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Integration of a metallic interstitial co-catalyst (Ni₃Mo₃N) onto CdS nanorods accelerated charge separation and efficient photocatalytic hydrogen evolution

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A metallic interstitial compound Ni₃Mo₃N was synthesized as a co-catalyst modified CdS nanorod for the first time. Photocatalytic studies show that the efficient charge separation and transfer from CdS to Ni₃Mo₃N enables high visible-light-driven hydrogen evolution at 6.56 mmol g⁻¹ h⁻¹. The Schottky heterojunction between CdS and Ni₃Mo₃N might be the key factor for the high photocatalytic activity.

1. Introduction

Photocatalytic water splitting into hydrogen is a promising route for transforming solar energy into clean and sustainable chemical fuel.^{1–3} A typical water-splitting photocatalyst contains two components: a light-harvesting semiconductor and a hydrogen evolution co-catalyst.^{4,5} The semiconductor absorbs photons and converts them to electron–hole pairs (*i.e.*, carriers), while the co-catalyst plays a crucial role in the photocatalytic process: accelerating the charge separation of photo-excited charge carriers at the co-catalyst/semiconductor interface, providing active sites to suppress back reaction, and lowering the activation energy of the hydrogen evolution reaction.

Recently, cadmium sulfide (CdS) has been proven to be one of the most promising candidate semiconductors for visible-light response photocatalytic properties, owing to its narrow band gap ($E_g = 2.4$ eV) and appropriate conduction band edge.^{6–8} However, the bare CdS exhibited low photocatalytic efficiency due to its photocorrosion and fast recombination of photogenerated electron–hole pairs.⁹ To overcome these bottlenecks, a co-catalyst loaded onto semiconductor surfaces not only serves as an active site for hydrogen evolution but also contributes to promoting the charge transfer. So far, platinum (Pt) has been proven to be the most efficient noble metal co-catalyst, benefiting from its small overpotentials and low Fermi energy levels. However, its widespread application is

limited by their high cost and rare earth-abundance. Therefore, it is a central and urgent issue to find novel highly efficient and noble-metal-free co-catalyst. To date, transition-metal nonoxides (*e.g.*, carbides, sulfides, phosphides and nitrides) have been extensively studied as efficient co-catalysts due to their d-band states' resemblance to platinum.^{10–14} Among them, transition-metal nitride is highlighted in view of its superior activity and high stability, which makes it a very promising candidate for photocatalytic hydrogen evolution.^{15,16} Typically, Ni–Mo bimetallic nitrides, a class of metallic interstitial compounds, have attracted much attention in the field of electrocatalysis.¹⁷ For example, Ren and co-workers reported the use of Ni–Mo nitrides (NiMoN) nanorods as electrocatalysts for hydrogen evolution, with reaction activity close to that of Pt/C electrodes.¹⁸ The outstanding performance was ascribed to their excellent electronic conductivity and low adsorption free energy of H*, which facilitates electron transportation to the absorbed protons and reduction to hydrogen release. However, to the best of our knowledge, Ni–Mo bimetallic nitride (Ni₃Mo₃N) have not been employed as the co-catalyst for photocatalytic hydrogen evolution.

In this work, we report for the first time noble-metal-free Ni₃Mo₃N as a highly co-catalyst for photocatalytic H₂ production under visible light. After Ni₃Mo₃N (10%) was coupled with CdS, the H₂ evolution activity is remarkably increased to 6.56 mmol g⁻¹ h⁻¹, which was about 25 times higher than that of bare CdS sample. Moreover, the Ni₃Mo₃N/CdS composite showed excellent stability during the photocatalytic hydrogen evolution reaction for six consecutive cycles. A series of photo-electrochemical characterizations and Kelvin probe measurements prove that the Ni₃Mo₃N nanoparticles anchoring on the CdS surface facilitates photoinduced electron–hole pair separation and transfer, and therefore contributing to the improved photocatalytic activity for hydrogen evolution rate.

Fig. S1a shows the XRD pattern of the obtained orthorhombic Ni₃Mo₃N nanoparticles and no other impurities such as Ni and Ni₃N are detected in the sample. As shown in Fig. S1b, all diffraction peaks of CdS can be corresponded to

