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ARTICLE TYPE

Preparation of g-C₃N₄/ZnMoCdS hybrid heterojunction catalyst with outstanding nitrogen photofixation performance under visible light via hydrothermal post-treatment

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Nitrogen fixation as the second most important chemical process in nature next to photosynthesis. Here, we report a novel g-C₃N₄/ZnMoCdS heterojunction photocatalysts with outstanding nitrogen

10 photofixation ability under visible light prepared by hydrothermal post-treatment. The as-prepared ZnMoCdS is the ternary metal sulfide Zn_{0.12}Mo_{0.12}Cd_{0.9}S_{1.14} with many sulfur vacancies, not a mixture of ZnS, MoS₂ and CdS. Strong electronic coupling, as evidenced by the UV-Vis, XPS and EIS results, exists between two components in the g- $C_3N_4/ZnMoCdS$ heterojunction photocatalysts, leading to more effective separation of photogenerated electron-hole pairs and faster interfacial charge transfer. The sulfur

15 vacancies on ternary metal sulfide not only serve as active sites to adsorb and activate N₂ molecules but also promote interfacial charge transfer from the catalyst to N₂ molecules, thus significantly improving the nitrogen photofixation ability. With the optimal ZnMoCdS mass percentage of 80%, the as-prepared heterojunction photocatalyst exhibits the highest NH_4^+ generation rate under visible light, which is 13.5fold and 1.75-fold greater than those of individual g-C₃N₄ and ZnMoCdS.

20 Introduction

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Nitrogen is the necessary element for the growth of plants and animals. Nitrogen fixation is the second most important chemical process in nature next to photosynthesis. Haber-Bosch process is used for the artificial nitrogen fixation in the past decades, in

- 25 which hydrogen gas reacts with nitrogen gas to produce ammonia in the presence of Fe-based catalysts under high pressure and temperature. Not only the energy consumption but the raw material cost is high for this process. Therefore, artificial nitrogen fixation under milder conditions is great significant, since the
- 30 reduction in the input energy during the fixation process and no use of hydrogen gas may be preferred from the viewpoints of cost and environmental protection.

In recent years, the photocatalytic nitrogen fixation technology has become the best alternative to traditional Haber-Bosch 35 process for its green cleaning, mild conditions, low power consumption, and low cost etc. In 1977, Schrauzer et al.¹ first reported that N₂ can be reduced to NH₃ over Fe doped TiO₂ under UV light. The reaction is as follow:

 $2N_2+6H_2O\rightarrow 4NH_3+3O_2$

40 Since then, many Ti-based metal oxides and composite catalyst were reported.²⁻⁶ Ranjit et al.² investigated the nitrogen photofixation activity of precious metals modified TiO2, and found that Ru modified TiO₂ exhibited the best photofixation performance. A linear relationship observed between the

 $_{45}$ concentration of NH₄⁺ and the strength of metal-H bond. Rusina et al.³ investigated the N_2 photofixation performance using

Fe₂Ti₂O₇ as catalyst and ethanol as the hole-trapping agent. Hoshino et al.4,5 prepared conducting polymer/TiO2 hybrid material for nitrogen photofixation under white light. The main 50 product is NH₄ClO₄. Zhao et al.⁶ prepared Fe-doped TiO₂ nanoparticles with highly exposed (101) facets by two-step hydrothermal method. They found the quantum yields of nitrogen photofixation depend on the partial pressure of nitrogen in the reaction. However, because of the poor visible light absorption 55 caused by the wide band gap energy, the nitrogen fixation ability of the Ti-based metal oxides and composite catalyst is still low under visible light.

Two-dimensional (2D) graphitic carbon nitride (g-C₃N₄), the most stable allotrope of covalent carbon nitride,7 have been 60 widely used as a new metal-free visible light photocatalyst for organic pollutant degradation,⁸ water reduction and oxidation,⁹ CO₂ capture¹⁰ and organic synthesis.¹¹ The tunable condensation degree and distinctive heptazine ring structure make g-C₃N₄ possess good physicochemical stability, fascinating electronic 65 structure and medium band gap (2.7 eV). However, the rapid photogenerated electron-hole pair recombination and low electrical conductivity lead to its low activity in practical applications.

