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Use of synergistic effects of the co-catalyst, p-n heterojunction, and porous structure for improvement of visible-light photocatalytic H₂ evolution in porous Ni₂O₃/ $Mn_{0.2}Cd_{0.8}S/Cu_3P@Cu_2S$

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Use of synergistic effects of the co-catalyst, p-n heterojunction, and porous structure for improvement of visible-light photocatalytic H₂ evolution in porous Ni₂O₃/Mn_{0.2}Cd_{0.8}S/Cu₃P@Cu₂S Dafeng Zhang, Yunxiang Tang, Xiaoxue Qiu, Jie Yin, Changhua Su, Xipeng Pu^{*} School of Materials Science and Engineering, Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, Liaocheng University, Liaocheng 252000, P. R. China

Abstract

The efficient separation and transfer of photogenerated charge carriers play indispensable roles in improving the photocatalytic H₂ evolution activity. Herein, we designed a Ni₂O₃-modified $Mn_{0.2}Cd_{0.8}S/Cu_3P@Cu_2S$ (MCS/CPS) p-n heterojunction structure with a porous morphology for efficient and stable photocatalytic H₂ evolution under visible-light irradiation. Novel porous Cu₃P@Cu₂S was obtained using a vulcanization method and Cu₂S nanoparticles were grown uniformly in situ on the surface of Cu₃P. Ni₂O₃ was adopted as a co-catalyst on the MCS/CPS p-n heterojunction surfaces to promote electrons transfer. Due to the synergistic effects of the co-catalyst, p-n heterojunction, and porous morphology, the as-synthesized Ni₂O₃/MCS/CPS composite with 9 wt% Ni₂O₃ and 2.5 wt% CPS exhibits an optimal photocatalytic H₂ evolution rate of 9.2 mmol g⁻¹ h⁻¹, which is 14.4 and 2.4 times higher than those of pure MCS and 9%Ni₂O₃/MCS, respectively. Meanwhile, the optimal sample exhibits an apparent quantum efficiency of 33.5% at 420 nm and an excellent stability under 20 h of irradiation. Moreover, a possible mechanism for the improved photoactivity of the as-synthesized Ni₂O₃/MCS/CPS composite has been discussed in this paper.

Keywords: Mn_{0.2}Cd_{0.8}S; Cu₃P@Cu₂S; Co-catalyst; p-n heterojunction; Photocatalytic H₂ evolution

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1. Introduction

Hydrogen (H₂) as an ideal alternative to fossil fuels, has long been considered as one of the most promising, renewable and environmentally friendly energy carriers [1, 2]. Traditionally, H₂ was obtained via the gasification of coal and the catalytic conversion of heavy oil or natural gas. However, these methods are not only inefficient, but also require significant additional energy, rendering it impossible to produce H₂ commercially on a large scale. Owing to the recent materials advancements with regard to semiconductors, generation of H₂ from water by using solar energy has attracted significant attention [3, 4]. The key to photocatalytic H₂ evolution is the development of cheap, highly efficient, and visible-light-driven photocatalysts [5]. Thus far, various photocatalysts have been developed, including metal sulfides [6-8], metal oxides [9], carbon nitride [10] and metal organic frameworks [11, 12]. Among these materials, Mn_xCd_{1-x}S solid solutions have attracted significant attention based on their tunable compositions as well as a moderate band gap, and excellent visible light absorption capacity [13]. However, Mn_xCd_{1-x}S alone does not exhibit excellent photocatalytic activity due to the rapid charge carrier recombination and photocorrosion. Several approaches, including bandgap engineering [14], co-catalyst loading [15, 16], and the fabrication of heterojunction with other semiconductors [17-19], have been used to improve the photocatalytic activity.

In general, co-catalysts not only capture charge carriers to improve separation efficiency but also reduce the reaction energy barriers for H_2 evolution and provide additional active sites [20]. Noble metals, such as Pd [21], Pt [22], and Au [23], have been developed as efficient co-catalysts for photocatalytic H_2 evolution; however, those materials are too scarce and expensive to be applied on a large scale for photocatalytic water splitting [24]. Therefore, developing highly efficient and low-cost co-catalyst is crucial. Recently, nickel and its oxides, such NiO and Ni₂O₃, have been proved to be efficient electron traps that can improve

the charge separation of photocatalysis [25]. For example, Shangguan et al. reported that Ni₂O₃ can act as

an electron trap and can promote charge separation to enhance photocatalytic performance [26]. Li's group reported that the photocatalytic activity of $Cd_{1-x}Zn_xS/O-MoS_2$ heterojunction was improved by NiO_x decoration [27]. Therefore, NiO_x can be used as an eminent co-catalyst for improving photocatalytic H₂ evolution activity.

