Construction and performance of CdS/MoO₂@Mo₂C-MXene photocatalyst for H₂ production

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Abstract: Nowadays, photocatalytic technologies are regarded as promising strategies to solve energy problems, and various photocatalysts have been synthesized and explored. In this paper, a novel CdS/MoO₂@Mo₂C-MXene photocatalyst for H₂ production was constructed by a two-step hydrothermal method, where MoO₂@Mo₂C-MXene acted as a binary co-catalyst. In the first hydrothermal step, MoO₂ crystals with an egg shape grew on the surface of two-dimensional (2D) Mo₂C MXene via an oxidation process in HCl aqueous solution. In the second hydrothermal step, CdS nanorods were uniformly assembled on the surface of MoO₂@Mo₂C-MXene in ethylenediamine with an inorganic cadmium source and organic sulfur source. The CdS/MoO₂@Mo₂C-MXene composite with MoO₂@Mo₂C-MXene of 5 wt% exhibits an ultrahigh visible-light photocatalytic H₂ production activity of 22,672 μmol/(g·h), which is ~21% higher than that of CdS/Mo₂C-MXene. In the CdS/MoO₂@Mo₂C-MXene composite, the MoO₂ with metallic nature separates CdS and Mo₂C MXene, which acts as an electron-transport bridge between CdS and Mo₂C MXene to accelerate the photoinduced electron transferring. Moreover, the energy band structure of CdS was changed by MoO₂@Mo₂C-MXene to suppress the recombination of photogenerated carriers. This novel compound delivers upgraded photocatalytic H₂ evolution performance and a new pathway of preparing the low-cost photocatalyst to solve energy problems in the future.

Keywords: Mo₂C MXene; MoO₂; CdS; photocatalysis; H₂ production

1 Introduction

H₂ is a clean, eco-friendly, and pollution-free gas, which is considered as promising energy. Semiconductor photocatalysis is a convenient and low-cost approach of continuously obtaining H₂. Owing to the narrow bandgap, appropriate conduction band position, and good electronic charge transfer capability [1,2], CdS has been proved to be one of the most prominent semiconductor photocatalysts for H₂ production. However, the rapid recombination rate of the photoinduced electron–hole pairs restricts the performance of CdS [3,4]. Coupling CdS with other materials to form heterojunctions can effectively separate the photogenerated electron–hole pairs by electron trapping and proper band alignment. Noble metals, such as Pt, Au, Pd, etc. [5,6], have been deposited onto CdS to construct hybridized systems as co-catalysts, and accelerate reaction kinetics by facilitating the transfer of charge carriers and their spatial separation. Nonetheless, the limitation of high price, extreme scarcity, and complicated synthetic processes affect the
commercialization of current photocatalysts with the noble metals. Therefore, it is significant to develop high-performance CdS-based photocatalysts by coupling with low-cost materials, such as the transition metal sulfide [7–10], transition metal oxide [11,12], graphene oxide [13], hydroxide [14], carbide [15], etc.

MXenes are a series of two-dimensional (2D) transition metal carbides, nitrides, or carbonitrides with a general formula of $M_{n+1}X_nT_x$ ($n = 1, 2, 3$), where M is an early transition metal, X is a carbon or nitrogen, and $T_x$ stands for various surface terminations ($–OH$, $–O$, and $–F$). Normally, MXenes are prepared by etching A element from the MAX phase [16–20] and have shown great potential in various fields due to the numerous hydrophilic functionalities on the surface of MXenes, excellent metallic conductivity, and exposed terminal transition metal sites [21–24]. Theoretically, MXenes have been predicted as promising photocatalysts for water splitting in 2016 [25]. Subsequently, numerous research confirmed that MXene-based co-catalysts are promising candidates for the H$_2$ production [26–37]. Notably, among these works, only Ti$_2$C$_2$ MXene, the first member of MXenes, was considered, though there are many MXenes with different compositions. Mo$_2$C MXene is another MXene prepared by etching Mo$_2$Ga$_2$C [38–42]. In the previous work [43], we found that Mo$_2$C-MXene/CdS heterostructure exhibited an ultra-high H$_2$ production rate of 17,964 $\mu$mol/(g·h).

Although the photocatalytic performance of Mo$_2$C MXene as the co-catalyst is superior to most other MXenes, the photocatalytic activity tends to decrease within the irradiation time. This is because that MXenes are not stable during the irradiation. To increase the stability, Mo$_2$C MXene needs to be partly covered by a stable layer. Moreover, the layer needs to be very thin with high electrical conductivity and potential for faster charge-carrier transfer between MXene and CdS. Therefore, if a thin layer with high stability and high conductivity is introduced at the MXene–CdS interface, the deterioration tendency of the catalyst can be improved because of the high stability, and the catalytic performance can be improved due to the faster charge-carrier transferring.

