Research Progress in Photo functional Materials for Catalytic Carbon Dioxide Reduction Reactions

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Abstract. Since the turn of the twenty-first century, the need to find new energy sources to create a low-carbon society has grown urgently due to the ongoing rise in greenhouse gas emissions, which are mostly caused by CO_2. The technique that uses solar energy to convert CO_2 into hydrocarbon fuels can produce high-value hydrocarbon fuels like methane, methanol, formic acid, or C_{2+}. This is a promising method of achieving global carbon balance. One of the key elements influencing the process of photocatalytic CO_2 reduction is the presence of materials having photocatalytic properties. Therefore, exploring and developing efficient photocatalytic functional materials is the main direction of research today. This article first introduces the development history of photo-functional materials and analyzes their mechanisms in photocatalytic reactions. Then, different types of optical functional materials were classified and introduced in detail. Finally, the development trend of photo-functional materials in the catalytic reduction of CO_2 was emphasized.

Keywords: CO_2, reduction reaction, photocatalysis, optical functional materials.

1. Introduction

People have relied on fossil fuels to live a convenient and comfortable life from the 1860s to the present, thanks to the Industrial Revolution and other developments. They have also benefited greatly from the improved medical, educational, and transportation resources, as well as other aspects of the high standard of living that come with industrial civilization. However, energy usage is necessary for the growth and exploitation of these resources. Fossil fuels account for 80% of global energy use today [1], which has a severe greenhouse impact and causes CO_2 emissions to rise quickly. The ensuing environmental issues, such as melting glaciers and global warming, represent a danger to human growth and existence. For the time being, fossil fuels are a nonrenewable resource that must be used wisely because they were formed over millions of years through geological development. To address these global issues, CO_2 must be converted into a readily available resource. This implies that techniques for lowering CO_2 levels, resolving environmental issues, and recycling and reusing resources must be developed.

Transforming dioxin into other forms or substances using thermal catalysis, photocatalysis, electrocatalysis, biocatalysis, or mixed catalysis—such as organic carbon compounds, fuel carbon, and inorganic carbon compounds—is now the primary strategy for lowering dioxin. However, in real industrial production, the choice of catalysts must address problems with the environment, energy consumption, selectivity, competitive reactions, cost, and conversion efficiency [2-4]. Among them, electrocatalysis is the most efficient but also the most expensive, energy-intensive, and difficult to separate the products. Although biocatalysis is very selective, its stability is low. Therefore, photocatalysis has emerged as a highly significant direction, considering variables like time, efficiency, and materials.

Utilizing the distinct optical characteristics of optical functional materials, photocatalysis in the CO_2 reduction area may be accomplished with effectiveness. Because of their many material options, zero-emission, and pollution-free qualities, and promising future development, optical functional materials have drawn a lot of interest. They are anticipated to provide solutions for the primary issues with present CO_2 reduction, including difficult environmental catalysis, poor catalytic activity, product selectivity, and catalyst durability [5]. Thus, several photo functional materials are introduced in this article along with their classification and introduction. It also examines their reaction mechanisms in various photocatalytic processes.

2. Development and characteristics of optical functional materials

Materials are separated into functional and structural materials. The term "functional materials" refers to a class of substances that, when subjected to external fields, rely on their optical characteristics to generate exceptional effects. Optical functional materials fall within this category. It can recognize, transform, and manipulate signals of incident light. It is separated into categories such as electro-optical materials, magneto-optical materials, elastic-optical materials, acousto-optic materials, thermo-optic materials, nonlinear optical materials, and laser materials based on various modes of action. In addition, depending on its unique qualities, it is separated into organic light functional materials, inorganic light functional materials, and organic-inorganic light functional materials.

