Highly efficient and selective photoreduction of CO$_2$ to CO with nanosheet g-C$_3$N$_4$ as compared with its bulk counterpart

Yaxin Qin$^{a}$, Guohui Dong$^{b}$, Lizhi Zhang$^{c, *}$, Guying Li$^{a}$, Taicheng An$^{a, *}$

$^{a}$ Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou, 510006, China
$^{b}$ School of Environmental Science and Engineering, Shaanxi University of Science and Technology, Xi’an, 710021, China
$^{c}$ Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, Institute of Environmental Chemistry, College of Chemistry, Central China Normal University, Wuhan, 430079, China

**A B S T R A C T**

Artificial photoreduction of CO$_2$ to clean energy utilizing the unlimited solar energy has shown promise to suppress the greenhouse effect and alleviate the energy shortage. In this study, a simple one-step calcination method was utilized to synthesize ultrathin nanosheet g-C$_3$N$_4$ (NS-g-C$_3$N$_4$). The prepared NS-g-C$_3$N$_4$ with a thickness of 10 nm was demonstrated to exhibited higher efficiency and selectivity than that of bulk counterpart (B-g-C$_3$N$_4$) for the photocatalytic reduction of CO$_2$ to CO under visible light irradiation. The yield of CO in the system with obtained NS-g-C$_3$N$_4$ was 5.8 times higher than that of B-g-C$_3$N$_4$. CO was measured to be the sole product detected in the system with NS-g-C$_3$N$_4$, while CO$_2$ can be reduced into CO, CH$_4$ and CH$_3$OH in the system with B-g-C$_3$N$_4$ under the same photocatalytic reduction conditions. The ultrathin nanostructures and abundant surface defect sites of NS-g-C$_3$N$_4$ could enhance the visible light adsorption efficiency, favor the separation and transfer of photogenerated carriers, and provide strong chemisorption sites for CO$_2$. The prepared NS-g-C$_3$N$_4$ exhibited excellent stability for NS-g-C$_3$N$_4$. The obtained also NS-g-C$_3$N$_4$ exhibited excellent stability for CO$_2$ photoreduction. More importantly, the surface defects of nanosheet could shift the adsorption mode of CO$_2$ from N-CO$_2$ for the B-g-C$_3$N$_4$ to N-O-C-O for NS-g-C$_3$N$_4$, and eventually contributing the selective photoreduction of CO$_2$ to CO. The obtained also NS-g-C$_3$N$_4$ exhibited excellent stability for CO$_2$ photoreduction. No significant change in the photoreduction efficiency of CO$_2$ in the system with NS-g-C$_3$N$_4$ was observed after four cycles. This study could not only provide a novel strategy to realize the high selectivity and efficiency photocatalytic conversion CO$_2$ to CO, but also aims to clarify the interactions between the adsorption model of CO$_2$ on g-C$_3$N$_4$ surface and the selectivity and efficiency of CO$_2$ photoreduction.

1. Introduction

CO$_2$ is the main contributor to the global warming due to its greenhouse effect, which could result in a mean rise in global temperature of 2.4°C–4.5°C (Davis et al., 2010). About 80% of CO$_2$ emission is related with energy usage, for example, non-renewable and indispensable fossil fuel. With the slathness consumption of fossil fuels and the growing concern about the rising levels of CO$_2$ in the atmosphere, the green conversion of CO$_2$ into higher energy compounds, such as carbon monoxide, methanol, and methane, has been receiving increasing attention (Appel et al., 2013; Indrakanti et al., 2009; Tornow et al., 2012). Considering the inertness and stability of CO$_2$ ($\Delta G^\circ = -394.36$ kJ/mol), most conversion methods are found to difficult due to high energy input, such as high-temperature or high-pressure conditions (Goettmann et al., 2007; Habisreutinger et al., 2013; Luo et al., 2018). Therefore, the conversion of CO$_2$ under mild conditions is one of the most important and challenging topics in scientific and technological fields. Since Inoue et al. first reported the photoelectrochemical reduction of CO$_2$ to produce organic fuels, HCOOH, HCHO, CH$_4$, and CH$_3$OH using semiconductors as photocatalyst (Inoue et al., 1979), many researches have made considerable efforts to develop the effective CO$_2$ photoreduction technology (Jiang et al., 2018). In the past decades, several kinds of semiconductors, such asWO$_3$ (Jin et al., 2015), Ga$_2$O$_3$ (Kattel et al., 2017), TiO$_2$ (Ji and Luo 2016; Mei et al., 2020), ZnGa$_2$O$_4$ (Liu et al., 2010), and BaLa$_2$Ti$_4$O$_{15}$ (Iizuka et al., 2011), have been reported for efficient CO$_2$ photoreduction (Wang et al., 2012; Zhai et al., 2018).
2013; Zhang et al., 2012). However, these photocatalysts can only reduce CO\textsubscript{2} under UV light and/or require sacrificial reducing agents, such as trialkylamines and trialkanolamines (Wu et al., 2019; Yu et al., 2019; Yu et al., 2016). That is, these kind technologies reduce CO\textsubscript{2} still reminded a lot of challenges.