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hexagonal CdS. Compared with pristine CdS, the diffraction peak at 40.7° can be clearly seen in the $\text{Ni}_3\text{Mo}_3\text{N}/\text{CdS}$ composites, which corresponds to the (221) plane of $\text{Ni}_3\text{Mo}_3\text{N}$, indicating that $\text{Ni}_3\text{Mo}_3\text{N}$ was successfully anchored onto CdS. The TEM images clearly show that the $\text{Ni}_3\text{Mo}_3\text{N}$ nanoparticle and CdS are in close contact with each other (Fig. 1a). The HRTEM image further observed show lattice spacings at 0.32 and 0.30 nm, which corresponds to the (101) and (021) diffraction planes of CdS and $\text{Ni}_3\text{Mo}_3\text{N}$ (Fig. 1b). In addition, the corresponding EDX mapping of the $\text{Ni}_3\text{Mo}_3\text{N}/\text{CdS}$ composite as shown in Fig. 1c clearly indicates the existence of Cd, S, Ni, Mo and N elements in the sample and the uniform distribution of Ni, Mo and N elements. Collectively, it is conclusive from these experimental results that the $\text{Ni}_3\text{Mo}_3\text{N}$ nanoparticle was successfully loaded onto the CdS nanorod, forming heterojunction structure, and thus improves the rate of water reduction reaction.

X-ray photoelectron spectroscopy (XPS) reveals the presence of Cd, S, Ni and Mo elements in $\text{Ni}_3\text{Mo}_3\text{N}/\text{CdS}$ composite. This is in accordance with the TEM data. The high-resolution XPS spectra of Cd 3d and S 2p show that, the binding energy of Cd 3d and S 2p shift slightly toward higher binding energy, which are attributed to the increase in electronic density in CdS after loading $\text{Ni}_3\text{Mo}_3\text{N}$ and a strong interaction between CdS and $\text{Ni}_3\text{Mo}_3\text{N}$.^{14,19} For the high-resolution XPS of Ni 2p, the peak at 853.9 eV was assigned to the Ni^{2+} species in $\text{Ni}-\text{N}$,^{5,20} while the peaks located at 856.7 and 871.6 eV are ascribed to Ni 2p_{3/2} and Ni 2p_{1/2} of Ni^{2+} species.²¹ Furthermore, the two additional peaks at 862.6 and 876.2 eV are the relevant satellite peaks, demonstrating the existence of surface partial oxidation of the $\text{Ni}_3\text{Mo}_3\text{N}/\text{CdS}$ sample. In Fig. S2d, the binding energies of Mo 3d was observed at 228.1 eV could be attributed to the metal-nitride.²² The peak located at 225.9 eV corresponding to the characteristic binding energy of S 2s in sulfides.^{23,24} The peaks located at 227.2, 231.3, 232.3 and 235.4 eV are assigned to Mo^{4+} and Mo^{6+} due to the surface oxidation of $\text{Ni}_3\text{Mo}_3\text{N}$.^{25–28} In addition, the N 1s peak intensity is very low for $\text{Ni}_3\text{Mo}_3\text{N}$ (10 wt%)/CdS, and this may be due to the small amount of $\text{Ni}_3\text{Mo}_3\text{N}$ in the composite.^{29–31}

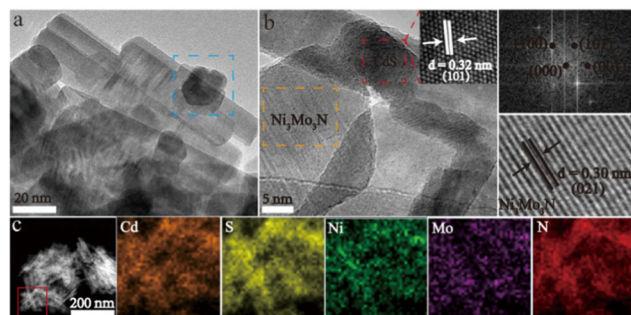


Fig. 1 (a and b) TEM and HRTEM images of the $\text{Ni}_3\text{Mo}_3\text{N}$ (10 wt%)/CdS sample and (c) EDX elemental mapping images of the $\text{Ni}_3\text{Mo}_3\text{N}$ (10 wt%)/CdS sample.

The UV-vis absorption spectra of the photocatalysts were employed to measure their light-harvesting abilities. As shown in Fig. 2a, there is a gradually enhanced absorption in the whole visible light region with the increase in the content of $\text{Ni}_3\text{Mo}_3\text{N}$. This can be attributed to the black metallic $\text{Ni}_3\text{Mo}_3\text{N}$ that absorbs all visible photons. Meanwhile, the behavior of charge trapping and separation in the CdS and $\text{Ni}_3\text{Mo}_3\text{N}/\text{CdS}$ composites was evaluated using photoluminescence. It can be observed that the $\text{Ni}_3\text{Mo}_3\text{N}$ co-catalyst loading results in a higher degree of quenching of CdS nanorod PL intensity, indicating that the recombination efficiency of the photogenerated electron-hole pairs in the CdS nanorods is greatly suppressed. This is reasonable because $\text{Ni}_3\text{Mo}_3\text{N}$ is able to accept and shuttle the photogenerated electrons from CdS because of its excellent electron conductivity and strong interaction between $\text{Ni}_3\text{Mo}_3\text{N}$ and CdS. Moreover, the $\text{Ni}_3\text{Mo}_3\text{N}/\text{CdS}$ composite shows a higher photocurrent density than bare CdS. In addition, $\text{Ni}_3\text{Mo}_3\text{N}/\text{CdS}$ exhibited a smaller semicircle than CdS in the Nyquist plots from electrochemical impedance spectroscopy (EIS), revealing that photo-excited charge carrier separation was promoted after the $\text{Ni}_3\text{Mo}_3\text{N}$ loading.

