Boosted charge transfer and photocatalytic CO₂ reduction over sulfur-doped C₃N₄ porous nanosheets with embedded SnS₂-SnO₂ nanojunctions

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ABSTRACT Two-dimensional porous nanosheet heterostructure materials, which combine the advantages of both architecture and components, are expected to feature a significant photocatalytic performance toward CO₂ conversion into useful fuels. Herein, we provide a facile strategy for fabricating sulfur-doped C₃N₄ porous nanosheets with embedded SnO₂-SnS₂ nanojunctions (S-C₃N₄/SnO₂-SnS₂) via liquid impregnation-pyrolysis and subsequent sulfidation treatment using a layered supramolecular structure as the precursor of C₃N₄. A hexagonal layered supramolecular structure was first prepared as the precursor of C₃N₄. Then Sn⁴⁺ ions were intercalated into the supramolecular interlayers through the liquid impregnation method. The subsequent annealing treatment in air simultaneously realized the fabrication and efficient exfoliation of layered C₃N₄ porous nanosheets. Moreover, SnO₂ nanoparticles were formed and embedded *in situ* in the porous C₃N₄ nanosheets. In the following sulfidation process under a nitrogen atmosphere, sulfur powder can react with SnO₂ nanoparticles to form SnO₂-SnS₂ nanojunctions. As expected, the exfoliation of sulfur-doped C₃N₄ porous nanosheets and ternary heterostructure construction could be simultaneously achieved in this work. Sulfur-doped C₃N₄ porous nanosheets with embedded SnO₂-SnS₂ nanojunctions featured abundant active sites, enhanced visible light absorption, and efficient interfacial charge transfer. As expected, the optimized S-C₃N₄/SnO₂-SnS₂ achieved a much higher gas-phase photocatalytic CO₂ reduction performance with high yields of CO (21.68 μmol g⁻¹ h⁻¹) and CH₄ (22.09 μmol g⁻¹ h⁻¹) compared with the control C₃N₄, C₃N₄/SnO₂, and S-C₃N₄/SnS₂ photocatalysts. The selectivity of CH₄ reached 80.30%. Such a promising synthetic strategy can be expected to inspire the design of other robust C₃N₄-based porous nanosheet heterostructures for a broad range of applications.

Keywords: sulfur-doped C₃N₄, porous nanosheets, SnO₂-SnS₂ nanojunctions, tunable composition, CO₂ photoreduction

INTRODUCTION

Today, serious environmental pollution accompanied by the sustained energy crisis has triggered considerable concern about the conversion of solar energy to fuels due to its inexhaustibility and relatively mild reaction conditions (normal pressure and

low temperature) [1–3]. Carbon dioxide (CO₂), as the main greenhouse gas, is expected to be converted into chemical fuels to address the energy crisis and climate deterioration via photocatalysis under sunlight irradiation [4]. Currently, semiconductor photocatalysts have received great attention due to their abundant resources, low cost, and stability in photocatalytic CO₂ reduction [5–7]. Except for the most widely studied TiO₂, other W-, Ce-, Ga-, and Zn-based semiconductor photocatalysts have been widely investigated [8–12]. However, most of the reported semiconductor-based photocatalyst materials suffer from various pertinent problems, such as mismatched band structures, inefficient spatial charge separation, and poor light-harvesting properties [13,14]. Therefore, fabricating suitable photocatalysts with an excellent photocatalytic CO₂ reduction performance is still challenging.

Recently, carbon nitride (C₃N₄) has been considered as a promising photocatalyst due to its high stability and nontoxicity [15–17]. However, C₃N₄ is generally prepared through calcination of nitrogen-containing materials. Therefore, the obtained bulk C₃N₄ suffers from an inefficiently low surface area, which will reduce the surface active sites [18–20]. Photocatalytic reactions occur at the active sites of catalysts; therefore, the active site is an important factor that influences the photocatalytic activity. Thus, increasing the surface active sites of C₃N₄ contributes to the enhancement of the photocatalytic performance, and the C₃N₄-based photocatalysts with rich active surface sites are expected. Apart from limited surface active sites, bulk C₃N₄ suffers from an inefficient charge separation, a low surface area, and poor visible light absorption [21,22]. These drawbacks lead to a relatively low photocatalytic activity. To overcome these problems, some effective routes, such as doping with metal or nonmetal atoms, controlling morphology, introducing defects, and fabricating g-C₃N₄-based heterostructures, have been explored to enhance its photocatalytic performance [23–27]. Among these strategies, sulfur doping can decrease the bandgap and generate surface defects. Therefore, this approach can enhance the visible light absorption of C₃N₄ and trap photoexcited carriers [28–30].

Constructing heterostructures by coupling C₃N₄ with other semiconductors with an appropriate bandgap is also a pivotal approach for improving the performance of photocatalysts [31–33]. The constructed heterostructure can effectively promote the migration and separation of charge carriers through a charge transfer. In recent years, many g-C₃N₄-based semi-

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conductor (e.g., TiO_2 , CdS and $\alpha\text{-Fe}_2\text{O}_3$) composites have been reported to enhance the photocatalytic activity [34–38]. Related experimental studies have demonstrated that $\text{g-C}_3\text{N}_4/\text{Sn}$ -based composites exhibit improved photocatalytic performances because of their excellent physicochemical properties and well-matched band positions [39]. However, the prepared $\text{g-C}_3\text{N}_4/\text{Sn}$ -based composites generally exist in an aggregation state and are large in size with deficient interfaces and active sites [40]. Therefore, it is still difficult to achieve a uniform incorporation and strong interfacial coupling between $\text{g-C}_3\text{N}_4$ and Sn-based nanoparticles. Moreover, small $\text{g-C}_3\text{N}_4$ nanosheets are apt to assemble into bulk aggregates, leading to decreased surface area and active sites. So, can we explore facile and effective strategies to fabricate ideal $\text{g-C}_3\text{N}_4/\text{Sn}$ -based hybrids with abundant exposed active sites and strong interactions between $\text{g-C}_3\text{N}_4$ and highly dispersed Sn-based nanomaterials? It remains highly desirable to achieve this goal.

