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Article

Construction of LSPR-enhanced 0D/2D CdS/MoO_{3-x} S-scheme heterojunctions for visible-light-driven photocatalytic H₂ evolution

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ABSTRACT

Plasmonic nonmetal semiconductors with localized surface plasmon resonance (LSPR) effects possess extended light-response ranges and can act as highly efficient H₂ generation photocatalysts. Herein, an LSPR-enhanced 0D/2D CdS/MoO_{3-x} heterojunction has been synthesized by the growth of 0D CdS nanoparticles on 2D plasmonic MoO_{3-x} elliptical nanosheets via a simple coprecipitation method. Taking advantage of the LSPR effect of the MoO_{3-x} elliptical nanosheets, the light absorption of the CdS/MoO_{3-x} heterojunction was extended from 600 nm to the near-infrared region (1400 nm). Furthermore, the introduction of 2D plasmonic MoO_{3-x} elliptical nanosheets not only provided a platform for the growth of CdS nanoparticles, but also contributed to the construction of an LSPR-enhanced S-scheme structure due to the interface between the MoO_{3-x} and CdS, accelerating the separation of light-induced electrons and holes. Therefore, the CdS/MoO_{3-x} heterojunction exhibited higher photocatalytic H₂ generation activity than pristine CdS under visible light irradiation, including under 420, 450, 550, and 650 nm monochromatic light, as well as improved photo-corrosion performance.

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1. Introduction

The consumption of fossil fuels and the environmental degradation produced by the combustion of fuels have become two significant challenges in the 21st century. Therefore, more and more attention has been paid to the research and development of clean and renewable energy [1–7]. Semiconductor-based photocatalytic technology is considered a potential approach to converting solar energy into clean and pollution-free energy in the form of H₂ to meet the growing global energy demand [8–12]. For a typical photocatalytic H₂ evolution reaction, semiconductor photocatalysts such as TiO₂, g-C₃N₄, and CdS adsorb

photons to produce photo-induced electrons and holes to take part in redox reactions [13,14]. However, due to restricted light response and rapid recombination of photo-induced electron-hole pairs, the aforementioned pristine semiconductors usually demonstrate unsatisfactory water splitting activities [15–18].

Recently, plasmonic semiconductor-based photocatalysts have attracted significant interest owing to their broad light-harvesting capacities, which range from visible to near-infrared light. Furthermore, they can harvest low-energy photons to generate extra high-energy “hot electrons,” allowing for full-spectrum-driven water reduction reactions [19]. Among

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the reported plasmonic semiconductors, nonstoichiometric molybdenum oxide with abundant oxygen vacancies (MoO_{3-x}) demonstrates a broad and intense localized surface plasmon resonance (LSPR) absorption centered at 700 nm, with adsorption tailing to 2000 nm. Accordingly, MoO_{3-x} has become one of the most attractive candidates for harvesting visible to near-infrared light for photocatalytic H_2 generation [20–23]. Nevertheless, the rapid recombination of charge carriers in pristine MoO_{3-x} still needs to be improved. The construction of MoO_{3-x} -based composite photocatalysts with type-II, Z-scheme, or S-scheme heterostructures has been evidenced as an effective tactic to simultaneously realize the expansion of light adsorption and the enhancement of spatial charge separation to improve photocatalytic H_2 evolution performance [24–28]. The advantage of Z-scheme and S-scheme heterostructures over traditional type-II heterostructures is that the photoexcited electrons preserved at higher reduction potentials would take part in water-splitting reactions, which is beneficial for achieving higher photocatalytic reaction efficiency [29–32]. It is worth mentioning that the migration distance between the electrons and holes can be further shortened in the S-scheme due to band bending caused by the internal electric field of the semiconductors, leading to faster separation of the photo-induced carriers in comparison to the Z-scheme [33]. The first S-scheme heterojunction, 2D/2D $\text{WO}_3/\text{g-C}_3\text{N}_4$, was published by Yu et al. [34], and it has been suggested that the construction of S-scheme heterojunctions relies on the band offset of the two semiconductors. Among the various semiconductors reported, CdS is a potential candidate as a photocatalyst due to its suitable bandgap ($E_g = 2.4$ eV) and high conduction band position, which make it able to reduce water to H_2 [35–41]. Moreover, CdS possesses an appropriate energy level that matches with MoO_{3-x} , satisfying the requirements for the construction of an S-scheme for photocatalytic H_2 evolution.

