Recent advances in g-C₃N₄-based photocatalysts for reduction of CO₂

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Abstract. The key to reduce the concentration of CO₂ in atmosphere by using the photocatalytic reduction method lies in the development of low-cost, stable, and environmentally friendly photocatalysts. Given that g-C₃N₄ has the advantages of non-toxic, no metal elements, narrow band gap, good thermal stability and so on, analysis shows that this is a very potential photocatalyst. However, at present, the photocatalytic efficiency of pure g-C₃N₄ is limited by small specific surface area, low visible-light utilization efficiency and high recombination rate of photogenerated charge carriers. In this review, we report the methods for improving photoactivity of the g-C₃N₄, for instance, loading precious metal cocatalysts, earth-abundant metal cocatalysts and non-metallic cocatalysts. Finally, the issues that should be paid attention to when further studying the photoreactivity of g-C₃N₄ and its future research directions are discussed.

1. Introduction

As a kind of greenhouse gas, the excessive emission of CO₂ has affected the balance of natural carbon cycle to a great extent, thus causing serious ecological problems, especially the Greenhouse Effect. Furthermore, with the development of today's society, countries all over the world are facing the present situation that coal, oil, natural gas and other energy fuels are increasingly scarce. Therefore, how to fundamentally control the emission of CO₂, capture the CO₂ to be discharged into the atmosphere and convert it into usable fuel has become one of the hot issues studied by scientists [1].

With the continuous exploration and research of CO₂ emission reduction technology, photocatalytic reduction technology came into being. Inoue et al. [2] reported the pioneering work, and since then the photocatalytic reduction of carbon dioxide has been widely studied. CO₂ photocatalytic reduction can use endless solar energy as the only energy source to directly convert CO₂ into CO or hydrocarbon fuel, providing people with a great strategy for solving energy crisis. Catalysts are core of photocatalytic technology. At present, hundreds of photocatalysts have been developed and synthesized. But most of the developed photocatalysts are wide-band gap semiconductors (such as TiO₂, etc.), resulting in low light utilization in the visible region, which accounts for about 43% of solar energy. At the same time, almost all of these photocatalysts are semiconductor photocatalysts based on transition metals, which are expensive and not conducive to large-scale use, and the leaching of metal ions is easy to cause secondary pollution to the environment. Researchers have been looking...
for and developing new low-cost, stable and environmentally friendly non-metallic photocatalysts to convert solar energy into fuel [3,4].

Graphite phase carbon nitride (g-C\(_3\)N\(_4\) or g-CN) photocatalytic materials have many advantages, such as non-toxic, no metal elements, good stability in aqueous solution with pH from 0 to 14, and belong to narrow band gap semiconductors. At the same time, it also has the advantages of strong mechanical properties and good thermal stability [5-7]. In 2009, Wang et al. [8] published the first report that hydrogen can be produced by photolysis of water under visible light using this non-metallic polymer g-C\(_3\)N\(_4\). However, the g-C\(_3\)N\(_4\) materials obtained by traditional preparation methods have small specific surface area, which causes small contact area with reactants during the catalytic reaction. Secondly, g-C\(_3\)N\(_4\) has the band gap of \(\sim 2.7\) eV, which can only absorb part of the visible-light with a wavelength of less than \(\sim 475\) nm in the solar spectrum, so the solar energy utilization efficiency is low. In addition, photogenerated charge carriers are very easily to recombine during the photocatalysis process, resulting in low catalytic efficiency. These seriously limit the practical industrial application of g-C\(_3\)N\(_4\)-based photocatalysts in the future [9,10]. In order to solve this problem, starting from the g-C\(_3\)N\(_4\)-based catalysts, this paper introduces the methods of loading precious metal cocatalysts, earth-abundant metal cocatalysts and non-metallic cocatalysts to improve the separation efficiency of charge carriers in g-C\(_3\)N\(_4\), thus promoting the conversion rate of CO\(_2\).