Continuous efforts have been made by the researchers to 70 improve this situation. In addition to doping selected heteroatoms into the framework (such as P, B, S, O, halogen and Fe),12-17 which could slightly modify the molecular orbital shape and position, promoting the photocatalytic performance, pristine g-C₃N₄ can be also engineered by charge-transfer complexation to

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form a nanocomposite which results in rearranging electron density within the catalyst. Nanostructural metal sulfide, including one-component ZnS,18 CdS,19 SnS2,20 and twocomponent $Zn_xCd_{1-x}S^{21}$ and $ZnIn_2S_4^{22}$, has received much s attentions in photocatalysis field in recent years. These metal sulfides possess moderate band gap which can absorb visible light directly. The energy level of conduction band and valence band of those metal sulfides match well with g-C₃N₄, leading to the efficient photogenerated charge interface migration and 10 increased activity of photocatalysts.²³ Thus, g-C₃N₄/metal sulfide hybrid catalysts have been reported in succession. Lu et al. prepared atomic layer g-C₃N₄-CdS nanoheterojunctions by a simple ultrasonic exfoliation approach. The enhanced photocatalytic MO degradation activity should be attributed to the 15 well-matched band structure and intimate contact interfaces between the g-C₃N₄ and CdS, which lead to the effective transfer and separation of the photogenerated charge carriers.²⁴ Ge et al. synthesized novel MoS₂/g-C₃N₄ composite via a facile impregnation method. The layered MoS2 co-catalysts were 20 decorated on the surface of g-C₃N₄ to form intimate interfaces facilitating charge transfer between the semiconductors. The 0.5wt% MoS₂/g-C₃N₄ sample shows the highest H₂ production ability, which is enhanced by 11.3 times compared to the unmodified g-C₃N₄.²⁵ Sun et al. prepared g-C₃N₄/Zn_{0.25}Cd_{0.75}S 25 composite photocatalyst for efficient degradation of dyes and reduction of Cr(VI) in water by a facile and template free in situ precipitation method.²⁶ The HRTEM images showing clear lattice fringes proved the formation of a heterojunction structure at the interfaces of g-C₃N₄ and Zn_{0.25}Cd_{0.75}S. The photoelectrochemical 30 measurements confirmed that the interface charge separation efficiency was greatly improved by coupling g-C₃N₄ with Zn_{0 25}Cd_{0 75}S.

Recently, Li et al. reported the photofixation of N₂ on BiOBr nanosheets.²⁷ They discovered that the introduction of oxygen ³⁵ vacancies could activate N₂ and promote interfacial electron transfer, thus significantly improving the nitrogen photofixation ability. We hypothesize that sulfur vacancies formed by the multi-component metal sulfide have a similar effect on nitrogen photofixation because oxygen and sulfur have the similar 40 chemical properties. To the best of our knowledge, no studies on the nitrogen photofixation performance over tri-component metal sulfide/g-C₃N₄ heterojunction photocatalysts have been reported. In this work, a novel g-C₃N₄/ZnMoCdS heterojunction photocatalyst with outstanding nitrogen photofixation ability 45 under visible light is prepared by hydrothermal post-treatment. The effects of heterojunction and sulfur vacancies on the

The effects of heterojunction and sulfur vacancies on the properties and N_2 photofixation ability of as-prepared catalysts are discussed.

Experimental

50 Preparation and characterization

In a typical experiment, 3 g dicyandiamide was annealed at 520 °C for 2 h (at a rate of 5 °C·min⁻¹). The obtained g-C₃N₄ was denoted as CN. The preparation procedure of the g-C₃N₄/ZnMoCdS heterojunction photocatalyst was as follow: a ⁵⁵ desired amount of zinc acetate, ammonium molybdate and

so desired amount of zinc acetate, ammonium molybdate and cadmium acetate (Zn/Mo/Cd molar ratio = 1 : 1 : 8) were

dissolved in deionized water to form a solution. Then 1 g of CN powders were added into above solution. The formed suspension was ultrasonicated for 30 min to completely disperse the g-C₃N₄. ⁶⁰ Stoichiometric Na₂S (0.5 M) was added dropwise into the suspension and stirred for 12 h at room temperature. The suspension was poured into 100 mL Teflon-lined container, sealed in a stainless steel autoclave and maintained at 160 °C for 16 h. The solids were washed for several times and dried at 80 °C. The obtained products were denoted as ZMCS-CN(x%), where x% stands for the mass percentages of CN. For comparison, the ZnMoCdS was prepared according to the same procedure mentioned above in the absence of CN. In order to investigate the effect of sulfur vacancies, the as-prepared 70 ZnMoCdS was calcined at 300 °C for 2 h in atmosphere and denoted as ZnMoCdSO.

