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Partially Oxidized SnS₂ Atomic Layers Achieving Efficient Visible-Light-Driven CO₂ Reduction

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ABSTRACT: Unraveling the role of surface oxide on affecting its native metal disulfide' CO_2 photoreduction remains a grand challenge. Herein, we initially construct metal disulfide atomic layers and hence deliberately create oxidized domains on their surfaces. As an example, SnS_2 atomic layers with different oxidation degrees are successfully synthesized. *In situ* FTIR spectra disclose the COOH* radical is the main intermediate, while density-functional-theory calculations reveal the COOH* formation is the rate-limiting step. The locally oxidized domains could serve as the highly catalytically active sites, which not only benefit for charge-carrier separation kinetics, verified by surface photovoltage spectra, but also result in electron localization on Sn atoms near the O atoms, thus lowering the activation energy barrier through stabilizing the COOH* intermediates. As a result, the mildly oxidized SnS₂ atomic layers exhibit the carbon monoxide formation rate of 12.28 µmol g⁻¹ h⁻¹, roughly 2.3 and 2.6 times higher than those of the poorly oxidized SnS₂ atomic layers and the SnS₂ atomic layers under visible light illumination. This work uncovers atomic-level insights into the correlation between oxidized sulfides and CO₂ reduction property, paving a new way for obtaining high-efficiency CO₂ photoreduction performances.

INTRODUCTION

The ever-increasing climate changes triggered by CO_2 is regarded as one of the major environmental challenges for our current society. Given this, converting CO₂ to value-added fuels has recently drawn massive attention since it could not only debase the environmental influences but also produce more useful fuels,¹⁻⁴ in which photoconversion of O_2 into hydrocarbon fuels is thought to be a promising 'green chemistry' approach.⁵ As is well-known, it is requisite that the practical implementation of CO₂ photoreduction should satisfy bargain price, high activity and persistent stability. In this respect, metal sulfides could be promising candidates for solar CO₂ reduction thanks to their earth abundance, high absorption coefficient as well as low-cost and environmentally friendly preparation procedures.⁶⁻⁷ In addition, the valence bands of metal sulfides are usually made up of S 3p orbitals, which possess much more negative potentials than that of the O 2p orbitals in metal oxides, thus ensuring narrow band gaps to harvest visible light. More importantly, the bottoms of conduction bands of metal sulfides are principally composed of the empty metal d orbitals, which enables the conduction band positions to be negative enough for reducing CO_2 into other available carbon forms.⁸⁻¹² Despite these advantages, metal sulfides still suffer from the woeful inefficiency and poor stability for CO₂ photoreduction as a result of the high

activation energy barrier to form intermediate such as CO_2^{-} or COOH* radicals as well as the fast recombination rate of photoexcited electron-hole pairs.¹³

Recently, considerable research efforts have been devoted to promote the photoactivity and photostability of metal sulfides by decorating their native oxides,¹⁴⁻¹⁵ which could not only accelerate the charge-carrier separation, but also refrain from the severe photocorrosion. For example, Wang et al. demonstrated that the photogenerated electrons could transfer from the conduction band of ZnS nanoparticles to that of ZnO nanorods, while the holes on the valence band of ZnO nanorods could transfer to that of ZnS nanoparticles, which dramatically boosted the electron-hole separation efficiency and hence acquired largely improved photocatalytic H_2 evolution.¹⁶ In addition, Wakerley *et al.* reported that the presence of CdO_x in CdS quantum dots helped to avoid photocorrosion during solar-driven reforming of lignocellulose.¹⁷ In spite of these advances, atomic-level role of how the native oxide domains confined in metal sulfides affect the photocatalytic performances still lacks a profound understanding up to now, chiefly because the previously fabricated catalysts usually contained multidimensionality, many undesirable defects, as well as exposing different crystal facets, which may bring about unexpected interference on the photocatalytic properties.

