In-Situ Hydrothermal Synthesis of SnS\textsubscript{2}/SnO\textsubscript{2}/rGO Nanocomposites with Enhanced Photogenerated Electron Transfer for Photoreduction of CO\textsubscript{2} to CH\textsubscript{4}

Yunfei Wang\textsuperscript{1} · Wei Feng\textsuperscript{1} · Qianyan Liu\textsuperscript{4} · Zeyang Li\textsuperscript{1} · Xiaolian Yang\textsuperscript{1} · Ping He\textsuperscript{1} · Haonian Wang\textsuperscript{1} · Qizhen Liu\textsuperscript{3} · Jiang Wu\textsuperscript{1,2} · Yongfeng Qi\textsuperscript{5}

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Abstract
As an extremely promising technology about decarburization, the reduction of CO\textsubscript{2} driven by sunlight shows a glamourous prospect, so it is valuable to design a sort of photocatalyst with excellent performance i.e., low cost, high photocatalytic activity and high product selectivity, which is the key factor to promote the further popularity of this technology in industry. In this work, the SnS\textsubscript{2}/SnO\textsubscript{2}/rGO ternary nanocomposites were successfully designed and fabricate through a simple one pot in-situ hydrothermal synthesis. It is worth noting that the XRD, SEM and Raman results indicate that the molar of SnS\textsubscript{2} to SnO\textsubscript{2} could be increased with the content of l-cysteine, and it is proved that the ternary material is simply adjustable. The separation and transference of photogenerated electrons and holes could be accelerated due to the reduced graphite oxide with outstanding electrical conductivity. At the same time, under the condition of inputting appropriate sulfur source precursors, appropriate pore size and pore volume structure characteristics are obtained, which further contributes the adsorption capacity of CO\textsubscript{2}. Moreover, the proper position of the conduction band improves the selectivity for photoreduction of CO\textsubscript{2} to CH\textsubscript{4} of SnS\textsubscript{2}/SnO\textsubscript{2}/rGO composite. Hence, under visible-near infrared light, the highest CH\textsubscript{4} productivity of SnS\textsubscript{2}/SnO\textsubscript{2}/rGO ternary composite is 5.52 μmol g\textsuperscript{-1} h\textsuperscript{-1}. This work provides some references for the field of photocatalytic decarburization.

Graphical Abstract

Keywords Photocatalysis · rGO · Tin-based compounds · CO\textsubscript{2} reduction · Electron transfer

Yunfei Wang and Wei Feng have contributed to the work equally and regarded as co-first authors.

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1 Introduction

Nowadays, with rapid consumption of hydrocarbon fuels, many problems have aroused great concern such as the greenhouse effect caused by the increased concentration of CO₂ in the atmosphere and the energy shortages. One of the most promising ways to tackle both the energy crisis and the ever-increasing climate change triggered by carbon dioxide is to convert it into renewable hydrocarbon fuels by photocatalysts [1]. The appropriate photocatalysts have always been a core issue in the study of photocatalysis, given this, tremendous efforts have been made to concentrate on developing photocatalysts in the last decades [2, 3]. Traditional semiconductor photocatalysts such as TiO₂ and ZnO, due to only responding under UV light and the high recombination rate of photoexcited electron–hole pairs, are just with low conversion efficiencies [4]. With the development of the study, some new photocatalysts such as ZnIn₂S₄, MOFs, Bi₃WO₆ and BiOIO₃ have also been reported to be applicable to the photocatalytic reduction of CO₂ [5–8]. Most of these semiconductor materials enhance photocatalytic activity, but lack the selectivity and quantum efficiency necessary for industrial application. Therefore, it is a great challenge to improve photocatalytic activity, selectivity and quantum efficiency of semiconductor photocatalysts.