In previous reports, both SnO_2 and SnS_2 exhibited relatively low CO_2 reduction efficiencies. Strikingly, constructing $\text{SnO}_2\text{-SnS}_2$ heterostructures has shown promise in terms of overcoming the drawbacks of single SnO_2 and SnS_2 [41]. However, most $\text{SnO}_2\text{-SnS}_2$ heterojunctions generally exist in an aggregation state and are large in size with deficient active sites [42]. To overcome these disadvantages, choosing appropriate materials with a high surface area and abundant sites as substrates to uniformly load $\text{SnO}_2\text{-SnS}_2$ nanojunctions is expected to be an effective approach for realizing efficient interfaces and high dispersity.

In our recent study, a layered rod-like supramolecular C_3N_4 precursor was prepared to acquire a large-size porous C_3N_4 nanosheet structure [43,44]. In the supramolecular precursor, interlamellar spacing exists in interlayers. It is therefore considered that if metal ions are intercalated into supramolecular interlayers and adsorbed on the surface of the interlayers, the following thermolysis process would make the metal ions convert into the corresponding metal oxide nanoparticles and anchor *in situ* onto the produced $\text{g-C}_3\text{N}_4$ porous nanosheets.

Based on the above demonstration, herein, we report a facile and effective synthetic route that fabricates sulfur-doped C_3N_4 porous nanosheets with embedded $\text{SnO}_2\text{-SnS}_2$ nanojunctions ($\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$) using a previously prepared hexagonal layered structure supramolecular as the precursor of $\text{g-C}_3\text{N}_4$. As expected, Sn^{4+} ions are successfully intercalated into the supramolecular interlayers through the liquid impregnation method. The subsequent pyrolysis process embeds the formed SnO_2 nanoparticles *in situ* between the well-exfoliated C_3N_4 porous nanosheets. The following sulfidation reaction leads to the formation of $\text{SnO}_2\text{-SnS}_2$ nanojunctions and sulfur-doped C_3N_4 porous nanosheets with controllable sulfidation degrees. The resultant sulfur-doped $\text{C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ composites possess abundant exposed active sites for catalysis, sufficient void space, and heterointerfaces. These advantages contribute to the transfer and separation of photogenerated charge carriers, CO_2 adsorption, and visible light harvesting. Impressively, the optimized sulfur-doped $\text{C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ ($\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$) exhibits an outstanding gas-phase photocatalytic conversion of CO_2 to CO and CH_4 with yield rates of 21.68 and $22.09\ \mu\text{mol g}^{-1}\text{h}^{-1}$, respectively, without an organic photosensitizer or noble metal, and are significantly superior to those of the control samples (C_3N_4 , $\text{S-C}_3\text{N}_4$, $\text{S-C}_3\text{N}_4/\text{SnO}_2$, and $\text{S-C}_3\text{N}_4/\text{SnS}_2$). The applicability of the synthetic strategy to $\text{g-C}_3\text{N}_4$ -based porous

nanosheet composites can also be expected.

EXPERIMENTAL SECTION

Synthesis of the layered supramolecular precursor

All reagents were of analytical grade and used without further purification. Phosphorous acid (0.6 g) and melamine (0.5 g) were added to 50 mL of deionized water. After stirring for 30 min, the mixture was added into an autoclave with a Teflon liner. The autoclave was then heated to 180°C and maintained for 10 h. The resulting product was washed with deionized water and dried for 10 h at 50°C .

Synthesis of C_3N_4 porous nanosheets with embedded SnO_2 nanoparticles

An appropriate amount of (0.1, 0.2, and 0.3 g) $\text{SnCl}_4\cdot\text{H}_2\text{O}$ and 0.8 g of the prepared precursor above were added to 10 mL of ethanol under stirring for half an hour. Then the mixture was allowed to stand for 12 h. The precipitate was filtered. After drying at 50°C , the powder was put into an alumina crucible and heated to 480°C for 4 h (2°C min^{-1}). The products obtained from 0.1, 0.2, and 0.3 g of $\text{SnCl}_4\cdot\text{H}_2\text{O}$ were labeled as $\text{C}_3\text{N}_4/\text{SnO}_2\text{-0.5}$, $\text{C}_3\text{N}_4/\text{SnO}_2$, and $\text{C}_3\text{N}_4/\text{SnO}_2\text{-1.5}$, respectively.

The synthetic method of pure C_3N_4 was similar to that of $\text{C}_3\text{N}_4/\text{SnO}_2$, but no $\text{SnCl}_4\cdot\text{H}_2\text{O}$ was introduced.