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Figure 1. (A) Diagram of the energy band structure and vectorial electron transfer in the SnS_2/SnO_2 composite semiconductors. Schematics of (B) the locally oxidized SnS_2 atomic layers and (C) the SnS_2 atomic layers, respectively. The differential charge density maps for (D) the locally oxidized SnS_2 atomic layers and (E) the SnS_2 atomic layers. In the differential charge density map, yellow and blue region indicate electron accumulation and depletion, respectively. (isosurface level: 0.03 e/Å^3)

To unveil the correlation between oxidized sulfides and CO₂ reduction property, and hence realize improved CO₂ photoconversion efficiency, for the first time, we built metal sulfide atomic layers with controllable oxidation degrees. In this respect, tin disulfide (SnS_2) would be a promising candidate: in addition to being nonpoisonous, relatively inexpensive, chemically stable,¹⁸⁻¹⁹ its suitable conduction band level and appropriate band gap can empower it to reduce CO₂ into other hydrocarbon fuels under visible light irradiation.²⁰ Importantly, as shown in Figure 1A, the coalescence of SnO2 and SnS2 could favor the vectorial displacement of electrons and holes travel from one to another owing to the close work functions for SnS₂ (4.2~4.6 eV) and SnO_2 (4.7 eV).²¹ Moreover, benefiting from the atomic thickness, the abundant surface atoms from SnS₂ and SnO₂ could be adequately exposed to serve as active sites for the catalytic reaction (Figure 1B-C),²²⁻²³ which could explicitly elucidate how the oxidized domains influence the CO₂ photoreduction. Besides, as revealed by density functional theory (DFT) calculation in Figure 1D-E and Figure S1-2, the SnS₂ atomic layers exhibited gradually increased charge density near the Fermi level with increasing oxidation degrees, and more interestingly, the charge tended to localize on Sn atoms near the O atoms, which was beneficial for CO₂ activation through effectively binding with COOH* intermediate. Motivated by the above consideration, it is imperative to initially prepare perfect SnS₂ atomic layers and then deliberately create oxidized domains on their surfaces, endeavoring to gain atomic-level insights into the role of locally oxidized domains in affecting the solar-driven CO₂ reduction.

RESULTS AND DISCUSSION

To this end, SnS₂ atomic layers with surface Sn oxide domains have been successfully fabricated through a facile and straightforward hydrothermal process, while the oxidation degrees of SnS₂ atomic layers could be tailored by controlling the volumetric ratio of ethylene glycol to distilled water (EG: H₂O). Taking the products obtained at the EG: H₂O ratio of 1:1 as an example, their XRD pattern in Figure S3A could be readily indexed to hexagonal SnS2 (JCPDS card No.23-0677),²⁴ while the TEM image in Figure 2A clearly depicted their sheet-like morphology. As displayed in Figure S3B, the two nearest spots with an orientation angle value of 60° were fairly consistent with the theoretical values of (100) and (010) planes for hexagonal SnS2,25 which suggested the SAED pattern corresponded to the SnS_2 phase recorded from the [001] zone axis. Atomic force microscopic (AFM) image and the corresponding height profiles in Figure S3C-D illustrated their average thickness of 1.2 nm, close to the 1.18 nm thickness of a two-unit-cells SnS₂ slab along the [001] direction, further confirmed by the lateral high-resolution TEM image in Figure 2G.²⁶ Inconceivably, the high-resolution TEM images in Figure 2B-D showed the presence of two different structural domains, the overwhelming majority of which exhibited an interplanar spacing of 0.315 nm and a dihedral angle of 60° . corresponding to the (100) and (010) planes of hexagonal SnS_2 ; meanwhile, the other one displayed interplanar spacings of 0.335 nm and 0.159 nm as well as a dihedral angle of 90°, corresponding to the (110) and (002) planes of tetragonal SnO₂, which inferred the existence of SnO₂ phase confined in the SnS_2 atomic layers. $^{\rm 27}$ In addition, the main Raman peak at 310 cm^{-1} in Figure 3H could be assigned to SnS_2^{28} while the excrescent peaks at 438 and 466 cm⁻¹ could powerfully demonstrate the presence of SnO₂ phase confined in the SnS₂ atomic layers.^{29^{*}} Moreover, as shown in Figure 2I, the

 normalized S 2p spectra were related to an oxidized sulfur,³⁰ fully supporting the above conclusion. According to the peak area for S 2p XPS spectra in Figure S6A, the content of Sn oxide domains in the SnS₂ atomic layers could be quantified to be about 3.4% (mildly oxidized SnS2 atomic layers).³¹ Interestingly, when the volumetric ratio of ethylene glycol to distilled water was decreased to 1:4, the relative intensity of SnO₂ Raman peaks sharply depressed, implying a decrease in the content of SnO₂, while the corresponding S 2p XPS spectra in Figure S6B revealed its content to be ca. 1.7% (poorly oxidized SnS₂ atomic layers). In addition, the corresponding AFM image and lateral high-resolution TEM image in Figure S4 also affirmed their nearly the same thickness of ca.1.2 nm.