In our early work, we have reported that graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) could photochemically reduce CO\textsubscript{2} to CO in the presence of water vapor under visible light (λ > 420 nm) (Dong and Zhang 2012). However, the efficiency of the process was relatively low due to the low specific surface area and the weak charge separation property of g-C\textsubscript{3}N\textsubscript{4}. Numerous attempts have been also made to modify g-C\textsubscript{3}N\textsubscript{4} by doping with metals and constructing heterojunction for the enhancement efficiencies of CO\textsubscript{2} photoreduction (Lin et al., 2014; Mao et al., 2013; Ohno et al., 2014; Wang et al., 2020b). For example, the modification of Pd and Pt could reduce the reaction barrier of g-C\textsubscript{3}N\textsubscript{4} for CO\textsubscript{2} reduction (Ghosh et al., 2020; Yang et al., 2021), and WO\textsubscript{3}, CeO\textsubscript{2}, ZnO, etc. were also employed to construct g-C\textsubscript{3}N\textsubscript{4} based heterostructure photocatalysts for CO\textsubscript{2} reduction (Ray et al., 2020; Wen et al., 2020). Notably, all these attempts aimed to inhibit the recombination of photogenerated electron-hole pairs and improve the transfer efficiencies of photogenerated carriers. However, besides photogenerated carriers transfer efficiencies, the CO\textsubscript{2} photoreduction efficiencies also depends on the CO\textsubscript{2} adsorption capability and adsorption model (Guo et al., 2020; Rodríguez et al., 2012; Wang et al., 2020a). The strong adsorption bond between CO\textsubscript{2} and semiconductor facilitates easier CO\textsubscript{2} reduction. Meanwhile, the model of electron reception may be related to the adsorption model of CO\textsubscript{2}. Therefore, the different adsorption approaches may contribute to different CO\textsubscript{2} photoreduction efficiencies and different reduction products. However, to the best of our knowledge, no systematic studies were reported in the literature about the relationship between the CO\textsubscript{2} photoreduction efficiency and the CO\textsubscript{2} adsorption capability as well as adsorption model on C\textsubscript{3}N\textsubscript{4} has been reported to date. Therefore, it is of great importance and challenge to understand the effect of adsorption mechanism of CO\textsubscript{2} onto g-C\textsubscript{3}N\textsubscript{4} photocatalyst.