With the advent of photochemistry came the creation of optical functional materials. Beginning in the early 20th century, Italian scientists Ciamician and Silber used the most basic photocatalysis to create compounds that were difficult to produce in the absence of light, then isolated and classified them. Consequently, scores of research articles on relevant topics were also published. The need for chemicals and pharmaceuticals has grown as a result of technological advancement, which has indirectly aided the growth of photochemistry. Artificial light sources, spectroscopic tools, identification tools, and the ability to synthesize some substances that were previously thought to only be produced naturally have all been developed by researchers, which has also sparked speculation about elements like chlorophyll that interact with light. New materials, such as alloys, organic polymer materials, and composite materials made of cement and glass have all surfaced recently. Currently, there are 8 million different types of materials, and they continue to expand at a rate of around 250000 each year. Among these, the study of optical functional materials has recently emerged as one of the most intriguing fields.

Optical functional materials operate according to several principles in the field of CO_2 reduction [6]. Materials based on photothermal effects also provide catalytic effects for CO_2 reduction, and artificial photosynthesis mimicking chloroplasts is another extremely promising CO_2 reduction technique [7]. Photo functional materials, represented by semiconductor materials, provide photo-generated electrons and catalytic active sites for CO_2 photo reduction reactions [8]. Therefore, photo functional materials have received widespread attention in the field of CO_2 reduction.

3. Mechanism of photocatalytic reduction of CO2 using optical functional materials

The current method of achieving CO_2 reduction mainly relies on specific material catalytic reduction reactions to convert CO_2 into other substances, such as ethylene, formic acid, and carbon, achieving the recovery and reuse of CO_2. The basic reaction equation is shown in Figure 1.

$$\begin{aligned}
&2H^{+} + 2e^{-} \Leftrightarrow H_2 && E^{\theta} = 0.0V \\
&2CO_2 + 12H^{+} + 8e^{-} \Leftrightarrow C_2H_4 + 4H_2O && E^{\theta} = 0.079V \\
&CO_2 + 8H^{+} + 8e^{-} \Leftrightarrow CH_4 + 2H_2O && E^{\theta} = 0.169V \\
&CO_2 + 2H^{+} + 2e^{-} \Leftrightarrow CO + H_2O && E^{\theta} = -0.103V \\
&CO_2 + H^{+} + e^{-} \Leftrightarrow HCOO^{-} + H_2O && E^{\theta} = -0.225V
\end{aligned}$$

Figure 1. CO_2 reduction reaction equation

The graph makes it obvious that the CO_2 reduction reaction and the hydrogen evolution reaction compete with one another. As a result, the selectivity of the catalysts should be taken into account while choosing them. Additionally, Table 1 demonstrates that the yield and selectivity of the CO_2

reduction process vary significantly in the presence of common catalysts. Additionally, it shows that the catalyst has to be controlled and modified.

Table 1. Faradaic Efficiencies of Products in CO_2 Reduction at various metal electrodes. Electrolyte: 0.1 M $KHCO_3$, T=18.5℃.

Electrode	Potential vs. SHE V	Current density mA cm^{-2}	Faradaic efficiency, %							
			CH_4	C_2H_4	EtOH	PrOH	CO	$HCOO^-$	H_2	Total
Pb	-1.63	5.0	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	-1.51	0.5	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
In	-1.55	5.0	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
Sn	-1.48	5.0	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
Cd	-1.63	5.0	1.3	0.0	0.0	0.0	13.9	74.4	9.4	103.0
Bi	-1.56	1.2	-	-	-	-	-	77	-	-
Au	-1.14	5.0	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
Ag	-1.37	5.0	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.6
Zn	-1.54	5.0	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
Pd	-1.20	5.0	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
Ga	-1.24	5.0	0.0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
Cu	-1.44	5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5
Ni	-1.48	5.0	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4
Fe	-0.91	5.0	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
Pt	-1.07	5.0	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
Ti	-1.60	5.0	0.0	0.0	0.0	0.0	-	0.0	99.7	99.7

Based on these problems, the fundamental challenge facing CO_2 reduction now is the creation of highly selective, active, and stable catalytic materials. These materials can be classified as inorganic, organic, or composite materials based on their chemical composition. TiO_2-based photocatalytic materials are an example of inorganic materials [8], whereas C_3N_4 is an example of an organic material that is mostly a polymer. Metal-organic compounds like V, W, Ge, and Ga-based materials are examples of composite materials.