Synthesis of sulfur-doped C_3N_4 porous nanosheets with embedded $\text{SnO}_2\text{-SnS}_2$ nanojunctions ($\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$)

Appropriate amounts of sublimed sulfur powders (0.3, 0.6, 0.8, and 1 g) and 0.1 g of $\text{C}_3\text{N}_4/\text{SnO}_2$ were put into alumina ceramic boats, respectively. Then the two boats were put into a ceramic tube next to one another, with the boat containing sulfur powders placed upstream of the ceramic tube. The tube furnace was then heated to 400°C (5°C min^{-1}) and maintained for 30 min under N_2 conditions. The products obtained from 0.3, 0.6, 0.8, and 1 g of sulfur powder were labeled as $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2\text{-0.3}$, $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2\text{-0.6}$, $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2\text{-0.8}$, and $\text{S-C}_3\text{N}_4/\text{SnS}_2$, respectively. Typically, the optimized sample used for characterizations and photocatalytic reactions was the $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2\text{-0.6}$ sample ($\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ for clarity) unless otherwise stated.

Characterization

X-ray diffraction (XRD) patterns were obtained from an X-ray powder diffractometer (SmartLab 9 kW, Rigaku) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15405\text{ nm}$, 40 kV, and 100 mA). The morphology and microstructure were characterized *via* scanning electron microscopy (SEM, Sigma 500). The morphologies of the samples were obtained using a JEM-F200 transmission electron microscope (TEM). The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Kratos-AXIS UL TRA DLD. Fourier transform infrared spectra (FT-IR) were obtained from a Spectrum One spectrometer (Perkin-Elmer). The photoluminescence (PL) spectra were taken from an Edinburgh FL920 spectrofluorometer. Nitrogen adsorption and desorption isotherms were measured on a Micrometrics ASAP 2420 analyzer. Ultraviolet-visible (UV-vis) absorption spectra were obtained from a Lambda 950 UV-vis spectrophotometer (Perkin Elmer). Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on an Optima 7000 analyzer (Perkin

Elmer). *In situ* diffuse reflectance FT-IR (DRIFTS) were obtained from an infrared spectrometer (Nicolet IS-50) with an *in situ* Harrick IR cell.

Photoelectrochemical test

Photoelectrochemical tests were recorded using a BAS100B electrochemical analyzer (USA). A standard three-compartment (counter electrode: Pt slice; reference electrode: saturated Ag/AgCl) cell was applied. The working electrodes were prepared using a previous method [45]. The electrolyte was a Na_2SO_4 (0.1 mol L^{-1}) solution. The transient photocurrent curves were obtained under a static potential of -1.00 V . The light source was a 300 W xenon lamp (with an AM1.5 filter). Electrochemical impedance spectrum (EIS) tests were conducted over a frequency range from 0.1 to 10^5 Hz .

Photocatalytic tests for CO_2 reduction

The CO_2 photoreduction experiments were conducted in a gas-solid reactor (80 mL, PLS-SXE300, Perfectlight, China). A 300 W Xe lamp with an AM1.5 filter was used as the visible light source. The light intensity was then controlled to 100 mW cm^{-2} using an NREL-calibrated Si solar cell. Before the tests, the photocatalyst powder (10 mg) was placed on a glass sheet ($1 \text{ cm} \times 1 \text{ cm}$) support in the reactor. High-purity CO_2 was then bubbled into the reactor to reach ambient pressure through deionized water. After equilibration for 30 min, the reactor was sealed and exposed to visible light. A circulation water system was applied to maintain the reaction temperature at approximately 293 K. After every 1 h of reaction, 1 mL of the reactant gas was taken and quantified with a GC7900 gas chromatograph. $^{13}\text{CO}_2$ gas was then applied to determine the carbon source by using an Agilent 6890N/5973N gas chromatography-mass spectrometry (GC-MS) analyzer.

RESULTS AND DISCUSSION

Characterization of the catalysts

The crystalline structures of the samples were confirmed *via* XRD analysis. As shown in Fig. 1a, the diffraction peaks located at 26.6° , 33.9° and 51.8° correspond to the (110), (101), and (211) planes of rutile SnO_2 (JCPDS 41-1445), respectively, indicating the formation of SnO_2 [46]. In the XRD patterns of $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ and $\text{S-C}_3\text{N}_4/\text{SnS}_2$, the diffraction peaks at 15.0° , 28.2° , 32.1° , 41.9° , 50.0° and 52.5° belong to hexagonal SnS_2 (JCPDS 23-0677), while the diffraction peaks belonging to SnO_2 tend to be weaker and disappear with the amount increase of

sulfur powder (Fig. S1), indicating the successful transformation of SnO_2 to SnS_2 [47,48]. The wide diffraction peak (27.4°) corresponding to the (002) reflection of C_3N_4 can be observed in the XRD patterns of all the composites, and no XRD diffraction peaks that are ascribed to the supramolecular precursor exist (Fig. S2), demonstrating the successful conversion of the supramolecular precursor into C_3N_4 [49]. FT-IR spectroscopy measurements were also conducted to reveal the chemical structure and intense coupling between different components in the composites. For the $\text{C}_3\text{N}_4/\text{SnO}_2$, $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$, and $\text{S-C}_3\text{N}_4/\text{SnS}_2$ composites, the band at approximately $500\text{--}700 \text{ cm}^{-1}$ originates from the Sn-O(S) stretching vibration mode [50]. The characteristic bands (e.g., 810, 1247, 1329, 1423, 1569, and 1636 cm^{-1}) of C_3N_4 could be observed [51,52]. The broadband from 3000 to 3300 cm^{-1} is assigned to the stretching vibration modes of the adsorbed H_2O molecules and terminal NH groups of the aromatic ring [53]. The results demonstrate that the structural characteristics of C_3N_4 are not changed after sulfur doping and loading of SnO_2 and SnS_2 .