Meanwhile, when distilled water was used as the sole solvent, SnS_2 atomic layers with the same thickness can be expectedly synthesized (Figure S5), while the corresponding Raman and S 2p XPS spectra in Figure 2H-I did not detect the presence of SnO_2 phase, insinuating there was no Sn oxide domains confined in the SnS_2 atomic layers. Moreover, as depicted by the TEM images and Raman spectra for the products obtained in other different ratios of EG to H₂O in Figure S7-8, it was concluded that the ratio of H₂O/EG could indeed play a vital role in tailoring the sulfide to oxide ratio, and the 1:1 ratio helps to obtain the SnS_2 atomic layers with the largest amount of Sn oxides.



Figure 2. Characterizations for the mildly oxidized SnS_2 atomic layers obtained from a mixed solvent of EG and H_2O (EG: $H_2O=1:1$): (A) TEM image, (B) high-resolution TEM image, and (C, D) the corresponding enlarged high-resolution TEM images, as well as (E, F) the related schematic atomic models, clearly showing the distinct atomic configuration corresponding to hexagonal SnS_2 and tetragonal SnO_2 , (G) lateral high-resolution TEM image. (H) Raman spectra and (I) S 2p XPS spectra for the three products acquired from different solvents.

To disclose how the locally oxidized domains affect on the CO₂ photoreduction properties of the SnS₂ atomic layers, the solar CO₂ reduction experiments for these three samples were performed under a 300 W Xe lamp with a standard AM 1.5 filter and a 420 nm cut-off filter. Gas chromato graphy (GC) was executed to identify and quantify the gas products, in which the predominant reaction product was carbon monoxide accompanied by a trace amount of methane. Control experiments demonstrated that there was no detectable carbon monoxide generation in the dark or in the absence of CO₂, verifying that carbon monoxide was derived from CO₂ reduction driven by solar light irradiation. As revealed by the synchrotron-based vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) in the inset of Figure 3A, the full spectrum obtained by SVUV-PIMS at the photon energy of 14.5 eV clearly displayed the signal of m/z=29, which

corresponded to the ¹³CO. Owing to the fact that the photon energy of 14.5 eV can not associate CO2 into CO (Figure S10A), the detected ¹³CO could undoubtedly be attributed to the reduction of ¹³CO₂ reduction. Of note, as displayed in Figure 3A, the mildly oxidized SnS₂ atomic layers exhibited the carbon monoxide formation rate of 12.28 μ mol g⁻¹ h⁻¹, roughly 2.3 and 2.6 times higher than those of the poorly oxidized SnS₂ atomic layers and the SnS₂ atomic layers, respectively, which convincingly demonstrated the superiority of the mildly oxidized SnS₂ atomic layers. In addition, the overall conversion yields for the SnS₂ atomic layers, the poorly oxidized and the mildly oxidized SnS₂ atomic layers were calculated to be about 0.016%, 0.018% and 0.042%, respectively. Interestingly, all these three samples could concurrently realize H₂O oxidation into O₂ (Figure S11), with average O_2 evolution rates of about 2.1, 2.4, and 5.2 µmol g⁻¹

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 h^{-1} for the SnS₂ atomic layers, the poorly oxidized and the mildly oxidized SnS₂ atomic layers, respectively. More importantly, the CO₂ photo-reduction activities for these three SnS₂ atomic layers samples were not passivated after 20 h photocatalysis. In this respect, the TEM images, XRD patterns,

Raman spectra, UV-vis diffuse reflectance spectra and XPS spectra in Figure S12-14 strongly demonstrated the morphology, the phase as well as the oxidation degrees of the three samples did not occur any obvious variation after 20 h photoreduction test, verifying their favorable photostability.



Figure 3. Photoreduction of CO₂ into CO under visible light irradiation for the SnS₂ atomic layers, the poorly oxidized and the mildly oxidized SnS₂ atomic layers. (A) 1 h, (B) stability test for 1, 4, 8, 12, 16, and 20 h, respectively, (C) UV-vis diffuse reflectance spectra, (D) secondary electron cutoff of the SRPES spectra, (E) SPV spectra, and (F) room-temperature PL spectra. Inset in (A) denotes SVUV-PIMS spectrum of the products after ¹³CO₂ photoreduction for the mildly oxidized SnS₂ atomic layers at hv = 14.5 eV and inset in (C) denotes the band gaps that estimated by a related curve of $(\alpha hv)^2$ versus photon energy plotted.