Two-dimensional (2D) layered materials have received extensive attention in the field of photocatalytic reduction of carbon dioxide, due to the short electron transport distance in the direction of thickness, which are conducive to the rapid transport of carriers to the surface and restrain the recombination of charge-carrier [9]. Moreover, they also have a large specific surface area, which can adsorb a large number of reactant molecules and provide abundant active sites. Among them, SnS₂, a metal sulfide of layered CdI₂-type structure with a narrow band gap of 2.2 eV, is considered to be a promising and efficient visible light photocatalyst [10]. In addition, its suitable positions of conduction band (CB) edges for redox reactions, long term stability, low cost, and non-toxicity give many advantages for a fine photocatalysts under visible light. However, photocorrosion as well as the fast photoexcited electron–hole pairs of SnS₂ results in its poor photocatalytic performance [9]. Charge-carrier [12, 13]. However, it suffers from difficulty in controlling the photoreduction for one CO₂ molecule selectivity to one CH₄ molecule production that demands eight electrons and eight hydrogen protons, involving multiple reaction steps, lacking of enough photogenerated electrons and adsorbed CO₂ molecules [14]. Reduced graphene oxide (rGO), a metal-free semiconductor, is generally used as high-efficiency acceptor and transporter of photogenerated electrons, which in turn improves the separation efficiency of photoexcited electron–hole pairs, and the result is the improvement of photocatalytic activity [15]. Moreover, rGO with the abundant surface hydroxyl can boost the adsorption and activation capacity for CO₂.

The large specific surface area provides enough space for supporting other semiconductor materials as substrate and the possibility of sufficient contact with other materials [16]. Integrating the above attributes of excellence, the construction of SnS₂/SnO₂/rGO nanocomposites synthesis by one step in-situ hydrothermal method is expected to bring inspiration for other photocatalytic systems for photocatalytic CO₂ reduction.

In present work, we reported a highly efficient and stable photocatalyst, SnS₂ and SnO₂ nanosheets in-situ growing on rGO prepared by hydrothermal method, for the photoconversion of CO₂ to CH₄ at a rate of 5.52 µmol g⁻¹ h⁻¹ under visible-light irradiation. During the facile hydrothermal process, GO was reduced to rGO and SnS₂/SnO₂ sheets were anchored on the rGO. The surface morphology, structural properties, optical and photoelectrochemical characteristics of the SnS₂/SnO₂/rGO nanocomposites were studied. Moreover, the mechanism of enhanced CH₄ production selectivity was discussed in detail.

2 Results and Discussion

As shown in the Fig. 1, SnS₂/SnO₂/rGO have been successfully prepared through a straightforward one-step in situ hydrothermal method, in which the proportion of SnS₂ to SnO₂ sheets could be controlled by adjusting the molar ratio of L-cysteine to Tin (IV) chloride pentahydrate.
(SnCl₄·5H₂O). The as-prepared samples with different molar ratios of l-cysteine to SnCl₄·5H₂O at 1, 2, 3, and 4 were denoted as 5GS1, 5GS2, 5GS3 and 5GS4. During the reaction, graphene oxide with negatively charged and abundant oxygen-containing functional groups show strong electrical attraction to Sn⁴⁺, ensuring uniform distribution of tin-based compound intermediates, which provides sufficient growth space for tin-based compounds as substrates [17]. And the graphene oxide could be reduced to rGO by l-cysteine which possesses reducibility.