MoO$_2$ is a metallic oxide with high stability and high electrical conductivity. It can be *in-situ* generated from the oxidation of Mo$_2$C MXene. Therefore, the MoO$_2$ thin layer can be introduced at the interface between Mo$_2$C MXene and CdS to enhance and stabilize the photocatalytic activity. In view of this, a novel catalyst with the structure of CdS/MoO$_2$@Mo$_2$C was designed in this paper. The catalyst showed higher and more stable catalytic performance compared to CdS/Mo$_2$C. In the catalyst, MoO$_2$ and Mo$_2$C MXene act as dual co-catalysts to increase the catalytic activity of CdS.

To construct the novel dual co-catalyst system, Mo$_2$C MXene was oxidized and covered by the *in-situ* generated MoO$_2$ to obtain MoO$_2$@Mo$_2$C-MXene structure. Then the CdS nanocrystals are assembled with the MoO$_2$@Mo$_2$C-MXene. A two-step hydrothermal method was used to make the catalyst. In the first step, the MoO$_2$ nanoparticles *in-situ* grew on the surface of Mo$_2$C MXene sheets to form MoO$_2$@Mo$_2$C-MXene hybrid via an oxidation process in HCl aqueous solution. Subsequently, in the second step, in the ethylenediamine with an inorganic cadmium source (Cd(NO$_3$)$_2$·4H$_2$O) and an organic sulfur source (thiourea), Cd$^{2+}$ and S$^{2−}$ were self-assembled on the surface of MoO$_2$@Mo$_2$C-MXene to form a heterostructure of CdS/MoO$_2$@Mo$_2$C. The heterostructure indeed possessed better photophysical and photoelectrochemical properties compared to CdS/Mo$_2$C, and exhibited an ultra-high photocatalytic activity.

### 2 Experimental

#### 2.1 Synthesis of Mo$_2$C MXene

Highly pure Mo$_2$C MXene was made by a hydrothermal strategy [44]. Briefly, Mo$_2$Ga$_2$C powders (lab-made) of 1 g [39–41] were mixed with HF (40%) solution of 40 mL and sealed in a Teflon-lined autoclave. The autoclave was ultrasonically treated for 30 min and kept at 160 °C for 24 h. Then the black sediments in the solution were washed with de-ionized water and ethanol until pH = 6. Finally, the obtained powders were dried at 60 °C for 12 h in vacuum, which were Mo$_2$C MXene powders.

#### 2.2 Synthesis of MoO$_2$@Mo$_2$C-MXene composite

NaBF$_4$ (99.9%, Macklin, China) of 0.2 g, as the directing reagent, was dissolved in 1.0 M HCl solution of 15 mL (36–38 wt%, Yantai Shuangshuang Chemical, China) and stirred for 30 min. Mo$_2$C MXene powders of 0.1 g were added into the above mixed solution, and the solution was stirred for 30 min, followed by ultrasonication for 30 min. The suspension was sealed
in a Teflon-lined autoclave and hydrothermally treated at 180 °C for 24 h. Thereafter, the powders of MoO2@Mo2C-MXene composite were collected, which were washed with the de-ionized water and ethanol until neutral and dried at 60 °C for 12 h in vacuum.

2.3 Assembly of CdS with MoO2@Mo2C-MXene

Cd(NO3)2·4H2O (analytical reagent (AR) 99%, Macklin, China) of 1.53 g and thiourea (AR 99%, Shanghai Aladdin Biochemical Technology, China) of 1.14 g, as the precursors of CdS, were dissolved in the de-ionized water of 40 mL and stirred for 30 min. A certain amount of MoO2@Mo2C-MXene powders were dispersed in the solution and strongly ultrasonic treated for 1 h. Thereafter, the ethylenediamine (AR 99%, Luoyang Chemical Reagent Factory, China) of 10 mL was added into the above solution and stirred for another 30 min. Then the mixed solution was sealed in a Teflon-lined autoclave and kept at 180 °C for 24 h to synthesize CdS/MoO2@Mo2C by a solvothermal process. The final precipitates with golden color were separated from the solution by centrifugalizing. The powders were washed with the de-ionized water and ethanol several times until neutral, and dried at 60 °C in vacuum for 12 h. According to the mass ratio of MoO2@Mo2C-MXene composite to CdS (0.1, 1, 2.5, 5, and 7 wt%), the prepared samples were labelled as CMMx (x = 0.1, 1, 2.5, 5, and 7). As reference samples, CdS/Mo2C and CdS/MoO2 with the optimal loading of co-catalyst (Mo2C MXene of 2.5 wt% for CdS/Mo2C and MoO2 of 5 wt% for CdS/MoO2) were made through the identical preparation process.

