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Article

Fabrication of hierarchical $\text{ZnIn}_2\text{S}_4@\text{CNO}$ nanosheets for photocatalytic hydrogen production and CO_2 photoreduction

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ABSTRACT

Photocatalytic H_2 production and CO_2 reduction have attracted considerable attention for clean energy development. In this work, we designed an efficient photocatalyst by integrating lamellar oxygen-doped carbon nitride (CNO) nanosheets into ZnIn_2S_4 (ZIS) microflowers by a one-step hydrothermal method. A well-fitted 2D hierarchical hybrid heterostructure was fabricated. Under visible light irradiation, the ZIS@CNO composite with 40 wt% CNO (ZC 40%) showed the highest hydrogen evolution rate from water ($188.4 \mu\text{mol}\cdot\text{h}^{-1}$), which was approximately 2.1 times higher than those of CNO and ZIS (88.6 and $90.2 \mu\text{mol}\cdot\text{h}^{-1}$, respectively). Furthermore, the selective CO production rates of ZC 40% ($12.69 \mu\text{mol}\cdot\text{h}^{-1}$) were 2.2 and 14.0 times higher than those of ZIS ($5.85 \mu\text{mol}\cdot\text{h}^{-1}$) and CNO ($0.91 \mu\text{mol}\cdot\text{h}^{-1}$), respectively, and the CH_4 production rate of ZC 40% was $1.18 \mu\text{mol}\cdot\text{h}^{-1}$. This enhanced photocatalytic activity of CNO@ZIS is due mainly to the formation of a heterostructure that can promote the transfer of photoinduced electrons and holes between CNO and ZIS, thereby efficiently avoiding recombination of electron-hole pairs.

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1. Introduction

Rapid economic development has resulted in increasing resource depletion, and serious environmental pollution have recently become common problems worldwide. Solar-based photocatalytic technology can convert solar energy directly into chemical energy, enabling the conversion of clean energy and the purification of environmental pollutants [1,2]. Conventional semiconductor photocatalysts such as titanium dioxide and zinc oxide have been widely used in degradation of organic pollutants [3], heavy metal ion reduction [4], photolysis of water to hydrogen [5], carbon dioxide photoreduction [6], and so on.

The very high recombination rate of photoexcited electron-hole pairs in single-component photocatalysts is the major obstacle to achieving high quantum efficiency and photocatalytic activity; it thus limits the practical application of photocatalysis technology. Single pristine bulk graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has attracted considerable attention because of its facilely tunable electronic structure, attractive electronic and optical properties, remarkable chemical and thermal stability, low cost, and environmental friendliness; however, it exhibits very low photocatalytic activity, with a quantum efficiency of approximately 0.1% under visible light irradiation as a result of its high photogenerated charge recombination rate and low solar light utilization rate [7–9]. Therefore, designing and de-

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veloping new and efficient catalysts with wide visible light responses has become an important goal for researchers.

Doping can tune the electronic structure and band gap of carbon nitride (CN) to broaden the light-responsive range, prolong the charge carrier lifetime, and enhance charge separation and transport [10,11]. Numerous experimental studies have shown that doping with non-metallic elements such as P, B, C, F, or S is an effective method of improving the photocatalytic performance of g-C₃N₄ [12–16]. Li et al. [17] used a simple H₂O₂ hydrothermal method to introduce oxygen atoms into g-C₃N₄ and successfully synthesized O-doped g-C₃N₄ with a hierarchical structure, which effectively enlarged the surface area and enhanced the visible-light response. Huang et al. [18] premixed melamine and H₂O₂ to produce O-doped g-C₃N₄ with a novel porous network through thermal polymerization; its photohydrolysis activity was 6.1 times higher than that of bulk g-C₃N₄.