Figure 2a shows the XRD patterns of the as-prepared samples synthesized via in situ hydrothermal process in different molar ratios of l-cysteine to SnCl₄·5H₂O. When the molar ratio of l-cysteine to SnCl₄·5H₂O is 4:1, all the XRD peaks could be readily indexed to pure hexagonal phase of SnS₂ (JCPDS No. 23-0677) [18]. All peaks of the other molar ratios are attributed to SnS₂ and tetragonal SnO₂ (JCPDS No. 41-1445) [19], and with the increase of l-cysteine amounts, it can be seen from the patterns that the relative proportion of SnO₂ in the nanocomposites decreases gradually. However, there are no obvious characteristic peaks of rGO could be observed in the pattern of samples, which could be attributed to the low content and high dispersion of rGO. For further insight of the phase structure of nanocomposites, Raman spectra was recorded and shown in Fig. 2b. The Raman peak at 301 cm⁻¹ could be attributed to SnS₂, whereas the bands peaking at 430, 467, 704 and 779 cm⁻¹ in Fig. 2b are all assigned to SnO₂, and with the increase of molar ratio of l-cysteine to SnCl₄·5H₂O, the characteristic peaks of SnO₂ peter out, which is consistent with the observation from XRD patterns [12, 20, 21]. Moreover, as displayed in Fig. S1a–d, the surface of SnS₂ gradually becomes smooth, which suggests that the contents of SnO₂ in the decreases gradually. The Raman spectrum of as-prepared GO exhibited two prominent peaks, the D band (1343 cm⁻¹) and G band (1585 cm⁻¹), being with an intensity ratio (I_D/I_G) of 0.96. Generally, the ratio of I_D/I_G was proportional to the sp² hybridized domains [22]. The I_D/I_G of SnS₂/SnO₂/rGO was higher than that of GO. In addition, compared with GO, the D and G bands of rGO in SnS₂/SnO₂/rGO appeared blue shift. The result confirmed the successful reduction of GO to rGO in SnS₂/SnO₂/rGO after hydrothermal process [23–25]. What’s more, FT-IR analysis was further carried out to verify bond characteristics of functional groups in the nanocomposites. As shown in Fig. 2c, the strong and wide transmittance peak at 3440 cm⁻¹, could be attributed to the O–H. There is also a strong peak at 1635 cm⁻¹, which is attributed to the stretching vibration of C=O. There are two extremely weak peaks at 1399 and 1110 cm⁻¹, which are attributed to the C–O in carboxyl group and C–O–C. No obvious C=O and C–OH vibration peaks are observed, which indicates that the GO was reduced to rGO by l-cysteine, agreeing well with the analysis of the XRD and Raman spectrum [26, 27]. In addition, as shown in Fig. 2e, the C 1s spectra can be well fitted to oxygen-containing groups such as –COOH and –OH, which is fully of compliance with the above conclusion. The shift in the peaks of Sn 3d of Fig. 2f in SnS₂/SnO₂/rGO may be attributed to the coupling effect of SnS₂ and SnO₂ in the the SnS₂/SnO₂ heterostructures. As indicated in Fig. 3 and Fig. S1, the SEM image of the as-prepared SnS₂/SnO₂/rGO showed that large amount of flower-like nanosheets can be observed uniformly distributed on the 2D rGO nanosheets. The TEM pictures of the lattice distance 0.316, 0.278 and 0.215 nm can be attributed to (100), (101) and (102) planes of the SnS₂, respectively. And the lattice distances of 0.335 and 0.264 nm match well with that of SnO₂ (111) and (101) planes, which is consistent with the fast Fourier transform (FFT) patterns [28, 29]. Base on the above, the TEM and HRTEM images, SEM images, XRD patterns, Raman spectra, FT-IR spectra and XPS spectra in Figs. 2 and 3 strongly demonstrated the flowerlike SnS₂/SnO₂ sheets heterostructure uniformly anchored on rGO sheets in SnS₂/SnO₂/rGO nanocomposites by in situ hydrothermal process, shown in Fig. 1, in which GO was reduced to rGO by l-cysteine.

The specific surface area, pore volume, and pore size of 5GS1-5GS4 was determined by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) method, relevant information is listed in Table 1. The specific surface areas of 5GS1, 5GS2, 5GS3 and 5GS4 was respectively calculated as 141.2354 m²/g, 74.7922 m²/g, 42.1753 m²/g, 37.4526 m²/g, the decrease in specific surface area can be attributed to the agglomeration between tin sulfide and tin oxide [30].