2.4 Materials characterizations

All the samples were tested by X-ray diffraction (XRD, Smart-lab, Rigaku Corporation, Japan) by using Cu Ka (λ = 1.5406 Å) radiation, observed by a scanning electron microscope (SEM, Merlin Compact, Zeiss, Germany) equipped with an energy dispersive spectroscopy (EDS, X-MaxN, Oxford Instruments, UK) and a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) with an accelerating voltage of 200 kV. The chemical components of the products were characterized by an X-ray photoelectron spectrometer (XPS, ESCALAB 250X, Thermo Fisher Scientific, USA) with an Al Kα source (hv = 1486.6 eV) of 12.5 kV. The Brunauer–Emmett–Teller specific surface area (SBET) was measured by N2 adsorption at 77 K using an adsorption analyzer (ASAP2460, Micromeritics Instruments, USA). The ultraviolet–visible (UV–Vis) diffuse reflectance spectra (DRS) were tested by dry-pressing disk samples with an ultraviolet–visible spectrophotometer (UH4150, Hitachi, Japan) and using BaSO4 as the reflectance standard. The photoluminescence (PL) spectra were evaluated by a spectrofluorophotometer (Fluoromax-4, Horiba, Japan) under the excitation of 350 nm at room temperature.

2.5 Photocatalytic H2-production measurements

The photocatalytic experiments were tested by a photocatalytic activity evaluation system (CEL-SPH2N, Beijing China Education Au-light Technology, China). A quartz vessel of 250 mL was used to carry out the water-splitting reaction. The quartz vessel was maintained at room temperature and vacuumed until the pressure was maintained at ~0.1 MPa during the reaction. A Xe lamp of 300 W equipped with a cut-off filter (λ ≥ 420 nm) was utilized as the light source (ca. 80 mW/cm² for the focused intensity on the sample in the mixed solution). The photocatalyst of 20 mg was added into the aequous solution of 50 mL containing the lactic acid (AR 85%) of 10 mL as the sacrificial reagent solution and the de-ionized water of 40 mL with stirring continuously in the range of 15–20 °C. The generated H2 during irradiation was analyzed by a gas chromatograph (TCD, TDX01 column, CEL-GC7920, Beijing China Education Au-light Technology, China) with N2 as a carrier gas. The apparent quantum efficiency (AQE) was measured under the identical photocatalytic conditions except for the replacement of the Xe lamp with a monochromatic cut-off filter (λ = 420 nm) as the light source to trigger the photocatalytic reaction. The focused intensity for 420 nm irradiation was ca. 6 mW/cm².

2.6 Electrochemical and photoelectrochemical measurements

The photoelectrochemical measurements were conducted on an electrochemical analyzer (CHI760E, Chenhua Instruments, China) in a standard three-electrode system by using the samples as the working electrodes, Ag/AgCl as the reference electrode, and the Pt wire as the counter electrode. The transient photocurrent (TPC) measurements were carried out under the visible light irradiation (λ ≥ 420 nm) with on/off switches at a bias of 0.2 V (vs. Ag/AgCl). The electrochemical
impedance spectra (EIS) experiments were performed at a bias of 0.9 V (vs. Ag/AgCl) under the visible light irradiation ($\lambda \geq 420$ nm). The Mott–Schottky plots were recorded over the AC frequency of 1000 Hz in the dark. The electrolytes in all the electrochemical measurements were 0.5 M Na$_2$SO$_4$ aqueous solution. The working electrodes were synthesized as follows: the as-prepared samples of 10 mg were dispersed in the mixed aqueous solution containing the de-ionized water of 375 μL, the ethanol of 125 μL, and the Nafion of 50 μL by ultrasonication for 2 h to make uniform slurry. Thereafter, the slurry was coated onto a fluorine doped tin oxide (FTO) glass plate of 10 mm × 25 mm, and the obtained electrodes were dried in air for 24 h.

3 Results and discussion

3.1 Synthesis and characterization of CdS/MoO$_2$@Mo$_2$C

The XRD patterns of as-prepared samples were shown in Fig. 1. The standard patterns of MoO$_2$ (PDF Card No. 78-1069) and wurtzite CdS (PDF Card No. 77-2306) are also shown in the figure. Mo$_2$Ga$_2$C is a new compound found in 2015 [38]. The standard pattern of Mo$_2$Ga$_2$C reported in Ref. [38] is shown in the figure. As shown in Fig. 1, the Mo$_2$Ga$_2$C powders made in this paper for starting material are highly pure Mo$_2$Ga$_2$C [41]. After etching, the powders converted to Mo$_2$C MXene with the feature of the strong characteristic peak of (002) that shifts to a low angle [43,44]. From the comparison of the two patterns, Mo$_2$C MXene was successfully made from Mo$_2$Ga$_2$C. The top pattern in Fig. 1(a) is the pattern of Mo$_2$C MXene oxidized by the hydrothermal process (MoO$_2$@Mo$_2$C-MXene). Compared with the XRD patterns of Mo$_2$C MXene and standard MoO$_2$, the emergence of MoO$_2$ is evidenced by the obvious diffraction peaks of MoO$_2$ (PDF Card No. 78-1069). The co-existence of Mo$_2$C MXene and MoO$_2$ indicates the successful synthesis of the MoO$_2$@Mo$_2$C-MXene composite.