Heterojunction formation is advantageous for improving the charge migration efficiency and improving the photocatalytic activity of a catalyst. As a ternary metal sulfide with good properties and photocatalytic activity, ZnIn₂S₄ has been widely used in several research fields [19]. ZnIn₂S₄ has the same band gap structure as g-C₃N₄, which makes it possible for a heterojunction to form between them, improving the charge separation and migration efficiency of g-C₃N₄ [20]. In recent work, Liu et al. [21] used a hydrothermal strategy to construct g-C₃N₄ nanosheet@ZnIn₂S₄ nanoparticles, which exhibited high photocatalytic hydrogen evolution efficiency. Liu et al. [22] also reported the synthesis of ZnIn₂S₄@g-C₃N₄ nanocomposites with improved photocatalytic activity using a hydrothermal method. However, although simple doping or heterojunction formation can significantly improve the photocatalytic performance of g-C₃N₄, there are few reports on combining these two methods.

In this study, an oxygen-doped carbon nitride (CNO) nanosheet catalyst was synthesized using a two-step thermal polymerization method, which enhanced the light absorption properties and reduced the band gap of g-C₃N₄. Next, a series of ZnIn₂S₄@CNO composites with different CNO contents was synthesized by a simple hydrothermal method. The structure and morphology of the ZnIn₂S₄/CNO composites were investigated by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) analysis, X-ray photoelectron spectroscopy (XPS), and so on. The photocatalytic H₂ production from water and photocatalytic CO₂ reduction performance were used to evaluate the properties of the composites. The results presented here are expected to be valuable for potential applications in energy conversion.

2. Experimental

2.1. Materials

All of the materials were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received without further purification.

2.2. Synthesis of oxygen-doped g-C₃N₄ (CNO) samples

In a typical experiment, 4 g of dicyandiamide, 4 g of urea, and 3.2 g of oxalic acid were dissolved in 20 mL of ultrapure water. After 30 min of stirring at room temperature, followed by oil bath evaporation, the solid was obtained for further use. The product was then ground to a powder, placed in a crucible with a cover, heated at 550 °C for 2 h at a ramp rate of 5 °C/min, and naturally cooled to room temperature. The collected product (CNO) was heated at 550 °C for another 2 h without a cover to obtain thinner nanosheets. CN was prepared under identical conditions without oxalic acid.

2.3. Preparation of ZnIn₂S₄@CNO (ZC) nanocomposites

A target amount of CNO was dissolved in 80 mL of ultrapure water and sonicated for 4 h, 1.5 mmol Zn(CH₃COO)₂·2H₂O and 3 mmol InCl₃ were added. After 30 min of stirring, 8 mmol thiocetamide was added, and stirring continued for 30 min. The mixed solution was transferred to a Teflon-lined stainless-steel autoclave and held at 120 °C for 10 h in an electric oven. After naturally cooling to room temperature, the products were collected, washed several times with ethanol and deionized water, and finally dried in an electric oven at 60 °C overnight. The as-synthesized ZnIn₂S₄@CNO samples with 20, 30, 40, and 50 wt% CNO are labeled ZC 20%, ZC 30%, ZC 40%, and ZC 50%, respectively. For comparison, ZnIn₂S₄ (ZIS) was prepared under identical conditions without the addition of CNO.

2.4. Characterization

The powder XRD patterns of the samples were measured using a Bruker D8 Advance diffractometer with Cu K α radiation (λ = 0.1541 nm). The morphology of the samples was observed by SEM (Nova Nano SEM 230) and TEM (JEOL JEM-2100). The specific surface area and pore size distribution of the products were measured using a JW-BK122W instrument and analyzed by the BET method. Ultraviolet-visible (UV-vis) diffuse reflectance spectroscopy (DRS) was performed using a UV-vis spectrophotometer (UV-2550, SHIMADZU). XPS was conducted using a Thermo ESCALAB 250Xi spectrometer with Mg K α radiation as the excitation source. Photoluminescence (PL) emission spectra were recorded on a QuantaMaster™ fluorescence spectrometer. Electrochemical experiments were performed on a CHI660D workstation.

2.5. Photocatalytic tests

The photocatalytic activity was evaluated by observing the photocatalytic hydrogen evolution from water and CO₂ photo-reduction reactions under visible light irradiation (λ > 400 nm).

