

Contents lists available at ScienceDirect

Separation and Purification Technology



journal homepage: www.elsevier.com/locate/seppur

SnO₂ nanodots-embedding and KSCN-assisted re-calcination synergistically boost photocatalytic CO₂ reduction of carbon nitride

Mianmian Zhai^{a,b}, Huawei Fang^{a,b}, Jun Xing^{a,b}, Jixiang Xu^{a,b,*}, Haifeng Lin^{a,b}, Lei Wang^{a,c,*}

^a Key Laboratory of Eco-chemical Engineering, Taishan Scholar Advantage and Characteristic Discipline Team of Eco-Chemical Process and Technology, Qingdao University of Science and Technology, Qingdao 266042, China

^b College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

^c College of Environment and Safety Engineering, Qingdao University of Science and Technology, Qingdao, Shandong 266042, China

ARTICLE INFO

Editor: Dr. S Yi

Keywords: Carbon nitride SnO₂ embedding KSCN-assisted calcination CO₂ photoreduction Mechanism

ABSTRACT

In this work, a heterojunction of SnO₂ nanodots embedded on K-doped carbon nitride (CN) was prepared via wet chemistry and two-step calcination processes for photoreduction of CO₂. Experiments and theoretical calculations confirmed that both of SnO2-embedding and KSCN-assisted re-calcination could enhance visible light absorption and facilitate photogenerated charge separation, enabling constructed SnO2/K-CN had good CO2 adsorption and activation performances. The optimized photocatalyst loaded with 1.92 wt% SnO₂ displayed high CO_2 reductive activity with CO and CH_4 yields of 80.4 and 1.4 µmol g⁻¹, respectively after 3 h in the presence of 0.5 mL water. Such CO₂ reductive activity was not reduced in four repeated tests within the 45 day period. This work provides a new method to construct CN-based heterojunction for enhancing CO2 reductive capacity and stability.

1. Introduction

Conversion of CO2 to useful chemicals via photocatalytic process is a sustainable approach to mitigate the greenhouse effect [1–4]. Among the derived chemicals (e.g., CO, CH₄, and CH₃OH, ethanol), CO produced via two-electron reduction of CO₂ can integrate to the Fischer-Tropsch synthesis to produce syngas, presenting fascinating applications. Employing cheap photocatalysts for efficient reducing CO₂ to CO are expected. These photocatalysts should have strong light utilization, efficient charge separation, high CO2 adsorption/activation and CO selectivity performances.

In the developed photocatalysts, carbon nitride (CN) is extensively used to photoreduce CO₂ owing to its facile synthesis, tunable structure, and appropriate band gap [5-8]. However, the structural defects of fast electrons-holes recombination and low visible light absorption impair its photocatalytic performance. Thus, various strategies like morphology/ defect/doping engineering, copolymerization, and heterostructure construction were adopted to modify CN for facilitating charge separation and enhancing catalytic performance [9-20]. In addition, in order to avoid CN decomposition during CO2 reduction, enhancing its crystallnity was proposed [21,22]. Our previous work found that recalcination CN with KSCN could enhance its structural order and avoid its decomposition, meanwhile, the CO₂ adsorption and reduction performance were increased [23].

CN with two-dimensional nanosheet morphology and larger surface area is a promising support to load active species. Its pyridinic N with lone pair electrons in heptazine rings can capture metal ions. Based on the structural features of CN, many metal atoms, metal nanoparticles. and metal oxide/sulfide/phosphide have loaded/anchored on CN via wet chemistry and calcination steps for enhancing its photocatalytic performances [24–29]. Among the used various metal species in CO₂ reduction, Sn-based materials arouse many interest due to its low cost, nontoxicity, and high selectivity toward CO [30]. Tian et al. prepared Sdoped CN/SnO₂-SnS₂ nanojunction to photoreduce CO₂ [31]. The yields of CO and CH₄ reached to 21.68 and 22.09 μ m g⁻¹ h⁻¹, respectively. Liu et al. prepared carbon dots-doped CN/SnS2 heterojunction to reduce CO2 via gas-liquid process. They confirmed that formation of g-C3N4/ SnS₂ could increase CO₂ adsorption and promote the electrons-holes separation [32]. In addition, Ag-loading [33], Sb-doping [34], and diazanyl modification [35] were also employed to improve CO₂ reduction performance of the SnO₂/CN, but they still showed inferior CO₂ reduction activity. Employing new strategies to prepare and decorate

https://doi.org/10.1016/j.seppur.2024.127185

Received 29 January 2024; Received in revised form 29 February 2024; Accepted 19 March 2024 Available online 20 March 2024 1383-5866/© 2024 Elsevier B.V. All rights reserved.

^{*} Corresponding authors at: Key Laboratory of Eco-chemical Engineering, Taishan Scholar Advantage and Characteristic Discipline Team of Eco-Chemical Process and Technology, Qingdao University of Science and Technology, Qingdao 266042, China.