2. Reaction mechanism of photocatalytic reduction of CO\(_2\) with g-C\(_3\)N\(_4\) supported by cocatalysts

When it comes to g-C\(_3\)N\(_4\) semiconductor material, its conduction band position is about -1.23 eV (vs. NHE, pH=7), which is more negative than potential of the photocatalytic reduction of CO\(_2\) to CO (CO\(_2\)/CO, -0.53 eV), CH\(_4\) (CO\(_2\)/CH\(_4\), -0.24 eV), CH\(_3\)OH (CO\(_2\)/CH\(_3\)OH, -0.38 eV), HCHO (CO\(_2\)/HCHO, -0.48 eV) and HCOOH (CO\(_2\)/HCOOH, -0.61 eV) [11]. However, the photocatalytic reduction of CO\(_2\) is a typical uphill reaction, which leads to slow surface kinetics of bulk g-C\(_3\)N\(_4\). Therefore, the unfavorable factor can be conquered by loading an appropriate cocatalyst on the external of g-C\(_3\)N\(_4\), which not only reduces activation energy of the reaction, improves separation and transmission of the charges, but also accelerates reaction kinetics of the surface reduction reaction, thereby greatly enhancing the photoreactivity [12]. The schematic diagram of CO\(_2\) reduction of g-C\(_3\)N\(_4\)-based photocatalysts supported by cocatalysts is illustrated in Figure 1: (1) After being excited by light, g-C\(_3\)N\(_4\) absorbs photons whose energy is equal to or higher than the band gap energy of the semiconductors, and generates electron-hole pairs; (2) the electron-hole pairs are separated, and the electrons move to surface of the catalyst and finally migrate to the cocatalysts; (3) the photogenerated electrons react with CO\(_2\) on the cocatalysts and reduce it to various fuels such as CO, CH\(_4\) and so on. Therefore, the g-C\(_3\)N\(_4\) supported by the cocatalysts shows great application prospects in the field of CO\(_2\) photocatalytic reduction.

![Figure 1. Schematic diagram of CO\(_2\) reduction of g-C\(_3\)N\(_4\)-based photocatalysts supported by cocatalysts.](image-url)
3. Research status

3.1. Loading precious metal cocatalysts

Loading precious metal nanoparticles such as Pt, Pd, etc. on surface of the g-C3N4-based photocatalysts, as cocatalysts for photocatalytic reaction, is an important strategy to ensure the effective separation of photogenerated charge carriers. The impact of cocatalysts loading technology on the photoactivity of g-C3N4 is essentially led by a fact that the Fermi energy level of precious metal cocatalysts is usually lower than that of semiconductors. After the precious metal cocatalyst is deposited on the semiconductor surface to form contact, the Schottky barrier is formed at the interface of metal-semiconductor, which can effectually prevent the recombination of photogenerated charge carriers and prolong their lifetime [13].