The use of photoelectric effects to make semiconductor materials absorb electron-hole pairs produced by light and cause them to undergo redox reactions, achieving the conversion of light energy and chemical energy, and thereby promoting the progress of the reaction, is one of the mechanisms by which these materials achieve catalysis. Only when the energy of the incident light exceeds or equals the bandgap width (Eg) of the material can electrons transition into the high-energy conduction band. The widely generated electrons then separate from the photogenerated holes to produce electron-hole pairs, which then move to the surface-active sites. Due to the strong reduction ability of photogenerated electrons migrating to surface active sites, they can facilitate the easy hydrogenation of CO_2 and photogenerated electrons in water [7,9].

Additionally, certain substances act as co-catalysts, such as Pt and RuO_2, which act as electron enrichment areas and hole enrichment regions, respectively. This increases the lifespan of charge carriers and boosts catalytic efficiency. Another catalytic process achieves thermal increase by using techniques like the photothermal effect. Using plasmonic elements simultaneously can increase light absorption, promote carrier separation, and speed up the kinetics of surface reactions. For instance, focusing sunlight through an external heat source can significantly improve the efficiency of product generation, improve energy utilization, and reduce energy consumption [10].

4. Different types of optical functional materials

4.1. Inorganic materials

For the most part, metal materials, which may be further broken down into metal elements, metal oxides, metal sulfur compounds, perovskite, etc., are utilized as inorganic catalysts for CO_2 reduction processes nowadays. The catalytic products also differ depending on the properties of the metal itself, for example, Au and Ag with CO as the primary product, Sn, In, and Pb with formic acid as the main product, etc.

4.1.1. Metal element

The earliest type of catalyst for CO_2 reduction processes that has been examined is one that uses metal elements as catalysts. It has a long history of great performance. While selectivity keeps getting stronger, it is challenging to increase efficiency when employing only metal components as catalysts. Consequently, raising the specific surface area to enhance active sites has had positive benefits in several investigations. According to research by Mistry et al. on the size dependency of CO_2 reduction on gold nanoparticles, when catalyst particle size is reduced, the current density rises, increasing the CO selectivity. Meanwhile, Strasser et al. investigated the comparable size dependency of copper nanoparticles. The selectivity of CO_2 likewise rises when the particle size is decreased. On particles smaller than 5 nm, this behavior is inhibited, which is connected to the large density of poor coordination sites on small nanoparticles. Therefore, while taking into account the catalytic activity of nanoparticles, particle size optimization is another crucial factor [10].

4.1.2. Metal semiconductors

In the realm of CO_2 reduction, a variety of semiconductor materials have recently seen widespread application. Narrow energy gaps and good light absorption properties of common metal semiconductor materials including copper oxide (Cu_2O), bismuth phthalate ($BiVO_4$), and bismuth oxide (Bi_2O_3) aid in the generation of photogenerated carriers and facilitate reactions. Particularly titanium dioxide has drawn a lot of interest because of its low cost, high effectiveness, and non-toxic qualities. To make the band gap of CO_2 smaller, the absorption stronger, and the yield greater, Nematollahi et al. developed a variety of titanium dioxide catalysts doped with Ni and Bi with varied concentrations using the solution gel technique [11].

4.1.3. Perovskite

Perovskite materials such as perovskite oxide ($CaTiO_3$) and bismuth barium titanate oxide ($Ba_xBi_{1-x}TiO_3$) also show potential in photocatalytic CO_2 reduction. These materials have excellent photoelectric performance and light absorption ability, which can improve the efficiency of photocatalytic reactions.

In addition, sulfides, nitrides, phosphides, etc. have also been studied for photocatalytic CO_2 reduction.

4.2. Organic and composite materials

Since inorganic materials often have superior photostability and chemical stability and can resist reactions under high temperature and light conditions, they are typically used in photocatalytic CO_2 reduction rather than organic materials. Inorganic materials are useful for photocatalytic reactions because they also have greater catalytic activity and electron transport characteristics. Organic materials do, however, have a few uses in photocatalytic CO_2 reduction. For instance, certain organic compounds can behave as co-catalysts or photosensitizers when combined with inorganic substances to boost the effectiveness of photocatalytic processes. These organic compounds often perform well at absorbing light and transferring electrons, which can improve the production and transmission of photogenerated charge carriers [12].