To uncover the underlying reasons for the enhancement of CO_2 photoreduction properties of locally oxidized SnS_2 atomic layers, it is indispensable to investigate their energy band structures that determine the generation, separation and transport of photoexcited carriers. It is well known that the energy band structures could be efficiently resolved by the synchrotron radiation photoemission spectroscopy (SRPES).³²⁻

³³ As shown in Figure 3D, the work functions for the SnS_2 atomic layers, the poorly oxidized and the mildly oxidized SnS_2 atomic layers could be calculated to be 4.10, 4.11 and 4.14 eV, respectively, while the valence band spectra in Figure S15 depicted their VBMs were 2.17, 2.21 and 2.25 eV, respectively. Thus, the VBMs vs. the vacuum level for the SnS_2 atomic layers, the poorly oxidized and the mildly oxidized SnS_2 atomic layers located at 1.77, 1.82 and 1.89 eV, respectively. Base on the band gaps obtained by UV–vis

diffuse reflectance spectra in Figure 3C, the electronic band structures vs. normal hydrogen electrode (NHE) can be exhibited in Figure S16, from which one can clearly observe that all these samples possessed the abilities to realize both CO_2 reduction and O_2 evolution occurring at the same time.³⁴ More importantly, Figure S16 also illustrated that both the VBM and conduction band minimum (CBM) gradually decreased with increasing oxidation degrees of SnS₂ atomic layers, fairly consisting with the positively shifted band edges of SnO_2 shown in Figure 1A, which convincingly demonstrated that the locally oxidized domains confined in SnS₂ atomic layers could effectively modulate the electronic structures. This could be further confirmed by their gradual shift of X-ray absorption threshold to lowered energy with increasing oxidation degrees in Figure S17, indicating the increment



Figure 4. (A-C) *In situ* FTIR spectra for co-adsorption of a mixture of CO_2 and H_2O vapor on the mildly oxidized SnS_2 atomic layers, in which the (A) 3D colormap surface with projection and (B) 2D contour color fill correspond to the line plots in (C). (D-E) Amplification of the selected areas in Figure 4C. (F) CO TPD spectra, and (G) free energy diagrams of CO_2 photoreduction to CO for the SnS_2 atomic layers, the poorly oxidized and the mildly oxidized SnS_2 atomic layers. Inset in (F) denotes the enlargered selected areas in Figure 4F.

of electron concentration³⁵, which would help to tailor the electron-hole separation efficiency. To support this view. surface photovoltage spectroscopy (SPV), a powerful tool to reflect the separation and transport behaviors of photoinduced charge carriers, was employed to evaluate these three samples.³⁶⁻³⁷ As revealed in Figure 3E, the mildly oxidized SnS₂ atomic layers displayed the highest SPV response intensity relative to the poorly oxidized SnS₂ atomic layers and the SnS₂ atomic layers, indicating that the presence of Sn oxide domains favored the separation of photogenerated electron-hole pairs in SnS₂ atomic layers, which matched well with the results uncovered by the room-temperature photoluminescence (PL) spectroscopy in Figure 3F. Therefore, the above results forcefully indicated that the local oxidation of SnS₂ atomic layers could be conducive to enhancing the separation efficiency of photoexcited electron-hole pairs.

To dive deep into CO₂ photoreduction process on SnS₂ atomic layers, *in situ* Fourier transform infrared spectroscopy

(FTIR) measurements were performed for the three samples (Figure 4A-C and Figure S18), with efforts to gain in-depth understanding on the reaction intermediates during the photocatalytic process. Taking the mildly oxidized SnS₂ atomic layers as an example, one can clearly see that several bands appeared with the extension of irradiation time from 0 to 20 min in Figure 4A-E. Importantly, a new IR peak at 1550 cm⁻¹ arose and gradually strengthened accompanied with increasing irradiation time, in which such a peak could be assigned to the COOH* groups, one of the key intermediates during photoreduction of CO_2 to CO, further verified by their characteristic peaks at 1200 cm⁻¹.³⁸⁻⁴⁰ Meanwhile, the peaks at 1510 and 1379 cm⁻¹ could be attributed to monodentate carbonate $(m-CO_3^{2-})$ groups, while the band for asymmetric OCO stretches of b-CO₃²⁻ groups located at 1337 cm⁻¹, which derived from the CO₂ dissolving in water.⁴¹ On the basis of the FTIR spectra analysis, CO₂ photoreduction on the mildly SnS₂ atomic layers may undergo the following steps. Initially, CO₂