As shown in Fig. 4, the N₂ adsorption–desorption isotherms of 5GS1 and belong to the type IV with the type-H2 hysteresis cycle, in the low pressure region of P/P₀, 5GS1 have a high adsorption volume, which indicates that there are many micropores in the sample. The isotherms of 5GS2, 5GS3 and 5GS4 appear as the type IV with the type-H3 hysteresis loops according to the classification standard of the IUPAC [31], which can be considered a characteristic of mesoporous materials. It is worth noting that the results show that the specific surface area is not directly related to the activity of the catalyst. The photocatalytic performance of 5GS1 with the largest specific surface area is not the best, which may be due to its small pore size, and the narrow hole neck can prevent CO₂ from adsorbing into the hole. However, 5GS3 has larger pore size and volume, which may increase the adsorption capacity of CO₂ on the catalyst surface. In order to verify this guess, the CO₂ adsorption isotherms was conducted. Fig. S3 displays the CO₂ adsorption capacities of the 5GS1, 5GS2, 5GS3 and 5GS4, and the larger CO₂ adsorption capacity on the 5GS3 than others indicate a possible synergistic effect.
Fig. 2  a–d XRD patterns, Raman spectra and FTIR spectra and Survey XPS spectra of 5GS1, 5GS2, 5GS3 and 5GS4, respectively; e–f High-resolution XPS spectra C 1s and Sn 3d of in 5GS1, 5GS2, 5GS3 and 5GS4, respectively
For evaluating the photocatalytic activity of the as-prepared samples, the CO2 photoreduction experiments were performed under a 300 W Xe lamp (λ > 420 nm). Gas products was detected to qualify and quantify by the gas chromatography (GC) with FID and TCD detector, in which the reaction products preferred to CH4 and O2 with trace amount of H2. Compared to the SnS2 and partially oxidation SnS2 in literature which the reaction products preferred to CO and O2 [13]. These lead us to conclude that the exist of rGO in nanocomposites plays an important role in enhancing the photocatalytic activity. Control experiments were also conducted in the dark and in the absence of photocatalyst, and no hydrocarbon products were detected in the control experiments, which suggests that the CO2 photocatalytic reduction process is not substitutable owing to above factors. In order to further eliminate the influence of the carbon element of rGO in the ternary composite on the photocatalytic experiment process, we used N2 instead of CO2 for photocatalytic experiment, as shown in Fig. S3. The results show that there is no generation of carbon containing substances, which confirms that CO2 is the only carbon source of CH4. Furthermore, in the GC–MS spectrum (Fig. S4), there is
a peak of CO$_2$ corresponding to 1.436 min, and no other obvious liquid products are produced.

Figure 5 exhibits the amount of CH$_4$ and O$_2$ generation on the photocatalyst without sacrificial agent. The 5GS3 exhibits the CH$_4$ formation rate of 5.52 μmol g$^{-1}$ h$^{-1}$, approximately 3.76, 2.36 and 2.17 times than those of the 5GS1, 5GS2 and 5GS4, which convincingly certify the superiority of the 5GS3. Moreover, the overall conversion yields for the 5GS1, 5GS2, 5GS3, 5GS4 were calculated to be about 0.0147%, 0.0234%, 0.0553%, and 0.0254%. The overall conversion yields of 5GS3 is greater than poorly oxidized SnS$_2$ in literature [13]. In addition, all these as-prepared samples could photooxidize H$_2$O into O$_2$ at the meantime, with the molar ratio of O$_2$ to CH$_4$ being roughly to 2, which is strongly consistent with the reaction of CO$_2$ with H$_2$O, i.e., CO$_2$ + 2 H$_2$O = CH$_4$ + 2 O$_2$. More importantly, the CH$_4$ evolution of the 5GS3 were not passivated during 24 h reaction in the aggregate at least 6 cycles, showing the high stability of the photocatalyst.

To unveil the underlying principle for the enhancement of CO$_2$ photoreduction selectivity and activity of SnS$_2$/SnO$_2$/rGO, the bandgaps and conduction band (CB) potentials of pristine SnS$_2$ and SnO$_2$ were determined by the UV–Vis DRS (Fig. S5) in ambient temperature and Mott–Schottky plots (Fig. S6). The band gaps of all photocatalysts can be calculated according to Eq. (1) [32]:

$$ahv = A(hv - E_g)^{n/2},$$

where $\alpha$ is the light absorption coefficient, $h$ represent Planck constant, $\nu$ represents frequency of the light, $E_g$ is the band gap of all samples, $A$ is a constant, and $n$ is evaluated as 1, which is due to pristine SnS$_2$ and SnO$_2$ are direct semiconductors [33]. Consequently, pure SnS$_2$ and SnO$_2$ were determined as 2.2 eV and 3.69 eV. According to Mott–Schottky plots of pure SnS$_2$ and SnO$_2$, the flat band potentials were −0.95 eV and −0.46 eV (vs. Ag/AgCl), respectively, and equal to −0.75 eV and −0.26 eV (vs. NHE) [34]. In general, the potential at the bottom of n-type semiconductor conduction band is generally equal to the flat band potential [35], so the conduction band of SnS$_2$ and SnO$_2$ is −0.75 eV and −0.26 eV, respectively. Based on Eq. (2) [36],

$$E_g = E_{CB} - E_{VB}$$

the valence bands of SnS$_2$ and SnO$_2$ are 1.45 eV and 3.43 eV, respectively.

Based on the above, the schematic illustration of electronic band structure vs normal hydrogen electrode (NHE) has been obtained (Fig. S7), from which we can clearly observe that the conduction potential of SnS$_2$ is more negative than that of SnO$_2$, and electrons can be transferred from SnS$_2$ to SnO$_2$ through the heterojunction interface and conduction band potential energy of pristine SnO$_2$ is more negative than the reduction potential of CO$_2$/CH$_4$ (−0.24 eV vs. NHE), but more positive to the reduction potential of CO$_2$/CO (−0.48 eV vs. NHE) [37], which adjusts energy conduction band to an appropriate position that makes samples possess the power to reduce CO$_2$ selectively to CH$_4$ instead of CO.

Moreover, the lifetime and enrichment of photogenerated electrons during the photocatalytic process are also indispensable factors for the enhanced selectivity and activity to CH$_4$ production [38, 39]. It was well-known that the introducing of rGO could enhance the utilization efficiency of visible light, and could improve the transformation of photoexcited electrons, which make more electrons participate in the reaction. The existence of –OH on rGO could boost the absorption of CO$_2$ and decrease the energy barrier for the formation of HCOOH*, which is the conclusive intermediates during overall process due to the massive energy cost [40, 41], and it was confirmed by CO$_2$ adsorption measurements. Hence, to verify the above viewpoint, photoluminescence emission spectra and time-resolved fluorescence emission decay spectra for samples were conducted and shown in Figs. 6 and 7. The photoluminescence (PL) measurements excited by 320 nm ultraviolet light and the transient photocurrent responses with several 30 s on–off cycles by using a 300 W
Xe lamp as a light source were detected, and the results are shown in Fig. 8, which demonstrated that 5GS3 has the most effective separation of the photoexcited electron–hole pairs and the largest photocurrent density. Moreover, the photoexcited charge carrier transfer dynamics of 5GS1, 5GS2, 5GS4 and 5GS3 are further investigated by time-resolved fluorescence emission decay (Fig. 7), similarly to the decay tendency in time-resolved fluorescence emission decay spectra, 5GS1, 5GS2, 5GS4 show fast decay with average PL lifetime of 1.082 ns, 0.994 ns and 1.146 ns, respectively, while the average PL lifetime of 5GS3 prolong to 1.686 ns, implying the greatly improving of the transformation in photoexcited electron. According to the literature in contrast to SnS2/SnO2 [17], the addition of graphene can provide excellent electrical conductivity to provide more electrons to participate in the reaction, which greatly improve the selectivity and activity of CO2 photoreduction. Combined with the results of above, in contrast to SnS2/SnO2, the as-prepared SnS2/SnO2/rGO showed more appropriate energy conduction band and possess the power to realize CO2 selectively reduction to methane instead of CO. The existence of rGO in SnS2/SnO2/rGO nanocomposites enhances the photogenerated electron transfer and enlarges the lifetime and enrichment of photogenerated electron, which in turn promotes the selectivity and activity of CO2 photoreduction.