E-mail addresses: xujix47@163.com (J. Xu), inorchemwl@126.com (L. Wang).

SnO₂/CN for efficient photoreduction of CO₂ is still pursuit.

It has been confirmed that more reactive sites can be constructed by decreasing the size of active species [36]. Controlling the interface structures of two semiconductors for maximizing their contact surfaces is benefit for charge transfer [37]. Zhang et al. embedded SnO₂ nanodots on CN nanosheets [30] via calcining SnCl₂ and melamine mixture, and demonstrated that p-p orbital couplings of SnO₂ and CN could facilitate electron transfer and electroreduce CO₂ to formate. Based on above discussion, it is expected that in situ embedding small-sized SnO₂ particles on CN nanosheets followed by calcination with KSCN can not only achieve effective contact between them to promote electrons-holes separation, but also provide abundant active sites to adsorb and activate CO₂. But, there are no reports regarding this until now.

Herein, a heterojunction of SnO₂ nanodots embedded on K-doped CN (K-CN) was prepared via impregnation and two-step calcination steps. Benefiting from the pyridine N in heptazine rings, the Sn²⁺ ions and then SnO₂ dots could tightly anchor on nanosheets. After second calcination with KSCN, the K⁺ ion was introduced in CN, and the resulted SnO₂/K-CN sample with SnO₂ content of 1.92 wt% exhibited excellent CO₂ reductive performance and stability in the presence of water, with CO yield of 80.4 µmol g⁻¹ in 3 h light irradiation. The enhanced CO₂ reduction mechanism was unveiled.

2. Experimental section

2.1. Preparation of SnO₂/K-CN photocatalyst

CN was synthesized via pyrolysis of melamine-cyanuric acid supermolecular at 600 °C for 3 h. The detail steps were provided in supplementary materials. Sn species was anchored on CN nanosheets via impregnation and calcination processes (Fig. 1a). Specifically, 6 μ mol SnCl₂ was dispersed in 100 mL distilled water under stirring, then 50 mg CN were added and stirred for 12 h. Afterward, the suspension was transferred to an autoclave and kept at 160 °C for 10 h. After natural cooling, the solid was collected, washed with water, and dried at 60 °C. Finally, the powder was calcined at 400 °C for 2 h under N₂ atmosphere, and was denoted Sn/CN. $\rm SnO_2$ was prepared with the same process but without addition of CN.

60.0 mg of Sn/CN and 60.0 mg KSCN were mixed and calcined at 300 °C for 2 h in a tube furnace. The obtained powder was thoroughly washed with water, dried at 60 °C, and was labeled SnO₂/K-CN. Control sample of K-CN was prepared with similar steps but mixing CN and KSCN.

2.2. Photocatalytic CO₂ reductive test

 CO_2 reduction test was carried out in a 370 mL closed glass reactor (Labsolar-6A, Perfectlight Co., Beijing). 10.0 mg catalyst was dispersed in water, then coated on the FTO and dried. The FTO was put on a quartz support (the height was 5.5 cm). 0.5 mL distilled water was added into the reactor. Afterward, the reactor was vacuumed and filled with highpurity CO_2 for the pressure up to 80 kPa. A 300 W Xenon lamp was used as light source. The circuit cooling equipment was maintained at 10 °C. The products were analyzed by a gas chromatograph (Techcomp GC 7900). In the stability test, the used catalyst was recovered, washed with distilled water, and dried before the next test.

3. Results and discussion

3.1. Structural characterization

Scanning electron microscopy (SEM) image revealed the CN had nanosheet morphology (Fig. S1). Transmission electron microscopy (TEM) image demonstrated the Sn/CN still had nanosheet structure (Fig. 1b), but some dispersed black dots were observed on nanosheests. When Sn^{2+} was dispersed in distilled water and reacted at 160 °C for 10 h, the obtained product was SnO₂, as verified by its X-ray diffraction (XRD) pattern (Fig. S2). So, the loaded particles on the nanosheets of Sn/CN might be Sn oxide. After re-calcination Sn/CN with KSCN, nanodots with sizes of about 3.0–7.0 nm were observed in nanosheets of SnO₂/K-CN, as shown in its TEM image (Fig. 1c). In the HRTEM image of SnO₂/K-CN, the lattice fringe with spacing of 0.336 nm was corresponded to



Fig. 1. (a) Synthesis routes of the SnO₂/K-CN, (b) TEM image of the Sn/CN, (c) TEM and (d) HRTEM images of the SnO₂/K-CN sample.

the (111) plane of SnO₂ (Fig. 1d). The content of SnO₂ in the SnO₂/K-CN was 1.92 wt%, determined by an inductively coupled plasma-optical emission spectrometer. N₂ adsorption–desorption isotherms of the samples were measured (Fig. S3), and the Brunauer-Emmett-Teller (BET) surface areas of Sn/CN and SnO₂/K-CN were 106.1 and 92.5 m² g⁻¹, respectively, which were lower than the previously reported CN (132.2 m² g⁻¹) [38]. It was likely that loading SnO₂ and KSCN-assisted re-calcination weakened the dispersion of nanosheets. The pore volumes of Sn/CN and SnO₂/K-CN were 0.38 and 0.31 cm² g⁻¹, respectively.