Interface design is another critical factor in the construction of highly efficient S-scheme hybrid materials. 0D/2D heterojunctions have demonstrated some unique features, with 0D nanoparticles having short charge-migration distances while 2D nanosheets act as supports that improve contact area and prevent the self-aggregation of 0D nanoparticles [42–46]. Inspired by this, there is motivation to rationally design and investigate 0D/2D CdS/ MoO_{3-x} S-scheme heterojunctions to enhance the visible-light photocatalytic activity to levels suitable for possible practical utilization. In the present work, a 0D/2D CdS/ MoO_{3-x} S-scheme heterojunction composing of 0D CdS nanoparticles and 2D MoO_{3-x} elliptical nanosheets were prepared by a simple coprecipitation route. The photocatalytic H_2 generation performances of the photocatalysts were evaluated under visible light irradiation (including monochromatic 420, 450, 550, and 650 nm light). The CdS/ MoO_{3-x} composite containing 15 wt% MoO_{3-x} was recognized to be the most active photocatalyst for H_2 evolution ($7.44 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) under visible-light irradiation, which is about 10.3 times as much as that of pristine CdS nanoparticles. The improvement in photocatalytic efficiency can be accredited to a LSPR-enhanced S-scheme charge transfer mechanism.

2. Experimental

2.1. Materials

Molybdenum metal powder (99.5%) was bought from Aladdin Industrial Corporation. Hydrogen peroxide (H_2O_2 , 30 wt%), 1-butanol ($\geq 99.5\%$), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ($\geq 99.0\%$), $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ($\geq 98.0\%$), and lactic acid ($\geq 85.0\%$) were bought from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without purification.

2.2. Sample preparation

MoO_{3-x} elliptical nanosheets were synthesized via a solvothermal process [23]. Two mmol of molybdenum metal powder was intermixed with 24 mL of 1-butanol in a beaker of capacity 50 mL, and then 3 mL of H_2O_2 (30 wt%) was added and stirred for 30 min to form a clear yellow solution. The final solution was shifted to a 50 mL autoclave and heated to 140°C for 12 h. The sediments were concentrated via centrifugation and rinsed thrice with absolute ethanol and DI water, and then dried at 60°C overnight.

CdS/ MoO_{3-x} composites were synthesized through a secure in-situ coprecipitation method (Scheme 1). Initially, MoO_{3-x} elliptical nanosheets were dispersed into 150 mL of DI water, followed by the addition of 0.525 g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ under stirring for 1 h to form Suspension I. A solution containing 0.4156 g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in 20 mL of DI water was poured into Suspension I with vigorous stirring for 2 h, and the mixture was then settled for 12 h at room temperature. The product was centrifuged, washed, and dried at 60°C overnight. The mass of MoO_{3-x} was adjusted to be 2, 10, 20, 30, or 40 mg in the first step, with these being denoted MC-1, MC-5, MC-10, MC-15, and MC-20, respectively. The corresponding mass ratios of MoO_{3-x} in the as-obtained samples were 1, 4, 8, 10, and 14 wt%, respectively. For comparison, the pure CdS was synthesized without the addition of MoO_{3-x} under identical experimental conditions.

