migration of carriers.

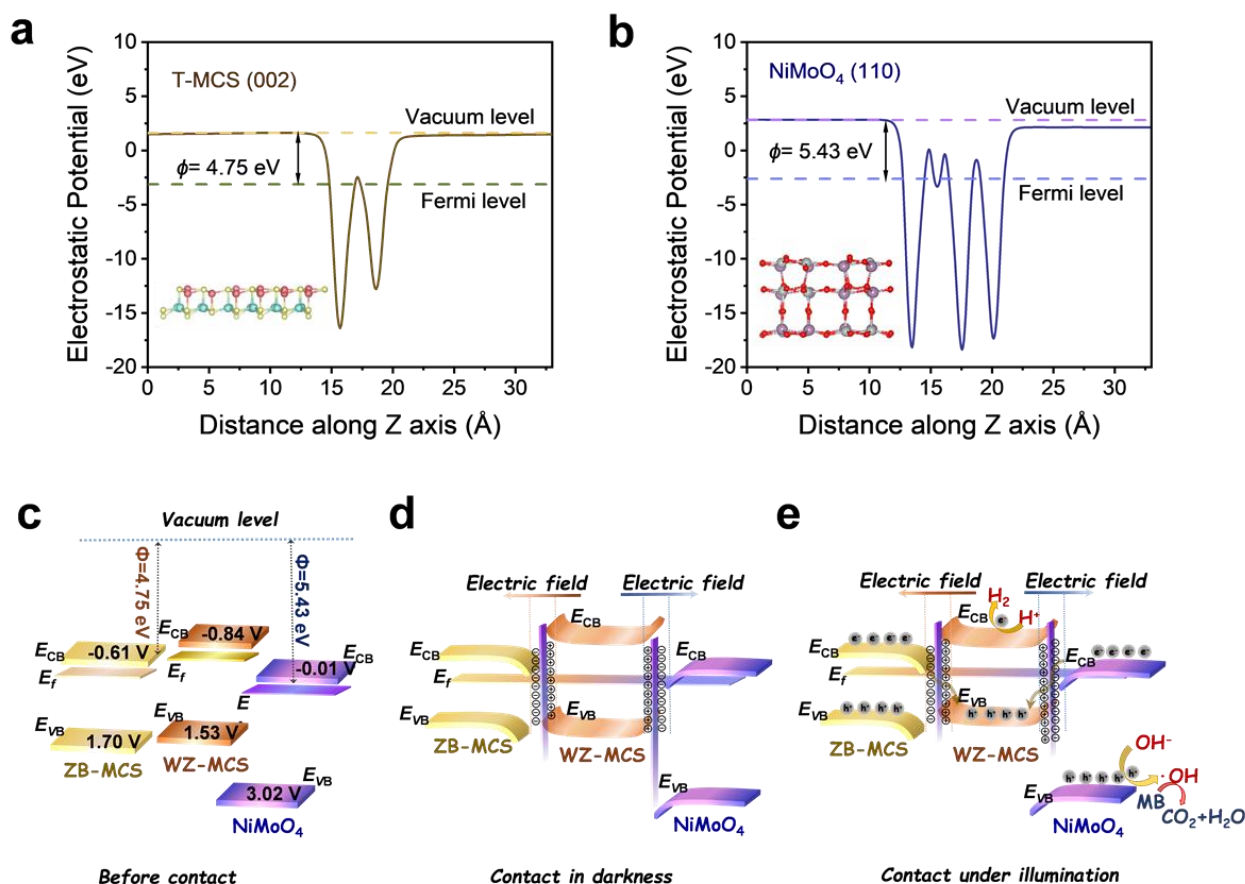


Fig. 7. The electrostatic potentials of (a) T-MCS (002) and (b) NiMoO₄ (110) as calculated. (c-e) Mechanisms of charge transfer for

NiMoO₄/T-MCS under illuminated conditions.

Subsequently, under light illumination, the e^- from both VB are photoexcited to their respective CB, while h^+ are retained on VB. The h^+ on the VB of T-MCS with low redox ability and the e^- on the CB of NiMoO₄ spontaneously recombine at the interface due to the influence of the interface electric field, Coulomb interactions, and band bending. Therefore, the photogenerated e^- and h^+ with strong redox reaction capabilities are respectively retained in the CB of T-MCS and the VB of NiMoO₄. This process adheres to the S-scheme charge transfer pathway. The e^- in the CB of T-MCS engage in the H^+ reduction reaction to form H_2 , whereas the highly oxidative h^+ in NiMoO₄ undergo oxidation reactions to convert OH^- to $\cdot OH$. The generated $\cdot OH$ can oxidize MB into CO_2 and H_2O . Therefore, the construction of S-scheme NiMoO₄/T-MCS heterojunctions effectively promotes carrier separation and transfer, preserves the maximum redox capacity, and significantly improves the kinetics of H_2 production.

Analogous to the NiMoO₄/T-MCS S-scheme heterojunction, T-MCS, a material consisting of two distinct crystal phases, also demonstrates a characteristic band alignment. This phenomenon is supported by the MS curves of ZB-MCS and WZ-MCS. As presented in Fig. S9b, owing to the variation in EF, e^- located on the CB of WZ-MCS transfer to ZB-MCS; this results in the buildup of positive charges on the WZ-MCS side and negative charges on the ZB-MCS side. Consequently, this redistribution of charges triggers band bending and brings about the formation of an internal electric field at the interface. Upon illumination (Fig. S9c), under the combined influence of the Coulomb force, band bending, and the built-in electric field, the e^- on the CB of ZB-MCS recombine with the h^+ on the VB of WZ-MCS. This mechanism ensures that carriers with strong redox capabilities are retained within T-MCS, following a bulk-phase S-scheme charge transfer route [66-67].