The XRD patterns of CdS assembled with different amounts of MoO$_2$@Mo$_2$C-MXene, named as CMM$\chi$ (x = 0.1, 1, 2.5, 5, and 7), are shown in Fig. 1(b). Compared with the standard wurtzite CdS shown in the bottom of Fig. 1(b), all patterns correspond well with the wurtzite phase (PDF Card No. 77-2306). Thus, CdS with the wurtzite crystal structure was obtained by this method. In general, CdS has two crystal structures: wurtzite (high-temperature phase) and sphalerite (low-temperature phase). Normally, the wurtzite CdS, the phase obtained in this work, has better photocatalytic performance compared to the sphalerite CdS [45].

The microstructure images of as-prepared samples are shown in Fig. 2. As shown in Fig. 2(a), the microstructure of Mo$_2$C MXene is 2D flakes, similar to its precursor Mo$_2$Ga$_2$C [39–41]. From Fig. 2(b), for MoO$_2$@Mo$_2$C-MXene sample, egg-shaped MoO$_2$ crystals appear on the surface of Mo$_2$C MXene flakes, which grew during the hydrothermal oxidation with the assistance of NaBF$_4$ as the directing reagent. As shown in Fig. 2(c), the CdS/MoO$_2$@Mo$_2$C sample exhibits an acanthosphere structure that consists of the rod-like CdS crystals. Besides, a bare 2D Mo$_2$C MXene sheet was observed among several acanthospheres in Fig. S1(a) in the Electronic Supplementary Material (ESM), which is marked by a red cycle. In the corresponding high magnification image (Fig. S1(b) in the ESM), a few immature CdS particles appear on the surface of Mo$_2$C MXene, illustrating how the CdS nanorods grew up at the beginning of the hydrothermal reaction.

It is worth noting that, the hydrothermal oxidation not only facilitated the growth of MoO$_2$ on Mo$_2$C.
MXene, but also made Mo2C MXene flakes more transparent to electrons in the SEM observation. Figure S2(a) in the ESM shows that some loose Mo2C MXene sheets in the red block diagram exhibit the transparent feature of electrons. The high magnification SEM image (Fig. S2(b) in the ESM) shows that the below flakes can be observed due to the electron transparency of Mo2C MXene sheets. Besides, abundant cracks, which are similar to defects, are observed clearly on the 2D sheets. On the contrary, the Mo2C MXene before the hydrothermal oxidation shows a smooth layered morphology without obvious cracks (Fig. S2(c) in the ESM). According to the previous research, the defects and nanopores in the Mo2C MXene flakes are beneficial to the energy storage or catalysis [46].

The TEM image of MoO2@Mo2C-MXene is shown in Fig. 2(d). Many 2D crystals with the typical MXene structure were observed (marked by a red rectangle), and a crystal with an egg shape was observed (marked by a yellow rectangle). The high-resolution TEM (HRTEM) image of the yellow rectangle is shown in Fig. 2(e). The lattice plane with $d$ spacing of 0.34 nm is attributed to the (011) plane of MoO2. The electron diffraction pattern in the inset of Fig. 2(e) confirms that it is a monoclinic phase of MoO2 with the P21/c space group [47]. The HRTEM image of the red rectangle is shown in Fig. 2(f). The $d$-spacing estimated in Fig. 2(f) is 0.26 nm, corresponding to the (100) planes of Mo2C MXene. The electron diffraction pattern in the inset of Fig. 2(f) shows that it is the hexagonal crystal of Mo2C MXene. Based on the above analysis, the two type crystals in Fig. 2(d) correspond to the MoO2 and Mo2C MXene. As shown in Fig. S3 in the ESM, the MoO2 crystal with the egg shape was derived from Mo2C MXene and gradually grew up until the Mo2C MXene sheets were completely covered.

The TEM image of CdS/MoO2@Mo2C with an acanthosphere shape is shown in Fig. 2(g). To observe the core of the acanthosphere, the sample was further treated by ultrasound for breaking the particles. The TEM image is shown in Fig. S4 in the ESM, which reveals that the CdS nanorods with a radial arrangement
grew on the core of MoO$_2$@Mo$_2$C-MXene composite. A high magnification TEM image in Fig. 2(h) shows the formed heterostructures between CdS and MoO$_2$@Mo$_2$C-MXene composite. The lattice fringes of 0.36 nm of the nanoparticle observed by the HRTEM in Fig. 2(i) are attributed to the (100) facets of hexagonal wurtzite CdS, which further indicates that the CdS nanorods synthesized in this work are the dominant wurtzite phase. Besides, the lattice fringes of 0.28 nm agree well with the (102) facets of MoO$_2$. The scanning transmission electron microscopy (STEM) image (Fig. 2(j)) and the corresponding element mappings focusing on the heterostructures clearly identify the component distribution. Mo and O are mainly distributed in the bottom crystal in Fig. 2(j), corresponding to MoO$_2$. The distribution of Cd and S in the top crystal confirms the existence of CdS.