The adsorption capability and adsorption manner of CO\textsubscript{2} are dependent on the surface structure of the photocatalysts (Mishra and Nanda 2020; Sun et al., 2020; Tang and Luo 2013). According to previous reports, bulk g-C\textsubscript{3}N\textsubscript{4} (B-g-C\textsubscript{3}N\textsubscript{4}) typically exhibit bulk semiconductor behavior (Dong et al., 2012; Kong et al., 2018). Recent experimental studies have demonstrated that nano-sheet semiconductor would have quite different gas sensing pattern than bulk semiconductor due to different surface structures (Andringa et al., 2011; Na et al., 2011). So, nanosheet g-C\textsubscript{3}N\textsubscript{4} (NS-g-C\textsubscript{3}N\textsubscript{4}) may have considerably different from B-g-C\textsubscript{3}N\textsubscript{4} in CO\textsubscript{2} photoreduction pattern. However, this effect has yet to be deeply investigated in the literature. For this reason, a simple method was developed in this study to distinguish the g-C\textsubscript{3}N\textsubscript{4} structure from bulk to nanosheet. The detailed structural information and CO\textsubscript{2} photoreduction activity of NS-g-C\textsubscript{3}N\textsubscript{4} are systemically discussed and compared with B-g-C\textsubscript{3}N\textsubscript{4}. Simultaneously, the CO\textsubscript{2} photoreduction mechanisms with different types of g-C\textsubscript{3}N\textsubscript{4} are also carefully attempted to clarify the factors affecting the efficiency and selectivity of CO\textsubscript{2} conversion. The purpose of this study aims to provide more detail information of NS-g-C\textsubscript{3}N\textsubscript{4} as a potential catalyst for the CO\textsubscript{2} photoreduction and open new avenues for further exploration of CO\textsubscript{2} selective conversion.

2. Materials and methods

2.1. Preparation of catalysts

All chemicals used in this study were analytical-grade reagents without further purification. Nanosheet graphitic carbon nitride (NS-g-C\textsubscript{3}N\textsubscript{4}) was synthesized by mixing melamine (1 g) with cyanuric acid (2 g) in an agate mortar. The resultant mixture was put into a combustion boat. Then, this boat was placed in a tube furnace and heated to 550 °C for 4 h under the N\textsubscript{2} atmosphere to obtain the final samples. For the comparison, bulk graphitic carbon nitride (B-g-C\textsubscript{3}N\textsubscript{4}) was also prepared by heating melamine (3 g) with the same heating procedures.

2.2. Characterisation

The crystal structures of the prepared catalysts were analyzed by Bruker D8 Advance X-ray diffractometer (XRD) with Cu K\textalpha radiation. The morphology of the final samples was analyzed by transmission electron microscopy (TEM, JEOL JSM-5510), and the elementary composition of resulted samples was measured by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C). The defects of result samples were analyzed by Electron paramagnetic resonance (EPR) at room temperature (298 K) with a Bruker ESR A300 spectrometer. The light absorption of prepared samples was obtained using a UV–vis spectrometer (Shimadzu UV-3600) by using BaSO\textsubscript{4} as a reference. The recombination rate of photogenerated carriers was obtained using a fluorescence spectrometer (Hitachi F-4500) at 293 K. The nitrogen adsorption and desorption isotherms were measured at 77 K using Micrometrics ASAP2020 system after samples were vacuumly dried at 180 °C overnight. Infrared spectroscopy (IR) spectra were also recorded on a Nicolet iS50 spectrometer (Thermo) equipped with a liquid nitrogen cooled MCT detector.

2.3. Photocatalytic activity measurement

The experiments of CO\textsubscript{2} photoreduction with H\textsubscript{2}O on NS-g-C\textsubscript{3}N\textsubscript{4} and B-g-C\textsubscript{3}N\textsubscript{4} were carried out in a homemade closed gas system. Compressed CO\textsubscript{2} (99.999%, Praxair) was used as the carbon source. In the experiment, 0.1 g of photocatalyst was added into 50 mL of 50 g/L KHCO\textsubscript{3} aqueous solution in a reaction cell with cooling water jacket outside. CO\textsubscript{2} was bubbled through this solution for 1 h to establish an adsorption-desorption balance and saturate the solution with CO\textsubscript{2}. Then, the reactor was sealed and shined with visible light. A 300 W Xenon lamp with a 420 nm cut-off filter was chosen as a visible light source. During the irradiation, about 0.5 mL of gas was taken from the reaction cell at given intervals for subsequent CO concentration analysis with a gas chromatograph (GC-14B, Shimadzu Corp., Japan) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID).