Previous studies have reported that CO2 molecules dissolve into aqueous solution to generate HCO3−, H2CO3, and CO32− in the liquid phase system, which is more conducive to the generation of methanol and ethanol liquid fuels in thermodynamics [42–44]. In addition, the photocatalytic reduction of CO2 to CO, which requires only two electrons to participate in the reaction, is kinetically easier to occur [45]. However, no CO methanol and ethanol were observed in the GC and GC−MS spectra, which may be attributed to the presence of −OH on rGO, which is not only conducive to more local electrons being stabilized around CO2 molecules, but also promotes the hydrogenation activation of CO2, further improving the selectivity and catalytic efficiency of CO2 photocatalytic reduction to CH4 [46]. As described in Fig. 9, CO2 molecule was first adsorbed at the surface and converted into one CH4 molecule through four successive hydrogenation steps by eight protons and eight electrons (CO2 + 8e− + 8H+ → CH4 + 2H2O).

Upon visible-light irradiation, only SnS2 in SnS2/SnO2/rGO is excited to generate electrons and holes. SnS2 and SnO2 sheets could form heterojunction, which is favorable
to promote separation of photoexcited electrons-holes. And the photoexcited electrons in the conduction band of SnS$_2$ sheets could transfer to the conduction band of SnO$_2$ sheets because of positively shifted conduction band edges of SnO$_2$ to SnS$_2$. Then the photoexcited electrons can further transfer to rGO sheets with strong electrical conductivity rather than stay in the conduction band of SnO$_2$ sheets [47]. As a result, the photogenerated electrons transfer in principle from SnS$_2$ sheets to SnO$_2$ sheets and to rGO sheets (SnS$_2$ → SnO$_2$ → rGO) or from SnS$_2$ sheets to rGO (Fig. 9). The photogenerated electrons are of enrichment on the surface of rGO sheets, while the photogenerated holes would stay in the valence band of SnS$_2$, which could restrain recombination of the photoexcited charge-carrier, meanwhile the photogenerated electrons subsequently react with the adsorbed CO$_2$ to produce CH$_4$ and the photogenerated holes react with the H$_2$O to produce O$_2$.

3 Conclusions

In summary, by adjusting the molar ratio of l-cysteine to SnCl$_4$·5H$_2$O, SnS$_2$/SnO$_2$/rGO have been successfully fabricated with simple one-step in situ hydrothermal process, which have been demonstrated that flower-like SnO$_2$/SnS$_2$ sheets heterostructure uniformly anchor on rGO sheets in SnS$_2$/SnO$_2$/rGO nanocomposites. We describe a new strategy to enhance the selectivity and activity of CO$_2$ photoreduction so as to selectively CH$_4$ through enhancing photogenerated electron transfer and CO$_2$ adsorption capacity. In addition, the transferring of the photogenerated electrons (SnS$_2$ → SnO$_2$ → rGO or SnS$_2$ → rGO) can efficiently enhance the charge separation. In this situation, it allows most electrons to be driven to surface of rGO, which photoreduce CO$_2$ selectively to CH$_4$. This strategy will provide inspiration for other photocatalytic systems for the utilization of CO$_2$.

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Authors and Affiliations

Yunfei Wang¹ · Wei Feng¹ · Qianyan Liu⁴ · Zeyang Li¹ · Xiaolian Yang¹ · Ping He¹ · Haonan Wang¹ · Qizhen Liu³ · Jiang Wu¹,² · Yongfeng Qi⁵

Qizhen Liu
liuqz@sheemc.cn

Jiang Wu
wjcf2002@163.com

¹ College of Energy and Mechanical Engineering, Shanghai University of Electric Power, No. 2103 Pingliang Road, Shanghai 200090, China
² Shanghai Non-carbon Energy Conversion and Utilization Institute, Shanghai 200240, China
³ Shanghai Environmental Monitoring Center, No. 55 Sanjiang Road, Shanghai 200030, China
⁴ Technical Center for Mechanical and Electrical Product Inspection and Testing of Shanghai Customs District, Shanghai 200135, China
⁵ School of Electrical, Energy and Power Engineering, Yangzhou University, Yangzhou 225009, China