The XRD patterns of the prepared samples were recorded on a Rigaku D/max-2400 instrument using Cu-K α radiation ($\lambda = 1.54$ Å). The scan rate, step size, voltage and current were 0.05 °/min, 75 0.01°, 40 kV and 30 mA, respectively. UV-Vis spectroscopy was carried out on a JASCO V-550 model UV-Vis spectrophotometer using BaSO₄ as the reflectance sample. ICP was performed on a Perkin-Elmer Optima 3300DV apparatus. TEM images were taken on a Philips Tecnai G220 model microscope. TPD studies ⁸⁰ were performed using a CHEMBET-3000 (Quantachrome, U.S.A.) instrument. The photoluminescence (PL) spectra were measured at room temperature with a fluorospectrophotometer (FP-6300) using a Xe lamp as the excitation source. The XPS measurements were performed on a Thermo Escalab 250 XPS ⁸⁵ system with Al Kα radiation as the excitation source. The binding energies were calibrated by referencing the C 1s peak (284.6 eV) to reduce the sample charge effect. Nitrogen adsorption was measured at -196 °C on a Micromeritics 2010 analyser. All the samples were degassed at 393 K prior to the measurement. The 90 BET surface area (S_{BET}) was calculated based on the adsorption isotherm. The water contact angle was measured at 25 °C using an OCA 20 contact angle system (Dataphysics, Germany). The electrochemical impedance spectra (EIS) were recorded using an EIS spectrometer (EC-Lab SP-150, BioLogic Science 95 Instruments) in a three electrode cell by applying a 10 mV alternative signal versus the reference electrode (SCE) over a frequency range of 1 MHz to 100 mHz. The cyclic voltammograms were measured in a 0.1 M KCl solution containing 2.5 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) as a redox ¹⁰⁰ probe at a scanning rate of 20 mV s⁻¹ in the same three electrode cell as the EIS measurement. The photocurrents were measured using an electrochemical analyser (CHI 618C Instruments) equipped with a rectangular shaped quartz reactor $(20 \times 40 \times 50)$ mm) using a standard three electrode system. The prepared 105 sample film was used as the working electrode, a Pt flake was used as the counter electrode, and Ag/AgCl was used as the reference electrode. A 500 W Xe lamp was used to irradiate the working electrode from the back side. The light intensity on the working electrode was 120 mW cm⁻². In addition, a mechanical 110 shutter was used to minimize the light exposure of the sample. A 1.0 M Na₂SO₄ solution was used as the electrolyte. The applied potential was 0.00 V vs. Ag/AgCl. All the measurements were performed at room temperature (298 K).

Photocatalytic Reaction

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Evaluation of nitrogen photofixation property is refered to previous literature.⁶ The nitrogen photofixation experiments were carried out in a double-walled quartz reactor in air. 0.2 g of photocatalyst was added into 500 mL solution of 0.789 g/L s ethanol as hole scavenger.⁶ The suspension was dispersed in an ultrasound generator for 10 min. In the photoreaction under

- visible light irradiation, the suspension was exposed to a 250 W high-pressure sodium lamp with main emission in the range of 400-800 nm, and air was bubbled at 130 ml/min through the 10 solution. The UV light portion of sodium lamp was filtered by 0.5
- M NaNO₂ solution. All runs were conducted at ambient pressure and 30 °C. At given time intervals, 5 ml suspension was taken and immediately centrifuged to separate the liquid samples from the solid catalyst. The concentration of ammonia was measured ¹⁵ using Nessler's reagent spectrophotometry method (JB7478-87)

by a UV-2450 spectrophotometer (Shimadzu, Japan).²⁷

Results and discussion

Figure 1 shows the nitrogen photofixation performance over the as-prepared catalysts under visible light. The results of the control $_{20}$ experiment indicate that the NH₄⁺ generation rate can be ignored in the absence of irradiation, N_2 or photocatalyst, indicating that nitrogen photofixation occurs via a photocatalytic process. CN and ZnMoCdS display the NH₄⁺ generation rates of 0.26 and 2.0 mg $L^{-1} h^{-1} g_{cat}^{-1}$. For as-prepared heterojunction catalysts, the $_{25}$ NH₄⁺ generation rate are 2.48, 3.5, 1.11 and 0.75 mg·L⁻¹·h⁻¹·g_{cat}⁻¹ for ZMCS-CN(10%), ZMCS-CN(20%), ZMCS-CN(50%) and ZMCS-CN(80%). ZMCS-CN(20%) shows the highest NH_4^+ generation rate, which is which is 13.5-fold and 1.75-fold greater than those of CN and ZnMoCdS. This hints that the probably 30 active sites for nitrogen photofixation is on ZnMoCdS but not CN. The Figure 1 insert shows the photocatalytic stability of ZMCS-CN(20%). No obvious decrease in nitrogen photofixation ability is observed after 20 h, hinting its good stability. It is noted that ZnMoCdSO shows the NH₄⁺ generation rate of only 0.32 ³⁵ mg·L⁻¹·h⁻¹·g_{cat}⁻¹, obviously lower than that of ZnMoCdS. The possible reason is discussed later. The influence of metal ratio on the nitrogen photofixation performance is present in Table 1. The result shows that the optimal metal molar ratio is Zn : Mo : Cd of 1:1:8.