molecules were adsorbed on the catalyst surfaces (Figure S19) and at the same time, H_2O molecules dissociated into hydroxyl and hydrogen ions on the surfaces. Upon the adsorbed CO₂* molecules interacted with the surface protons, the COOH* intermediate would be gradually generated, while the further protonation of COOH* intermediate could yield the CO* molecules. The final step in the catalytic reaction was desorption of adsorbed CO* from the catalyst surface. Similar to that of the mildly oxidized SnS₂ atomic layers, the *in situ* FTIR spectra of the poorly oxidized SnS₂ atomic layers and the SnS₂ atomic layers in Figure S10 manifested the same

$$\begin{array}{ll} \text{CO}_2(\text{g}) \rightarrow \text{CO}_2^* & (1a) \\ \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- & (1b) \\ \text{CO}_2^* + e^- + \text{H}^+ \rightarrow \text{COOH}^* & (2) \\ \text{COOH}^* + e^- + \text{H}^+ \rightarrow \text{CO}^* + \text{H}_2\text{O} & (3) \\ \text{CO}^* \rightarrow \text{CO} & (4) \end{array}$$

where "*" represents the corresponding adsorption state on the catalyst surface.



Scheme 1. Schematic representation of CO₂ photoreduction mechanism on the mildly oxidized SnS₂ atomic layers.

To deeply investigate the full CO₂ catalytic reduction cycle, DFT calculations were further carried out on the above reaction steps. As indicated by the calculated reaction Gibbs free energies (ΔG) in Figure 4G and table S1-2, both the formation of COOH* and CO* for the three samples were highly endergonic processes, in which the formation of COOH* intermediate was the rate-limiting step. Importantly, compared with the poorly oxidized SnS₂ atomic layers and the SnS₂ atomic layers, the mildly oxidized SnS₂ atomic layers possessed the lowest formation energy of COOH*, which indicated that the increasing oxidation degree of the SnS₂ atomic layers can lead to the decreased formation energy of COOH* intermediate. This might be primarily attributed to the indraught of O atom, which enabled a mass of electrons to locate around Sn atom, and hence enhanced the bonding effect between Sn and COOH*, thus favoring to reach a more stable configuration (Scheme 1). Moreover, since CO desorption process is also regarded as a significant factor that may influence the whole CO_2 reduction processes,⁴² it is also essential to assess the CO desorption ability for the three samples. As revealed by the CO temperature programmed desorption (TPD) measurements in Figure 4F, the lowest CO onset desorption temperature and the highest total amount of detected CO for the mildly oxidized SnS2 atomic layers meant the formed CO* molecules could liberate from the surface much easier than those on the poorly oxidized SnS₂ atomic layers and the SnS₂ atomic layers, exactly consistent with the DFT calculations in Figure 4G. Besides, the DFT calculations in Figure S20 and Table S1, 3 also uncovered that increasing oxidation degree of SnS₂ atomic layers could also tailor the rate-determining step for the water oxidation process, which would immensely enhance the activity of oxygen production.

Consequently, both theoretical and experimental results demonstrated that the introduction of native oxide domains, which could act as the highly catalytically active sites, could benefit for the rate-limiting COOH* adsorption step via stabilizing the COOH* intermediate, hence lowering their activation energy and explicitly facilitating CO_2 reduction catalysis.