Yu et al. [14] reduced CO2 to hydrocarbons through g-C3N4 deposited by Pt and found that different contents of Pt had a great effect on photoactivity and selectivity of the g-C3N4. The maximum production of CH3OH and HCHO was observed at 0.75wt% Pt content, while the maximum yield of CH4 occurred at 1wt% Pt content. Pt acts as a cocatalyst, which not only promotes the electron transfer, but also promotes the enrichment of photogenerated electrons on surface of the g-C3N4, thereby reducing CO2 better. Wang et al. [15] prepared CN-PA catalyst deposited by Pd–Ag bimetallic nanoparticles for photoreduction of CO2. The molar ratio of Pd-Ag bimetal greatly affects the photocatalytic activity and product selectivity. A lower Pd content is beneficial to the production of CO, while a higher Pd content preferably produces CH4. In addition, the yields of the CNPA photocatalyst with a Pd-Ag molar ratio of 1:2 to CO and CH4 were 5.42 μmol g⁻¹ h⁻¹ and 4.03 μmol g⁻¹ h⁻¹, respectively. This selective transformation and high productivity can be ascribed to the superior charge collection ability, distinctive optical characteristics of Pd-Ag bimetal, and activation of the g-C3N4 surface by plasmonic effect of the Pd and Ag NPs. Gao et al. [16] first studied the catalytic performance of Pt/g-CN and Pd/g-CN photocatalyst for CO2 reduction by DFT (i.e. density functional theory). It was found that HCOOH is the preferred product for photocatalytic reduction of CO2 over Pd/g-CN catalyst, while Pt/g-CN photocatalyst is more inclined to convert CO2 to CH4, which provides a novel route for experimental verification to use solar energy to transform carbon dioxide into fuel. Kuriki et al. [17] synthesized a heterogeneous photocatalyst system comprised of g-C3N4 and ruthenium complex, which can convert CO2 into HCOOH under the irradiation of visible-light. At 400 nm, the apparent quantum yield is 5.7%, which is the best value of heterogeneous photocatalyst reported so far for reducing CO2 under visible-light irradiation. In addition, many researchers have studied the mixture of ruthenium complex and g-C3N4, and found that they all show better selectivity for photocatalytic reduction of the CO2 [18-20]. Table 1 summarizes the precious metal cocatalysts supported on g-C3N4 and their photocatalytic activity.

3.2. Loading earth-abundant metal cocatalysts

Depositing precious metal cocatalysts such as Pt, Pd, etc. on g-C3N4 is a common choice to improve its photocatalytic activity. However, precious metals are scarce and expensive, which confines their large-scale practical application in the future. Therefore, it is necessary to study the earth-abundant metal cocatalysts which have both the advantages of low price and high performance. Recently, earth-abundant metal cocatalysts, such as transition metal dichalcogenide (MoS2 [21,22], WS2 [23,24]), Ni(OH)2 [25,26], etc., have attracted wide concern in the field of photocatalytic H2 evolution and pollutant degradation. However, in contrast, there are relatively few studies on the application of these earth-abundant metal cocatalysts to photocatalytic reduction of CO2 over the g-C3N4-based photocatalysts.

Metal-based cocatalysts have been used in photocatalytic CO2 reduction (CO2RR), and the combination of cocatalysts/semiconductors is expected to improve the selectivity of the reaction. Through extensive theoretical calculation and comprehensive study of the performance, reaction kinetics and adsorption/desorption thermodynamics of the catalyst, Li et al. [27] proved that compared with Au/CN which produces both CO and CH3OH, CO2 can be selectively reduced to CH4 on Cu/CN.
This is mainly due to the significantly enhanced electronic interaction between Cu and adjacent N atoms compared with Au, which provides a highly active site for selective CO$_2$RR. Zhang et al. [28] further improved its photocatalytic activity by loading Co- and Ni- species upon the surface of g-C$_3$N$_4$. The Co- species is used for the oxidation of water by capturing holes, while the Ni- species is used for the CO$_2$ reduction through capturing photogenerated electrons. The g-C$_3$N$_4$ co-modified by Co and Ni shows a significant synergistic effect and its photoactivity is 3.1 times as high as that of unmodified g-C$_3$N$_4$. Huang et al. [29] proposed that loading molybdenum nanospheres onto the surface of g-C$_3$N$_4$ is able to effectually take advantage of a wide spectral range from the ultraviolet to the near-infrared region (NIR, up to 800 nm). The enhancement of photoreactivity is due to such a fact that Mo nanospheres promote adsorption of CO$_2$ through the photothermal effect, activate the surface CO$_2$, promote the transfer of photogenerated electrons from g-C$_3$N$_4$ to Mo nanospheres, and thus prolong the lifespan of photo-generated carriers. Table 1 summarizes the earth-abundant metal cocatalysts supported on g-C$_3$N$_4$ and their photocatalytic activity.