2.5.1. Photocatalytic H₂ production

The photocatalyst powder (50 mg) was dispersed in 100 mL of an aqueous solution containing 10% (v/v) of triethanolamine (TEOA), and 100 μ L of an aqueous solution of chloroplatinic acid (H₂PtCl₆·6H₂O, 0.04 g/mL) was added to the above solu-

tion and stirred for 30 min. After evacuation, a 300 W xenon lamp source (400 nm cutoff filter) was used for illumination, and 3% (w/w) of Pt was photodeposited on the surface of the catalyst. The amount of H_2 produced was automatically sampled online by gas chromatography (thermal conductivity detector, with N_2 as the carrier gas) every 20 min.

2.5.2. Photocatalytic CO_2 reduction

The photocatalyst powder (50 mg), 20 mg of bpy, a solvent (6 mL, acetonitrile: H_2O = 2:1), TEOA (1 mL), and $CoCl_2$ (1 μ mol) were added to a gas-closed quartz glass reactor (200 mL in volume). The reaction system was filled with high-purity CO_2 gas (1 atm). A 300 W Xe lamp was used as the light source (400 nm cutoff filter). The reaction temperature was kept at 40 $^{\circ}C$ by water cooling. During photocatalysis, the reaction system was stirred vigorously. After the reaction, the generated gaseous products (CO and CH_4) were sampled and quantified by gas chromatography (flame ionization detector, with N_2 as the carrier gas).

3. Results and discussion

3.1. Morphological and structural characterizations

The XRD patterns of the as-synthesized CN, CNO, ZIS, and ZC composites are shown in Fig. 1. CN and CNO had the same characteristic structure, where the (100) peak at 12.9° indicates the typical in-plane repeating motifs of continuous heptazine frameworks [23,24]. The (002) peak of CNO (27.3° , d = 0.328 nm) showed a slight downshift compared with that of CN (27.6° , d = 0.321 nm). This finding suggests that O doping results in a larger graphite layer spacing, which favors the formation of shredded CNO nanosheets. At the same time, the significant decrease in intensity indicates that O doping reduces the long-range order of the stack structure between the catalyst layers, which is attributed to the introduction of structural defects [25]. The diffraction peaks of $ZnIn_2S_4$ are identical to those of the hexagonal phase (JCPDS No. 65-2023) [26]. The XRD pattern of ZC shows the diffraction peaks of both $ZnIn_2S_4$ and CNO, where the feature peaks of $ZnIn_2S_4$ (27.5°) and CNO (27.3°) are very close and overlap each other. With increasing CNO loading, the intensity of the diffraction peaks of CNO increased. The results show that ZIS and CNO coexist in the

Fig. 1. XRD patterns of CN, CNO, ZIS, and ZC samples.

composite materials.

SEM images are shown in Fig. 2. In Fig. 2(a), CN prepared by the thermal polymerization method shows a typical block distribution, which is formed by stacking of tight sheets. The particle packing density of CNO after O doping is significantly reduced, and the nanosheets constituting the catalyst are smaller, which is consistent with the XRD result that O doping increased the CN layer spacing. The pure ZIS exhibits a distinct agglomerated structure consisting of many smaller ZIS nanocrystals, as shown in Fig. 2(b). When CNO was loaded on the ZIS microspheres, several nanosheets markedly adhered to the surface of ZIS (Fig. 2(c)). Fig. 2(d) clearly shows that the CNO nanosheets (relatively thin and small) were well combined with ZIS nanosheets, which indicates that heterojunctions formed.

To further confirm the formation of junctions, TEM images of the microstructure of the samples are shown in Fig. 2(e) and (f). The CNO sample was randomly combined with "velvety" nanosheets, in which porous ZIS microspheres are well embedded. The tight junctions could serve as transport media to accelerate the transport of photogenerated charge carriers. A high-resolution TEM image of ZC 40% is presented in Fig. 2(f); the lattice spacing is 0.328 nm, which corresponds well to the (002) plane of CNO. The marked lattice spacings of 0.32 and 0.41 nm are in good agreement with the (102) and (006) planes of hexagonal ZIS, respectively [27], which are tightly attached to CNO to form the heterojunction. The ZC heterojunctions with close contact between ZIS and CNO nanosheets are indeed fabricated by the in-situ growth process and may facilitate photoinduced interfacial charge transfer between the nanosheets, enhancing the photocatalytic activity of the catalysts. Furthermore, as shown in Fig. 2(g), the elemental mapping images clearly reveal the uniform spatial distribution of many elements, including carbon, nitrogen, oxygen, sulfur, indium, and zinc, indicating that flat CNO nanosheets are uniformly distributed on the surfaces of ZIS, strongly supporting the SEM and TEM observations.