The photocorrosion of sulfide semiconductors is an unavoidable problem that reduces their photostability. Constructing heterojunctions with other semiconductors for facilitating the separation and transfer of photogenerated charge carriers has been proved to be an efficient approach to improve photocatalytic activity and photostability [28]. Recently, Cu-based materials, such Cu₃P [29], CuS [30] and Cu₂S [6], have been applied in the photocatalytic field based on their low cost and natural abundance. Thus far, several Cu-based heterojunction photocatalysts, including Cu₃P/g-C₃N₄ [29], CuS/ZnS [30], and Cu₂S/CdS [31], have been reported. Additionally, the recent studies indicated that the synergy of P-S anions can provide a powerful mechanism for catalyst production [32, 33]. For example, Fu and coworkers reported that MoS₂@MoP core-shell heterojunctions can serve as high-performance catalysts for H₂ evolution reactions [34]. Wang et al. reported that MoS₂-MoP heterojunctions on polymer-derived carbon substrates show greater H₂ evolution activity than that of pure MoS₂ or MoP and that this improved catalytic performance can be attributed to the electronical interactions between MoS₂ and MoP [35].

Motivated by these reports, we loaded Cu₂S nanoparticles onto the surface of porous Cu₃P to form Cu₂S@Cu₃P (CPS) heterojunctions using a vulcanization method. Both Cu₃P and Cu₂S are p-type semiconductors and Mn_{0.2}Cd_{0.8}S (MCS) is a typical n-type semiconductor. MCS/CPS p-n heterojunctions were synthesized by combining MCS and CPS. Additionally, Ni₂O₃ nanoparticles were introduced as non-noble metal co-catalysts, and a porous Ni₂O₃/MCS/CPS composite photocatalyst was obtained. As expected,

the Ni₂O₃/MCS/CPS composites exhibited improved photoactivity as compared to those of pure MCS and

 Ni_2O_3/MCS . The enhanced photoactivity of $Ni_2O_3/MCS/CPS$ can be attributed to the synergistic effects of the co-catalyst, p-n junctions between CPS and MCS, and a porous morphology. Additionally, a possible mechanism for charge transfer over the $Ni_2O_3/MCS/CPS$ composite was discussed.

2. Experimental section

2.1. Synthesis of MCS and Ni₂O₃/MCS

MCS was prepared using a solvothermal method [36], as illustrated in Fig. 1. Typically, 1.1417 g of thiourea (CH₄N₂S), 4.3495 g of Cd(Ac)₂·4H₂O, and 0.2074 g of Mn(Ac)₂·2H₂O were dissolved in 60 mL of ethylenediamine under magnetic stirring for 1 h. This mixture was then transferred into a 100 mL stainless steel autoclave and held at 160 °C for 24 h. After cooling to room temperature, the resulting precipitates were collected and washed several times with deionized water and ethanol, and then dried at 80 °C for 12 h. The Ni₂O₃/MCS was prepared using an in situ photo-deposition method. Specifically, 0.3 g of MCS and a certain amount of NiCl₂·6H₂O (containing 1 wt%, 5 wt%, 9 wt%, or 13 wt% of Ni.) were dispersed in 30 mL of ethanol and ultrasonicated for 30 min. Subsequently, the mixed solution was injected with nitrogen for thorough degassing and then irradiated under a 300 W Xe lamp ($\lambda > 400$ nm) for 30 min with stirring. These samples were denoted as x%Ni₂O₃/MCS (x = 1, 5, 9, and 13).