CONCLUSION

In summary, metal sulfide atomic layers with different oxidation degrees were first proposed, with efforts to unveil how locally oxidized domains matter the native metal sulfide's CO_2 photoreduction properties. As a prototype, SnS_2 atomic layers with surface Sn oxide domains have been successfully fabricated. SPV and PL spectra verified the presence of Sn oxide domains benefited for charge-carrier separation kinetics, while in situ FTIR spectra fully revealed that the COOH* radical was the main intermediate during their CO₂ photoreduction. Most importantly, DFT calculations uncovered that the formation of COOH* intermediate was the rate-limiting step, while the electron localization on Sn atoms resulting from local oxidation could lower the CO₂ activation energy barrier through stabilizing the COOH* intermediates. On the strength of these advantages, the mildly oxidized SnS₂ atomic layers showed the carbon monoxide formation rate of 12.28 μ mol g⁻¹ h⁻¹, roughly 2.3 and 2.6 times higher than those of the poorly oxidized SnS₂ atomic layers and the SnS₂ atomic layers, respectively. Briefly, this work experimentally/theoretically demonstrates the locally oxidized domains could serve as the highly catalytically active sites, which not only boost the charge separation efficiency but also favor CO₂ activation, opening new avenues towards achieving robust solar-driven CO₂ conversion performances.

EXPERIMENTAL SECTION

Synthesis of the mildly oxidized SnS₂ atomic layers:

In a typical synthetic procedure, 0.6 mmol sodium dodecyl benzene sulfonate (SDBS), 0.25 mmol $SnCl_4 \cdot 5H_2O$ and 2 mmol L-cysteine were dissolved in a mixed solvent of 15 mL deionized water and 15 mL ethylene glycol in order under continuous magnetic stirring. After dozens of minutes, the mixed solution was transferred into a Teflon-lined autoclave, maintaining at 160 °C for 10 h, and then naturally cooled to room temperature. The obtained products were washed with water and ethanol for several times, and placed in the vacuum freeze-drying equipment overnight for further characterization.

Synthesis of the poorly oxidized SnS₂ atomic layers:

In a typical synthetic procedure, 0.6 mmol sodium dodecyl benzene sulfonate (SDBS), 0.25 mmol $SnCl_4 \cdot 5H_2O$ and 2 mmol L-cysteine were dissolved in a mixed solvent of 25 mL deionized water and 5 mL ethylene glycol in order under continuous magnetic stirring. After dozens of minutes, the mixed solution was transferred into a Teflon-lined autoclave, maintaining at 160 °C for 10 h, and then naturally cooled to room temperature. The obtained products were washed with water and ethanol for several times, and placed in the vacuum freeze-drying equipment overnight for further characterization.

Synthesis of the SnS₂ atomic layers:

In a typical synthetic procedure, 0.6 mmol sodium dodecyl benzene sulfonate (SDBS), 0.25 mmol $SnCl_4 \cdot 5H_2O$ and 2 mmol L-cysteine were dissolved in 30 mL deionized water in order under continuous magnetic stirring. After dozens of minutes, the mixed solution was transferred into a Teflon-lined autoclave, maintaining at 160 °C for 10 h, and then naturally cooled to room temperature. The obtained products were washed with water and ethanol for several times, and placed in the vacuum freeze-drying equipment overnight for further characterization.

Characterization: Transmission electron microscopy (TEM) images were performed with a JEOL-2010 TEM with an acceleration voltage of 200 kV. The high-resolution TEM images were carried out on a JEOL JEM-ARM200F TEM/STEM with a spherical aberration corrector. XRD patterns were obtained from a Philips X'Pert Pro Super diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å). Veeco DI Nano-scope MultiMode V system was employed to acquire atomic force microscopy (AFM) images. UV-vis diffuse reflectance spectroscopy were measured on a Perkin Elmer Lambda 950 UV-vis-NIR spectrophotometer. Room temperature photoluminescence (PL) spectra were recorded on a RenishawRM3000 Micro-Raman system, in which the excitation pulse was a 325-W Xe lamp. CO₂ adsorption isotherms were determined using an automatic microporous physical and chemical gas adsorption analyzer (ASAP 2020M PLUS). Micromeritics ChemiSorb 2720 with a thermal conductivity detector (TCD) were used to conduct temperature-programmed desorption (TPD) of the samples. In situ FTIR spectra were obtained by using a Thermo Scientific Nicolet iS50. SRPES, SVUV-PIMS, XANES and XPS spectra were executed in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China.