2.3. Material characterization

X-ray diffraction (XRD) data were procured using a Rigaku D/Max2500 X-ray powder diffractometer. X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Fisher ESCALAB 250Xi. The morphological peculiarities of the samples were investigated by utilizing scanning electron microscopy (SEM, JSM-7001F) and transmission electron microscopy (TEM, JEM-2100). The UV-vis diffuse reflectance spectra were

Scheme 1. Synthesis of the CdS/ MoO_{3-x} composites.

evaluated using a UV-visible spectrophotometer (DRS, UV-2600), with BaSO₄ as a reference. The linear sweep voltammograms (LSV), Mott-Schottky curves (M-S), photocurrents (PC), and electrochemical impedance spectra (EIS) of the catalysts were measured using an electrochemical workstation (CHI-660E, Shanghai, China) having a platinum plate counter electrode, a Ag/AgCl reference electrode, and a 0.5 M Na₂SO₄ solution as the supporting electrolyte. Electron spin resonance (ESR) experiments were carried out with a JES FA200 spectrometer and using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the radical-capture reagent.

2.4. Photocatalytic H₂ evolution experiments

Photocatalytic H₂-production investigations were conducted in a flask exposed to irradiation from a 350 W Xenon lamp. The sample (25 mg) was added to 80 mL of lactic acid solution (10 vol%), and the flask was pumped with N₂ to remove air before light illumination. After 1 h of illumination, 0.4 mL of gaseous products were extracted from the flask and measured by gas chromatography (GC-2014, Japan). The apparent quantum yield (AQY) was calculated as

$$\text{AQY} = \frac{2 \times \text{amount of released hydrogen molecules}}{\text{number of incident photons}} \times 100\%$$

3. Results and discussion

Fig. 1(a) shows the XRD patterns of MoO_{3-x}, CdS, and the CdS/MoO_{3-x} composites. The XRD peaks of pure MoO_{3-x} can be indexed as orthorhombic MoO_{2.69} (JCPDS# 70-0615), and the peaks at 23.4°, 25.5°, 27.2°, 33.8°, 38.7°, and 39.6° can be assigned to the (110), (040), (021), (111), (060), and (002) planes, respectively [23]. Only three diffraction peaks could be

found for pristine CdS at 26.7°, 43.9°, and 51.9°. These are attributed to the (111), (220), and (311) crystal reflection planes of cubic CdS (JCPDS# 10-0454) [47,48]. A small (021) MoO_{3-x} diffraction peak could be observed in the MC-15 sample, and the other CdS/MoO_{3-x} composites possess the diffraction peaks of cubic CdS due to the low diffraction intensity of MoO_{3-x}. To further confirm the existence of MoO_{3-x} in the CdS/MoO_{3-x} composites, XPS was employed to explore the surface compositions of CdS, MoO_{3-x}, and MC-15. Fig. 1(b) shows the survey spectra of these samples, where it is clear that Cd 3d and S 2p peaks can be observed in both CdS and MC-15, while Mo 3d and O 1s peaks can be seen in both MoO_{3-x} and MC-15, implying the coexistence of MoO_{3-x} and CdS in the CdS/MoO_{3-x} composite. In the Cd 3d XPS spectra of CdS and MC-15, two peaks at 404.9 and 411.6 eV pertain to Cd 3d_{5/2} and Cd 3d_{3/2}, respectively as shown in Fig. 1(c). Two characteristic peaks corresponding to S 2p_{1/2} (161.2 eV) and S 2p_{3/2} (162.3 eV) are observed in the S 2p spectra (Fig. 1(d)) [48,49]. In the Mo 3d spectrum of MoO_{3-x} (Fig. 1(e)), the two peaks at binding energies of 232.6 and 235.8 eV are respectively considered to be the Mo 3d_{5/2} and Mo 3d_{3/2} peaks of the Mo⁶⁺ state, while those at 231.3 and 234.1 eV are marked as the Mo 3d_{5/2} and Mo 3d_{3/2} peaks of the Mo⁵⁺ state [20,23]. The existence of Mo⁵⁺ ions evidences the abundant localized electrons in MoO_{3-x} and the MC-15 hybrid, and also supports LSPR in these systems. The high-resolution O 1s XPS spectra shows two peaks for MoO_{3-x}, one at 530.4 eV and the other at 531.4 eV. The former can be marked as the lattice oxygen of MoO_{3-x}, and the latter can be identified as surface-adsorbed species such as OH⁻ [50]. The atomic ratio of Mo to O was around 1:2.8, which is in accordance with the XRD results. The slight positive shifts in the Cd 3d and S 2p peaks and the negative shifts in the Mo 3d and O 1s peaks are caused by charge transfer from the CdS to MoO_{3-x}, resulting in CdS