⁴⁰ **Figure 1.** Nitrogen photofixation performance over the asprepared catalysts under visible light.

Table 1. Th	ne influence	of molar	ratio	of Zn	: Mo	: Cd	on	the
45 nitrogen pho	tofixation pe	erformanc	e					

Zn : Mo : Cd (molar ratio)	0.5:0.5:9	1:1:8	2:2:6	3:3:4
R_{NH4}^{+} (mg·L ⁻¹ ·h ⁻¹ ·g _{cat} ⁻¹)	2.2	3.5	2.94	2.55

The XRD patterns of as-prepared catalysts are shown in Figure 2. Two typical diffraction peaks of $g-C_3N_4$ are present in the CN. The peak at 13.1° corresponds to in-plane structural packing 50 motif of tri-s-triazine units, which is indexed as (100) peak. The distance is calculated as d = 0.671 nm. The peak at 27.5 ° corresponds to interlayer stacking of aromatic segments with distance of 0.324 nm, which is indexed as (002) peak. For ZnMoCdS, three diffraction peaks located at 26.9, 44.4 and 52.4° 55 are observed. It is known that the diffraction peaks of cubic phase CdS are located at 26.6, 43.9 and 52°, which are very close to those of the as-prepared ZnMoCdS.²⁴ In addition, no ZnS and MoS_2 diffraction peaks are observed.^{28,29} Thus it is deduced that Zn and Mo doped into the crystal lattice of CdS to form 60 the ternary metal sulfide ZnMoCdS but not the mixture of ZnS, MoS₂ and CdS. The doping of Zn and Mo causes the crystal lattice defects of CdS, leading to the shift of diffraction peaks. The XRD patterns of the g-C₃N₄/ZnMoCdS heterojunction photocatalysts show no difference to pure ZnMoCdS due to the 65 low X-ray diffraction intensity of the g-C₃N₄ and characteristic peaks overlapping between CdS (26.6°) and g-C₃N₄ (27.5°). The similar phenomenon has been reported by Sun and Ge.^{26,30}



Figure 2. XRD patterns of as-prepared catalysts.

The Zn, Mo, Cd and S concentrations of ZnMoCdS obtained by ICP are 4.8, 9.2, 63.5 and 22.5 wt.%, close to the theoretical values. The actual atomic ratio is Zn_{0.12}Mo_{0.12}Cd_{0.9}S_{1.14} for the asprepared ternary metal sulfide. Under this metal ratio, the number of sulfur atoms should be 1.26. Thus the crystal lattice defects in 75 ternary metal sulfide should be the sulfur vacancies. For ZnMoCdSO, the actual atomic ratio is Zn_{0.11}Mo_{0.12}Cd_{0.88}S_{1.12}O_{0.11} obtained by ICP, hinting the sulfur vacancies are oxidized during calcination process.

The morphologies of the representative samples were ⁸⁰ examined by using SEM analysis. Figure 3a indicates that CN exhibits layered structure, similar to its analogue graphite. In Figure 3b, the as-prepared ZnMoCdS displays uniform nanoparticles with the average size of ~50 nm. Interestingly, these ZnMoCdS nanoparticles self-assemble to 3D spherical ⁸⁵ nanostructure with an diameter of ~1 µm. For ZMCS-CN(20%) (Figure 3c), it can be seen that lots of nanoparticles are attached on the g-C₃N₄ surface. The average size of these nanoparticles are \sim 50 nm, which is consistent with as-prepared ZnMoCdS shown in Figure 3b. This hints the g-C₃N₄/ZnMoCdS hybrid heterojunction catalysts are successfully synthesized. The ⁵ elemental mapping has been conducted to investigate the element distribution in the ZMCS-CN(20%) (Figure 3d). The dark blue, light blue, yellow and red colour of the image is respectively acquired at the K-line spectra of C, N, S and Zn elements, while that for the green and purple colour are acquired at the L-line ¹⁰ spectra of Cd and Mo elements. The result indicates that all the elements are homogenously distributed in the whole sample.



Figure 3. SEM images of CN (a), ZnMoCdS (b), ZMCS-CN(20%) (c) and elemental mapping images of ZMCS-CN(20%) ³⁰ (d).