The microstructures of the samples were characterized *via* SEM and TEM. After calcining the hexagonal layered structure supramolecular precursor microrods (Fig. S3), pure C_3N_4 was prepared and exhibited a nanosheet structure with numerous wrinkles and some nanopores (Fig. 2a). The SEM image (Fig. 2b) of $\text{C}_3\text{N}_4/\text{SnO}_2$ shows a nanosheet morphology similar to pure C_3N_4 . The enlarged SEM image (Fig. 2c) and TEM images (Fig. 2d, e) show that many nanoparticles are uniformly anchored on the C_3N_4 porous nanosheets. This result indicates that C_3N_4 porous nanosheets could closely attach the SnO_2 nanoparticles and effectively inhibit their agglomeration and growth, benefiting the exposure of active sites. The scanning TEM (STEM) image (Fig. S4) and energy dispersive X-ray spectroscopy (EDX) elemental mappings further confirm the homogeneous distribution of the C, N, Sn, and O elements. In the high-resolution TEM (HRTEM) image (Fig. 2f), the lattice distance of 0.325 nm corresponds to the (110) plane of SnO_2 . The clear lattice fringes suggest the well-defined crystal structure of SnO_2 [54]. The particle size is approximately $3\text{--}5 \text{ nm}$. The results show that few layers of the C_3N_4 nanosheets can act as an effective buffer matrix for inhibiting the growth and agglomeration of SnO_2 nanoparticles while maintaining structural integrity.

The SEM and TEM images (Fig. 3a–f) reveal that $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ also possesses the wrinkled porous nanosheet structure of $\text{C}_3\text{N}_4/\text{SnO}_2$, which indicates the structural stability of the hybrid during the sulfidation process. In the HRTEM image

Figure 1 (a) XRD patterns and (b) FTIR spectra of C_3N_4 , $\text{C}_3\text{N}_4/\text{SnO}_2$, $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$, and $\text{S-C}_3\text{N}_4/\text{SnS}_2$.

Figure 2 (a) SEM and (d) TEM images of C_3N_4 . (b, c) SEM, (e) TEM and (f) HRTEM images of $S-C_3N_4/SnO_2$.

(Fig. 3f), two different structural domains can be observed. The lattice fringes of 0.325 and 0.316 nm match well with the (110) plane of SnO_2 and the (100) plane of SnS_2 , respectively, which signifies the formation of SnO_2-SnS_2 nanojunctions [55,56]. The STEM image (Fig. 3g) and EDX elemental mappings indicate homogeneous distribution of O, S, C, N, and Sn elements throughout the $S-C_3N_4/SnO_2-SnS_2$ porous nanosheet matrix, which unambiguously confirms that the SnS_2-SnO_2 nanojunctions were embedded *in situ* in sulfur-doped C_3N_4 porous nanosheets. The results indicate that the SnO_2-SnS_2 heterojunctions with strong interface interactions were constructed. The strong coupling interactions between $S-C_3N_4$, SnO_2 , and SnS_2 are expected to not only tune the optical/electronic band structure, but also improve the charge-separation efficiency of the $S-C_3N_4/SnO_2-SnS_2$ hybrid.

The overall synthetic procedure for the $S-C_3N_4/SnO_2-SnS_2$ is presented in Fig. 4. The hexagonal layered structure supramolecular microrods were first synthesized as the substrate material (Fig. S3). Then, the prepared supramolecular microrods were immersed in an anhydrous ethanol solution containing Sn^{4+} to make Sn^{4+} and ethanol molecules intercalate into the layered microrod precursors due to the existence of a large interlamellar distance (0.315 nm) between the tri-stiazine layers [43]. Substantial functional groups ($-NH_2$ and $-OH$) on the surface of the tri-stiazine layer are ideal sites for coordinating with Sn^{4+} species, which could easily adsorb the Sn^{4+} species through electrostatic interactions. The subsequent annealing treatment in air simultaneously realized the production and efficient exfoliation of the layered C_3N_4 porous nanosheets. Moreover, SnO_2 nanoparticles were formed and embedded *in situ* in C_3N_4 porous nanosheets (Fig. 2e, f). Furthermore, the amount of Sn^{4+} influences the microstructure of the C_3N_4/SnO_2 hybrids. A low amount of Sn^{4+} leads to the formation of small SnO_2 nanoparticles embedded in C_3N_4 porous nanosheets ($C_3N_4/SnO_2-0.5$) (Fig. S5). In contrast, a large amount of Sn^{4+} leads to a high density of interconnected SnO_2 nanoparticles anchored on the C_3N_4 porous nanosheet ($C_3N_4/SnO_2-1.5$) (Fig. S6). In the fol-

lowing sulfidation process under a nitrogen atmosphere, sulfur powder can react with SnO_2 nanoparticles with controllable tuning of the sulfidation degree to form SnO_2-SnS_2 nanojunctions and SnS_2 nanoparticles. Moreover, the doping of sulfur into C_3N_4 porous nanosheets was realized, producing $S-C_3N_4/SnO_2-SnS_2$. The optimized $S-C_3N_4/SnO_2-SnS_2$ composite was determined according to the performance of the photocatalytic CO_2 reduction. The optimized ratio of $SnS_2:SnO_2$ was measured to be approximately 1:1, and the C_3N_4 content was 60.6 wt% *via* EDX measurements (Fig. S7). The real composition of the optimized $S-C_3N_4/SnO_2-SnS_2$ photocatalyst was further determined *via* ICP-AES. According to the test results, in the optimized $S-C_3N_4/SnO_2-SnS_2$ photocatalyst, the C_3N_4 , SnO_2 , and SnS_2 contents are approximately 60.9, 18.2, and 20.9 wt%, respectively.