2.4. In-situ DRIFTS analysis for CO\textsubscript{2} photoreduction

The experiment of in-situ diffuse reflectance infrared Fourier transform spectroscopic (DRIFTS) of CO\textsubscript{2} adsorption and photoreduction was recorded on the NS-g-C\textsubscript{3}N\textsubscript{4} and B-g-C\textsubscript{3}N\textsubscript{4}. Typically, 5 mg of the above photocatalyst was pressed into the sample cell, which was then thoroughly vacuum-treated to completely remove air. Then, the background was collected at room temperature. After that, CO\textsubscript{2} and H\textsubscript{2}O vapor were passed through the sample cell at 2.0 mL/min for 1 h to establish an adsorption-desorption balance. Then, the sample cell was sealed shined with visible light. Meanwhile, the IR spectrum was recorded as a function of time.

2.5. Electrochemical and photoelectrochemical experiments

Electrochemical impedance spectroscopy Nyquist analysis Mott-Schottky analysis was conducted on CHI 660C electrochemical workstation (Shanghai Chenhua, China) to study the semiconducting behavior of the final samples. In measurement process, platinum plate (1 × 1 cm\textsuperscript{2}) and saturated calomel electrode were chosen as counter electrode and reference electrode, respectively. The working electrode (Preparation method was described in the next paragraph) was immersed in electrolyte solution (0.1 M KCl). Photocurrent curves of result samples were measured with i-t curve method. Nyquist plots were measured by using the AC impedance method. The visible light source using in this test was generated from a 300 W Xe lamp with a 420 nm
cutoff filter.

The working electrode was prepared as described in our previous report. Typically, the mixture of photocatalyst and distilled water was grinded into aqueous slurries, which were then spin-coated on indium tin oxide (ITO) glass substrate. This prepared electrode was dried in air and annealed at 200 °C for 1 h as the final working electrode.

3. Results and discussion

3.1. Characterization of prepared catalysts

As shown in Fig. 1a, the morphology of B-g-C₃N₄ synthesized with melamine was found to be thick plate structure by using TEM. Unexpectedly, when the mixture of melamine and cyanuric acid was used as precursor, the obtained NS-g-C₃N₄ sample was found to be composed of ultrathin nanosheets with a thickness of 10 nm (Fig. 1b). As the formation route of g-C₃N₄ shown in Fig. 1c, melamine could form B-g-C₃N₄ with thick plate structure by an assembly approach during calcination process. With the addition of cyanuric acid, the released NH₃ with thick plate structure by an assembly approach during calcination process. With the addition of cyanuric acid, the released NH₃ from the decomposition of cyanuric acid can burst the bulk B-g-C₃N₄ to form NS-g-C₃N₄ (Fig. 2a). As shown in Fig. 1a, the morphology of B-g-C₃N₄ was confirmed by TEM images of (a) B-g-C₃N₄ and (b) NS-g-C₃N₄. As shown in Fig. 1d, the EPR signal intensity of NS-g-C₃N₄ was 38 μmol/L with the same 6 h duration, which was about 5.8 times than that of B-g-C₃N₄ (Fig. 2a). Evidently, NS-g-C₃N₄ due to the formation of carbon vacancy after the layer-peeling decreased the number of unpaired electrons.

3.2. Photocatalytic reduction of CO₂

Then, the photocatalytic activities of both prepared g-C₃N₄ catalysts were comparably investigated in CO₂ photoreduction experiments under visible light. Control experiments showed that no other kinds of reduction products can be detected in the absence of either the photocatalyst or visible light irradiation, indicating that both photocatalysts and visible light are necessary for the present system of photocatalytic CO₂ reduction (Fig. 2). In the system with B-g-C₃N₄, CO₂ can be reduced into CO and CH₄ in the presence of water vapor (Fig. 2a and b). After visible light irradiation for 6 h, the yields of CO and CH₄ over B-g-C₃N₄ were obtained as 6.6 and 0.98 μmol/L, respectively. Aside from CO and CH₄, CH₃OH in the liquid phase was also detected (Fig. 2c). But CO was measured to be the sole product detected in the system with NS-g-C₃N₄ under the same photocatalytic reduction conditions. The yield of CO with NS-g-C₃N₄ was 38 μmol/L with the same 6 h duration, which was about 5.8 times than that of B-g-C₃N₄ (Fig. 2a). Evidently, NS-g-C₃N₄ exhibited higher reactivity in the photoreduction of CO₂ to CO. More importantly, no other products, such as CH₄ and CH₃OH, were observed.
for NS-g-C\textsubscript{3}N\textsubscript{4} (Fig. 2d), showing that NS-g-C\textsubscript{3}N\textsubscript{4} possessed high selectivity in the photoreduction of CO\textsubscript{2} to CO. In addition, no reduced C1 or C2 products were detected over both B-g-C\textsubscript{3}N\textsubscript{4} and NS-g-C\textsubscript{3}N\textsubscript{4} when CO\textsubscript{2} was replaced by Ar under visible light irradiation (Fig. 2e). These results strongly evidenced that CO\textsubscript{2} is the only source to generate CO and CH\textsubscript{4} in both g-C\textsubscript{3}N\textsubscript{4} systems.