- ⁴⁵ The typical TEM image of ZMCS-CN(20%) shown in Figure 4a displays that the CN exhibit a typical sheet-like morphology, which is similar to its analogue graphite. The ZnMoCdS consists of plenty of irregular particles. The two-dimensional ordering of CN is very weak and hard to find the lattice fringe in HRTEM
- ⁵⁰ image (Figure 4b). However, the clear lattice fringe is observed for ZnMoCdS. The measured lattice spacing is 0.330 nm, very close to the (1 1 1) crystal face of cubic phase CdS.²⁴ This tight coupling is favorable for the charge transfer between CN and ZnMoCdS and promotes the separation rate of electron-hole ⁵⁵ pairs.

Generally, a catalyst with high specific surface area (S_{BET}) is significant to the enhancement of catalytic performance. The nitrogen adsorption and desorption isotherms of g-C₃N₄ based

catalysts were measured (Figure 5). The isotherm of as-prepared ⁶⁰ catalysts are of classical type IV, suggesting the presence of mesopores (2-50 nm). Because of the agglomeration, CN shows a low S_{BET} of 8.8 m²·g⁻¹. The S_{BET} of ZnMoCdS is 27.5 m²·g⁻¹, which is probably due to the formation of larger pores accumulated by the ZnMoCdS nanoparticles. This is consistent ⁶⁵ with the SEM results. For ZMCS-CN(20%), the S_{BET} is 12.2 m²·g⁻¹, much lower than that of ZnMoCdS. This is reasonable because the ZnMoCdS nanoparticles did not self-assemble to microspheres but attach onto the g-C₃N₄ surface during the preparation process, as shown in Figure 3c. Thus the larger pores ⁷⁰ produced by the accumulation of ZnMoCdS nanoparticles is not



formed in ZMCS-CN(20%).

75

Figure 5. N_2 adsorption-desorption isotherm of CN, ZnMoCdS and ZMCS-CN(20%).



Figure 6. UV-Vis spectra of the as-prepared catalysts.

Figure 6 displays the UV-Vis spectra of the g-C₃N₄/ZnMoCdS heterojunction photocatalysts with different weight ratios of g- C_3N_4 , together with those of $g-C_3N_4$ and ZnMoCdS. The band gaps are estimated from the tangent lines in the plots of the ⁸⁰ square root of the Kubelka-Munk functions as a function of the photon energy.³¹ Pure g-C₃N₄ has an absorption edge at about 464 nm, corresponding to the band gap of 2.67 eV. The absorption edge value for ZnMoCdS is observed at 550 nm, and the corresponding band gap is estimated to be 2.25 eV. The 85 absorption edges of g-C₃N₄/ZnMoCdS heterojunction photocatalysts are located between g-C₃N₄ and ZnMoCdS, which confirms the electronic coupling of these two components in the g-C₃N₄/ZnMoCdS heterojunction. The similar phenomenon has been reported in other g-C₃N₄ based heterojunction materials.^{32,33} 90 Besides the red-shifted absorption edge, the intensity of the

absorbance of $g-C_3N_4/ZnMoCdS$ heterojunction photocatalysts are higher than that of CN in the full spectrum. This indicates that the $g-C_3N_4/ZnMoCdS$ heterojunction photocatalysts could absorb more visible light and produce more electron-hole pairs, which s will be favorable for a photocatalytic reaction.



Figure 7. XPS spectra of the as-prepared catalysts in the region of C 1s (a), N 1s (b), S 2p (c), Zn 2p (d), Mo 2p (e) and Cd 3d (f).

XPS are carried out to confirm the structure of as-prepared heterojunction catalyst. In Figures 7a, the spectrum of CN in C 1s region can be fitted with three contributions located at 284.6, 286 and 288.4 eV. They are attributed to the C-C bond, which ³⁵ originated from sp² C atoms bonded to N in an aromatic ring (N-C=N), C=N or C≡N, which could be ascribed to defectcontaining sp² hybridized carbon atoms present in graphitic domains, and pure graphitic sites in a CN matrix.³⁴ In Figure 7b, the main N 1s peak of CN located at 398.4 eV can be assigned to ⁴⁰ sp² hybridized nitrogen (C=N–C), thus confirming the presence of sp² bonded graphitic carbon nitride. The peak at higher binding energy 400.7 eV is attributed to tertiary nitrogen (N–(C)₃) groups.³⁵ In the case of ZMCS-CN(20%), the spectrum in N 1s region exhibit the red shift in the binding energy. This is probably ⁴⁵ due to the electron-rich g-C₃N₄ transfer partial electrons to