2.2. Synthesis of Cu₃P and CPS composite

As illustrated in Fig. 1, $Cu(OH)_2$ was first prepared using a simple precipitation method. Typically, 1.208 of g $Cu(NO_3)_2$ and 0.2 g of NaOH were dissolved in 100 mL and 20 mL of deionized water, respectively. Next, the aqueous solution of NaOH was slowly poured into the aqueous solution of $Cu(NO_3)_2$ under constant stirring. $Cu(OH)_2$ was then obtained via filtration and dried at 60 °C for 8 h under vacuum. Next, 0.3 g of $Cu(OH)_2$ and 1.5 g of NaH₂PO₂ were ground in an agate mortar and transferred into a porcelain

boat. The mixture was then calcined at 300 °C for 2 h at a rate of 2 °C min⁻¹ in a N_2 atmosphere. After

cooling, the black Cu_3P was washed several times with deionized water and ethanol, and then dried at 80 °C for 12 h.

To prepare the CPS composite, 0.15 g of Cu_3P and 1.5 g of CH_4N_2S were placed in square combustion boats. Next, the two square combustion boats were transferred into a tube furnace with CH_4N_2S loaded upstream and calcined at 300 °C for 2 h at a rate of 2 °C min⁻¹ in a N₂ atmosphere. Finally, after coolling to room temperature, the CPS composite was obtained.

2.3. Preparation of 9%Ni₂O₃/MCS/CPS composites

 $Ni_2O_3/MCS/CPS$ composites were synthesized as illustrated in Fig. 1. First, 0.1 g of 9% Ni_2O_3/MCS and a certain amount of CPS (1.0, 2.5, or 5.0 mg) were dispersed in 30 mL of ethanol solution and subjected to ultrasonication for 1 h (100 W, 40 KHz). After stirring for 4 h, the particles were centrifuged and dried at 60 °C for 8 h. Finally, the mixture was transferred into a muffle furnace and annealed in air at 100 °C for 2 h. The obtained composites were denoted as $Ni_2O_3/MCS/CPS$ -x, where x = 1, 2.5, and 5. For comparison, a $Ni_2O_3/MCS/Cu_3P$ -2.5 composite was prepared using the same procedure.

The corresponding characterizations, photoelectrochemical measurements, and photocatalytic H_2 evolution experiments have been presented in the Supporting Information.



Fig. 1. Schematic illustration of the Ni₂O₃/MCS/CPS preparation process.

3. Results and discussion

3.1. Characterization of the samples

The crystalline structures of the as-prepared photocatalysts were characterized by using X-ray powder diffraction (XRD). The XRD patterns of the MCS and Ni₂O₃/MCS photocatalysts are presented in Fig. S1. In the case of pure Cu₃P, three primary diffraction peaks at 36.0°, 45.1° and 46.1° are attributed to the (112), (300), and (113) reflections of hexagonal Cu₃P (JCPDS #71-2261), respectively [37]. After vulcanization of Cu₃P, in addition to the typical diffraction peaks of Cu₃P, three new peaks at 37.3°, 45.8° and 48.2° are attributed to the (102), (110), and (103) crystal planes of hexagonal Cu₂S (JCPDS #84-0206), respectively [38]. These results indicate that the coexistence of Cu₃P and Cu₂S phases in the material. Furthermore, the diffraction profiles of the Ni₂O₃/MCS/CPS composites are similar to those of MCS due to the low Cu₃P and Cu₂S content. With a high CPS content (Ni₂O₃/MCS/CPS-5), two additional humps can be observed at 45.1° and 46.1°, which can be ascribed to the Cu₃P phase. These results indicate that the Ni₂O₃/MCS/CPS





Fig. 2. XRD patterns of as-prepared photocatalysts.

The morphologies of the as-synthesized samples were investigated using scanning electron microscopy (SEM). As shown in Fig. 3a, Cu₃P exhibits a porous structure. After vulcanization of Cu₃P, Cu₂S nanoparticles were grown in situ and uniformly decorated onto the surface of Cu₃P (Fig. 3b), resulting in

Journal Pre-proof porous CPS. In Fig. 3c, the MCS is composed of nanorods. In the case of Ni₂O₃/MCS/CPS-2.5 (Fig. 3d),

Ni₂O₃/MCS particles can be observed on the CPS surface. Notably, the as-synthesized Ni₂O₃/MCS/CPS inherits a porous structure, which not only increases the number of active sites, but also enhances light absorption through multiple reflections in the structure [39]. Ni₂O₃ nanoparticles are difficult to observe, but the presence of Ni₂O₃ can be confirmed by the following transmission electron spectroscopy (TEM) and X-ray photoelectron spectroscopy (XPS) results. Additionally, the energy-dispersive X-ray spectroscopy (EDS) spectrum confirms the presence of Cd, Mn, S, Ni, O, Cu, and P elements in Ni₂O₃/MCS/CPS-2.5 (Fig. 3e). The EDS mapping images show the elemental distribution (Fig. 3f). The distribution patterns of P and Cu confirm the porous structures of the samples.