Photocatalytic CO₂ reduction measurement: In the typical CO₂ photocatalytic reduction process, 0.1 g of the sheet-like SnS₂ powders were initially dispersed in deionized water and then the dispersions were dripped onto the quartz glass. After one day's natural air drying, the SnS₂ powders could be dispersed onto a quartz glass homogeneously. Note that the SEM images in Fig. S9 clearly revealed the loosely arranged sheet-like SnS₂ on the quartz glass, which would ensure better contact with H₂O vaper and CO₂, and hence achieve efficient CO₂ photoreduction property. Then, the quartz glass was put in the reaction cell with 2 mL deionized water on the bottom, in which the volume of the reaction cell was approximately 400 mL. Hence, the reaction cell was vacuum-treated for three times, which was then pumped by high-purity CO_2 (99.99%) to reach an atmospheric pressure. The temperatures of the reaction cell were controlled at 10 °C by recirculating cooling water system during irradiation. The light source for the photocatalysis was a 300 W Xe lamp (PLS-SXE300/300UV, Beijing Perfectlight Technology Co., Ltd) with a standard AM 1.5 filter and a 420 nm cut-off filter, in which the outputting light density was about 50 mW/cm^2 . During the light irradiation, the product gases were by analyzed qualitatively Techcomp GC7900 gas chromatograph (FID detector, TDX-01 column) by identifying the chromatographic peaks. The overall conversion yield was calculated as follows:

 η (%) = [R(CO) × \triangle G°] / [P × S] × 100

where R(CO), ΔG° , P, and S denote the rate of carbon monoxide evolution (mol s⁻¹) in the photocatalysis, the change in the Gibbs free energy that accompanies the CO₂ photoreduction to CO (64.1 × 10³ J mol⁻¹), the energy intensity of the solar light irradiation (0.05 W cm⁻²), and the irradiation area (10 cm²), respectively.

SPV measurements: The surface photovoltage measurements were conducted on the basis of a lock-in amplifier. The measurement systems were composed of a simple chamber, a source of monochromatic light, a lockin amplifier (SR830, Stanford research systems, Inc.) and a light chopper (SR540, Stanford research systems, Inc.). A 500 W xenon lamp (CHF-XM-500 W, global xenon lamp power) with a grating mono-chromator (Omni-3007, No.16047, Zolix), chopping with a frequency of 23 Hz, served as the monochromatic light.

DFT calculation details: The first-principles calculations were executed with the Vienna ab initio simulation package.⁴³⁻ ⁴⁴ Projector augmented wave (PAW) potentials were used to describe the interaction between ions and valence electrons, while the exchange-correlation between electrons is treated by utilizing the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form.⁴⁵ The plane wave cutoff energy was 340 eV, and a $3 \times 3 \times 1$ for sheet k-point mesh were employed to achieve the accurate density of the electronic states. Ionic relaxations were performed under the conventional energy (10^{-4} eV) and force (0.01 eV/Å) convergence criteria. The two layers SnS₂ nanosheets along the [001] projection were adopted to imitate the synthetic 1.2-nm thick sheets, in which 1.5 nm vacuum layer was added to avert the interaction between adjacent layers.

Gibbs free energies for each gaseous and adsorbed species were calculated at 298.15 K, according to the expression:

 $G=EDFT + EZPE + \int CPdT - TS$

Where EDFT is the electronic energy calculated with VASP, EZPE is the zero-point energy, JCPdT is the enthalpic temperature correction, TS is the entropy contribution. EZPE, JCPdT, and TS from temperature, pressure, and calculated vibrational energies were computed by using standard ideal gas methods. All 3N degrees of freedom for adsorbates were regarded as frustrated harmonic vibrations with negligible contributions from the catalyst surfaces.

Each reaction step is considered as a concurrent transfer of the proton-electron pair as a function of the applied potential in the computational hydrogen electrode (CHE) model.⁴⁶ Thus, free energy changes with respect to an initial state of gaseous CO_2 freely above an empty surface can be represented by

 $\Delta \operatorname{G}[\operatorname{COOH}^*] = \operatorname{G}[\operatorname{COOH}^*] + \operatorname{G}[\operatorname{H}^+ + e^-] - (\operatorname{G}[*] + \operatorname{G}[\operatorname{CO}_2] + 2 \times \operatorname{G}[\operatorname{H}^+ + e^-])$

 $\Delta G[CO^*] = G[CO^*] + G[H_2O] - (G[^*] + G[CO_2] + 2 \times G[H^+ + e^-])$

 $G[H^+ + e^-] = 1/2 G[H_2] - eU$

where U is the applied overpotential and e is elementary charge.

ASSOCIATED CONTENT

Supporting Information

Details of DFT, XRD, TEM, AFM image and CO₂ adsorption isotherms. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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