To measure the photocatalytic activity of the $\text{Ni}_3\text{Mo}_3\text{N}/\text{CdS}$ composites, we carried out the photocatalytic hydrogen evolution experiments using Na_2S and Na_2SO_3 as the sacrificial agents under visible light irradiation ($\lambda > 420$ nm). As illustrated in Fig. 3a, the pristine CdS displayed a poor photocatalytic performance ($0.26 \mu\text{mol g}^{-1} \text{h}^{-1}$), possibly due to the fast charge carrier recombination. After coupling with $\text{Ni}_3\text{Mo}_3\text{N}$, the CdS showed significantly increased photocatalytic HER activity. Specifically, $\text{Ni}_3\text{Mo}_3\text{N}$ (10 wt%)/CdS with an optimal content of the $\text{Ni}_3\text{Mo}_3\text{N}$ co-catalyst exhibited the highest photocatalytic hydrogen evolution rate of $6.56 \text{ mmol g}^{-1} \text{h}^{-1}$, which is much higher than those of CdS and 1 wt% Pt modified CdS. However, further increasing the amounts of

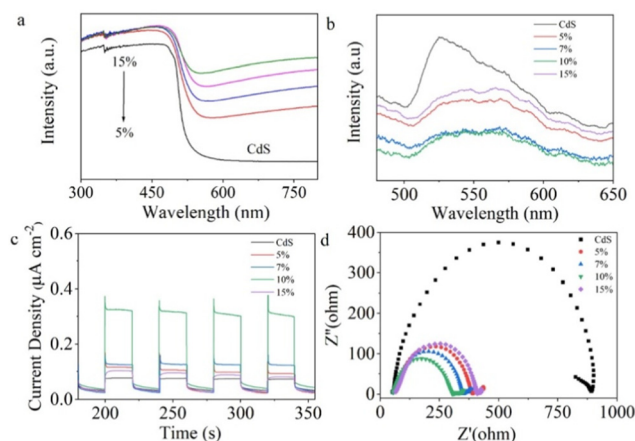


Fig. 2 (a) UV-vis absorption spectra of pristine CdS and $\text{Ni}_3\text{Mo}_3\text{N}$ (x wt%)/CdS ($x = 5, 7, 10$ and 15) samples; (b) photoluminescence emission spectra of CdS and $\text{Ni}_3\text{Mo}_3\text{N}$ (10 wt%)/CdS samples; photoelectrochemical measurements of CdS and $\text{Ni}_3\text{Mo}_3\text{N}$ (10 wt%)/CdS samples; (c) photocurrent response and (d) EIS Nyquist plots.

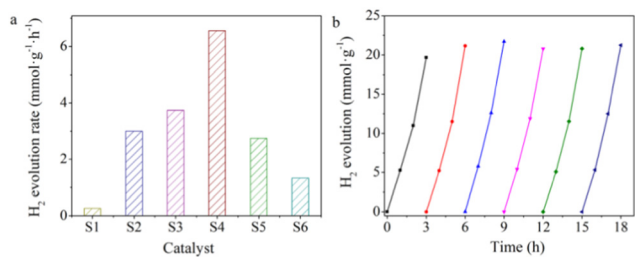


Fig. 3 Photocatalytic performance: (a) photocatalytic H₂ evolution rates of CdS and Ni₃Mo₃N (*x* wt%)/CdS (*x* = 0, 5, 7, 10 and 15; S1–S5) samples; Pt (1 wt%)/CdS (S6); (b) cyclic hydrogen evolution over the Ni₃Mo₃N (10 wt%)/CdS sample.