- ⁴⁵ due to the electron-field g-C₃N₄ transfer partial electrons to ZnMoCdS, leading to the decreased electron density. This shift in binding energy suggests an electronic interaction between the g-C₃N₄ and ZnMoCdS. In S 2p region (Figure 7c), the binding energy located at 162.1 eV for ZnMoCdS is associated with the ⁵⁰ S²⁻. In the case of ZMCS-CN(20%), a new peak located at 163.3
- $_{50}$ S · In the case of ZMCS-CN(20%), a new peak located at 165.5 eV is observed, which is attributed to the C-S bond.¹⁴ This bond should be formed between g-C₃N₄ and ZnMoCdS, which confirms the g-C₃N₄/ZnMoCdS heterojunction photocatalysts are successfully prepared. In Zn 2p, Mo 2p and Cd 3d regions of ZnMoCdS locate at the binding energies of ZnMoCdS locate at the successful sector.
- ⁵⁵ (Figure 7d, e and f), the binding energies of ZnMoCdS locate at 1021.7 and 1044.9 eV, 230.2 and 233.4 eV, and 404.7 and 411.5 eV, obvious different from that of single ZnS, MoS₂ and CdS in previous reports.³⁶⁻⁴⁰ This confirms the as-prepared metal sulfide

is not the mixture of ZnS, MoS₂ and CdS but the hybrid ternary ⁶⁰ metal sulfide. For ZMCS-CN(20%), the binding energies in the regions of Zn 2p, Mo 2p and Cd 3d display blue shifts compared with that of ZnMoCdS. This increased electron density is due to the electron transfer from electron-rich g-C₃N₄ to ZnMoCdS which is consistent with the results obtained from N 1s region. ⁶⁵ This confirms an electronic interaction between the g-C₃N₄ and ZnMoCdS.

EIS is a useful tool for characterizing the charge-carrier migration. Thus EIS was employed to further confirm the interfacial charge transfer effect of the as-prepared g-C₃N₄ based 70 catalysts. As shown in Figure 8, as-prepared heterojunction catalysts exhibit decreased arc radius compared to that of CN and ZnMoCdS. In general, the radius of the arc in the EIS spectra reflects the reaction rate on the surface of the electrode.⁴¹ The reduced arc radius indicates diminished resistance of working 75 electrodes, suggesting a decrease in the solid state interface layer resistance and the charge transfer resistance across the solidliquid junction on the surface between $g-C_3N_4$ and ZnMoCdS.⁴² ZMCS-CN(20%) shows the smallest arc radius. Since the radius of the arc on the EIS spectra reflects the migration rate occurring so at the surface, it suggests that a more effective separation of photogenerated electron-hole pairs and a faster interfacial charge transfer occurs on ZMCS-CN(20%) surface under this condition.43



Figure 8. EIS spectra of the as-prepared catalysts.



g-C₃N₄ Heterojunction ZnMoCdS

Figure 9. The schematic illustration of electron-hole separation ¹⁰⁰ and transport at the g-C₃N₄/ZnMoCdS heterojunction interface.

The valence band (VB) edge positions of ZnMoCdS is

estimated according to the concept of electronegativity. Herein, the electronegativity of an atom is the arithmetic mean of the atomic electron affinity and the first ionization energy. The VB edge potential of a semiconductor at the point of zero charge can ⁵ be calculated by the following empirical equation⁴⁴:

 $E_{\rm VB} = X - E_{\rm c} + 0.5E_{\rm g}$

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where E_{VB} is the VB edge potential, X is the electronegativity (geometric mean of the electronegativity of the constituent atoms), E_c is the energy of free electrons on the hydrogen scale ¹⁰ (4.5 eV), E_g is the band gap energy. The X value for $Zn_{0.12}Mo_{0.12}Cd_{0.9}S_{1.14}$ is 5.21 eV. Accordingly, the E_{VB} of $Zn_{0.12}Mo_{0.12}Cd_{0.9}S_{1.14}$ is +1.84 eV/NHE. Thus, the E_{CB} is estimated to be -0.41 eV/NHE. The E_{CB} and E_{VB} of g-C₃N₄ are -1.12 eV and +1.57 eV, respectively.⁴⁵ Therefore, once g-C₃N₄ and ¹⁵ ZnMoCdS are electronically coupled together, the band alignment between the two kinds of materials results in the formation of heterojunction with well-matched band structure. The schematic illustration of electron-hole separation and transport at the g-C₃N₄/ZnMoCdS heterojunction interface is ²⁰ shown in Figure 9. Upon visible-light irradiation, the