In conclusion, the enhanced H_2 production activity of the NiMoO₄/T-MCS heterojunction may be ascribed to the following aspects: First, the double S-scheme heterojunction, formed through the synergy between NiMoO₄ and T-MCS as well as within bulk T-MCS, serves as multiple carrier transfer pathways. This substantially reduces both bulk-phase and interfacial transfer resistance, thereby accelerating carrier transfer kinetics and optimizing the redox driving force of the system. Second, the incorporation of NiMoO₄ introduces additional active sites and decreases the H_2 production overpotential, which enhances surface

reaction kinetics. Lastly, the introduced OH^- serves as medium in an alkaline environment, promoting interfacial reactions and facilitating carrier migration, thus effectively boosting the kinetics of surface water decomposition and the purification rate of pollutants. Furthermore, this separation mechanism, combining intra-particle bulk homojunction and inter-component interfacial heterojunction, builds a global high-efficiency carrier transport network that single interfacial S-scheme structures cannot replicate. Consistently, Zhao *et al.* reported that morphology modulation of LaNiO₃ to enlarge heterojunction contact regions and streamline charge pathways remarkably improves S-scheme photocatalytic H_2 evolution performance, verifying that structural and morphological optimization of multi-level heterostructures is a powerful strategy to maximize S-scheme synergies [68]. Our dual S-scheme design advances this strategy by integrating internal twin homojunction engineering and external nanorod composite construction, simultaneously optimizing both bulk carrier migration and interfacial charge transfer, which fully demonstrates the rationality and cutting-edge advantage of the multi-scale dual S-scheme catalyst developed in this work.

4. Conclusions

Overall, this work reports the preparation of the double S-scheme NiMoO₄/T-MCS heterojunction prepared by means of a solution-based physical drying approach and its subsequent application for H_2 evolution coupled with MB purification. A key finding is the substantial enhancement of the catalyst's activity achieved through the simple modulation of the alkaline concentration in the reaction solution. This approach showcases a pronounced "photocatalyst-electrolyte" effect. The NiMoO₄/T-MCS heterojunction demonstrates exceptional H_2 production performance, achieving the peak level of activity of 28.22 $mmol \cdot g^{-1} \cdot h^{-1}$ under 4 M NaOH conditions. This represents a 2.1-fold increase compared to T-MCS (9.17 $mmol \cdot g^{-1} \cdot h^{-1}$) and an impressive 116.6-fold increase relative to NiMoO₄ (0.24 $mmol \cdot g^{-1} \cdot h^{-1}$). Meanwhile, the purification rate of MB can reach 98.57 % within 40 min, and MB can undergo full purification within a 50 min timeframe due to the generated $\cdot OH$ radicals in alkaline media. Dual S-scheme charge transfer pathways exert a synergistic action in the bulk phase and at the

interface, and this synergistic effect serves as the reason for the enhanced activity. These pathways effectively mitigate interfacial transfer resistance, promote carrier separation and migration, optimize the redox capacity of the system, and provide sufficient driving force for the reaction. Additionally, the introduction of NiMoO_4 increases the density of active sites, reduces the overpotential for H_2 evolution, and extends the carrier lifetime, thereby enhancing surface reaction kinetics. Additionally, the introduction of NaOH not only accelerates carrier migration by intensifying interfacial reactions but also improves the hydrophilicity of the catalyst, thereby effectively boosting the kinetics of water splitting on the catalyst surface. In addition to demonstrating high efficiency in both hydrogen evolution and pollutant degradation, this dual-function system achieves integrated resource and energy utilization within a single reactor, driven by the same light source. It simultaneously promotes two processes: water splitting for hydrogen production (energy storage) and organic pollutant mineralization (environmental remediation), enabling the synergistic use of solar energy, reactants (water and pollutants), and the catalyst. This design fully aligns with the principles of atom economy, process intensification, and sustainable development, reflecting an important trend in photocatalytic technology from single-target reactions toward multifunctional integrated systems. This work presents a novel strategy to design green and efficient double S-scheme heterojunctions based on T-MCS, specifically for photocatalytic H_2 production in an alkaline medium.

CRedit author statement

Zhuonan Lei: Writing - review & editing, Writing - original draft, Validation, Methodology, Formal analysis, Data curation, Conceptualization. **Wenhua Xue:** Writing - review & editing, Writing - original draft, Validation, Project administration, Methodology, Data curation, Conceptualization. **Haijiao Xie:** Writing - review & editing, Writing - original draft, Validation, Conceptualization. **Tao Sun:** Writing - review & editing, Validation, Conceptualization. **Enzhou Liu:** Writing - review & editing, Validation, Conceptualization.

Conflict of interest

Enzhou Liu is an editorial board member of Composite Functional Materials and was not involved in the editorial review or the decision to publish this article. Other authors declare that there are no competing interests.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (22378326). Natural Science Basic Research

Program of Shaanxi Province (2023-JC-YB-115). Qin Chuangyuan project of Shaanxi Province (QCYRCXM-2022-213). Key Research and Development Program of Shaanxi Province (2024GX-YBXM-449). Thanks to Shiyanjia Lab for the TEM, XPS, etc.

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