Fig. 3. SEM images of (a) Cu₃P, (b) CPS, (c) MCS, and (d) Ni₂O₃/MCS/CPS-2.5. (e) EDS spectrum and (f)

EDS mapping images of Ni₂O₃/MCS/CPS-2.5.

Furthermore, high-resolution TEM (HRTEM) was used to investigate the microstructures of the samples in greater detail, as shown in Fig. 4. For the pure MCS, the interplanar distance of 0.33 nm can be indexed to the (002) plane (Fig. 4a). In Fig. 4b, the interplanar distance of 0.23 and 0.35 nm can be indexed to the (102) and (100) planes of Ni₂O₃ (JCPDS #14-0481) and MCS, respectively. In the case of Ni₂O₃/MCS/CPS-2.5 (Fig. 4c), several lattice fringes with withs of 0.33 and 0.35 nm (corresponding to the (002) and (100) planes of MCS, respectively), 0.28 nm ((002) plane of Ni₂O₃) and 0.20 nm ((113) plane of Cu₃P or (110) plane of Cu₂S) can be observed, confirming the coexistence of MCS, Ni₂O₃, Cu₃P, and Cu₂S in the as-synthesized Ni₂O₃/MCS/CPS composites.



Fig. 4. HRTEM images of (a) MCS, (b) 9% Ni_2O_3/MCS and (c) $Ni_2O_3/MCS/CPS$ -2.5.

To investigate the chemical compositions and valence states of elements in Cu₃P and Ni₂O₃/MCS/CPS-2.5 in greater detail, the samples were characterized using XPS. As shown in Fig. 5a, the XPS survey spectrum of Ni₂O₃/MCS/CPS-2.5 indicates the presence of Cd, Mn, S, Ni, O, Cu, and P. In Fig. 5b, the high-resolution Cd 3d spectrum contains two peaks at 404.8 and 411.5 eV, which are attributed to the Cd $3d_{52}$ and Cd $3d_{32}$ of Cd^{2+} in the Ni₂O₃/MCS/CPS-2.5 composite, respectively [40]. The XPS peaks of Mn at 641.5 and 652.1 eV can be attributed to the Mn $2p_{32}$ and Mn $2p_{1/2}$ of Mn²⁺, respectively [13]. Two peaks at 161.1 (S $2p_{32}$) and 162.3 eV (S $2p_{1/2}$) are assigned to the S²⁻ species in the composite (Fig. 5d) [13]. As shown in Fig. 5e, the Ni 2p spectrum can be deconvoluted into four peaks. The peaks at 855.8 and 873.4 eV are attributed to Ni $2p_{3/2}$ and Ni $2p_{1/2}$, respectively, which are close to the peaks of Ni₂O₃ [27]. The two peaks at 861.5 and 879.6 eV are satellite peaks. For the Cu 2p spectrum (Fig. 5f), the two peaks at 932.5 ($2p_{3/2}$) and 952.3 ($2p_{1/2}$) eV correspond to the Cu₃P signal. The peaks at 934.3 eV ($2p_{3/2}$) and 954.3 eV ($2p_{1/2}$), as well as the additional satellite peaks, correspond to oxidized copper (Cu²⁺) generated by surface

oxidation [41, 42]. Fig. 5g presents the P 2p XPS spectrum, where the peaks at 129.0 and 133.3 eV can be



attributed to phosphide species and oxidized species, respectively [43].

Fig. 5. (a) XPS survey spectrum and high-resolution XPS spectra of (b) Cd 3d, (c) Mn 2p, (d) S 2p, (e) Ni

2p, (f) Cu 2p and (g) P 2p of Cu₃P and Ni₂O₃/MCS/CPS-2.5.