3.3. Loading non-metallic cocatalysts

Since g-C$_3$N$_4$ is a semiconductor with poor conductivity, it is not easy to transfer electrons to the surface of g-C$_3$N$_4$ during the photocatalytic reaction, which greatly reduces the catalytic activity. Carbon materials such as carbon nanotubes, graphene, graphene oxide, etc. not only have excellent electrical conductivity, but also have a low Fermi level. On the one hand, coupling g-C$_3$N$_4$ with carbon-based components can improve the electron transport properties, thus inhibiting the recombination of charge carriers; on another hand, carbon materials have large specific surface area and good light absorption properties, which are also very beneficial to the catalytic reaction.

For the first time, Wang et al. [30] prepared new hybrid graphite carbonitride carbon composites (H-g-C$_3$N$_4$/C) via a simple method of one-step pyrolysis using natural soybean oil and melamine as the precursors, and studied the photocatalytic activity of CO$_2$ reduction. These results show that introduction of the carbon components can greatly enhance the electronic conductivity and texture characteristics of the composites. Under 9 h simulated solar radiation, the highest yields of CO and CH$_4$ were 22.6 μmol/g and 12.5 μmol/g, which were more than twice that of bulk g-C$_3$N$_4$. Lu et al.[31] synthesized g-C$_3$N$_4$/MWCNTs, a stable and highly selective CO$_2$ reduction catalyst, by connecting g-C$_3$N$_4$ with multiwall carbon nanotubes. The prepared composite material can exclusively reduce CO$_2$ to CO, and no decrease in photocatalytic activity is found even after 50 hours of the reaction. The increase in photocatalytic activity is owing to the emergence of active C-N bonds, large specific surface area and better electrical conductivity of the material. Tan et al. [32] constructed a 2D/2D hybrid heterojunction photocatalyst rGO/PCN by introducing PCN (protonated g-C$_3$N$_4$) and rGO (reduced graphene oxide). Since rGO and PCN have sufficient contact on the interface of rGO/PCN heterojunction, the charge transferring can be carried out effectively, thereby inhibiting the recombination of charge carriers. As a consequence, the CH$_4$ yield of the optimized catalyst increased significantly, which was 5.4 and 1.7 times that of PCN and rGO/CN samples, respectively. In addition, some researchers have carried out research on new non-metallic cocatalysts such as Phosphate [33] and C(CN)$_3$ [34], which play important roles in the photoreduction of CO$_2$. Table 1 summarizes the non-metallic cocatalysts supported on g-C$_3$N$_4$ and their photocatalytic activity.
Table 1. Summary of g-C\textsubscript{3}N\textsubscript{4}-based photocatalysts loaded with various cocatalysts and their photocatalytic activity.