Fig. 1. (a) XRD patterns of MoO_{3-x}, CdS, and the CdS/MoO_{3-x} composites; (b) XPS survey spectra of MoO_{3-x}, CdS, and MC-15; (c) Cd 3d and (d) S 2p XPS spectra of CdS and MC-15; Mo 3d (e) and O 1s (f) XPS spectra of MoO_{3-x} and MC-15.

losing electrons while MoO_{3-x} gains them, producing an internal electric field at the interface between CdS and MoO_{3-x} .

SEM, TEM, and HR-TEM images of the MoO_{3-x} , CdS, and MC-15 samples are presented in Fig. 2. The pristine MoO_{3-x} crystallized into elliptical nanosheets with lengths of about 1.5 μm and widths of 300 nm (Fig. 2(a) and (b)), and several elliptical nanosheets could agglomerate to form olive-like aggregations. As shown in Fig. 2(c) and (d), pure CdS had irregular particle-like features with sizes of several nanometers. For the MC-15 composite (Fig. 2(e) and (f)), it can be observed that some nanoparticles were anchored and adhered to the surface of the MoO_{3-x} and h reveal that the inter-fringe distances of the MoO_{3-x} elliptical nanosheets were 0.18 nm, corresponding to the (002) planes of MoO_{3-x} , and the lattice fringes of the nanoparticles were 0.335 nm, which is consistent with the lattice spacing of the (111) planes of CdS [23,47,48]. The elemental mapping patterns (Fig. 2(i)) further substantiated the presence of Cd, S, Mo, and O in the MC-15 composite, indicating the successful formation of a CdS/ MoO_{3-x} heterojunction with a compact interface via the growth of CdS nanoparticles on the MoO_{3-x} elliptical nanosheets.

The photocatalytic activities of MoO_{3-x} , CdS, and the CdS/ MoO_{3-x} composites with different ratios were investigated via photocatalytic H_2 -production in the presence of visible light. As outlined in Fig. 3(a) and (b), the pristine MoO_{3-x} demonstrated no H_2 production activity, while a tiny quantity of H_2 evolution was detected from the CdS sample. Compared with the pristine samples, the CdS/ MoO_{3-x} composites demonstrated enhanced photocatalytic H_2 production performances, and the CdS/ MoO_{3-x} composite containing 15 wt% MoO_{3-x} nanosheets showed the highest H_2 production rate of $7.44 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, roughly 10.3 times superior to that of pristine CdS. Furthermore, the photocatalytic H_2 production performances of MC-15 and pure CdS when irradiated using different monochromatic

Fig. 2. SEM and TEM images of MoO_{3-x} (a, b), CdS (c, d), and MC-15 (e, f); HRTEM images of CdS (g) and MoO_{3-x} (h); (i) EDX elemental mapping of MC-15.

Fig. 3. Photocatalytic H_2 evolution performances (a) and H_2 evolution rates (b) of CdS, MoO_{3-x} , and CdS/ MoO_{3-x} samples under visible light irradiation; Photocatalytic performances of CdS and MC-15 when irradiated using monochromatic light at 420 (c), 450 (d), 550 (e), and 650 nm (f).