The structure of the samples was further analyzed based on XRD and X-ray photoelectron spectroscopy (XPS) measurements. In the XRD patterns (Fig. 2a), the peaks at 13.2° and 27.2° were assigned to (210) and (002) planes of CN, respectively. No diffraction peaks related to Sn species were observed in Sn/CN, which was attributed to the low content and amorphous state of Sn oxide. Whereas, the diffraction peak of SnO₂ at 52.0° (JCPDS No. 71-0652) was observed in pattern of SnO₂/K-CN, indicating SnO₂ is embedded on nanosheets. In addition, the characteristic peaks of melon in SnO₂/K-CN become strong, implying its structure become orderly after calcination with KSCN [39]. In the XPS survey spectra, signals of C 1s, N 1s, O 1s, and Sn 3d were presented (Fig. S4). Because the peaks of K 2p and C 1s were overlapped, the signal of K 2p was not distinguish in survey spectrum. In the high-resolution XPS spectra, Sn 3d spectrum of SnO₂ exhibited two fitting peaks at 495.1 and 486.7 eV, which were assigned to the Sn $3d_{3/2}$ and Sn $3d_{5/2}$ of Sn⁴⁺, respectively [32]. These two peaks were also existed in the Sn 3d of SnO₂/K-CN (Fig. 2b), but their binding energies negatively shifted, implying electrons can transfer from K-CN to SnO₂. In addition, the C 1s spectrum of SnO₂/K-CN was fitted into four peaks located at 284.4, 286.0, 287.8, and 288.9 eV, respectively (Fig. 2c), which were attributed to adventitious carbon, C bonded to NH_x , sp^2 carbon in N-C = N, and C = O bond, respectively. In the O 1 s spectrum (Fig. 2d), the lattice oxygen (Sn-O), surface absorbed oxygen, and C = O group at 530.0, 532.1, and 532.6 eV, respectively were found. In the N 1s spectrum (Fig. 2e), four peaks at about 398.2, 399.3, 400.8, and 403.8 eV,

corresponding to N in C–N = C, C–NHx, and N–(C)₃ groups, as well as π -excitation, respectively, were observed. K⁺ characteristic peaks at 292.7 and 294.6 eV were observed in the K 2p spectrum (Fig. 2f). The above results suggest the successful embedding SnO₂ on K-CN nanosheets.

Fig. 3a is the ultraviolet-visible (UV-Vis) diffuse reflectance spectra of the obtained samples. The light absorption of CN in 300-800 nm largely increased after embedding SnO2 nanodots then second calcination with KSCN, meanwhile, the absorption edge was red-shifted. These will facilitate photon excitation. Based to the Kubelka-Munk plots, the band gaps of SnO2 and K-CN were 3.01 and 2.86 eV, respectively (Fig. S5). Meanwhile, Mott-Schottky curves demonstrated that the flat band potentials of SnO2 and K-CN were -0.76 V and -0.91 eV (vs. Ag/ AgCl), respectively (Fig. S6). It was reported that the conduction band potentials (E_{CB}) of n-type semiconductor is more negative (~ -0.1 eV) than its flat band potential with $E_{\rm NHE} = E_{\rm Ag/AgCl} + 0.197$. Thus, the $E_{\rm CB}$ / valence band potentials (EVB) of SnO2 and K-CN were -0.66/2.35 eV and -0.81/2.05 eV, respectively. Based on these band potentials of SnO₂ and K-CN, it is inferred that the photogenerated electrons of K-CN can spontaneously diffuse to the CB of SnO₂, while the holes in the VB of SnO₂ can migrate to the VB of K-CN (Fig. 3b), then suppressing the recombination of electrons and holes. Such charge transfer at the SnO₂/ K-CN interface was also illustrated by the differential charge density diagram (Fig. S7). As shown in Fig. 3c, the electrons were accumulated on SnO₂, also implying that electrons can transfer from K-CN to SnO₂. This is consistent with the XPS analysis. To further illustrate the charge separation performance of CN after modification, photo-electrochemical measurements were performed. As shown in Fig. 3d, the transient photocurrent increased in order of CN < Sn/CN < K-CN < SnO₂/K-CN, indicating that embedding SnO_2 and K-doping realized via recalcination with KSCN can promote electrons and holes separation. In the electrochemical impedance spectrum (EIS) plots (Fig. 3e), SnO₂/K-CN had the smallest Nyquist semicircle among the four samples, and K-CN took second place, also demonstrating the charge transfer resistance



Fig. 2. XRD patterns of th obtained samples. High-resolution XPS spectra of (b) Sn 3d of the SnO₂ and SnO₂/K-CN; (c) C 1 s, (d) O 1 s, (e) N 1 s, and (f) K 2p of the SnO₂/K-CN.