Fig. 6a shows the ultraviolet-visible (UV-vis) diffuse reflectance absorption spectra (DRS) of the assynthesized photocatalysts. Cu₃P and CPS exhibit strong absorption over the entire visible light range owing to their narrow band gaps, whereas pure MCS exhibits an absorption edge at approximately 530 nm. For the Ni₂O₃/MCS/CPS composites, the absorption edge shows an obvious red shift due to the strong absorption of CPS. The enhanced visible light absorption of the Ni₂O₃/MCS/CPS composites has a beneficial effect on the improved utilization of visible light photons. Additionally, the corresponding energy band gaps (E_g) of MCS and CPS can be calculated according to the Kubelka-Munk function [44], as shown in Fig. 6b. The E_g values of Cu₃P, CPS and MCS are estimated to be 1.69, 1.67 and 2.38 eV,



Fig. 6. (a) UV-vis DRS spectra and (b) corresponding Tauc plots of the as-synthesized samples.

Fig. 7 presents the Fourier transform infrared (FTIR) spectra of MCS, $9\%Ni_2O_3/MCS$, and $Ni_2O_3/MCS/CPS-2.5$. The absorption peaks in the range of 3000–3500 cm⁻¹ and at 1647 cm⁻¹ are attributed to the O-H stretching vibrations of adsorbed water on the samples [45]. The characteristic peaks of MCS at 611 cm⁻¹ can be attributed to the typical vibrations of Mn-S bonds and the absorption bands at 1100 and 1383 cm⁻¹ correspond to the vibrations of Cd-S bonds [46-48]. For the 9%Ni₂O₃/MCS and

contents of Ni₂O₃ and CPS.



Fig. 7. FTIR spectra of MCS, 9%Ni₂O₃/MCS, and Ni₂O₃/MCS/CPS-2.5.

3.2. Photocatalytic activity and stability of as-synthesized photocatalysts

The photocatalytic H₂ evolution activities of the as-synthesized photocatalysts were tested under irradiation of a 300 W Xe lamp with a filter ($\lambda > 400$ nm), using a 0.35 M Na₂S/0.25 M Na₂SO₃ aqueous solution as a sacrificial agent (Fig. 8 and S2). As shown in Fig. 8b, the pure MCS and CPS exhibit low photocatalytic H₂ evolution rates of 0.64 mmol g⁻¹ h⁻¹ and 0.15 mmol g⁻¹ h⁻¹, respectively. After loading Ni₂O₃ as a co-catalyst, the Ni₂O₃/MCS composites exhibit enhanced H₂ evolution activities, which can be attributed to enhanced charge separation (Fig. S2). The optimal content of Ni₂O₃ is 9 wt%, resulting in the best H₂ evolution rate of 3.8 mmol g⁻¹ h⁻¹, which is 5.9 times greater than that of the pure MCS. The photocatalytic activities of 9%Ni₂O₃/MCS hybridized with different amounts of CPS were investigated further. It can be seen that the H₂ evolution activity is further enhanced (Fig. 8a) due to the formation of MCS/CPS p-n heterojunctions. With the increase in CPS content from 1 wt% to 5 wt%, the H₂ evolution rate of Ni₂O₃/MCS/CPS first increases and then decreases. The maximum H₂ evolution rate (9.2 mmol g⁻¹ h⁻¹) is obtained at 2.5 wt%. This rate is 14.4 and 2.4 times greater than those of pure MCS and 9%Ni₂O₃/MCS, respectively. The corresponding apparent quantum efficiency (AQE) is 33.5% at 420 nm.

Increasing the amount of CPS to 5 wt% results in a significant decrease in the H₂ evolution rate (6.3 mmol

 g^{-1} h⁻¹), which can be attributed to excessive CPS hindering the light absorption of Ni₂O₃/MCS. For comparison, the photocatalytic activity of Ni₂O₃/MCS/Cu₃P-2.5 was also evaluated. The H₂ evolution rate of Ni₂O₃/MCS/Cu₃P-2.5 (5.6 mmol g⁻¹ h⁻¹) is clearly lower than that of Ni₂O₃/MCS/CPS-2.5. This suggests that the formation of a CPS composite has a beneficial effect on the photoactivity of Ni₂O₃/MCS/CPS. Furthermore, some reported photoactivity of Mn_xCd_{1-x}S (0≤x≤1) based photocatalysts for photocatalytic H₂ evolution are listed in Table S1. Apparently, our Ni₂O₃/MCS/CPS photocatalysts have a better photocatalytic activity than most other reported materials.