Ni₃Mo₃N in the Ni₃Mo₃N/CdS composite leads to a reduced photocatalytic activity, which could be attributed to the blocking incident light absorption and the coverage of active sites by the excessively loaded Ni₃Mo₃N co-catalyst. In addition, the quantum efficiency of Ni₃Mo₃N (10 wt%)/CdS at 420, 450 and 500 nm was evaluated to 10.6, 8.5 and 6%, respectively (Fig. S3a). Hydrogen cannot be detected under 550 nm light illumination, which confirms that the reactions were driven by photoabsorption of the photocatalyst. The Ni₃Mo₃N (10 wt%)/CdS sample demonstrates a stable photocatalytic hydrogen evolution activity, with no obvious activity loss after six cycling runs (Fig. 3b). Furthermore, we characterized the Ni₃Mo₃N (10 wt%)/CdS sample after six cycling durability tests. The corresponding XRD pattern matches well with the fresh Ni₃Mo₃N (10 wt%)/CdS catalyst, suggesting that its crystallinity and structure are well retained (Fig. S3b). Also, the XPS studies of Ni₃Mo₃N (10 wt%)/CdS before and after the photocatalytic hydrogen evolution stability tests were conducted and the results are shown in Fig. S4 of the SI. It shows that the catalyst is stable under the experimental conditions. Based on the result above, the photocatalytic activity of CdS is actually improved by loading an appropriate amount of Ni₃Mo₃N, and photostability was retained after six cycling runs.

The improvement of the photogenerated charge separation efficiency of CdS by a Ni₃Mo₃N co-catalyst can be ascribed to the Schottky heterojunction between Ni₃Mo₃N and CdS in the composites. To further confirm the direction of photoinduced electron transfer, the surface electronic potentials of CdS and Ni₃Mo₃N were measured using Kelvin probe technology. The work function (WF) of CdS and Ni₃Mo₃N is 4.99 and 5.23 eV, respectively, calculated using the equation: WF (eV) = WF (Au) + CPD/1000. The work function of Ni₃Mo₃N is greater than that of CdS, indicating that the Fermi level of Ni₃Mo₃N is more negative than that of CdS. It is well known that the interfacial electric field is the primary driving force for charge separation (Fig. 4a). When CdS and Ni₃Mo₃N are in contact, the free electrons will transfer from CdS to Ni₃Mo₃N until an equilibrium state is formed, which will induce an interfacial electric field orienting from CdS to Ni₃Mo₃N (Fig. 4b). In addition, the space charge layer formed on the CdS side will cause the band to bend upwards and form the Schottky barrier. The Schottky barrier and band bending effect make charge transfer more

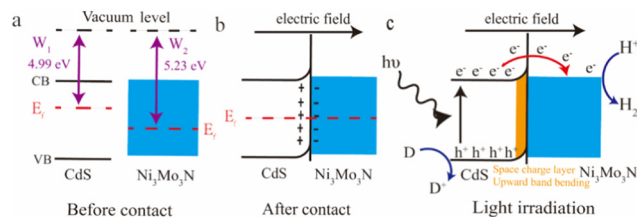


Fig. 4 Schematic illustration of the photocatalytic H₂ evolution and charge transfer process of the Ni₃Mo₃N/CdS composite.

effective between Ni₃Mo₃N and CdS, and prevent the electrons captured by Ni₃Mo₃N from returning to CdS. In other words, the Ni₃Mo₃N sides can accumulate negative charges, whereas positive charges accumulate on the CdS side (Fig. 4b). When the Ni₃Mo₃N/CdS composite was under light irradiation, electrons were excited to the conduction band of CdS, leaving the holes in the valence band. The photogenerated electrons migrate to Ni₃Mo₃N driven by the interfacial electric field between CdS and Ni₃Mo₃N. Moreover, the electrons will be captured by the H⁺ ions absorbed onto the Ni₃Mo₃N nanoparticles, and hydrogen molecules would form and release on the Ni₃Mo₃N nanoparticle surface (Fig. 4c). The hydrogen molecule is released through one of the two processes: 2H* → H₂ + 2* or H⁺ + e⁻ + H* → H₂ + *, where * denotes a catalytically active site on the surface of the Ni₃Mo₃N nanoparticles. Meanwhile, the holes will be consumed by the sacrificial agent. For these reasons, the photogenerated carriers in the CdS were suppressed and the photocatalytic hydrogen evolution was enhanced remarkably.

In conclusion, a noble-metal-free Ni₃Mo₃N/CdS photocatalyst was successfully fabricated, and it showed remarkably enhanced visible light photocatalytic activity for hydrogen evolution. Due to the formation of the Schottky heterojunction between CdS and Ni₃Mo₃N, the migration and separation of photogenerated electron–hole pairs are significantly promoted in the Ni₃Mo₃N/CdS composite. As a consequence, the Ni₃Mo₃N (10 wt%)/CdS composite shows the highest hydrogen evolution rate of 6.56 mmol g⁻¹ h⁻¹, which is 25 times higher than that of pure CdS. A high apparent quantum efficiency of 10.6% is reached at 420 nm. Moreover, the photocatalyst also exhibited high photocatalytic activity stability for six consecutive cycles of measurements. This work provides a facile strategy for the synthesis and application of Ni₃Mo₃N nanoparticles as an alternative co-catalyst to Pt in photocatalytic water splitting for hydrogen production.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its supplement.

tary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5dt02653a>.

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