The chemical composition and bonding states of CMM5 were tested by an X-ray photoelectron spectrometer (XPS). The XPS survey spectrum is shown in Fig. S5 in the ESM, which displays that Cd, O, C, Mo, and S are dominant elements. Figure 3(a) shows the XPS spectra in the Mo 3d region before and after the combination of MoO$_2$@Mo$_2$C-MXene and CdS. The Mo 3d spectrum of MoO$_2$@Mo$_2$C-MXene can be divided into two main peaks, as clearly shown in Fig. 3(a). The peaks centered at 229.6 and 232.8 eV can be ascribed to the Mo–C species in Mo$_2$C MXene [46]. Significantly, the binding energy of Mo–C species at 229.6 eV is 1.5 eV higher than that of the Mo–C species (228.1 eV) in Mo$_2$Ga$_2$C [48], indicating the replacement of the Ga element by plenty of electronegative surface functional groups (O, OH, and/or F) during the etching process [49]. The binding energy peaks of Mo 3d$_{5/2}$ (230.0 eV) and Mo 3d$_{3/2}$ (233.1 eV) components are characteristics of Mo$^{4+}$ [50], i.e., MoO$_2$ derived from Mo$_2$C MXene, while the other two weaker peaks at 231.2 and 235.6 eV correspond to Mo$^{6+}$ or Mo$^{3+}$ [48,51], suggesting that a small number of other forms of molybdenum oxide, such as MoO$_3$, co-exist in the generated MoO$_2$ during the hydrothermal treatment. For the CMM5 sample, a strong peak at 225.45 eV appears in the Mo 3d experimental signal, which is intensively associated with the formation of Mo–S bonds [52].

The XPS spectra in S 2p and Cd 3d are shown in Figs. 3(b) and 3(c), respectively. Compared with the pure CdS, the peaks of S 2p and Cd 3d in the CMM5 sample both shift towards a higher binding energy direction, owing to the decreased electronic density of Cd and S after coupling with MoO$_2$@Mo$_2$C-MXene and the formed heterojunction interaction [53].

The N$_2$ adsorption–desorption isotherms and the pore size distributions are shown in Fig. S6 in the ESM. All the samples exhibit similar type IV isotherms with a well-defined H3 hysteresis loop (Fig. S6(a) in the ESM), demonstrating the presence of mesopores [54]. According to Barrett–Joyner–Halenda method, the calculated distribution curves of CMMx samples are shown in Fig. S6(b) in the ESM. The pore sizes of all samples are mainly in the range of 4–30 nm (mesopores), while a small number of pores have a size above 50 nm, even 100 nm (macropores). The presence of such a hybrid pore size of mesopores and macropores is beneficial to the contact between the reactant and the photocatalyst and facilitates the photocatalytic process [55]. The $S_{BET}$ of all the CdS/MoO$_2$@Mo$_2$C is shown in Table S1 in the ESM. The results reveal that all the samples have similar $S_{BET}$ from 14.3 to 15.5 m$^2$/g.

According to the experimental results and discussion above, the typical synthesis route of CdS/MoO$_2$@Mo$_2$C nanoparticles is schematically depicted in Fig. 4. MoO$_2$ was formed on the surface of Mo$_2$C MXene due to oxidation with the help of HCl in the first hydrothermal

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**Fig. 3** (a) High resolution XPS spectra of MoO$_2$@Mo$_2$C-MXene and CMM5 in the Mo 3d region. High resolution XPS spectra of CdS and CMM5 in (b) S 2p region and (c) Cd 3d region.
process. Thus, the MoO$_2$@Mo$_2$C-MXene composite was obtained. Then, the CdS nanocrystals nucleated and grew up on the surface of the MoO$_2$@Mo$_2$C-MXene composite in the second hydrothermal process. Finally, the CdS/MoO$_2$@Mo$_2$C nanoparticles in the acanthosphere shape were obtained.

3.2 Photocatalytic properties

The photocatalytic H$_2$ production of CdS/MoO$_2$@Mo$_2$C samples (20 mg) was evaluated at room temperature under the visible light with the lactic acid as the sacrificial agent. The activities of each sample for the H$_2$ production (illumination for 4 h) are displayed in Fig. 5(a), and the H$_2$ production rates are shown in Fig. 5(b). The pure CdS sample presents a low H$_2$ production rate of 1923 μmol/(g·h) in Fig. 5(b), while the H$_2$ evolution performance is significantly boosted with the addition of MoO$_2$@Mo$_2$C-MXene for CMM$\times$ ($\times$ = 0.1, 1, 2.5, 5, and 7). The number of formed heterostructures between CdS and MoO$_2$@Mo$_2$C-MXene increases with the loading of MoO$_2$@Mo$_2$C-MXene, which is beneficial to the enhancement of photocatalytic activity. In particular, the optimal sample of CMM5 exhibits the best H$_2$ production rate of 22,672 μmol/(g·h), which is ~21% higher than that of CdS/Mo$_2$C [43]. The reduction of photocatalytic activity with the further increase of MoO$_2$@Mo$_2$C-MXene is probably because excessive MoO$_2$@Mo$_2$C-MXene can cover the active sites of the catalysts [28,56]. Furthermore, the photocatalytic activity of CMM5 was repeatedly observed under the same reaction conditions for the three recycling tests (Fig. 5(c)). High stability of photocatalytic activity for CMM5 was maintained during each cyclicity experiment, indicating the excellent photo-stability of heterostructure between CdS and MoO$_2$@Mo$_2$C-MXene.