Fig. 3. (a) UV–Vis diffuse reflectance spectra of the obtained samples, (b) schematic diagram of band positions and charge transfer pathways of the K-CN and SnO_2 samples, (c) the calculated differential charge density diagram of SnO_2/K -CN (K, C, N, O, and Sn atoms are represented by purple, light gray, brown, red, and grayish purple balls, respectively; The isosurface of charge density is set to 0.0004 e/Å³). (d) Photocurrent, (e) EIS, and (f) PL curves of the obtained samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. (a) Comparison the yields of CO and CH₄ under different catalysts catalysis after 3 h light irradiation, (b) Comparison the CO_2 reduction performance of SnO_2/K -CN with previously reported CN-based photocatalysts, (c) effect of Sn^{2+} dosage on CO_2 reduction, (d) reusability of SnO_2/K -CN in reduction of CO_2 .

decreased after increasing the order of melon structure and embedding SnO₂ [23]. In addition, the photoluminescence (PL) spectra revealed that SnO₂/K-CN exhibited the lowest PL emission peak compared to the other samples, implying the recombination of photogenerated charge is largely inhibited in SnO₂/K-CN (Fig. 3f). It can be seen that coupling of SnO₂, especially re-calcination with KSCN can facilitate photogenerated charge transfer and separation in CN. Thus, more holes and electrons could take part in protons formation and CO₂ conversion reactions.

3.2. CO_2 reduction performance

CO₂ reduction tests were performed under full-spectrum irradiation without photosensitizers and sacrificial agents. Fig. 4a shows the evolved CO and CH₄ yields after 3 h reaction under different samples catalysis. No products were detected using SnO2 and CN alone as catalyst owing to poor photogenerated charge separation. When 6 µmol Sn²⁺ was introduced to modify CN, the yields of CO and CH₄ over Sn/CN were 14.6 and 0 μ mol g⁻¹, respectively. The CO₂ conversion efficiency largely increased after re-calcination with KSCN, and the yields of CO and CH4 under SnO₂/K-CN catalysis reached to 80.4 and 1.4 µmol g⁻¹, respectively, which was 5.5 times higher than that of Sn/CN, and higher than those yields generated under K-CN catalysis (CO: 32.6 μ mol g⁻¹ and CH₄: 0 μ mol g⁻¹) [40], and some of the previously designed catalysts (Table S1 and Fig. 4b). Correspondingly, the apparent quantum efficiency (AQE) of SnO₂/K-CN at 400 nm was 7.0%, and the CO selectivity was 93.0%. In addition, optimal experiments confirmed that introducing 6 μ mol Sn²⁺ to form heterojunction with CN exhibited the best CO₂ reduction performance (Fig. 4c). For the reusability of SnO₂/K-CN, as shown in Fig. 4d, the yields of CO and CH₄ did not decrease during consecutive three cyclic tests. Moreover, the yields of CO and CH₄ also not decrease after the sample was placed for 45 day. Meanwhile, compared to the fresh sample, no obvious changes were found in the XRD pattern of the used SnO₂/K-CN (Fig. S8). All the fitting peaks were existed in the XPS spectra of the used sample (Fig. S9), and the corresponding binding energies not obviously change. No products were detected when SnO₂/K-CN was used to catalyze CO₂ reduction in N₂filled reactor or without light irradiation (Fig. S10). These results confirm that the SnO2/K-CN cannot self-decompose and has good activity and reusability in reduction of CO₂.

To explain the good CO₂ reduction performance of SnO₂/K-CN, its CO₂ adsorption behavior was analyzed based on temperature programmed CO₂ desorption (CO₂-TPD) curves and DFT calculation. As shown in Fig. 5a, only one peak centered at about 140 °C was observed in both samples, but the SnO₂/K-CN showed slight larger CO₂ desorption amount (0.0345 mmol g⁻¹) than that of Sn/CN (0.0317 mmol g⁻¹), implying re-calcination with KSCN then doping of K⁺ ions into melon

can enhance its CO₂ adsorption capacity. In our previous work, the free energy for adsorption of CO₂ (ΔE_{ads}) on the K-CN was -0.24 eV obtained by DFT calculation [40], whereas, the CO₂ molecules adsorbed on the SnO₂/K-CN yielded a more negative ΔE_{ads} of -2.09 eV (Fig. 5b), indicating embedding SnO₂ is favor for CO₂ adsorption. Furthermore, the bond angle of CO₂ adsorbed on SnO₂/K-CN was changed to 172.5°, and the C = O bond lengthened to 1.37 Å (1.17 Å in K-CN [40]), implying CO₂ activation also become easy after embedding SnO₂ on CN and recalcination with KSCN.