Fig. 4. (a) Cycle stability experiments for CdS and MC-15; (b) AQYs of MC-15 at 420, 450, 550, and 650 nm.

light sources for 5 h are compared and shown in Fig. 3(c)–(f). MC-15 demonstrated higher activity than pure CdS regardless of the wavelength used. When irradiated at 420 and 450 nm, the photocatalytic H₂ productions of MC-15 were 15.7 and 10.9 mmol·g⁻¹, i.e., 6.8 and 5.0 times higher than CdS at those wavelengths, respectively. Even when the photon energy was decreased to 550 and 650 nm, MC-15 still demonstrated higher H₂ evolution activity than CdS, illustrating that coupling the MoO_{3-x} elliptical nanosheets capable of LSPR with CdS nanoparticles is a feasible method of improving photocatalytic water reduction performance over a broad solar spectrum from 420–650 nm.

Fig. 4(a) shows cycling tests for photocatalytic H₂-production using MC-15 and CdS under visible light irradiation. After four consecutive runs without renewing the reagents and photocatalysts, a slight decrease in H₂ generation was found due to the consumption of sacrificial agents [49]. However, after the addition of a certain amount of lactic acid as a sacrificial agent, a H₂-production rate 6.65 mmol·g⁻¹·h⁻¹ could still be achieved for MC-15, demonstrating that it possessed

stable performance over 25 h. However, the photocatalytic H₂ evolution of the pristine CdS was significantly reduced from 3.93 to 1.65 mmol·g⁻¹ over this period. In the light of the above experimental results, the introduction of MoO_{3-x} elliptical nanosheets not only effectively enhanced the photocatalytic H₂-production performance but also improved the photostability of CdS. Figure 4(b) reveals the wavelength-dependent apparent quantum yield (AQY) values of MC-15, with the calculated AQYs at 420, 450, and 550 nm being 8.8%, 14.3%, and 0.08%, respectively.

It is generally recognized that photocatalytic activity is primarily determined by the charge separation efficiency, which can be reflected in the photoelectrochemical performance as measured by techniques such as LSV, PC, and EIS. MC-15 demonstrated an improved polarization curve and a higher current density when compared to CdS, as depicted in Fig. 5(a). Furthermore, CdS and MoO_{3-x} possessed weak photocurrent intensities ascribable to the expeditious recombination of carriers, while MC-15 demonstrated a higher photocurrent intensity that can be ascribed to the introduction of the MoO_{3-x} ellip-

Fig. 5. LSV curves (a) and transient photocurrent responses (b) of CdS, MoO_{3-x}, and MC-15; (c) Transient photocurrent responses of MC-15 under different monochromatic wavelengths; (d) EIS plots of CdS, MoO_{3-x}, and MC-15.

tical nanosheets (Fig. 5(b)) [51–54]. The photocurrent of the MC-15 sample under light irradiation at 420, 520, and 650 nm is also exhibited in Fig. 5(c), which shows that the photocurrent density decreased as the wavelength of the incident light increased. As revealed in Fig. 5(d), the MC-15 composite showed smaller EIS semicircles than CdS and MoO_{3-x}, indicating lower charge transfer resistance and faster interfacial charge separation [55,56]. The improved photoelectrochemical performances (LSV, PC, and EIS) show the improved charge separation efficiency of MC-15, and elucidate the enhanced photocatalytic H₂ evolution activity of this sample [57–59].

Extending the light response range is also beneficial for improving the activities of photocatalytic materials. Accordingly, the optical absorption behaviors of CdS, MoO_{3-x}, and the CdS/MoO_{3-x} composites were explored by UV-vis spectroscopy, as presented in Fig. 6(a) and (b). Pristine CdS demonstrated visible light absorption with a bandgap energy of 2.14 eV, while the MoO_{3-x} elliptical nanosheets possessed an intrinsic absorption edge at around 410 nm and a broad absorption band ranging from 600–1400 nm, which is caused by the LSPR effect induced by the copious oxygen vacancies of MoO_{3-x} [60–62]. All the CdS/MoO_{3-x} composites had similar absorption tails in the 600–1400 nm region due to the introduction of the MoO_{3-x} elliptical nanosheets, and the intensity of this absorption tail increased as the amount of MoO_{3-x} in the composites was increased. The flat band potentials (E_{fb} , vs. Ag/AgCl) of CdS and MoO_{3-x} were –1.11 and –0.18 V, respectively, based on the Mott-Schottky plots (Fig. 6(c)), and the flat potentials characterized with Ag/AgCl could be converted into the normal hydrogen electrode (NHE) potentials via the equation $E_{fb} = E_{Ag/AgCl} + 0.059 \times \text{pH} + E^0_{Ag/AgCl}$ (pH = 6.8 and $E^0_{Ag/AgCl} = 0.197$ V). The conduction band (E_{CB}) of *n*-type semiconductors is usually 0.3 V