4.2.1. Supported catalysts

Catalysts that attach active ingredients, such as metal nanoparticles or organic complexes, to the surfaces of inert carriers, such as oxides, carbon compounds, or metal-organic frameworks, are referred to as supported catalysts. Supported catalysts in photocatalytic reactions can use photogenerated charge carriers to excite the active components on the catalyst surface, facilitating the reduction of CO_2 in the process. The carrier's strong conductivity and optical qualities can produce enough photogenerated charge carriers and deliver them to the catalyst's active sites. Furthermore, it can make the catalyst last longer by fixing the active ingredients on a reliable carrier.

4.2.2. Organic dyes

Some organic dyes can operate as photosensitizers in photocatalytic processes due to their high light absorption efficiency and capacity for photoelectric conversion. They can absorb near-infrared or visible light, converting the energy into photogenerated charge carriers that support CO_2 reduction activities. For instance, the investigation of photocatalytic CO_2 reduction has utilized organic dyes like Rhodamine B and methyl orange.

4.2.3. Organic ligands

Some organic ligands can coordinate with transition metal ions to form coordination compounds, serving as co-catalysts in photocatalytic reactions. These organic ligands can regulate the electronic structure, stability, and reactivity of the catalyst. For example, some nitrogen-containing ligands such as pyridine and imidazole have been used in photocatalytic CO_2 reduction reactions.

4.2.4. Organic semiconductor materials

Excellent photoelectric conversion and electron transport characteristics may be found in organic semiconductor materials. To increase the effectiveness of CO_2 reduction, they can be coupled with inorganic catalysts to create composite materials. For instance, synthetic organic semiconductor materials like perovskite materials and polymers have both been investigated for photocatalytic CO_2 reduction.

4.2.5. Metal-organic framework

Metal ions or clusters combined with organic ligands form crystalline structures known as metal-organic frameworks (MOFs). Because of their very adaptable and varied structural makeup, it is possible to control their photoelectric performance and catalytic activity by changing the choice, ratio, and connection style of the metal ions and organic ligands. The choice, ratio, and connecting style of metal ions and organic ligands may be changed to control the photoelectric performance and catalytic activity of MOFs, which have extremely adaptable and diversified structures.

5. Conclusion

Even while partial industrialization and the reduction of CO2 have been accomplished in recent years using a variety of materials and techniques, there is still room for improvement in terms of industry speed, utilization rate, cost, and sustainability. This page gives a thorough introduction to various materials and primarily categorizes them into organic, inorganic, and composite materials based on their chemical makeup.

Currently, several issues need to be resolved to use functional materials for photocatalytic CO_2 reduction: (1) Low efficiency: The high stability and inertness of CO_2 provide a high energy barrier in the reduction reaction, which results in a large energy loss during the photocatalytic reduction of CO_2. (2) Low selectivity: During the photocatalytic reduction of CO_2, various byproducts may be created in addition to the target product. (3) Low catalyst stability: In the process of photocatalytic CO_2 reduction, catalysts must resist circumstances of intense light and chemical reactions. However, many catalysts may experience structural deterioration or activity loss over an extended period of time, resulting in a decline in reaction efficiency. (4) Thorough investigation of reaction mechanism: The photocatalytic reduction of CO_2 involves a complicated reaction mechanism, and there is still considerable confusion surrounding the crucial stages and the process by which intermediate intermediates occur.

Methods like logical catalyst structure design, control of optical and electrical characteristics, and reaction condition optimization can be employed to overcome these difficulties. Moreover, techniques like photocatalysis and photocatalysis can be applied as multidisciplinary research continues to advance. Future studies on opt functional materials can also continue to concentrate on enhancing the effectiveness, selectivity, and stability of photocatalytic CO_2 reduction while also learning more about the reaction process. Better options for attaining sustainable CO_2 conversion may potentially result from this.

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