### 3.3. Catalytic activity and selectivity mechanism

As well-known, semiconductor photocatalysts mediating CO\textsubscript{2} reduction need to absorb light energy, generate electrons, and then transfer these electrons to CO\textsubscript{2}. The generation of photogenerated electrons strongly depends on the band gap of the photocatalyst. Therefore, the UV–vis absorption spectra of B-g-C\textsubscript{3}N\textsubscript{4} and NS-g-C\textsubscript{3}N\textsubscript{4} were measured to verify their absorption edges and band gaps (Fig. 3a). Compared with B-g-C\textsubscript{3}N\textsubscript{4}, the intrinsic absorption edge of NS-g-C\textsubscript{3}N\textsubscript{4} showed an obvious blue shift. Therefore, the band gap of NS-g-C\textsubscript{3}N\textsubscript{4} (2.8 eV) is slightly bigger than that of B-g-C\textsubscript{3}N\textsubscript{4} (2.7 eV). Additionally, the light absorption range of NS-g-C\textsubscript{3}N\textsubscript{4} extended to the whole visible light region, even in the infrared region. The light absorption in the long

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**Fig. 2.** CO (a), CH\textsubscript{4} (b), and CH\textsubscript{3}OH (c) generation in different systems. (d) The species of CO\textsubscript{2} photoreduction products with B-g-C\textsubscript{3}N\textsubscript{4} and NS-g-C\textsubscript{3}N\textsubscript{4}. (e) CO, CH\textsubscript{4}, and CH\textsubscript{3}OH generation in the B-g-C\textsubscript{3}N\textsubscript{4}/Ar and NS-g-C\textsubscript{3}N\textsubscript{4}/Ar systems.

**Fig. 3.** UV–vis absorption and diffuse reflectance spectra (inset) of B-g-C\textsubscript{3}N\textsubscript{4} and NS-g-C\textsubscript{3}N\textsubscript{4} (a). The Photoluminescence spectra (b), photocurrent response (c), and Nyquist plots (d) of B-g-C\textsubscript{3}N\textsubscript{4} and NS-g-C\textsubscript{3}N\textsubscript{4}.
wavelength may be caused by the electronic excitation from the valence band of NS-g-C\textsubscript{3}N\textsubscript{4} to the defect state of NS-g-C\textsubscript{3}N\textsubscript{4}. Based on above characterization results and analysis, we believe that NS-g-C\textsubscript{3}N\textsubscript{4} exhibited higher yields of photogenerated electrons than B-g-C\textsubscript{3}N\textsubscript{4}.