more negative than $E_{fb, NHE}$, and the E_{CB} positions of CdS and MoO_{3-x} were therefore calculated to be –0.81 and 0.12 V (NHE, pH = 0), respectively [63,64]. Finally, the bandgap structures and relative band positions of CdS and MoO_{3-x} are illustrated in Fig. 6(d).

The Fermi energy level (E_F) of the semiconductor that in a heterojunction affects the charge transfer. Accordingly, the work functions of CdS and MoO_{3-x} were calculated using first-principles density functional theory (DFT) [65,66], with the work functions of the CdS (001) and MoO_{3-x} (001) surfaces being determined as 4.07 (Fig. 7(a)) and 7.56 eV (Fig. 7(b)), respectively. Due to the fact that the E_F of MoO_{3-x} is more negative than that of CdS, when these two semiconductors are brought into contact electrons would migrate from CdS to MoO_{3-x}, and thus the energy bands of CdS and MoO_{3-x} would bend upward and downward, respectively, until their E_F values are at equilibrium (Fig. 7(c) and (d)) [34]. Such upward and downward band bending is one of the characteristics of the S-scheme structure [67,68]. Furthermore, an internal electric field would be created between the positively charged CdS and the negatively charged MoO_{3-x}, which agrees with the XPS analyses.

ESR measurements were employed to investigate the mechanism of photocatalytic enhancement [69,70]. No ESR signal was observed for the MC-15 composite in the dark (Fig. 8(a) and (b)), while strong ESR signals for both DMPO- $\cdot\text{O}_2^-$ and DMPO- $\cdot\text{OH}$ could be detected for the MC-15 composite under light irradiation, suggesting that both $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals can be generated on the surface of the MC-15 composite. For comparison, the ESR signals of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals generated by CdS and MoO_{3-x} were also investigated (Fig. 8(c) and (d)), and it was found that DMPO- $\cdot\text{O}_2^-$ signals were only detected for CdS

Fig. 6. (a) UV-vis spectra of CdS, MoO_{3-x}, and the CdS/MoO_{3-x} composites; (b) bandgaps of CdS and MoO_{3-x}; Mott-Schottky plots (c) and corresponding band alignments (d) of CdS and MoO_{3-x}.

Fig. 7. Work functions of CdS (001) surface (a) and MoO_{3-x} (001) surface (b); the band alignments of MoO_{3-x} and CdS before (c) and after (d) contact.

and MC-15, while almost no DMPO- $\cdot\text{O}_2^-$ signal was generated by pristine MoO_{3-x}. This may be due to the conduction band of MoO_{3-x} (0.12 V, NHE), which is more positive than the O₂/ $\cdot\text{O}_2^-$ redox potential (−0.33 V, NHE) [34,64]. The intensities of both the DMPO- $\cdot\text{O}_2^-$ and DMPO- $\cdot\text{OH}$ signals of MC-15 were stronger than those of CdS and MoO_{3-x}, proving that MC-15 can produce more $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals. Furthermore, the ESR results also

suggest that the light-induced electrons and holes remain in the conduction band of CdS and the valence band of MoO_{3-x}, respectively, and that the photo-induced charge separation mechanism of the CdS/MoO_{3-x} composite would follow the S-scheme mechanism rather than the traditional type-II heterojunction mechanism.