Increasing the surface area and porosity of the catalyst are particularly important for heterogeneous photocatalysis. The

Fig. 2. SEM images of CN and CNO (a), ZIS (b), ZC 40% (c, d); TEM images of CNO and ZC 40% (d, e), and elemental mapping images of ZC 40% (g).

Fig. 3. N₂ adsorption-desorption isotherms (a) and the corresponding Barrett-Joyner-Halenda pore size distribution (b) of various samples.

textural properties of the CN, CNO, and ZC 40% samples were analyzed using a nitrogen adsorption-desorption spectrometer. As illustrated in Fig. 3(a), all the photocatalysts exhibit typical IV N₂ adsorption-desorption isotherms with an H₃-type hysteresis loop, indicating the presence of mesopores [28]. The specific surface area and pore volume of CNO were 58 m²/g and 0.202 cm³/g, respectively, which were larger than those of CN (23 m²/g, 0.115 cm³/g). This result verifies the lower degree of polymerization of CNO with abundant porosity. The porous structure with an increased specific surface area provides more active sites for the catalytic reaction and more contact points for the formation of the ZC heterojunction. The specific surface area and pore volume of ZC 40% (50 m²/g, 0.128 cm³/g) are larger than those of pure ZIS (17 m²/g, 0.042 cm³/g), probably because of the combination of ZIS and CNO.

To further investigate the chemical states of typical ele-

ments in the ZC 40% composite samples, XPS profiles were obtained. The C 1s spectrum (Fig. 4(a)) for the ZC 40% composite can be deconvoluted into three peaks. The weak peak at 284.6 eV can be interpreted as C–C coordination of the surface adventitious carbon. The peak at 286.3 eV can be attributed to C–O bonds and indicates the doping of O atoms in the hybrid unit. The main peak centered at 288.4 eV is attributed to sp²-bonded carbon (N=C=N) in the composite [29]. The peaks at binding energies of 398.8, 399.6, and 401.3 eV in the N 1s region (Fig. 4(b)) correspond to sp²-hybridized nitrogen in C–N=C bonds, tertiary nitrogen N–(C)₃ groups, and C–N–H amino groups, respectively [30]. In the O 1s XPS profile (Fig. 4(c)), the peak at 532.8 eV corresponds to the adsorption of water or oxygen on the surface of the catalyst, and the peak at 531.5 eV suggests the generation of N–C–O/C–O bonds resulting from the incorporation of O [31]. Fig. 4(d) shows that the

Fig. 4. High-resolution XPS profiles of ZC 40%. (a) C 1s, (b) N 1s, (c) O 1s, (d) S 2p, (e) In 3d, (f) Zn 2p.

high-resolution S 2p spectrum of ZC 40% has two peaks at 161.2 eV (S 2p_{3/2}) and 162.4 eV (S 2p_{1/2}) for S²⁻ [32]. The In 3d XPS profile (Fig. 4(e)) has two peaks at 444.9 eV (In 3d_{5/2}) and 452.4 eV (In 3d_{3/2}), suggesting the presence of In³⁺ [33]. The Zn 2p XPS profile of (Fig. 4(f)) can be divided into two independent peaks centered at 1021.8 and 1044.8 eV and associated with Zn²⁺ (2p_{3/2} and 2p_{1/2}, respectively) [34]. These results, along with the SEM, TEM, and BET results, suggest that ZIS was hybridized with CNO by the successful formation of heterojunctions, which provide suitable channels for photoinduced charge transfer between them.