In order to determine the reductive pathways of CO₂, the possible intermediates during CO₂ reduction were determined via in situ diffuse reflectance infrared Fourier-transform (DRIFT) spectra measurement. As shown in Fig. 6, the characteristic peaks of CO_2^* (1249 cm⁻¹), CH_3O^* (1076 and 1136 cm⁻¹), *CH₂ (1477 cm⁻¹), COOH* (1260 and 1598 cm⁻¹), HCOOH* (1457 and 1540 cm⁻¹), CHO* (1706 cm⁻¹), and CO* $(1940 \text{ and } 2078 \text{ cm}^{-1})$ were observed [24,41-43]. Thus, the mechanism of CO₂ reduction was proposed [44,45]. First, gaseous CO₂ molecules are adsorbed on the K-CN. Under light illumination, K-CN and SnO₂ generate electrons and holes (Eq. (1)). The electrons gather on the SnO₂, while the holes gather on the VB of K-CN driven by their band positions difference. Then, the holes oxide H_2O to H^+ (Eq. (2)), and the electrons transfer into the CO₂* to form COOH* and CO* with H⁺, then CO is released (Eqs. (3)-(6)). On the other hand, a little of COOH* can gradually transform into HCOOH*, CHO*, CH₃O*, and *CH₂, then few CH₄ is formed (Eqs. (7)-(11)).

$SnO_2/K-CN + h\nu \rightarrow electrons + holes$	(1)

$$H_2O + 2 \text{ hole} \rightarrow 2H^+ + 1/2O_2$$
 (2)

 $CO_2 \rightarrow CO_2^*$ (3)

$$CO_2^* + H^+ + electron \rightarrow COOH^*$$
 (4)

 $COOH^* + H^+ + electron \rightarrow CO^* + H_2O$ (5)

 $CO^* \rightarrow CO + *$ (6)

 $COOH^* + H^+ + electron \rightarrow HCOOH^*$ (7)

 $\text{HCOOH}^* + \text{H}^+ + \text{electron} \rightarrow \text{CHO}^* + \text{H}_2\text{O}$ (8)

 $CHO^* + 2H^+ + 2 \text{ electron} \rightarrow CH_3O^*$ (9)

 $CH_3O^* + H^+ + electron \rightarrow *CH_2 + H_2O$ (10)

$$*CH_2 + 2H^+ + 2 \text{ electron} \rightarrow CH_4 \tag{11}$$

Control sample of SnO₂ + K-CN was prepared via mixing SnO₂, CN, and KSCN, which then calcined at 300 $^{\circ}$ C for 2 h, washed and dried. Experiment found that 53.6 CO and 1.47 μ mol g⁻¹ CH₄ were evolved



Fig. 5. (a) CO₂-TPD curves of Sn/CN and SnO₂/K-CN samples, (b) Optimized configurations of CO₂ adsorption on the SnO₂/K-CN (inset is the bond length and bond angle of the adsorbed CO₂).



Fig. 6. In situ DRIFTS spectra of photocatalytic CO_2 reduction under SnO_2/K -CN catalysis in the dark (0 min) and under 300 W Xe lamp irradiation (30, 60, and 90 min).

under SnO₂ + K-CN catalysis, lower than those yields of SnO₂/K-CN (Fig. S11). Besides, sample of SnO₂/CN obtained by calcining SnO₂ and CN at 300 °C for 2 h only produced 20.2 μ mol g⁻¹ CO in 3 h. Thus, the good CO₂ reduction activity of SnO₂/K-CN was attributed to (i) enhanced light absorption in 300–800 nm after SnO₂-emdeding then recalcination with KSCN; (ii) easily charge transfer and efficient electronsholes separation via *in situ* formation of SnO₂ on K-CN; (iii) good CO₂ adsorption and activation ability.

4. Conclusions

A new strategy of SnO₂ nanodots *in situ* embedding and KSCNassisted re-calcination was adopted to modify CN. The optimized SnO₂/K-CN heterojunction coupling 1.92 wt% SnO₂ exhibited good CO₂ reduction performance and stability. 80.4 CO and 1.4 μ mol g⁻¹ CH₄ were evolved after 3 h light irradiation, which was 5.5 times larger than those yields of Sn/CN, and higher than that of CN (0). The high CO₂ reduction capacity was attributed to the synergism of SnO₂-embedding and KSCN-assisted re-calcination, as well as their intimate interface, increasing light absorption, making structure of CN more order, providing more electrons and holes, as well as high CO₂ activation ability. This work provides a new CN-based heterojuction for overcoming structural defects of CN, increasing its photo-reduction performance.

CRediT authorship contribution statement

Mianmian Zhai: Writing – original draft, Methodology, Data curation. Huawei Fang: Supervision, Software. Jun Xing: Supervision, Methodology. Jixiang Xu: Writing – review & editing, Supervision, Methodology, Funding acquisition. Haifeng Lin: Software, Funding acquisition. Lei Wang: Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

The authors are grateful for the financial support of the National Natural Science Foundation of China (52171140, 52072197, and 22179068), the Natural Science Foundation of Shandong Province (ZR2021ME022), Outstanding Youth Foundation of Shandong Province, China (ZR2019JQ14).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2024.127185.