Considering the band alignments of CdS and MoO_{3-x} and the

Fig. 8. DMPO- $\cdot\text{O}_2^-$ (a) and DMPO- $\cdot\text{OH}$ (b) ESR spectra of MC-15; comparison of DMPO- $\cdot\text{O}_2^-$ (c) and DMPO- $\cdot\text{OH}$ (d) ESR spectra of MoO_{3-x}, CdS, and MC-15.

Fig. 9. Mechanism of photocatalytic H_2 -production using $\text{CdS}/\text{MoO}_{3-x}$ composites.

radical generation results, an S-scheme mechanism is proposed for the $\text{CdS}/\text{MoO}_{3-x}$ composites (Fig. 9). When irradiated with visible light, both CdS and MoO_{3-x} can generate electron-hole pairs for photocatalytic reactions. If the photo-induced electrons followed the type-II route, the electrons would transfer from the conduction band of CdS to the conduction band of MoO_{3-x} . However, the conduction band of MoO_{3-x} is located at 0.12 V (NHE), which is not high enough for water reduction and $\cdot\text{O}_2^-$ generation since the redox potentials of H^+/H_2 and $\text{O}_2/\cdot\text{O}_2^-$ are 0 and -0.33 V (NHE), respectively [71]. Accordingly, the $\text{CdS}/\text{MoO}_{3-x}$ composite must follow the S-scheme charge transfer mechanism. Based on the XPS and DFT results, an internal electric field is established between the positively charged CdS and the negatively charged MoO_{3-x} ; therefore, the band edges of CdS and MoO_{3-x} bend upward and downward, respectively. Under light irradiation, the internal electric field and band edge bending cause electrons to accumulate on the conduction band of MoO_{3-x} and combine with the holes of CdS , leaving electrons with stronger redox capacities on the conduction band of CdS to take part in photocatalytic water reduction, leading to more efficient H_2 generation.

4. Conclusions

In summary, an LSPR-enhanced 0D/2D $\text{CdS}/\text{MoO}_{3-x}$ heterojunction composed of 0D CdS nanoparticles grown on 2D plasmonic MoO_{3-x} elliptical nanosheets has been successfully fabricated. The 0D/2D $\text{CdS}/\text{MoO}_{3-x}$ heterojunction exhibits improved photocatalytic H_2 generation activity under a wide range of visible light irradiation, including using 420, 450, 550, and 650 nm monochromatic light, and the optimal $\text{CdS}/\text{MoO}_{3-x}$ demonstrates 10.3 times higher photocatalytic H_2 evolution ($7.44 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) than that of pristine CdS under visible light irradiation ($>420 \text{ nm}$). The key factor affecting such high efficiency can be ascribed to an S-scheme mechanism enhanced by the LSPR effect of the 2D plasmonic MoO_{3-x} elliptical nanosheets. Additionally, the light response capacity of the $\text{CdS}/\text{MoO}_{3-x}$ heterojunction is extended from 600 to 1400 nm, and furthermore, the S-scheme charge-transfer mechanism of

the 0D CdS nanoparticles and 2D plasmonic MoO_{3-x} can both retain the strong redox ability of CdS and accelerate charge separation due to the interface between the MoO_{3-x} and CdS . This study may lead to new approaches and insights into wide-spectrum-driven photocatalysis of water-splitting using plasmonic semiconductors.

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Graphical Abstract

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Construction of LSPR-enhanced 0D/2D CdS/MoO_{3-x} S-scheme heterojunctions for visible-light-driven photocatalytic H₂ evolution

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The MoO_{3-x}/CdS heterojunctions exhibit improved photocatalytic H₂ generation activity, which is accredited to an LSPR-enhanced S-scheme charge transfer mechanism.