3.2. Photocatalytic activity and stability

3.2.1. Photocatalytic H₂ evolution

The photocatalytic H₂ production activity of the prepared samples was evaluated in a conventional closed-circulation system under visible light ($\lambda > 400$ nm) irradiation using TEOA and 3 wt% of chloroplatinic acid as the sacrificial reagent and co-catalysts, respectively. As shown in Fig. 5(a), the H₂ evolution rate of CNO (88.6 $\mu\text{mol/h}$) is approximately 3.9 times that of CN (22.6 $\mu\text{mol/h}$). The photocatalytic H₂ generation activity of ZIS is close to that of CNO, and 90.2 μmol H₂ was detected after 1 h of irradiation. After hybridization of CNO and ZIS, the photocatalytic activity for H₂ generation on the composite material improved significantly. This finding implies that in-situ growth of ZIS nanosheets on CNO nanosheets could noticeably enhance the photocatalysis activity for H₂ production. The rate of H₂ evolution over the ZC composites increases with increasing CNO content, reaching a maximum of 188.4 $\mu\text{mol/h}$ for the ZC 40% sample (where the CNO content is 40 wt%), which is approximately 2.1 times higher than those of ZIS and CNO. The quantum efficiency of H₂ evolution by CNO, ZIS, and ZC 40% measured at 420 nm was 0.96%, 0.98%, and 2.04%, respectively. Compared to that in various reports on the use of NiS or MoS_x as co-catalysts, the photocatalytic activity enhancement in our work is significant (Table S1) [35–37]. A further increase in the CNO content results in a decrease in photocatalytic activity, which is probably attributable to the fact that the active sites on the surface of ZIS were covered by an excessive amount of CNO [38]. Therefore, an appropriate amount of CNO loading is criti-

cal to enhancing the photocatalytic activity of the ZIS photocatalyst.

In addition, H₂ production catalyzed by ZC 40% was performed for five cycles to evaluate the stability and reusability (Fig. 5(b)). After repeated use of the catalyst for several cycles, the H₂ yield remained stable, indicating that the catalyst has good hydrogen production stability and strongly confirming the stability of the ZC 40% heterojunction nanosheets for use as a photocatalyst. The slight decrease in the rate of H₂ production at the beginning of the reaction may be due to hydration of the catalytic surface and a decrease in the number of active sites. When the liquid–solid interface reached an equilibrium state, very stable activity was maintained.

3.2.2. Photocatalytic CO₂ reduction

Photocatalytic CO₂ reduction to CO and CH₄ under visible light ($\lambda > 400$ nm) irradiation was observed. Fig. 6(a) shows the photocatalytic CO and CH₄ evolution rates of CN, CNO, ZIS, and ZC 40%. The pure CN or CNO nanosheets clearly exhibit poor photoreduction activity. However, the ZC composite photocatalyst exhibits greatly improved CO and CH₄ generation. It is clear that ZC 40% shows the strongest reducing activity, which is consistent with its photocatalytic H₂ evolution performance. The CO production rate of ZC 40% (12.69 $\mu\text{mol/h}$) is 2.2 and 14.0 times those of ZIS (5.85 $\mu\text{mol/h}$) and CNO (0.91 $\mu\text{mol/h}$), respectively. Additionally, the measured CH₄ production rates of CNO and ZIS are only approximately 0.64 and 0.82 $\mu\text{mol/h}$, respectively, whereas the CH₄ production rate of ZC 40% (1.18 $\mu\text{mol/h}$) is much higher. The amount of CH₄ and CO production under light irradiation increased with time, although the rate gradually decreased. In summary, the enhanced photoreduction activity of the ZC composite materials for H₂ generation from H₂O and selective CO generation from CO₂ is thought to result mainly from the formation of well-designed charge transfer nanochannels, which contribute to the high photoinduced charge separation and migration efficiency [39].

3.3. Photoelectrochemical response

The optical absorption properties of the CN, CNO, ZIS, and ZC 40% composites were examined by UV-vis DRS, as shown in

Fig. 5. Photocatalytic H₂ production of catalysts. (a) Cumulative amount of H₂ versus light irradiation time; (b) H₂ production stability of ZC 40%.