References

- [1] T.K. Kong, Y.W. Jiang, Y.J. Xiong, Photocatalytic CO₂ conversion: What can we learn from conventional CO_x hydrogenation? Chem. Soc. Rev. 49 (2020) 6579–6591.
- [2] J.Y. Zhang, J.Y. Jiang, Y.R. Lei, H.H. Liu, X.L. Tang, H.H. Yi, X.B. Huang, S.Z. Zhao, Y.S. Zhou, F.Y. Gao, Photocatalytic CO₂ reduction reaction: Influencing factors, reaction pathways and dominant catalysts, Sep. Purif. Technol. 328 (2024) 125056–125074.
- [3] P. Prabhu, V. Jose, J.M. Lee, Heterostructured catalysts for electrocatalytic and photocatalytic carbon dioxide reduction, Adv. Funct. Mater. 30 (2020) 1910768–1910870.
- [4] L.X. Wang, B.C. Zhu, J.J. Zhang, J.B. Ghasemi, M. Mousavi, J.G. Yu, S-scheme heterojunction photocatalysts for CO₂ reduction, Matter 5 (2022) 4187–4211.
- [5] Q.L. Xu, Z.H. Xia, J.M. Zhang, Z.Y. Wei, Q. Guo, H.L. Jin, H. Tang, S.Z. Li, X.C. Pan, Z. Su, S. Wang, Recent advances in solar-driven CO₂ reduction over g-C₃N₄ based photocatalysts, Carbon Energy 5 (2022) 1–43.
- [6] C. Prasad, N. Madkhali, V. Govinda, H.Y. Choi, I. Bahadur, S. Sangaraju, Recent progress on the development of g-C₃N₄ based composite material and their photocatalytic application of CO₂ reductions, J. Environ. Chem. Eng. 11 (2023) 1097273–1097304.
- [7] Q.Q. Lu, K. Eid, W.P. Li, A.M. Abdullah, G.B. Xu, R.S. Varma, Engineering graphitic carbon nitride (g-C₃N₄) for catalytic reduction of CO₂ to fuels and chemicals: strategy and mechanism, Green Chem. 23 (2021) 5394–5428.
- [8] Z.R. Zhou, W.Y. Guo, T.Y. Yang, D.D. Zheng, Y.X. Fang, X.H. Lin, Y.D. Hou, G. G. Zhang, S.B. Wang, Defect and nanostructure engineering of polymeric carbon nitride for visible-light-driven CO₂ reduction, Chin. J. Struct. Chem. (2024) 100245–100255.
- [9] S.J. Wang, J.Q. Zhang, B. Li, H.Q. Sun, S.B. Wang, X.G. Duan, Morphologydependent photocatalysis of graphitic carbon nitride for sustainable remediation of aqueous pollutants: A mini review, J. Environ. Chem. Eng. 10 (2022) 107438–107450.
- [10] X.J. Xu, Y.S. Xu, Y.H. Liang, H.Y. Long, D.C. Chen, H.W. Hu, J.Z. Ou, Vacancymodified g-C₃N₄ and its photocatalytic applications, Mater. Chem. Front. 6 (2022) 3143–3173.
- [11] C. Lu, X. Chen, Nanostructure engineering of graphitic carbon nitride for electrochemical applications, ACS Nano 15 (2021) 18777–18793.
- [12] S. Patnaik, D.P. Sahoo, K. Parida, Recent advances in anion doped g-C₃N₄ photocatalysts: A review, Carbon 172 (2021) 682–711.
- [13] X.N. Yu, S.F. Ng, L.K. Putri, L.L. Tan, A.R. Mohamed, W.J. Ong, Point-defect engineering: Leveraging imperfections in graphitic carbon nitride (g-C₃N₄)

M. Zhai et al.

photocatalysts toward artificial photosynthesis, Small 17 (2021) 2006851–2006896.