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LSPR增强0D/2D CdS/MoO_{3-x} S型异质结的构建及其可见光光催化活性研究

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摘要: 近年来, 等离子体半导体光催化剂因其具有从可见光到近红外光的光响应而引起了人们极大的研究兴趣. 含有丰富氧空位的非化学计量的氧化钼(MoO_{3-x})具有中心位于700 nm和尾部吸收拓展至2000 nm强的局域表面等离子体共振(LSPR)效应, 因此, MoO_{3-x}或将成为实现全光谱响应光催化制氢技术最有吸引力的候选材料之一. 然而, 单一MoO_{3-x}中电荷载流子的复合快速. 具有II型、Z型或S型异质结构的MoO_{3-x}基复合光催化剂的构建被证明是同时实现拓展光吸收和分离光生载流子改善光催化析氢性能的有效策略. 与传统的II型异质结构相比, Z型或S型可在较高还原电位上进行水分解反应, 又可以实现光生载流子的有效分离. 相比于Z型, S型由于内部电场导致的半导体的能带弯曲可以进一步缩短电子与空穴之间的迁移距离, 从而导致光诱导载流子的更快分离. 基于此, 本文选择了与MoO_{3-x}能带匹配的CdS半导体催化剂, 通过简单的共沉淀法在具有LSPR效应的二维(2D) MoO_{3-x}椭圆纳米片上生长零维(0D) CdS纳米粒子, 制备了LSPR增强的0D/2D CdS/MoO_{3-x}S型异质结. 由于MoO_{3-x}的引入, 0D/2D CdS/MoO_{3-x}复合材料展现出了一个因LSPR效应而具有的从600到1400 nm的尾部吸收, 并且这种尾部吸收强度随着复合材料中MoO_{3-x}含量的增加而增加.

在可见光光催化反应中, CdS/MoO_{3-x}复合材料的产氢速率为7.44 mmol·g⁻¹·h⁻¹, 为单一CdS的10.3倍. 当采用不同波段的单色光作为激发光源, 在420, 450和550 nm单色光的照射下, CdS/MoO_{3-x}复合材料的产氢效率为15.7, 10.9和193.4 mmol·g⁻¹, 分别比CdS高6.8, 5.0和3倍. 当激发波长拓展至650 nm时, CdS/MoO_{3-x}复合材料的产氢效率为6.83 mmol·g⁻¹, 而CdS则不具有产氢活性, 侧面体现了MoO_{3-x}的LSPR效应在提升光解水产氢活性方向的有效作用.

我们利用肖特基和固体紫外测试确定了CdS和MoO_{3-x}的能带结构, 并通过第一原理密度泛函理论模拟计算了CdS和MoO_{3-x}的功函数, 分别为4.07和7.56 eV, 当这两个半导体接触时, MoO_{3-x}的费米能级比CdS的更负, 电子将从CdS迁移到MoO_{3-x}, 因此CdS和MoO_{3-x}的能带将分别向上和向下弯曲, 直到其费米能级达到平衡. 这种向上和向下的带弯曲是S型结构的特征之一. XPS分析也证实在带正电荷的CdS和带负电荷的MoO_{3-x}之间会产生内部电场, 这也符合S型结构.

此外, 还利用电子自旋共振(ESR)进一步研究了CdS, MoO_{3-x}和CdS/MoO_{3-x}在光照下自由基的产生情况, CdS/MoO_{3-x}产生的DMPO-·O₂⁻和DMPO-·OH信号强度均强于CdS和MoO_{3-x}, 证明CdS/MoO_{3-x}能产生更多的·O₂⁻和·OH自由基. ESR结果还表明, 在CdS/MoO_{3-x}复合材料中光诱导电子和空穴仍然分别停留在CdS的导带和MoO_{3-x}的价带中, CdS/MoO_{3-x}复合材料的光诱导电荷分离机制将遵循S型机制, 而不是传统的II型异质结. 在光照下, 内部电场和弯曲能带促使积聚在MoO_{3-x}导带上的电子与CdS的空穴结合, 在CdS的导带上留下具有较强氧化还原能力的电子参与光催化水还原反应, 实现高效的光催化产氢.

关键词: CdS; MoO_{3-x}; 光催化产氢; S型; LSPR效应

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