photogenerated electrons tend to transfer rapidly from g-C₃N₄ to ZnMoCdS driven by CB offset of 0.71 eV, whereas the photogenerated holes transfer from ZnMoCdS to g-C₃N₄ driven by VB offset of 0.27 eV. The potential difference is the main ²⁵ driving force for efficient charge separation and transfer. These two charge transfer processes are beneficial for overcoming the high dissociation barrier of the Frenkel exciton and stabilizing electrons and holes. The redistribution of electrons on one side of the heterojunction (ZnMoCdS) and holes on the opposite side (g-³⁰ C₃N₄) could establish a steady internal electric fields, which reduces the electron/hole pairs recombination. As the photogenerated electrons and holes are spatially separated into two components, the charge recombination is drastically inhibited, which is of great benefit for enhancing the ³⁵ photocatalytic activity.



Figure 10. The N₂-TPD of CN, ZnMoCdS, ZnMoCdSO and ZMCS-CN(20%) (a). The comparison of PL intensity of ZnMoCdS and ZnMoCdSO under Ar and N₂ atmospheres (b). ⁵⁵ Photocurrent responses of as-prepared catalysts under N₂ or Ar atomsphere (c and d).

Because the chemical adsorption sites are considered to be reaction centers capable of activating N_2 , chemisorption is an

- 60 essential step in photocatalytic N₂ fixation. TPD investigations were performed to understand N₂ chemisorption on the surface of the as-prepared catalysts. In Figure 10a, the N₂-TPD results on CN, ZnMoCdS, ZnMoCdSO and ZMCS-CN(20%) are compared. Two adsorbed N₂ species in ZnMoCdS and ZMCS-CN(20%) and
- 65 only one adsorbed N₂ species in CN and ZnMoCdSO are observed. The peak at ~120 °C is related to physical adsorption. The peak at 270 °C, which is related to the strong chemisorption species of N₂, is observed for ZnMoCdS and ZMCS-CN(20%) but not for CN and ZnMoCdSO. This result indicates that sulfur
- ⁷⁰ vacancies could introduce many chemical adsorption sites on the surface of ZnMoCdS. Because chemisorption is generally associated with activation, these chemical adsorption sites will activate N₂ for nitrogen photofixation. Figure 10b compares the PL intensity of ZnMoCdS and ZnMoCdSO under Ar and N₂ ⁷⁵ atmospheres. The emission peak of ZnMoCdS is weaker than that of ZnMoCdSO under both atmospheres, indicating that sulfur
- vacancies can act as electron trappers to improve carrier separation. Under N₂ atmosphere, the PL intensity of ZnMoCdS has been sharply reduced compared with that under an Ar atmosphere. This hints that sulfur vacancies may promote photogenerated electron transfer from ZnMoCdS to adsorbed N₂. By contrast, no difference is observed for ZnMoCdSO between the PL spectra under N₂ and Ar atmospheres, confirming this point of view.
- Figure 10c shows the photocurrent densities of CN, ZnMoCdS, ZMCS-CN(20%) and ZnMoCdSO under a N₂ atmosphere. Because of the formation of heterojunction, ZMCS-CN(20%) shows the highest photocurrent. The photocurrent of ZnMoCdSO is lower than that of ZnMoCdS, confirming that sulfur vacancies
- ⁹⁰ can trap the electrons to promote the separation rate. Note that the photocurrent generated on the CN and ZnMoCdSO electrode remains unchanged with irradiation time. However, the photocurrent densities of ZMCS-CN(20%) and ZnMoCdS gradually decrease at the beginning and then remain stable. This photocurrent decrease is probable due to the computation between the photocurrent decrease at the beginning and then remain stable. This photocurrent decrease is probable due to the computation between the photocurrent decrease at the beginning and then remain stable. This photocurrent decrease is probable due to the computation between the photocurrent decrease at the beginning and then remain stable.
- ⁹⁵ photocurrent decay is probably due to the competition between N₂ and FTO glass for trapped electrons. Li and his coworkers reported that oxygen vacancies can trap electrons and promote interfacial charge transfer from BiOBr nanosheets to N₂.²⁷ We hypothesize that sulfur vacancies have a similar effect because ¹⁰⁰ they are the congeners. The photogenerated electrons that arrived ¹⁰⁰ they are the congeners.
- at the surface of ZnMoCdS are trapped by the sulfur vacancies, and then transferred immediately from the catalysts to the adsorbed N2, causing the photocurrent decay. In Figure 10d, the photocurrents of ZnMoCdSO under N2 and Ar atmosphere are ¹⁰⁵ almost the same. Whereas, the photocurrent of ZnMoCdS does not decay under Ar atmosphere. This result confirms the fast electron transfer process from the catalyst to the adsorbed N₂. Thus, the possible nitrogen activation process over ZMCS-CN(20%) is as follows. First of all, N₂ molecules are 110 chemisorbed on the sulfur vacancies of ternary metal sulfide. When ZMCS-CN(20%) is excitated by the irradiation, the formed photogenerated-electrons are transferred from g-C₃N₄ to ternary metal sulfide, and then trapped by the sulfur vacancies. Those photogenerated-electrons are transferred immediately from the 115 catalyst to the adsorbed N₂. Because the bonding orbitals of N₂ molecule are occupied by four electrons, this photogenerated-