To investigate the photostability and reusability of the synthesized photocatalysts, a typical cycle test of H_2 evolution was performed using a Ni₂O₃/MCS/CPS-2.5 sample. As shown in Fig. 8c, after 20 h of irradiation under visible light, the Ni₂O₃/MCS/CPS-2.5 retains almost 100% of its photocatalytic activity. In addition, no obvious changes in crystalline structure or morphology can be observed following photocatalytic reaction (Figs. S3 and S4). This result suggests that the photostability of the Ni₂O₃/MCS/CPS photocatalyst is acceptable.





Fig. 8. (a) Photocatalytic H₂ evolution performance and (b) average rates of H₂ evolution of the different

photocatalysts, as well as (c) cycling tests of the Ni₂O₃/MCS/CPS-2.5 composite.

3.3. Photocatalytic mechanism

To investigate the separation of photogenerated charge carriers, photoluminescence (PL) and timeresolved PL (TRPL) decay spectra were recorded. The results are plotted in Figs. 9a and 9b. The PL intensity of Ni₂O₃/MCS/CPS-2.5 is clearly weaker than that of MCS, 9%Ni₂O₃/MCS, and Ni₂O₃/MCS/Cu₃P-2.5 under 410 nm light excitation, indicating suppressed charge recombination in Ni₂O₃/MCS/CPS-2.5 (Fig. 9a) [49]. The TRPL decay spectra reveal that the charge carrier lifetime of Ni₂O₃/MCS/CPS-2.5 is longer than that of pure MCS (Fig. 9b). The long charge carrier lifetime of Ni₂O₃/MCS/CPS-2.5 ensures that more electrons can participate in photocatalytic reaction [50].

To verify the improved separation efficiency of charge carriers in Ni₂O₃/MCS/CPS-2.5, electrochemical characterizations were conducted. As shown in Fig. 9c, the transient photocurrent response of Ni₂O₃/MCS/CPS-2.5 exhibits the largest current density. This enhanced photocurrent response can be ascribed to the higher separation efficiency of charge carriers [51], which is consistent with the highest H₂ evolution rate. Additionally, the electrochemical impedance spectroscopy (EIS) result for Ni₂O₃/MCS/CPS-2.5 (Fig. 9d), 2.5 reveals a smaller arc radius compared to MCS, 9%Ni₂O₃/MCS, and Ni₂O₃/MCS/Cu₃P-2.5 (Fig. 9d),

indicating reduced charge transport resistance in the Ni₂O₃/MCS/CPS ternary composites [52]. Fig. S5

presents the linear sweep voltammetry curves of MCS, 9%Ni₂O₃/MCS, and Ni₂O₃/MCS/CPS-2.5. One can see that Ni₂O₃/MCS/CPS-2.5 has a much lower overpotential for H₂ evolution compared to MCS and 9%Ni₂O₃/MCS, indicating that loading Ni₂O₃ and CPS can effectively increase H₂ evolution reaction activity [53, 54].



Fig. 9. (a) PL spectra, (b) TRPL decay spectra, (c) photocurrent densities and (d) EIS Nyquist plot of MCS,

9%Ni₂O₃/MCS, Ni₂O₃/MCS/Cu₃P-2.5 and Ni₂O₃/MCS/CPS-2.5.

The surface photovoltage (SPV) technique is a powerful technique for understanding the dynamic behavior of photogenerated charge carriers [5]. As shown in Fig. 10, all samples exhibit responses in the wavelength range of 300–550 nm, which is consistent with the E_g values of samples. The as-synthesized composites exhibit stronger SPV signals than pure MCS, indicating that the recombination of charge

highly efficient separation of charge carriers.



Fig. 10. SPV spectra of the as-synthesized photocatalysts.