| Material               | Cocatalyst | Main products\(^a\) | Photocatalytic activity\(^b\) | Ref. |
|------------------------|------------|----------------------|-------------------------------|------|
| Au-CN                  | Au         | CH\textsubscript{4}   | 1.55\textmu molg\(^{-1}\)h\(^{-1}\) | [13] |
| Pt/CN                  | Pt         | CH\textsubscript{4}   | 1.30\textmu molg\(^{-1}\)h\(^{-1}\) | [35] |
| C-CN                   | Pd         | CH\textsubscript{3}OH | 2.23\textmu molg\(^{-1}\)h\(^{-1}\) | [36] |
| T-CN                   | Pd         | CH\textsubscript{3}OH | 3.17\textmu molg\(^{-1}\)h\(^{-1}\) |      |
| Pd-g-C\textsubscript{3}N\textsubscript{4}/RGOA | Pd         | CH\textsubscript{4}   | 6.4\textmu molg\(^{-1}\)h\(^{-1}\) | [37] |
| Au-T/S-PCN             | Au         | CH\textsubscript{4}   | 365\textmu molg\(^{-1}\)h\(^{-1}\) | [38] |
| Cu/g-C\textsubscript{3}N\textsubscript{4} | Cu         | CH\textsubscript{4}   | 109\textmu molg\(^{-1}\)h\(^{-1}\) | [39] |
| Cu-SCN                 | Cu         | CO                   | 2.4\textmu molg\(^{-1}\)h\(^{-1}\) | [40] |
| rGO/PCN                | rGO        | CH\textsubscript{4}   | 1.393\textmu molg\(^{-1}\)h\(^{-1}\) | [32] |
| CNGA                   | GO         | CO                   | 3833\textmu molg\(^{-1}\)h\(^{-1}\) | [41] |
| GCN                    | graphene   | CH\textsubscript{4}   | 0.587\textmu molg\(^{-1}\)h\(^{-1}\) | [42] |
| MPCN                   | phosphate  | CO                   | 38.5\textmu molg\(^{-1}\)h\(^{-1}\) | [33] |
| ACNNG                  | nitrogen-doped | CH\textsubscript{3}OH | 21.178\textmu molg\(^{-1}\)h\(^{-1}\) | [43] |
| H-g-C\textsubscript{3}N\textsubscript{4}/C | carbon     | CH\textsubscript{4}   | 2.51\textmu molg\(^{-1}\)h\(^{-1}\) | [30] |

\(^a\) Only main products of the experiment are summarized here, the actual products are not limited to this.

\(^b\) The unit of photocatalytic activity is uniformly converted to \textmu molg\(^{-1}\)h\(^{-1}\).

4. Conclusions and prospect

In the past, most of the research on g-C\textsubscript{3}N\textsubscript{4}-based catalysts focused on hydrogen production [44] and pollutant degradation [45]. In contrast, there are few studies on the photoreduction of CO\textsubscript{2} over g-C\textsubscript{3}N\textsubscript{4}-based catalysts [46]. CO\textsubscript{2} is reduced by photocatalysis, and greenhouse gas is converted into fuel, thus reducing the emission of CO\textsubscript{2}, which provides a new scheme for reducing greenhouse gas emission. The excellent characteristics of g-C\textsubscript{3}N\textsubscript{4} determine its broad prospect in the field of CO\textsubscript{2} mitigation. This paper introduces the methods of loading precious metal cocatalysts, earth-abundant metal cocatalysts and non-metallic cocatalysts to enhance the photoreactivity of g-C\textsubscript{3}N\textsubscript{4}.

In the field of CO\textsubscript{2} photocatalytic reduction, some progress has been made in the design of CO\textsubscript{2} photoreduction catalysts with high reactivity and product selectivity by supporting cocatalysts. However, before the photocatalysts are applied to industry, there are still many problems to be further considered and studied. For example: (1) since precious metal cocatalysts are scarce and expensive, it will be an arduous task to study earth-abundant metal cocatalysts and non-metallic cocatalysts with the advantages of low price and high performance; (2) compared with the hydrogen evolution reaction, the process of the reduction of CO\textsubscript{2} is much more complicated and difficult, because the reduction of carbon dioxide needs a big overpotential to drive the reaction. What’s more, CO\textsubscript{2} photocatalytic reduction is a complex multi-product reaction, and the accurate detection of intermediate products is crucial to the interpretation of the complex reaction pathway and mechanism; (3) when designing semiconductor photocatalysts, the product selectivity of CO\textsubscript{2} reduction should also be an important factor to be considered. Density functional theory (DFT) serves as a bridge between theory and experiment. The in-depth study of electron band structure, charge transfer kinetics and reaction path by DFT calculation plays a crucial role in improving the selectivity of CO\textsubscript{2} photocatalytic reduction. With the continuous development of theoretical and experimental research related to g-C\textsubscript{3}N\textsubscript{4}, it is of great significance to further develop the application of g-C\textsubscript{3}N\textsubscript{4}-based catalysts in the field of photocatalytic reduction of CO\textsubscript{2}. 
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