The AQE of the samples was evaluated under the identical photocatalytic conditions except that a
monochromatic light resource ($\lambda = 420$ nm) was employed to trigger the photocatalytic reactions. As shown in Table S2 in the ESM, the results of AQE are in accordance with the photocatalytic H\(_2\) production experiments that CMM5 can more effectively transform the absorbed photons into H\(_2\) molecules (49.2%).

To further investigate the effect of the structure of CdS/MoO\(_2@\)Mo\(_2\)C in the photocatalysis process, the photocatalysis of CdS coupled with only MoO\(_2\) (99%, Shanghai Aladdin Biochemical Technology, China) or Mo\(_2\)C MXene under the identical preparation technology was evaluated in the same photocatalytic measurements and compared with that of the CMM5 sample in Fig. S7(a) in the ESM. The H\(_2\) production rates of optimal CdS/MoO\(_2\) and CdS/Mo\(_2\)C are 8002 and 17,472 \(\mu\)mol/(g·h), respectively. The results show that CdS/MoO\(_2@\)Mo\(_2\)C (CMM5) has much better photocatalytic performance than CdS/Mo\(_2\)C and CdS/MoO\(_2\). The faster transfer of excited charge carriers and efficient charge separation caused by MoO\(_2\) between CdS and Mo\(_2\)C MXene can extensively increase the photocatalytic performance of CdS/Mo\(_2\)C.

### 3.3 Photophysical and photoelectrochemical properties

The light response and photoelectric characters were investigated to understand the photocatalytic processes. Firstly, the UV–Vis diffuse reflectance spectra (DRS) were measured to investigate the photoabsorption behaviors of the photocatalysts. The UV–Vis DRS of the samples are shown in Fig. 6(a). As shown in Fig. 6(a), the light-harvesting capabilities of all CMMx samples appeal in the wavelength range of > 520 nm. Moreover, the absorption intensity in the light region ($\lambda > 520$ nm) increases gradually with the loading of the MoO\(_2@\)Mo\(_2\)C-MXene compound. This is due to the inherent optical property of the MoO\(_2@\)Mo\(_2\)C-MXene compound and the interface between MoO\(_2@\)Mo\(_2\)C-MXene and CdS. The light-harvesting capabilities of the CdS/Mo\(_2\)C sample are also shown in Fig. 6(a). This CdS/Mo\(_2\)C sample with Mo\(_2\)C MXene of 2.5 wt% presented the best H\(_2\) production rate of 17,964 \(\mu\)mol/(g·h) among the CdS/Mo\(_2\)C samples [43]. As shown in Fig. 6(a), CMM5 has better light-harvesting capability.

![Fig. 6](https://example.com/fig6.png)  
(a) UV–Vis DRS of CMM\(_x\) samples and CdS/Mo\(_2\)C. (b) PL spectra of CdS, CMM5, and CdS/Mo\(_2\)C. The inset without the CdS spectrum is used to show the PL intensity difference between CMM5 and CdS/Mo\(_2\)C. (c) EIS plots and (d) TPC responses of CdS and CMM5.
compared to CdS/Mo2C, which corresponds to a better H2 production rate (22,672 μmol/(g·h)). Besides, compared with the pure CdS, the loading of MoO2@Mo2C-MXene makes a gradual absorption edge red-shift and promotes the visible absorption, which is more helpful to promote the progress of the photocatalytic reaction.

The PL spectroscopy was used to analyze the separation efficiencies of photogenerated carriers. The PL spectra of CdS, CMM5, and CdS/Mo2C are shown in Fig. 6(b). The pure CdS exhibits a strong PL peak at 435 nm, indicating the quick photoinduced carrier recombination. In comparison, the PL intensities of CMM5 and CdS/Mo2C decline dramatically, which implies that the photoinduced carrier recombination is effectively suppressed owing to the existence of co-catalyst. Besides, compared with CdS/Mo2C, CMM5 presents the lowest PL intensity, suggesting that CdS/MoO2@Mo2C has a lower electron–hole recombination rate probably due to the “long” reversed flow path of electrons from Mo2C MXene to CdS caused by the MoO2 separation [57].

The charge-transfer efficiency was investigated by the EIS and TPC density measurements, which are shown in Figs. 6(c) and 6(d), respectively. As indicated in Fig. 6(c), CMM5 has a smaller arc radius of charge transfer resistance than CdS, which is indicative of higher separation efficiency of carriers. The TPC responses of CdS and CMM5 were tested by several on–off cycles under illumination. As shown in Fig. 6(d), the photocurrent intensity of CMM5 was significantly higher than that of CdS. This is because the MoO2@Mo2C-MXene composite, as the binary co-catalyst, was effectively to receive photogenerated electrons from CdS. Thus, the photoelectrochemical experiments demonstrate that the introduction of MoO2@Mo2C-MXene can obviously promote the light absorption, charge separation, and transfer.