Fig. 6. Photocatalytic CO₂ reduction of catalysts. (a) CO and CH₄ production rates of CN, CNO, ZIS, and ZC 40%; (b) gas production stability of ZC 40%.

Fig. 7(a). The light absorption band of CN is near 450 nm. For CNO, the light absorption band is distinctly red-shifted to nearly 480 nm, and the absorbance of light is also significantly improved after O doping. ZIS has an absorption edge with a longer wavelength than those of the other catalysts. An increase in CNO content caused a slight blue shift of the absorption edge of the ZC composites. In particular, although the light utilization of the composite catalyst may be slightly lower than that of ZIS, ZC 40% exhibited a high absorption capacity in visible light, which may result in generation of sufficient photoinduced electron-hole pairs. The band gaps of the CN, CNO, ZIS, and ZC 40% composites can be estimated using the Kubelka-Munk function [40], and the results are shown in Fig. 7(b). The band gap of CN is 2.92 eV, and that of CNO is distinctly shifted to a lower position (2.82 eV), promoting the transition of photogenerated carriers under wide visible light illumination. The band gap difference between the ZIS and ZC samples is comparatively small, suggesting that the optical properties of ZIS are not markedly changed by hybridization with CNO. The lower band gaps of the ZC composites compared to that of CNO plays a crucial role in charge generation and thus directly affects their photocatalytic performance [41].

The separation efficiency of photogenerated charges is an important factor affecting photocatalysis performance. The PL emission spectrum can provide useful information about charge carrier trapping and recombination. Fig. 8(a) shows the steady-state PL spectra of the CN, CNO, ZIS, and ZC 40% sam-

ples at an excitation wavelength of 320 nm. It can be seen that pure CN has a strong PL emission peak at 440–470 nm, which results from band-edge fluorescence caused by light excitation. Clearly, the PL emission peak of CNO appears at the same position but at a much lower intensity, indicating that O doping greatly inhibits the recombination of photogenerated electron-hole pairs. For the composite samples, the PL intensity of ZC 40% is weak, predicting much more efficient separation of photocarriers in the ZnIn₂S₄-CNO samples [42]. Similar results were observed by other groups in ZnS/g-C₃N₄ [43], ZnFe₂O₄/g-C₃N₄ [44], and Mo₂C@C/2D g-C₃N₄ [45] heterojunction systems.

In addition, time-resolved transient PL spectroscopy was performed at room temperature to obtain further information on the photoinduced interfacial charge transfer process (Fig. 8(b)). Pure ZIS exhibited very little fluorescence emission, so its decay lifetime can be ignored. By fitting the decay spectra using double-exponential kinetics, the intensity-averaged lifetimes (τ) of CNO and ZC 40% are 1.81 and 1.88 ns, respectively. The slightly longer lifetime of ZC 40% indicates that the radiative lifetime for charge carriers was effectively extended by combining CNO and ZnIn₂S₄, which could be beneficial for photocatalytic reactions.

The generation efficiency of photoinduced electrons for photocatalytic reduction was evaluated by photocurrent measurements. At the same time, electrochemical impedance spectroscopy (EIS) was also used to visually represent the charge

Fig. 7. UV-vis diffuse reflectance absorbance spectra (a) and band gaps of the as-synthesized samples (b).

Fig. 8. Steady-state PL emission spectra of CN, CNO, ZIS, and ZC 40% (a) and time-resolved PL decay spectra of CNO, ZIS, and ZC 40% (b).

Table 1

Structural parameters and photocatalytic activities of samples.