After the photoexcitation, the photogenerated electrons could either recombine with photogenerated holes, or migrate to the surface of photocatalyst for subsequent chemical reactions. The transfer distance of photogenerated electrons between excitation sites and surface depends on the morphology of the semiconductors. As a kind of stratified material, the electron transfer from bulk phase to the surface of g-C\textsubscript{3}N\textsubscript{4} must consume energy to span the space between different layers. The fewer g-C\textsubscript{3}N\textsubscript{4} layers would lead the easier electron transfer from bulk phase to the surface. Therefore, the change of morphology from thick plate to ultrathin nanosheets may shorten the migration distance, decrease the required energy, and favor the separation and transfer of photogenerated carriers, and thus help the migration of bulk phase electrons to the surface of NS-g-C\textsubscript{3}N\textsubscript{4}. So, photoluminescence (PL) measurements were further employed to study the separation efficiencies of photogenerated carriers in B-g-C\textsubscript{3}N\textsubscript{4} and NS-g-C\textsubscript{3}N\textsubscript{4} samples. Fig. 3\textit{b} shows the PL emission spectra of the two compared samples under the excitation of 330 nm wavelength light. The strong emission peak of B-g-C\textsubscript{3}N\textsubscript{4} around 455 nm was derived from the direct electrons photoexcitation and separation of photogenerated carriers, and eventually produce more photoelectrons than B-g-C\textsubscript{3}N\textsubscript{4}, indicating that the resistances of charge recombine with photogenerated holes, or migrate to the surface of ground phase to the surface. Therefore, the change of morphology from thick plate to ultrathin nanosheets may shorten the migration distance, decrease the required energy, and favor the separation and transfer of photogenerated carriers, and thus help the migration of bulk phase electrons to the surface of NS-g-C\textsubscript{3}N\textsubscript{4}.

Based on the result of UV-vis absorption spectra and PL emission spectra of these two samples, the layer-peeling would favor the generation and separation of photogenerated carriers, and eventually produce more electrons to reduce CO\textsubscript{2}. Unexpectedly, the photocurrent generated on NS-g-C\textsubscript{3}N\textsubscript{4} electrode was significantly lower than that of the B-g-C\textsubscript{3}N\textsubscript{4} (Fig. 3\textit{c}). Meanwhile, NS-g-C\textsubscript{3}N\textsubscript{4} exhibited lower reactivity in the photoreduction of Cr(VI), whose activity was merely 1/4.6 that of B-g-C\textsubscript{3}N\textsubscript{4}. These results confirmed that the defects on the NS-g-C\textsubscript{3}N\textsubscript{4} surface were the chemical adsorption sites of CO\textsubscript{2}. Stronger adsorption bond facilitated easier electron transfer. Thus, the chemisorption site on NS-g-C\textsubscript{3}N\textsubscript{4} surface could facilitate the transfer of confined photogenerated electrons to the adsorbed CO\textsubscript{2} to, and thus accelerate its photocatalytic reduction (Fig. 4\textit{b}).
In order to further demonstrate that the CO$_2$ chemical adsorption sites of NS-g-C$_3$N$_4$ are presented as the defects, photodeposition of Pd was carried out to cover the defect sites. If the defects are the chemical adsorption sites of CO$_2$, the deposition of Pd will inhibit the photoreduction of CO$_2$. As shown in Fig. 4c, the loading of Pd onto NS-g-C$_3$N$_4$ can completely suppress the formation of CO. These results may be attributed to two reasons. The first reason is that photogenerated electrons are confined in the defect sites. The Pd particles selectively deposited on the defect sites would cover the defect sites, and thus block the transfer of confined photogenerated electrons to CO$_2$ (Fig. 4d). The second reason is that the platinum group metals are generally difficult to absorb CO$_2$ due to their considerable work function as the similar results from the reference (Liu et al., 1991). Therefore, these results further confirming that CO$_2$ was mainly chemi-adsorbed on the surface defects of NS-g-C$_3$N$_4$.

According to previous reports, the carbon atom of CO$_2$ has a partial positive charge, making its gas behave as a Lewis acid. Meanwhile, the bridging N atom of g-C$_2$N$_4$ could act as a Lewis base (Kim and Kim 2007). We therefore supposed that CO$_2$ can interact with the bridging N atom via Lewis acid-base interactions. To test this speculation, the bridging N was replaced with a C atom using a previous method (Dong et al. 2012; Zhang et al., 2010). Fig. 5a shows that the substation of CO$_2$ from the reference (Liu et al., 1991). Therefore, these results further confirming that CO$_2$ was mainly chemi-adsorbed on the surface defects of NS-g-C$_3$N$_4$.