Additionally, the semiconductor types and flat band potentials (E_{fb}) of MCS, CPS, and Cu₃P were measured based on Mott-Schottky plots. It is known that semiconductor types can be concluded from the slopes of the Mott-Schottky plots. As shown in Fig. 11(a, b), MCS is an n-type semiconductor with a positive slope, whereas both Cu₃P and CPS exhibit p-type characteristics with negative slopes. The E_{fb} values of MCS, Cu₃P and CPS are approximately -1.08, 0.66 and 0.83 V versus a saturated calomel electrode, respectively (-0.84, 0.90 and 1.08 V versus NHE, respectively). Generally, the conduction band potentials (E_{CB}) of n-type semiconductors and valence band potentials (E_{VB}) of p-type semiconductors are believed to be approximately 0.1 V above and below E_{fb} , respectively [55]. Therefore, the E_{CB} value of MCS as well as E_{VB} values of Cu₃P and CPS were estimated to be -0.94, 1.0 and 1.18 V vs. NHE, respectively. Based on the E_g values, the E_{VB} value of MCS was calculated to be 1.44 V and the E_{CB} values of Cu₃P and CPS were calculated to be -0.69 and -0.49 V, respectively. According to our previous report, the E_{CB} and E_{VB} values of Cu₂S are -0.22 and 1.06 V, respectively [38]. Furthermore, the Mott-Schottky

n heterojunctions (Fig. 11c) [56].



Fig. 11. Mott-Schottky plots of (a) MCS, (b) CPS and Cu₃P (inset), and (c) Ni₂O₃/MCS/CPS-2.5.

Based on the analysis above, both the Ni_2O_3 co-catalyst and formed p-n heterojunctions are responsible for the enhanced photocatalytic H₂ evolution of the $Ni_2O_3/MCS/CPS$ composites. A possible mechanism for photocatalytic H₂ evolution is presented in Fig. 12. The energy band structures of the MCS, Cu_2S , and Cu_3P prior to contact are presented in Fig. 12a. The Fermi levels (E_f) of MCS and CPS are close to the conduction band (CB) and valence band (VB), respectively. However, when the p-type CPS and n-type MCS contact each other, a p-n heterojunction is formed at the phase interface (Fig. 12b). Furthermore, electrons from the n-type region flow into the p-type region and holes migrate from the p-type region to the

n-type region owing to their different Fermi levels. Consequently, an equilibrium between the Fermi levels of MCS and CPS is achieved. Under visible light irradiation, photogenerated electrons are generated in Cu_3P , Cu_2S , and MCS, and then transfer from the CB of Cu_3P to the CB of MCS through the CB of Cu_2S due to the E_{CB} level differences. Furthermore, electrons migrate to the Ni_2O_3 co-catalyst due to the relatively lower overpotential of Ni_2O_3 [27]. Finally, the accumulated electrons in Ni_2O_3 can reduce H^+ into H_2 . Conversely, the holes in the VB of the MCS transfer spontaneously to the VB of the CPS and are consumed by sacrificial agents. Combined with the Ni_2O_3 co-catalyst and formed p-n heterojunctions, the synthesized porous structure can capture more incident light through multiple reflections and provide more active sites, which is also beneficial to improved photoactivity.



Fig. 12. (a) Energy band diagrams of MCS, Cu₂S and Cu₃P. (b) Possible charge transfer mechanism for H₂

evolution over the Ni₂O₃/MCS/CPS-2.5 photocatalyst.

4. Conclusions

In this study, we successfully synthesized a novel Ni₂O₃/MCS/CPS ternary photocatalyst by coupling Ni₂O₃/MCS and CPS. Cu₂S nanoparticles were grown in situ and uniformly attached to the surface of Cu₃P by using the vulcanization method. Ni₂O₃/MCS/CPS-2.5 exhibits an optimal photocatalytic H₂ evolution rate of 9.2 mmol g⁻¹ h⁻¹, which is 14.4 and 2.4 times higher than those of pure MCS and 9%Ni₂O₃/MCS, respectively. Additionally, Ni₂O₃/MCS/CPS-2.5 exhibits a high AQE of 33.5% at 420 nm and an excellent

photostability over 20 h in a Na₂S/Na₂SO₃ solution. This improved photocatalytic activity and stability can

be attributed to synergistic effects offered by the p-n heterojunctions that are formed between MCS and CPS, the favorable co-catalytic activity of Ni₂O₃, and a porous structure, which facilitates the separation and transfer of photogenerated charge carriers and improves the light absorption. This work provides a new avenue for the development and design of highly efficient visible-light-driven photocatalysts.

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Highlights

- 1. Ni₂O₃/MCS/CPS composite show excellent photocatalytic activity and stability.
- 2. Ni₂O₃ as a cocatalyst favors the charge transfer and provides active sites.
- 3. The p-n heterojunction between MCS and CPS boosts charge separation.

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Declaration of interests

□ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Declarations of interest: none.

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