Sample	E_g (eV)	BET surface area (m^2/g)	PL life-time (ns)	H_2 evolution rate ($\mu mol/h$)	CH_4 evolution rate ($\mu mol/h$)	CO evolution rate ($\mu mol/h$)
CN	2.92	23	—	22.6	0.61	0.75
CNO	2.82	58	1.81	88.6	0.64	0.91
ZIS	2.20	17	—	90.2	0.82	5.85
ZC 40%	2.19	50	1.88	188.4	0.98	12.67

transport properties of the semiconductors. Fig. 9(a) shows the photocurrent transient response for CN, CNO, ZIS, and ZC 40% electrodes under visible light irradiation. As the light was switched on and off repeatedly, all the samples responded quickly to the photocurrent, demonstrating their excellent photoelectric conversion properties. The photocurrent response of CNO was much higher than that of CN, indicating that O doping facilitates the generation of photogenerated charges. Compared to CNO and ZIS, the ZC 40% sample exhibits the highest photocurrent transient response under visible light irradiation, implying improved intensity of photoinduced electrons. The enhanced photocurrent of ZC 40% could be attributed to the efficient heterojunction interaction between ZIS and CNO [46]. As shown in Fig. 9(b), the diameter of the semicircular portion of the Nyquist plot of CNO is significantly smaller than that of pure CN, indicating that O doping reduces the transmission resistance. Furthermore, for the ZC 40% sample, the semicircular portion has a smaller diameter than those of the CNO and ZIS samples, suggesting that the hybrid composite has a lower charge transfer resistance than either semiconductor alone.

The PL and photoelectrochemical results confirm that the ZC 40% composite photocatalyst exhibits superior charge production, transfer, and recombination inhibition. These features are responsible for the enhanced photocatalytic activity and are consistent with the fact that the ZC 40% composite exhibits the highest photocatalytic performance owing to its efficient separation of electron-hole pairs in the heterostructure formed between CNO and ZIS.

The Mott-Schottky analysis was employed to determine the flat potential close to the conduction band (CB) of the prepared samples [47]. The results are shown in Fig. 10(a); the plot slopes are positive for all the samples, indicating that they exhibit n-type behavior. The CBs of the CNO and ZIS are determined to be at -1.32 and -1.10 eV, respectively. By combining this information with the band gap values obtained from the UV-vis plot, the valence band (VB) positions of the samples were determined. As illustrated in Fig. 10(b), type-I binary heterojunction interfaces are formed owing to the suitable CB and VB positions of the CNO and ZIS nanosheets, providing the conditions for generation of a heterojunction with high-speed charge transfer nanochannels. Under visible light illumination,

Fig. 9. EIS (a) and photocurrent spectra (b) of CN, CNO, ZIS, and ZC 40%.

Fig. 10. Mott-Schottky plots of CNO and ZIS (a) and schematic diagram showing the photoinduced charge transfer at the interface between ZIS and CNO nanosheets (b).

both the CNO and ZIS nanosheets could be excited to produce many photogenerated electron-hole pairs [48].

The photoinduced electrons and holes on CNO would move thermodynamically to the CB and VB of the ZIS nanosheets, respectively, via the heterojunction interfaces. As a result of the photosynergistic effect of the ZC heterojunction, the recombination of photoinduced charge carriers in CNO can be effectively inhibited, and because of the photoinduced interfacial charge transfer, the number of photoinduced charge carriers on ZIS increases remarkably. Consequently, more reductive electrons would accumulate in the CB of ZIS, resulting in enhanced photocatalytic reduction activity for generation of H₂ and CO. The photogenerated holes on the VBs of the CNO and ZIS nanosheets are quickly quenched by the sacrificial electron donor (TEOA). The charge migration distance and transfer time are greatly decreased by these charge transfer nanochannels afforded by the heterojunction, significantly increasing the charge transport and separation efficiency, and ultimately leading to remarkable photocatalytic activity.

4. Conclusions

In conclusion, ZIS/CNO (ZC) heterojunction nanosheets were successfully synthesized by in-situ growth of CNO on ZnIn₂S₄ nanosheets. The resulting heterojunctions provide abundant charge transfer channels in the ZC composites, which contribute to the relatively high efficiency of photoinduced charge generation, separation, and migration, ultimately leading to remarkably enhanced visible-light-driven activity for photocatalytic reduction. The best-performing as-synthesized composite, ZC 40% (with a CNO content of 40%), exhibited enhanced visible-light-driven photocatalytic H₂ generation (188.4 μmol/h), which is 2.1 times those of ZIS and CNO. The measured quantum efficiencies of H₂ evolution for CNO, ZIS, and ZC 40% are 0.96%, 0.98%, and 2.04%, respectively. ZC 40% also exhibited excellent efficient and selective visible-light photocatalytic activity for CO₂ reduction to CO at a rate of 12.69 μmol/h, which is 2.2 and 14.0 times higher than those of ZIS and CNO, respectively. Therefore, this study offers a new insight for designing and preparing high-efficiency visible-light-responsive composite semiconductors with highly

efficient photocatalytic reduction activity.