### 3.4 Photocatalytic mechanism

The energy band structure of semiconductor samples is crucial to comprehending the mechanism in the photocatalytic system for the H2 evolution activity. The band gap energy (Eg) of the samples is calculated by Eq. (1) [58]:

\[(αhv)^{1/n} = A(hv - E_g)\]

where α, h, ν, and A are the absorption constant, the Planck constant, the frequency, and the constant, respectively. Here, the variable n is 1/2 because the nature of CdS is a direct band gap material, and CdS has a characteristic of the n-type semiconductor [59]. Figure 7(a) draws the extrapolated Tauc plots according to Eq. (1) and the corresponding UV–Vis DRS in Fig. 6(a). The E_g of CdS, CMM5, and CdS/Mo2C can hence be estimated at 2.26, 2.23, and 2.25 eV, respectively. Compared with the pure CdS, the E_g of CMM5 and CdS/Mo2C were tuned to be relatively narrow after the loading of MoO2@Mo2C-MXene or Mo2C MXene, resulting in the absorption of the majority of visible light [60].
The positions of conduction band (CB) are determined by the Mott–Schottky plots (Fig. 7(b)). From the Mott–Schottky plots, the flat band potentials ($E_{fb}$) of the photoelectrodes of CdS, CMM5, and CdS/Mo2C can be found to be $-0.64$, $-0.77$, and $-0.73$ V (vs. Ag/AgCl), respectively. Thus, the CB values of CdS, CMM5, and CdS/Mo2C are equivalent to be $-0.44$, $-0.57$, and $-0.53$ V vs. normal hydrogen electrode (NHE), respectively, according to the formula of $E_{NHE} = E_{Ag/AgCl} + 0.197$ V, because of the little difference between the $E_{fb}$ and the lower CB edge for the n-type semiconductor [61]. According to the $E_{g}$ values from the Tauc plots in Fig. 6(a) and the calculated CB, the calculated valance band (VB) levels of CdS, CMM5, and CdS/Mo2C are $1.82$, $1.66$, and $1.72$ V vs. NHE, respectively. According to these, the energy band structure can be schematically described in Fig. 7(c). Compared with the pure CdS, CMM5 and CdS/Mo2C have more negative CB levels, while CMM5 exhibits the most negative value of CB. Thus, the photoinduced electrons in the CB region of CdS/Mo2C have a stronger reduction capability compared to the case in CdS/Mo2C.

In the n-type semiconductor, the $E_{fb}$ potential is close to the Fermi level ($E_f$) [62]. Therefore, the $E_f$ levels of CdS, CMM5, and CdS/Mo2C can be regarded as $-0.44$, $-0.57$, and $-0.53$ V vs. NHE, respectively. According to the previous works, the $E_f$ values of MoO2 and Mo2C MXene are calculated to be $0.57$ V [63] and $1.09$ V [43], respectively. Hence, the electrons migrate from CdS with the electronegative $E_f$ to MoO2@Mo2C-MXene or Mo2C MXene with the electropositive $E_f$ after their combination. Based on the above analysis, the changes in the band structure before and after the combination between CdS and MoO2@Mo2C-MXene or Mo2C MXene are schematically shown in Fig. 8. After the combination, the $E_f$ of pure CdS is much more negative than those of MoO2 and Mo2C MXene (Figs. 8(a) and 8(d)). After coupling with co-catalysts, the charges are redistributed among them until equilibrium with the reduction of the band gap of CdS (Figs. 8(b) and 8(e)). Thus, their Fermi levels reach the same value [63]. Then, the CB and VB of CdS in CMM5 and CdS/Mo2C are bent “upward”. In view of this, a Schottky junction is formed between CdS and co-catalyst due to the remain of positive charges in CdS near the interface, where a space charge layer is formed [64]. Under the visible-light illumination (Figs. 8(c) and 8(f)), CdS is excited to produce electrons and holes. Then the excited photoinduced electrons can be transferred from the VB to the CB in CdS, building up the separation of photoexcited electron–hole pairs. In general, the semiconductor material with a narrow band gap is more beneficial to the solar energy conversion under visible light [60], indicating that it should be possible to irradiate CMM5 with the light of MoO2 and Mo2C MXene.

![Fig. 8](https://www.springer.com/journal/40145)

**Fig. 8** Schematic illustration of the changes of the band structures before and after coupling in the case of (a, b) CdS/MoO2@Mo2C and (d, e) CdS/Mo2C. (c, f) Schematic illustration of separation and transfer of photoinduced electrons and holes in the CdS/MoO2@Mo2C and CdS/Mo2C systems under the visible light irradiation.
lower energy than that needed to electronically excite CdS/Mo2C, i.e., the formed separation of photogenerated carriers can be readily achieved for CdS/MoO2@Mo2C in CdS as compared to CdS/Mo2C.