In this reaction system, $S-C_3N_4/SnO_2-SnS_2$ composites with different Sn dosages can also be prepared. For the hybrid sample ($S-C_3N_4/SnO_2-SnS_2-0.5$) with a low Sn^{4+} dosage, apart from the strong C_3N_4 phase-related XRD diffraction peaks, only weak peaks of SnO_2 and SnS_2 could be observed in the XRD pattern (Fig. S8). Moreover, no obvious particles could be observed in the TEM images (Fig. S9). When the Sn dosage exceeded a certain value, many interconnected nanoparticles (but not porous C_3N_4 nanosheets) were found in the TEM images (Fig. S10). This indicates that a high Sn^{4+} dose can promote the decomposition of the supramolecular precursor.

The elemental compositions, together with the chemical structure of $S-C_3N_4/SnO_2-SnS_2$, were determined *via* XPS characterization. The survey XPS spectrum of $S-C_3N_4/SnO_2-SnS_2$ proves the coexistence of C, N, Sn, S, and O elements (Fig. 5a). In the high-resolution C 1s XPS spectra (Fig. 5b), the peaks located at 284.8 and 288.3 eV correspond to the C-C in $C-C\equiv N$ and $N-C=N$, respectively [22]. In the N 1s spectrum of g- C_3N_4 , the divided peaks at 400.5, 399.1, and 398.2 eV can be assigned to amino functions bonding with hydrogen (C-N-H) in the heterocycles, tertiary nitrogen $N-(C)_3$ groups, and sp^2 -hybridized nitrogen in the triazine rings (C-N=C) (Fig. 5c), respec-

Figure 3 (a–c) SEM images, (d, e) TEM images, and (f) HRTEM image of S-C₃N₄/SnO₂-SnS₂. (g) STEM image and elemental mappings of (h) C, (i) N, (j) Sn, (k) O, and (l) S of S-C₃N₄/SnO₂-SnS₂.

Figure 4 Illustration of the formation of S-C₃N₄/SnO₂-SnS₂.

Figure 5 XPS spectra analysis. (a) Survey XPS spectra and high-resolution XPS spectra of (b) C 1s, (c) N 1s, (d) Sn 3d, (e) O 1s, and (f) S 2p in different samples.

tively [57,58]. The three peaks have some slight shift for S-C₃N₄/SnO₂-SnS₂, revealing the subtle change in the chemical environment around the N atoms. In the spectrum of Sn 3d (Fig. 5d), the binding energy difference between Sn 3d_{3/2} and Sn 3d_{5/2} is 8.4 eV, which indicates that Sn⁴⁺ exists in the samples [59]. Similarly, the binding energies of the Sn 3d peaks were found to show some slight shift in S-C₃N₄/SnO₂-SnS₂ compared with those in SnO₂ and SnS₂, suggesting strong interactions between SnS₂/SnO₂ and C₃N₄ (Fig. 5d). Therefore, the XPS results indicate the successful synthesis of the S-C₃N₄/SnO₂-SnS₂ porous nanosheet architecture and manifest the establishment of coupling interfaces. In the O 1s XPS spectra (Fig. 5e), two peaks at 530.6 and 532.3 eV can be attributed to the lattice oxygen and the adsorbed OH groups in SnO₂, respectively [60,61]. In the S 2p XPS spectra (Fig. 5f), the peaks centered at 161.2 and 162.3 eV are assigned to S 2p_{3/2} and S 2p_{1/2}, respectively, indicating the existence of S²⁻ [62].

The UV-vis diffuse reflectance spectroscopy (DRS) spectra are

shown in Fig. 6a. The sharp absorption edges of SnO₂, C₃N₄, and SnS₂ rise at 400, 500, and 600 nm, respectively. For the C₃N₄-based samples, C₃N₄/SnO₂, S-C₃N₄/SnO₂-SnS₂, and S-C₃N₄/SnS₂ exhibit an increased light absorption in the wavelength range of 400–800 nm compared with SnO₂. In particular, S-C₃N₄/SnS₂ shows the highest visible light absorption ability. This indicates that the introduction of C₃N₄, SnS₂, and surface defects can improve the visible light absorption properties of the composites. According to the curves of (αhν)² against hν (Fig. 6b), the optical band gaps (E_g) of SnO₂, SnS₂, C₃N₄, and S-C₃N₄ were also calculated to be 3.69, 2.66, 2.54, and 2.46 eV, respectively. The existence of surface defects in S-C₃N₄/SnO₂-SnS₂ can be proven by the electron paramagnetic resonance (EPR) spectra in Fig. 6d. In addition, the higher EPR signal intensity of S-C₃N₄/SnO₂-SnS₂ indicates its higher concentration of oxygen vacancies compared with that of other samples.