- [14] X.T. Xu, Y. Huang, K. Dai, Z.L. Wang, J.F. Zhang, Non-noble-metal CuSe promotes charge separation and photocatalytic CO₂ reduction on porous g-C₃N₄ nanosheets, Sep. Purif. Technol. 317 (2023) 123887–123896.
- [15] M. Majdoub, Z. Anfar, A. Amedlous, Emerging chemical functionalization of g-C₃N₄: Covalent/noncovalent modifications and applications, ACS Nano 14 (2020) 12390–12469.
- [16] Y. Zuo, Y.J. Wang, G. Dai, F. Ge, L.Y. Fang, X.T. Zhou, C.M. Li, H.J. Dong, Dual interfacial build-in electric field effect induced by sandwich-type heterojunction for propelling photocatalytic fuel extraction from CO₂ in water, Sep. Purif. Technol. 308 (2023) 122971–122980.
- [17] J.K. Lin, W.J. Tian, H.Y. Zhang, X.G. Duan, H.Q. Sun, S.B. Wang, Graphitic carbon nitride-based Z-Scheme structure for photocatalytic CO₂ reduction, Energy Fuels 35 (2020) 7–24.
- [18] S. Li, Y. Yang, S.P. Wan, R.N. Wang, M.Y. Yu, F.J. Song, Q. Zhong, Supramolecular self-assemble deficient carbon nitride nanotubes for efficient photocatalytic CO₂ reduction, J. Colloid Interf. Sci. 651 (2023) 726–733.
- [19] Q.J. Ye, R. Yang, L.H. Huang, Q. Li, Q. Zhang, D. Li, D. Tian, D.L. Jiang, Bridging engineering of polymeric carbon nitride for boosting photocatalytic CO₂ reduction, J. Colloid Interf. Sci. 652 (2023) 813–824.
- [20] Z.L. Wang, R.L. Liu, J.F. Zhang, K. Dai, S-scheme porous g-C₃N₄/Ag₂MoO₄ heterojunction composite for CO₂ photoreduction, Chin. J. Struct. Chem. 41 (2022) 2206015–2206022.
- [21] F.Y. Yang, J.F. Qu, Y. Zheng, Y.H. Cai, X.G. Yang, C.M. Li, J.D. Hu, Recent advances in high-crystalline conjugated organic polymeric materials for photocatalytic CO₂ conversion, Nanoscale 14 (2022) 15217–15241.
- [22] P. Chen, X.A. Dong, M. Huang, K.L. Li, L. Xiao, J.P. Sheng, S. Chen, Y. Zhou, F. Dong, Rapid self-decomposition of g-C₃N₄ during gas-solid photocatalytic CO₂ reduction and its effects on performance assessment, ACS Catal. 12 (2022) 4560–4570.
- [23] M. Chen, M.R. Guo, M.M. Zhai, J.X. Xu, L. Wang, Manipulating electronic structure and light absorption of carbon nitride via P-doping and local crystallization for efficient photocatalytic reduction of CO₂, J. CO₂ Util. 68 (2023) 102392–102402.
- [24] A.X. Deng, E. Zhao, Q. Li, Y. Sun, Y.Z. Liu, S.G. Yang, H. He, Y. Xu, W. Zhao, H. O. Song, Z.P. Xu, Z. Chen, Atomic cobalt–silver dual-metal sites confined on carbon nitride with synergistic Ag nanoparticles for enhanced CO₂ photoreduction, ACS Nano 17 (2023) 11869–11881.
- [25] S. Hu, P.Z. Qiao, X.L. Yi, Y.M. Lei, H.L. Hu, J.H. Ye, D.F. Wang, Selective photocatalytic reduction of CO₂ to CO mediated by silver single atoms anchored on tubular carbon nitride, Angew. Chem. Int. Ed. 62 (2023) 202304585–202304605.
- [26] X.L. Shi, P.F. An, Q. Zhang, Q. Song, D.L. Jiang, D. Tian, D. Li, Synergy of nitrogen vacancies and Fe₂P cocatalyst on graphitic carbon nitride for boosting photocatalytic CO₂ conversion, Chem. Eng. J. 446 (2022) 137096–137105.
- [27] X.D. Zhang, J. Yan, F.Y. Zheng, J. Zhao, L. Lee, Designing charge transfer route at the interface between WP nanoparticle and g-C₃N₄ for highly enhanced photocatalytic CO₂ reduction reaction, Appl. Catal. B: Environ. 286 (2021) 119879–119887.
- [28] W.C. Wang, Y. Tao, L.L. Du, Z. Wei, Z.P. Yan, W.K. Chan, Z.C. Lian, R.X. Zhu, D. L. Phillips, G.S. Li, Femtosecond time-resolved spectroscopic observation of long-lived charge separation in bimetallic sulfide/g-C₃N₄ for boosting photocatalytic H₂ evolution, Appl. Catal. B: Environ. 282 (2021) 119568–119576.