Owing to the restriction of the “upward” bending of the CB and the VB in CdS resulting from the reduced space charge layer thickness [65], the photoinduced electrons in the CB of CdS can still keep going to migrate across the Schottky junction to co-catalyst, leaving the photoinduced holes in the VB of CdS. As a result, the Schottky junction can serve as an electron sink to capture the photoinduced electrons effectively and restrict electrons from diffusing back to CdS. As depicted in Fig. 8, the CB position of CdS becomes more negative, from $-0.44$ (pure CdS) to $-0.57$ or $-0.53$ V vs. NHE after coupling with MoO2@Mo2C-MXene or Mo2C MXene. The more negative CB position in the heterostructure, especially in CdS/MoO2@Mo2C, indicates the formation of a “higher” Schottky junction, which can more effectively prevent electrons from returning to CdS. In view of this, more holes left in the VB can be consumed by the sacrificial reagent, and the further suppressive recombination is achieved.

The contrastive experiments in Fig. S7(a) in the ESM confirm that two CdS samples coupled with MoO2 and Mo2C MXene exhibit lower H2 production capacity than that of CdS/MoO2@Mo2C. Obviously, the formed double heterointerface (CdS–MoO2 and MoO2–Mo2C) plays an important role in the photocatalysis process. After being transferred to the MoO2@Mo2C-MXene composite, the electrons further rapidly shuttle to Mo2C MXene through MoO2.

Both heterointerfaces (CdS–MoO2 and Mo2–Mo2C) are essential for the photocatalysis process. Single CdS–MoO2 heterointerface does not have excellent performance. This is because MoO2 has a high carrier-density. The high carrier-density is often accompanied by a faster recombination rate of photoexcited electron–hole pairs in MoO2 due to the small band gaps [63]. Thus, if there is no Mo2C MXene with a high reduction capability of H+ into H2 as electron trapping, the CdS/MoO2 shows low photocatalytic activity due to the faster recombination rate of photoexcited electron–hole pairs in MoO2. In the CdS/MoO2@Mo2C system, it is more likely that MoO2 should be regarded as an electron-transport bridge for the fast photoinduced electron transferring from CdS to Mo2C MXene due to the existence of the double heterointerface, which is similar with the role of carbon species in some photocatalytic systems [66–68]. Moreover, in the case of Mo2C MXene being as the single co-catalyst, the migration rate of photoinduced electrons from CdS to Mo2C MXene is “slower” owing to the lack of MoO2 as the electron-transport bridge. The mechanism discussed above and the charge-transfer efficiency are further evidenced by the EIS and TPC in Figs. S7(b) and S7(c) in the ESM, respectively.

Last but not the least, Mo2C MXene has been proved to be an excellent candidate among various MXenes for the photocatalytic H2 production due to its near-zero $\Delta G_{\text{H}}^{\text{f}}$ and more activity of Mo element. In this case, Mo2C MXene can serve as an electron trapping because of its electropositive $E_{\text{f}}$ position and excellent conductivity. The photoinduced electrons arrive in Mo2C MXene finally and transfer to the active sites on the MXene surface, where the protons in the aqueous solution are efficiently reduced and the reduction of H+ into H2 is achieved by the photoinduced electrons.

Table S3 in the ESM makes a comparison between CdS/MoO2@Mo2C and various state-of-the-art MXene-based and CdS-based photocatalysts previously reported. It is evident that CdS/MoO2@Mo2C made in this paper outperforms most other MXene-based photocatalysts with the best H2 evolution performance, even superior to the noble metal catalysts. Therefore, the novel CdS/MoO2@Mo2C photocatalyst modified based on CdS/Mo2C successfully achieves the further improvement of photocatalytic H2 production and provides new ideas for the application of MXenes in the photocatalysis.

4 Conclusions

In summary, the CdS/MoO2@Mo2C photocatalyst was successfully prepared by a two-step hydrothermal method. In this system, CdS grew on the surface of the MoO2@Mo2C-MXene composite and formed an acanthosphere structure. Remarkably, the optimal CdS/MoO2@Mo2C (CMM5) exhibits an ultrahigh H2 production rate of 22,672 $\mu$mol/(g·h) under visible light, which is 11.8 times that of CdS. Moreover, the binary co-catalyst of MoO2@Mo2C-MXene based CdS also has higher photocatalytic H2 production activity than that of Mo2C MXene as the single co-catalyst. The experimental results illustrate that CdS/MoO2@Mo2C possesses better photophysical and photoelectrochemical properties compared to CdS/Mo2C due to the presence of MoO2 with excellent electrical conductivity as the
electron-transport bridge between CdS and Mo2C MXene, thereby leading to faster photoinduced electron transfer. The energy band structure reveals that the CB of CdS is tuned to be more negative after coupling with MoO2@Mo2C-MXene compared to the case of CdS/Mo2C, indicating that the resultant “higher” Schottky junction can more effectively restrict electrons from diffusing back to CdS and further achieve the suppressive recombination. Besides, the relatively narrow band gap in CdS/Mo2C@Mo2C is beneficial to supressive recombination. Besides, the relatively narrow band gap in CdS/Mo2C is beneficial to the visible light absorption. These factors greatly enhance the H2 production of this novel photocatalytic system with the binary co-catalyst as compared to CdS/Mo2C.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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