The adsorption-desorption isotherms of the samples show type IV isotherms (Fig. 6c). Sn-based C₃N₄ composites, includ-

Figure 6 (a) DRS spectra and (b) Tauc plots. (c) N₂ adsorption-desorption isotherms and the pore-size distribution curves (inset). (d) Room-temperature EPR spectra. (e) CO₂ adsorption isotherms. (f) CO₂-TPD plots of different samples.

ing C_3N_4/SnO_2 , $S-C_3N_4/SnO_2-SnS_2$, and $S-C_3N_4/SnS_2$, possess much higher large surface areas and pore volumes than pure C_3N_4 (Table S1). Undoubtedly, the increased surface area and pore volume come from layer-by-layer exfoliation and the formation of porous heterostructure nanosheets during the pyrolysis process of Sn^{4+} -intercalated supramolecular microrods. The large surface area, abundant porous structure, surface defects, and sufficient nanoscale heterointerfaces endow $S-C_3N_4/SnO_2-SnS_2$ with more active sites for a remarkably enhanced CO₂ adsorption, which was confirmed by the CO₂ adsorption isotherms (Fig. 6e). This indicates the existence of an interaction between CO₂ molecules and $S-C_3N_4/SnO_2-SnS_2$, which was revealed by the CO₂ temperature-programmed desorption (CO₂-TPD) measurement (Fig. 6f). The initial desorption temperature of CO₂ molecules on $S-C_3N_4/SnO_2-SnS_2$ is higher than that on C_3N_4 , C_3N_4/SnO_2 , and $S-C_3N_4/SnS_2$. In particular, the desorption temperature at 300 °C is relatively high, indicating a rather strong CO₂ chemisorption ability of $S-C_3N_4/SnO_2-SnS_2$ [63]. Moreover,

the largest peak area of the CO₂-TPD profile of $S-C_3N_4/SnO_2-SnS_2$ indicates that it has more basic sites for CO₂ adsorption.

Photocatalytic CO₂ reduction

Photocatalytic CO₂ reduction tests of the samples were conducted in a gas-solid reaction setup under AM1.5 irradiation in the absence of cocatalysts or sacrificial agents. As shown in Fig. 7a–c, all the samples exhibit CO₂ photoreduction activity in generating CO and CH₄. Single C_3N_4 shows a normal photocatalytic activity. The evolution rates of CO and CH₄ are 4.62 and 1.27 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. Compared with pristine $g-C_3N_4$, the coupling of SnO_2 nanoparticles with C_3N_4 porous nanosheets can trigger a significantly improved photocatalytic CO₂ reduction performance. The low CO and CH₄ evolution rates of C_3N_4 could be attributed to the inefficient charge separation/transfer. In C_3N_4/SnO_2 , the introduction of wide-bandgap SnO_2 nanoparticles slightly decreases the visible light absorption (Fig. 6a), but the enhanced photoinduced charge

Figure 7 Time-yield plots of (a) CO and (b) CH₄ generated from photocatalytic CO₂ reduction with different catalysts under AM1.5 irradiation. (c) The average production rates of CO and CH₄ catalyzed by different samples under AM1.5 irradiation. (d) CO generation rates under different reaction conditions. (e) Stability test of the photocatalytic CO₂ reduction over S-C₃N₄/SnO₂-SnS₂. (f) Mass spectra of ¹³CO and ¹³CH₄ generated using ¹³CO₂ as the starting carbon source over S-C₃N₄/SnO₂-SnS₂.

separation efficiency enables more electrons to participate in the CO₂ reduction reactions. Comprehensive factors lead to the improvement of the photocatalytic activity. The control experiments show that the content of SnO₂ nanoparticles also influences the photocatalytic CO₂ reduction performance. As shown in Fig. S11, C₃N₄/SnO₂ with a moderate SnO₂ content yields the highest CO and CH₄. C₃N₄/SnO₂ hybrids with SnO₂ contents too low or too high (C₃N₄/SnO₂-0.5 or C₃N₄/SnO₂-1.5) exhibit decreased photocatalytic performances. The control experiments also confirm that pure SnO₂ and SnS₂ exhibit very low photocatalytic CO₂ reduction performances (Fig. S12).

After sulfidation treatment, the obtained optimal S-C₃N₄/SnO₂-SnS₂ exhibits significantly enhanced yields of CO (23.5 μmol g⁻¹ h⁻¹) and CH₄ (22.6 μmol g⁻¹ h⁻¹), which exceed those of C₃N₄/SnO₂ and S-C₃N₄/SnS₂. The selectivity of CH₄ reaches 80.30%. In general, two electrons are required to produce one CO molecule, and eight electrons are needed to produce one CH₄ molecule. Therefore, the apparent quantum yield (QE) is defined as the ratio of the number of reacted electrons

(forming CO and CH₄ molecules) to the number of incident photons. The QEs of the samples were calculated and provided using the equation in Table S2. Compared with the relatively low QE and the overall conversion yields (CE) of bare C₃N₄, C₃N₄/SnO₂, and S-C₃N₄/SnS₂, the QE and CE of the optimized S-C₃N₄/SnO₂-SnS₂ were calculated to be 2.58% and 0.043%, respectively, using methods described in previous reports (Table S2) [64]. In addition, the molar ratios of SnO₂:SnS₂ in S-C₃N₄/SnO₂-SnS₂ also influence the photocatalytic performance. Both low and high ratios (2:1 and 1:2) of SnO₂:SnS₂ can lead to a decrease in the photocatalytic activity (Fig. S13). Because S-C₃N₄/SnO₂-SnS₂ has a porous nanosheet structure and surface area similar to those of C₃N₄/SnO₂ and S-C₃N₄/SnS₂, its superior photocatalytic CO₂ reduction activity can be attributed directly to the unique two dimensional (2D) porous ternary heterostructured features with nanosized interfacial contacts, which accelerate photo-induced charge transfer and separation. Moreover, the surface defects produced by sulfur doping effectively favor the separation of photoinduced charge carriers and act as active sites for