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Graphical Abstract

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Fabrication of hierarchical $\text{ZnIn}_2\text{S}_4@\text{CNO}$ nanosheets for photocatalytic hydrogen production and CO_2 photoreduction

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Hydrothermally synthesized 2D hierarchical $\text{ZnIn}_2\text{S}_4@\text{CNO}$ nanosheet composite is highly efficient and exhibits stable photocatalytic H_2 generation and CO_2 reduction.

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$\text{ZnIn}_2\text{S}_4 @ \text{CNO}$ 多级纳米片用于光催化分解水制氢和还原 CO_2

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摘要: 光催化分解水制氢和还原 CO_2 是太阳能利用领域的研究热点, 对清洁能源的转化具有重要意义. 石墨相氮化碳(CN)作为一种非金属半导体, 是一种非常有开发潜力的光催化材料. 然而限于其聚合物本质, 光催化效率仍有待进一步提高. 原位非金属掺杂可以利用元素电子结构调控电荷分布, 优化光生电荷传输性能. 同时, 半导体复合, 尤其是2D层状复合结

构的构筑,可充分发挥2D半导体的优势,合适的能带交错有利于光生电荷的传输,可在一定程度上加速催化反应的进行。

本文首先以草酸为氧掺杂源,采用二步煅烧法合成氧掺杂氮化碳纳米片催化剂(CNO)。在二次煅烧和氧掺杂共同作用下,增大了CN层间距和多孔性,颗粒尺寸减小,同时增强了对光的吸光性,拓展了可见光吸收范围。接下来采用一步水热合成法得到 ZnIn_2S_4 @CNO(ZC)复合材料,在可见光照射下通过分解水制氢和 CO_2 还原反应对复合材料进行光催化还原性能评价。采用X射线衍射(XRD)、透射电镜(TEM)、X射线光电子能谱(XPS)、荧光光谱(PL)、光电化学测试等方法对ZC进行详细的结构表征和分析。XRD和XPS结果表明,经过一步直接水热可得到层状ZC复合材料,高倍TEM进一步证实二者形成均一的2D异质复合材料。 N_2 -吸附-脱附曲线表明,复合材料具有较大的比表面积和均一的孔结构分布,主要得益于O掺杂CNO纳米片的多孔性结构。光电性质测试结果表明,相比于CNO,复合材料具有降低的荧光发射强度和延长的荧光寿命,表明复合产物显著抑制了光生电荷的复合。电化学测试进一步表明,复合异质结的构筑有利于光生载流子的产生,同时降低了界面电荷转移电阻,提高了电荷迁移速率。因此,多孔2D异质结构的构筑对促进CN基半导体光催化还原具有重要作用。

在可见光照射下($\lambda > 400 \text{ nm}$),复合材料表现出优异的光催化还原性能,且随着CNO含量的增加催化活性不断提高,其中ZC 40%(CNO质量比40%)具有最佳的催化活性,其产氢速率达 $188.4 \mu\text{mol/h}$,约是 ZnIn_2S_4 和CNO的2.1倍。同时,光催化还原 CO_2 测试表明,复合材料具有显著提高的CO和 CH_4 产率,其中CO为主要反应产物。ZC 40%的CO产生速率为 $12.69 \mu\text{mol/h}$,分别是 ZnIn_2S_4 和CNO的2.2倍和14.0倍。对催化剂进行连续光反应,结果表明,复合催化剂具有优异的结构稳定性和活性稳定性,能够持续发生光还原反应制取 H_2 和CO。

关键词: ZnIn_2S_4 ; 氧掺杂氮化碳; 光催化; 产氢; CO_2 还原

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