electron has to occupy the anti-bonding orbitals, leading to the

nitrogen activation (Figure 10d insert).

CdS, MoCdS and ZnCdS were prepared using the same method and metal molar ratio. Figure 11a compares the nitrogen photofixation performance of CdS, MoCdS and ZnCdS. The $_{5}$ NH₄⁺ generation rate are 0.19, 0.70 and 1.01 mg·L⁻¹·h⁻¹·g_{cat}⁻¹ for CdS, MoCdS and ZnCdS, obviously lower than as-prepared ternary metal sulfide ZnMoCdS. Considering the sulfur vacancies are regarded as the active centers for nitrogen photofixation, the NH_4^+ generation rate should be highly dependent on the amount 10 of sulfur vacancies. More metal components causes the more crystal lattice defects, leading to the formation of more sulfur vacancies. The actual atomic ratio obtained by ICP is $CdS_{0.98}$, Mo_{0.11}Cd_{0.89}S_{1.06} and Zn_{0.12}Cd_{0.92}S_{0.98} for CdS, MoCdS and ZnCdS, respectively. The difference of the theoretical and actual 15 number of sulfur atoms stands for the concentration of sulfur vacancies. It is noted that the NH_4^+ generation rates of CdS, MoCdS and ZnCdS are linearly related to the concentration of sulfur vacancies (Figure 11a insert), confirming the significantly important role of sulfur vacancies on nitrogen photofixation.



Figure 11. Nitrogen photofixation performance over as-prepared ³⁰ catalysts under visible light.

In addition, MoNiCdS and NiSnCdS were also prepared using the same method and metal molar ratio. ICP results show that the actual atomic ratio is $Mo_{0.11}Ni_{0.12}Cd_{0.87}S_{1.15}$ and ³⁵ Ni_{0.13}Sn_{0.10}Cd_{0.85}S_{1.13}, indicating sulfur vacancies are also formed in these ternary metal sulfides. The as-prepared ternary metal sulfide combined with g-C₃N₄ to form the heterojunction catalyst MoNiCdS-CN(20%) and NiSnCdS-CN(20%). Nitrogen photofixation performance shown in Figure 11b indicates that the

⁴⁰ NH₄⁺ generation rate are 2.5 and 1.84 mg·L⁻¹·h⁻¹·g_{cat}⁻¹ for MoNiCdS-CN(20%) and NiSnCdS-CN(20%), obviously higher than that of CN, MoNiCdS and NiSnCdS (0.26, 1.47 and 1.18 mg·L⁻¹·h⁻¹·g_{cat}⁻¹). This result indicates that not only ZnMoCdS but other ternary metal sulfide can combine with g-C₃N₄ to form

⁴⁵ the heterojunction catalyst to promote the separation rate of electrons-holes.

Conclusions

- A novel g-C₃N₄/ZnMoCdS heterojunction photocatalysts with outstanding nitrogen photofixation ability under visible light were ⁵⁰ prepared by hydrothermal post-treatment. Strong electronic coupling exists between two components in the g-C₃N₄/ZnMoCdS heterojunction photocatalysts, leading to more effective separation of photogenerated electron-hole pairs and faster interfacial charge transfer. The sulfur vacancies on ternary
- $_{55}$ metal sulfide not only serve as active sites to adsorb and activate N₂ molecules but also promote interfacial charge transfer from catalyst to N₂ molecules, thus significantly improving the

nitrogen photofixation ability. With the ZnMoCdS mass percentage of 80%, the as-prepared heterojunction photocatalyst ⁶⁰ exhibits the highest NH₄⁺ generation rate under visible light, which is 13.5-fold and 1.75-fold greater than those of individual g-C₃N₄ and ZnMoCdS. This outstanding nitrogen photofixation ability is attributed to the synergy effect of heterojunctions and sulfur vacancies. Not only ZnMoCdS but other ternary ⁶⁵ metal sulfide can combine with g-C₃N₄ to form the heterojunction catalyst to promote the separation rate of electrons-holes.

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75 Notes and references

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