CO₂ chemisorption. Furthermore, the introduction of narrow-bandgap SnS₂ and surface defects can significantly enhance visible light absorption. As reported in previous studies, sulfidation can achieve sulfur doping of C₃N₄ and a controllable conversion of metal oxide to the corresponding metal sulfide, which can greatly influence the crystal phase component, surface state, and photocatalytic activity of the final products [65,66]. These favorable factors enable more electrons to react with the adsorbed CO₂ molecules, thus promoting the CO₂ photoreduction performance of S-C₃N₄/SnO₂-SnS₂. The CO and CH₄ evolution rates over S-C₃N₄/SnO₂-SnS₂ are higher than those of most reports and other state-of-the-art photocatalysts (Table S3). Control experiments, including no light illumination, no catalyst, and under an argon atmosphere, were also performed (Fig. 7d). The results show that no CO or CH₄ were detected, indicating that CO₂ photoreduction occurred in the presence of photocatalysts under light irradiation and a CO₂ atmosphere.

To evaluate the photocatalytic performance and structural stability of S-C₃N₄/SnO₂-SnS₂, cyclic performance tests were conducted. After five recycles, there was only a slight decrease in the yield rates of CO and CH₄ (Fig. 7e). The XRD, SEM, and TEM characterizations of S-C₃N₄/SnO₂-SnS₂ after stability tests reveal that S-C₃N₄/SnO₂-SnS₂ shows no noticeable alternation in the morphology and crystal/chemical structures, reaffirming its high recyclable stability (Fig. S14). To determine whether the carbon source of the resulting CO and CH₄ products is CO₂, an isotope-labeled CO₂ test was performed (Fig. 7f). A further GC-MS analysis reveals that the charge-mass ratios of 17 ($m/z = 17$) and 29 ($m/z = 29$) are assigned to ¹³CH₄ and ¹³CO, respectively, indicating that carbon originated from ¹³CO₂. The results confirm that the photocatalytic products are generated from CO₂ photoreduction.

To study CO₂ activation over the catalysts, *in situ* FT-IR spectra of CO₂ adsorbed on S-C₃N₄/SnO₂-SnS₂ under gas-solid conditions were collected (Fig. S15). The FT-IR background spectrum of S-C₃N₄/SnO₂-SnS₂ was first obtained before CO₂ adsorption. After adsorbing the CO₂ molecules, the IR spectra of the adsorbed species on S-C₃N₄/SnO₂-SnS₂ were acquired by subtracting the background spectrum of S-C₃N₄/SnO₂-SnS₂. Under light irradiation, CO₂ molecules were adsorbed and activated on S-C₃N₄/SnO₂-SnS₂. Peaks at 1726, 1577, 1390, and 1296 cm⁻¹ ascribed to the stretching vibration of the carboxy group (*COOH) intermediates were observed [67]. These peaks gradually became intense with extending light irradiation time. This indicates that CO₂ photoreduction over S-C₃N₄/SnO₂-SnS₂ undergoes a multistep process involving CO₂ adsorption, the production of intermediates, and the final conversion of CO₂ into carbon-containing chemicals. Because no formate species were detected, it can be deduced that *COOH was more likely to be further dehydrated to generate CO and CH₄.

The photoinduced charge transfer properties were further investigated by photoelectrochemical and PL spectroscopy techniques. Steady-state fluorescence spectra of the samples are shown in Fig. 8a. Compared with C₃N₄, significant PL quenching was found in the C₃N₄-based composites. In particular, S-C₃N₄/SnO₂-SnS₂ shows the lowest PL intensity, implying that the sulfur-doped 2D porous ternary heterostructure nanosheets significantly facilitate photoinduced charge separation. The delay times in the time-resolved PL spectra (Fig. 8b) were calculated by fitting the decay curves and are listed in Table S4. S-C₃N₄/SnO₂-SnS₂ shows a longer decay lifetime than single C₃N₄ and binary hybrids (C₃N₄/SnO₂ and S-C₃N₄/SnS₂), suggesting that ternary nano-heterojunctions can effectively elongate the lifetime of charge carriers. The long lifetime of charge carriers and the distinct PL quenching of S-C₃N₄/SnO₂-SnS₂ portend a

Figure 8 (a) Steady-state PL spectra. (b) Transient-state PL spectra. (c) Transient photocurrent action spectra. (d) EIS Nyquist plots.

Figure 9 (a–c) Mott-Schottky plots of different samples. (d) The charge transfer route and photocatalytic CO_2 reduction mechanism over the $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ photocatalyst.

higher chance for charge carriers to participate in CO_2 reduction reactions, thus improving the photocatalytic activity.

The charge-transfer kinetics of the samples was further characterized by electrochemical tests. The transient photocurrent action spectra (Fig. 8c) show that the transient photocurrent of $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ is significantly superior to that of the control samples, indicating its efficient charge transfer and separation. The EIS Nyquist plots are shown in Fig. 8d, where the inset is the corresponding equivalent circuit. The two resistances, R_{ct} and R_s , are the charge transfer and the series resistance, respectively. $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ possesses the smallest EIS semicircle, testifying its lowest interfacial R_{ct} and decreased R_s , which are effective in promoting the migration of charge carriers.