For the system with B-g-C$_3$N$_4$, the photoreduction rate, confirming that the bridging N atom of NS-g-C$_3$N$_4$ may prefer to interact with the O atom of CO$_2$ rather than C atom. To test this possibility, in-situ DRIFTS spectra of CO$_2$ photoreduction was also conducted on NS-g-C$_3$N$_4$. After 1 h CO$_2$ adsorption without light irradiation, the DRIFTS spectra for NS-g-C$_3$N$_4$ were found to contain peaks associated with CO$_2$, C=O, and O–N–O at 2350, 1644, and 1010 cm$^{-1}$ (Fig. 7a). Compared with the case of B-g-C$_3$N$_4$, the disappearance of –CO$_2$ confirmed that the adsorption mode of CO$_2$ on NS-g-C$_3$N$_4$ was really different from that on B-g-C$_3$N$_4$. Meanwhile, the formation of N–O further confirmed that CO$_2$ was adsorbed on NS-g-C$_3$N$_4$ by the interaction between the O atom of CO$_2$ and the bridging N atom of NS-g-C$_3$N$_4$. After visible light irradiation, the peak intensity of CO$_2$ decreased significantly, showing the excellent activity of NS-g-C$_3$N$_4$ for CO$_2$ photoreduction. Meanwhile, the apparent decrease found in the peak intensity of C=O was attributed to CO release. Moreover, the new band at 3452 cm$^{-1}$, which can be attributed to the surface hydroxyl group, was believe to be generated from the residual O atom of adsorbed CO$_2$. Aside from the hydroxyl group, no other bands were formed in the spectrum, confirming the high selectivity of NS-g-C$_3$N$_4$ in the photoreduction of CO$_2$ to CO. Based on the above mechanism analyses and experimental results, we concluded that the first step of CO$_2$ photoreduction over NS-g-C$_3$N$_4$ is the formation of the N–O=C=O group (Fig. 7b). Then, the C=O single bond of N–O=C=O is severed by the photogenerated electrons, thereby releasing the end product, CO. The change in adsorption mode of CO$_2$, which was mainly attributable to the defects, and was the origin of the high selectivity of NS-g-C$_3$N$_4$ in the photoreduction of CO$_2$ to CO.

![Fig. 5](https://example.com/fig5.png)  
Fig. 5. (a) CO generation amount in different systems. (b) The adsorption models of CO$_2$ on NS-g-C$_3$N$_4$. 

hand, the –C=O group can be stabilized by accepting proton and forming –CH=O. Subsequently, –CH=O accepts electrons and protons, thereby converting to –CH$_2$–OH. Evidently, the by-product at this stage is CH$_3$OH. Finally, –CH$_2$–OH can be further reduced to –CH$_3$ and release the end product, CH$_4$.