- [30] Q. Zhang, M.Z. Sun, C.Y. Yuan, Q.W. Sun, B.L. Huang, H. Dong, Y.W. Zhang, Strong electronic coupling effects at the heterojunction interface of SnO₂ nanodots and g-C₃N₄ for enhanced CO₂ electroreduction, ACS Catal. 13 (2023) 7055–7066.
- [31] X. Chen, Y.J. Chen, X. Liu, Q. Wang, L.G. Li, L.Z. Du, G.H. Tian, Boosted charge transfer and photocatalytic CO₂ reduction over sulfurdoped C₃N₄ porous nanosheets with embedded SnS₂-SnO₂ nanojunctions, Sci. China Mater. 65 (2022) 400–412.
- [32] Y. Li, Q. Yin, Y.S. Zeng, Z. Liu, Hollow spherical biomass derived-carbon dotted with SnS₂/g-C₃N₄ Z-scheme heterojunction for efficient CO₂ photoreduction into CO, Chem. Eng. J. 438 (2022) 135652–135666.
- [33] W. Ali, X.L. Zhang, X.X. Zhang, S. Ali, L.N. Zhao, S. Shaheen, L.Q. Jing, Improved visible-light activities of g-C₃N₄ nanosheets by co-modifying nano-sized SnO₂ and Ag for CO₂ reduction and 2,4-dichlorophenol degradation, Mater. Res. Bull. 122 (2020) 110676–110686.
- [34] L.Q. Yang, J.F. Huang, L. Shi, L.Y. Cao, H.M. Liu, Y.Y. Liu, Y.X. Li, H. Song, Y.N. Jie, J.H. Ye, Sb doped SnO₂-decorated porous g-C₃N₄ nanosheet heterostructures with enhanced photocatalytic activities under visible light irradiation, Appl. Catal. B: Environ. 221 (2018) 670–680.
- [35] F.Y. Su, Y.L. Chen, R.P. Wang, S. Zhang, K.C. Liu, Y.Z. Zhang, W. Zhao, C.H. Ding, H.Q. Xie, L.Q. Ye, Diazanyl and SnO₂ bi-activated g-C₃N₄ for enhanced photocatalytic CO₂ reduction, Sustain. Energy Fuels 5 (2021) 1034–1043.
- [36] F. Mo, Q.X. Zhou, W.D. Xue, W.T. Liu, S.Z. Xu, Z.L. Hou, J.L. Wang, Q. Wang, The optimized catalytic performance of single-atom catalysts by incorporating atomic clusters or nanoparticles: In-depth understanding on their synergisms, Adv. Energy Mater. 13 (2023) 2301711–2301733.
- [37] L.B. Wang, H.Y. Tan, L.Y. Zhang, B. Cheng, J.G. Yu, In-situ growth of few-layer graphene on ZnO with intimate interfacial contact for enhanced photocatalytic CO₂ reduction activity, Chem. Eng. J. 411 (2021) 128501–128513.
- [38] M.R. Guo, M. Chen, J.X. Xu, C. Wang, L. Wang, C, N-vacancies and Br dopant coenhanced photocatalytic H₂ evolution of g-C₃N₄ from water and simulated seawater splitting, Chem. Eng. J. 461 (2023) 142046–142053.
- [39] E. Alwin, W. Nowicki, R. Wojcieszak, M. Zieliński, M. Pietrowski, Elucidating the structure of the graphitic carbon nitride nanomaterials via X-ray photoelectron spectroscopy and X-ray powder diffraction techniques, Dalton Trans. 49 (2020) 12805–12813.
- [40] M.M. Zhai, Y. Zhang, J.X. Xu, H.F. Lin, J. Wang, L. Wang, Nickel hydroxidedecorating potassium-doped graphitic carbon nitride for boosting photocatalytic carbon dioxide reduction, J. Colloid Interf. Sci. 650 (2023) 1671–1678.
- [41] J.M. Luo, H.N. Han, X.L. Wang, X.Z. Qiu, B. Liu, Y.L. Lai, X.Y. Chen, R.M. Zhong, L. Wang, C.Y. Wang, Single-atom Nb anchored on graphitic carbon nitride for boosting electron transfer towards improved photocatalytic performance, Appl. Catal. B: Environ. 328 (2023) 122495–122509.
- [42] C. Yang, Q.Y. Tan, Q. Li, J. Zhou, J.J. Fan, B. Li, J. Sun, K.L. Lv, 2D/2D Ti₃C₂ MXene/g-C₃N₄ nanosheets heterojunction for high efficient CO₂ reduction photocatalyst: Dual effects of urea, Appl. Catal. B: Environ. 268 (2020) 118738–118749.
- [43] Y.Y. Yu, X.A. Dong, P. Chen, Q. Geng, H. Wang, J.Y. Li, Y. Zhou, F. Dong, Synergistic effect of Cu single atoms and Au–Cu alloy nanoparticles on TiO₂ for efficient, ACS Nano 15 (2021) 14453–14464.
- [44] X.Z. Feng, R.J. Zheng, C.Y. Gao, W.F. Wei, J.G. Peng, R.H. Wang, S.H. Yang, W. S. Zou, X.Y. Wu, Y.F. Ji, H. Chen, Unlocking bimetallic active sites via a desalination strategy for photocatalytic reduction of atmospheric carbon dioxide, Nature Commun. 13 (2022) 2146–2154.
- [45] X.Y. Wu, Y. Li, G.K. Zhang, H. Chen, J. Li, K. Wang, Y. Pan, Y. Zhao, Y.F. Sun, Y. Xie, Photocatalytic CO₂ conversion of M_{0.33}WO₃ directly from the air with high selectivity: Insight into full spectrum induced reaction mechanism, J. Am. Chem. Soc. 141 (2019) 5267–5274.