Based on the above discussion, a photocatalytic CO_2 reduction mechanism over the $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ photocatalyst was provided. The terraced-type charge transfer in $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ is shown in Fig. 9d. According to the flat band potential estimated by the Mott-Schottky plots (Fig. 9a–c), the XPS valence band spectra (Fig. S16), and the bandgap values calculated from the Tauc plots of the corresponding DRS spectra (Fig. 6b), the energy bands of $\text{S-C}_3\text{N}_4$, SnO_2 , and SnS_2 are determined (Table S5) and well aligned to form a type of terraced band alignment heterostructure. Under AM1.5 illumination, electron-hole pairs are produced on $\text{S-C}_3\text{N}_4$, SnS_2 , and SnO_2 . Because their different band structures create an internal electric field within the space charge region, effective electron-hole separation and migration in the $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ system is realized. The excited electrons can migrate from the conduction band (CB) of $\text{S-C}_3\text{N}_4$ and SnS_2 to that of SnO_2 . Moreover, the new impurity levels caused by sulfur doping between the valence band (VB) and the CB of C_3N_4 promote more photoinduced charge exci-

tation and transfer. The accumulated electrons in the CB of SnO_2 will participate in CO_2 reduction reactions to produce CO and CH_4 . Moreover, the holes in the VB of SnO_2 and SnS_2 transfer to the VB of $\text{S-C}_3\text{N}_4$ to oxidize H_2O . The synergistic effect of the terraced-type band alignment heterostructure with nanosized interfacial contacts and porous hybrid ultrathin nanosheets with rich surface defects could lower the reaction barrier and effectively promote the formation of intermediate species, leading to an excellent CO_2 reduction performance. Commonly, the generation rate of H_2 is lower than that obtained through the solid-liquid mode due to the exposed CO_2 atmosphere. The same is suitable for CH_3OH and other formate species. Generally, in gas-solid mode during the photocatalytic CO_2 reduction, for SnS_2 , surface oxidized SnS_2 ($\text{SnS}_2/\text{SnO}_2$), and C_3N_4 -based catalyst systems, the selectivities of CO and CH_4 are relatively high [42]. Similarly, in this work, no H_2 or formate species were detected, so it can be deduced that the intermediate $^*\text{COOH}$ is more likely to be further dehydrated to generate CO and CH_4 over the $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ hybrid.

CONCLUSIONS

In summary, $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ were rationally fabricated via liquid impregnation-pyrolysis following a sulfidation strategy using a supramolecular layered structure as the precursor. In this synthetic route, ultrathin C_3N_4 porous nanosheets and embedding of SnO_2 nanoparticles can be achieved simultaneously. The subsequent sulfidation treatment achieves sulfur doping and *in situ* formation of $\text{SnO}_2\text{-SnS}_2$ nanojunctions in C_3N_4 porous nanosheets with tunable $\text{SnO}_2/\text{SnS}_2$ ratios. The synthetic approach makes $\text{S-C}_3\text{N}_4/\text{SnO}_2\text{-SnS}_2$ possess abundant active sites, an enhanced CO_2 uptake capacity, an improved visible

light absorption, and an efficient interfacial charge transfer. As a result, the optimized S-C₃N₄/SnO₂-SnS₂ achieved an excellent CO₂ conversion efficiency with higher yields of CO (23.2 μmol g⁻¹ h⁻¹) and CH₄ (21.2 μmol g⁻¹ h⁻¹) compared with the control photocatalysts under gas-solid reaction conditions. Such a promising synthetic strategy can be expected to promote the design of other robust C₃N₄-based porous nanosheet heterostructures for a broad range of applications.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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硫掺杂 SnO_2 - SnS_2 纳米异质结镶嵌的 C_3N_4 多孔纳米片 提高电荷转移和光催化还原 CO_2 性能

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摘要 结合了多孔纳米片和异质结优点的二维多孔纳米片异质结构材料预计能在 CO_2 光催化还原为燃料过程中表现出优异的性能. 本文中, 我们提出了一种简便的合成方案, 即通过液体浸渍-热解和后续硫化处理, 将层状结构的超分子前驱体转变成 C_3N_4 , 形成了硫掺杂的原位嵌入的 SnO_2 - SnS_2 纳米异质结 C_3N_4 多孔纳米片($\text{S-C}_3\text{N}_4/\text{SnO}_2$ - SnS_2). 在这项研究中, 硫掺杂的 C_3N_4 多孔纳米片的剥离和 SnO_2 - SnS_2 纳米异质结同时获得. SnO_2 - SnS_2 纳米异质结的硫掺杂 C_3N_4 多孔纳米片具有丰富的活性位点、增强的可见光吸收能力和界面电荷转移效率. 正如预期, 与 C_3N_4 , $\text{C}_3\text{N}_4/\text{SnO}_2$ 和 $\text{S-C}_3\text{N}_4/\text{SnS}_2$ 光催化剂相比, 优化的 $\text{S-C}_3\text{N}_4/\text{SnO}_2$ - SnS_2 具有更高的气相光催化还原 CO_2 性能, CO 产率($21.68 \mu\text{mol g}^{-1} \text{h}^{-1}$)和 CH_4 产率($22.09 \mu\text{mol g}^{-1} \text{h}^{-1}$)显著提高. CH_4 的选择性可达80.30%. 这种合成策略有望推动其他 C_3N_4 基多孔纳米片异质结构的研究, 以实现更广泛的应用.