Based on the reduction pathway of CO$_2$ over B-g-C$_3$N$_4$, two possible reasons for the high selectivity of NS-g-C$_3$N$_4$ in the photoreduction of CO$_2$ to CO have been proposed. The first possible reason may be that the layer-peeling changed the surface charge situation from negative to positive. The positively charged surface of NS-g-C$_3$N$_4$ would not absorb protons, so the product of CO$_2$ photoreduction over NS-g-C$_3$N$_4$ is only CO. Therefore, we investigated the surface charge situation of B-g-C$_3$N$_4$ and NS-g-C$_3$N$_4$ by measuring their zeta potentials, and the zeta potentials of NS-g-C$_3$N$_4$ achieved the peak intensity of CO$_2$ at 3452 cm$^{-1}$, which is CH$_3$OH. Finally, –CH$_2$–OH can be further reduced to –CH$_3$ and release the end product, CH$_4$. The second possible reason is that the adsorption mechanism of CO$_2$ on NS-g-C$_3$N$_4$ is different from that on B-g-C$_3$N$_4$. Given that the NS-g-C$_3$N$_4$ defects are located on the bridging N atoms, the bridging N atom can be changed from being a Lewis base site to a Lewis acid site. In addition, the oxygen atoms of CO$_2$ can act as Lewis base due to the partial negative charges. As a result, the bridging N atom of NS-g-C$_3$N$_4$ may interact with CO$_2$ rather than C atom. To test this possibility, in-situ DRIFTS spectra of CO$_2$ photoreduction was also conducted on NS-g-C$_3$N$_4$. After 1 h CO$_2$ adsorption without light irradiation, the DRIFTS spectra for NS-g-C$_3$N$_4$ were found to contain peaks associated with CO$_2$, C=O, and O–N–O at 2350, 1644, and 1010 cm$^{-1}$ (Fig. 7a). Compared with the case of B-g-C$_3$N$_4$, the disappearance of –CO$_2$ confirmed that the adsorption mode of CO$_2$ on NS-g-C$_3$N$_4$ was really different from that on B-g-C$_3$N$_4$. Meanwhile, the formation of N–O further confirmed that CO$_2$ was adsorbed on NS-g-C$_3$N$_4$ by the interaction between the O atom of CO$_2$ and the bridging N atom of NS-g-C$_3$N$_4$. After visible light irradiation, the peak intensity of CO$_2$ decreased significantly, showing the excellent activity of NS-g-C$_3$N$_4$ for CO$_2$ photoreduction. Meanwhile, the apparent decrease found in the peak intensity of C=O was attributed to CO release. Moreover, the new band at 3452 cm$^{-1}$, which can be attributed to the surface hydroxyl group, was believe to be generated from the residual O atom of adsorbed CO$_2$. Aside from the hydroxyl group, no other bands were formed in the spectrum, confirming the high selectivity of NS-g-C$_3$N$_4$ in the photoreduction of CO$_2$ to CO. Based on the above mechanism analyses and experimental results, we concluded that the first step of CO$_2$ photoreduction over NS-g-C$_3$N$_4$ is the formation of the N–O=C=O group (Fig. 7b). Then, the C=O single bond of N–O=C=O is severed by the photogenerated electrons, thereby releasing the end product, CO. The change in adsorption mode of CO$_2$, which was mainly attributable to the defects, and was the origin of the high selectivity of NS-g-C$_3$N$_4$ in the photoreduction of CO$_2$ to CO.
3.5. Stability of NS-g-C$_3$N$_4$ for CO$_2$ photoreduction

The recycling test was also conducted to confirm the stability of NS-g-C$_3$N$_4$ for CO$_2$ photoreduction. According to the CO$_2$ photoreduction process over NS-g-C$_3$N$_4$, the effect of recycle utilization is poorly affected because newly formed hydroxyl groups may occupy the defect sites. However, no significant change in CO$_2$ photoreduction activity was found after four cycles (Fig. S4 in the Supporting Information). Thus, the hydroxyl group was supposed to be further reduced to hydroxyl anion and then the occupied defect sites can be freed for recycle utilization. To test this hypothesis, the CO$_2$ photocatalysis reaction was also carried out in the water suspension of NS-g-C$_3$N$_4$. After 6 h of visible light irradiation, the final pH values of NS-g-C$_3$N$_4$ suspension were obviously higher than that of the initial (7.3–8.2), indicating that the hydroxyl group can be reduced to hydroxyl anion. Therefore, NS-g-C$_3$N$_4$ catalyst possesses good stability in CO$_2$ photoreduction.

4. Conclusion

In this study, we successfully distinguished the ultrathin nanosheet g-C$_3$N$_4$ catalyst from bulk (B-g-C$_3$N$_4$) one. Compared with B-g-C$_3$N$_4$, NS-g-C$_3$N$_4$ exhibited higher reactivity and selectivity in the photoreduction of CO$_2$ to CO. The excellent activity of NS-g-C$_3$N$_4$ can be attributed to the ultrathin nanostructure and surface defect sites, which can induce good absorbance of light, efficient separation and quick transfer of photo-generated carriers, and strong chemisorption of CO$_2$. More importantly is that the surface defects are located on the bridging N atoms of NS-g-C$_3$N$_4$, which induced reversal of the acid-base character of bridging N atom, changed the adsorption mechanism of CO$_2$ on g-C$_3$N$_4$ from N–CO$_2$ to N–O–C==O, and eventually resulted in higher selectivity of NS-g-C$_3$N$_4$ than that of B-g-C$_3$N$_4$. Apart from providing a new strategy to tune the behavior of semiconductors, this study also prompts deeply understanding the relationship of surface structure of catalysts with the pathway of CO$_2$ photoreduction.

Author contributions section


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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2021.110880.