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Recent progress in the photocatalytic reduction of aqueous carbon dioxide

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ABSTRACT

Using solar energy to convert CO_2 to value-added chemicals and fuels can not only reduce carbon emission by the utilization of CO_2 as feedstock, but also store solar energy as high-energy-density fuels, being considered an ultimate strategy to solve environment and energy issues. Developing efficient photocatalysts and photocatalytic systems for CO_2 reduction is the most essential part in achieving this goal. Considerable developments in CO_2 photocatalytic reduction have been made over past decades. This article reviews the latest progresses in aqueous CO_2 photoreduction related to photocatalytically experimental design and photocatalyst materials, including TiO_2-based photocatalysts, metal oxide-based photocatalysts, sulfide-based photocatalysts, graphene-based photocatalysts, oxometallate-based photocatalysts and other photocatalysts. In addition, experimental and theoretical studies on the possible mechanisms of CO_2 photo-reduction reaction as well as the potential methods for mechanisms studies are also summarized. On the basis of the aforementioned discussions, we present the future prospects for further development of CO_2 photocatalytic reduction.

1. Introduction

Limited fossil fuel resources and global warming derived from increasing CO_2 in the atmosphere have emerged as major concerns in the worldwide [1–8]. The conversion of CO_2 into valuable chemicals and fuels serves as a promising route for mitigating the greenhouse effect of CO_2 and meeting energy demands. The carbon atom in CO_2 molecule exhibits the highest oxidation state and CO_2 itself with the C− O bond strength of 364 kJ/mol is chemically stable, so it is difficult to be activated and requires a large amount of energy to undergo conversion. In general, the reduction of CO_2 can be carried out by chemical methods, including catalyzed hydrogenation reduction, photocatalytic reduction, thermochemical reduction, electrochemical reduction and biological reduction etc. Among these, thermochemical reduction is more demanding for reaction instruments, while photocatalytic reduction of CO_2 is more attractive from the viewpoint of the utilization of clean and sustainable solar energy. Different from other CO_2 conversion processes, photocatalytic reduction can directly use sunlight to induce the CO_2 reduction, which is mentioned in the same breath with the photovoltaic processes accepted as desirable ways to convert solar energy efficiently. Under the irradiation of sunlight, photocatalysts can convert CO_2 into fuels and chemicals, showing the potentials to tackle both environmental and energy issues. The involving main products from CO_2 photo-reduction are CO, HCHO, HCOOH, CH_3OH, C_2H_5OH, CH_4, etc., depending on the number of transferred electrons, so it is essential to use catalysts to improve the selectivity and efficiency of CO_2 reduction reaction [2–6,8].

Many types of solvents such as H_2O [9], CCl_4 [10], CH_2Cl_2 [10] and C_2H_7NO (monoethanolamine) [11] have been tested for CO_2 photocatalytic reduction. While H_2O still remains the most naturally abundant source of hydrogen that is available and low-cost for CO_2 photoreduction, we solely discuss the situation with H_2O as the reactant in the aqueous solutions in this review.

The CO_2 photoreduction process is more complicated compared to other photocatalytic processes such as light-driven water splitting, organic degradation, etc. The CO_2 photoreduction efficiency is primarily determined by the thermodynamic and kinetic balance of light harvesting, charge separation, electronic potentials, and CO_2 adsorption/activation on the catalyst surface. In photocatalytic processes including CO_2 photoreduction, the energy band configuration of semiconductors plays an important role in the light harvesting. Bandgap engineering is an effective approach to adjust band position and bandgap for effectively utilizing solar energy, mainly including cation/anion doping, solid solution formation, sensitization, etc. The photon energy must be

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above the bandgap of the semiconductor photocatalyst to induce the electron jump. Therefore, the match between the photocatalyst bandgap and light wavelength should be firstly considered. Moreover, the photogenerated charge separation and transportation are widely considered to determine the efficiency of the CO_2 photocatalytic process. If the electron-hole pairs are not separated well, the high charge recombination will occur, resulting in the seldom electrons transferred to the surface-active sites for CO_2 reduction. The photocatalysts with smaller sizes, porous structures, are able to decrease the probability of charge recombination, and result in the improved CO_2 photocatalytic activities. Furthermore, water molecules are also involved in the CO_2 photoreduction to provide protons for the formation of various products, so both CO_2 reduction potentials and water oxidation potential should be met from the viewpoint of the electronic potentials of the photocatalysts. Thus, CO_2 and water can undergo reduction by photogenerated electrons and oxidation by holes, respectively, to produce various hydrocarbon and oxygenates in photocatalytic reduction of CO_2. Therefore, the bandgap of the photocatalyst needs to be engineered to satisfy both a high absorption of solar light and the sufficient built-in potential for water oxidation. On the other hand, the surface area, pore structure, exposed crystal facets, and surface defects in photocatalysts show significant impact on the adsorption and activation of CO_2 molecules, which also determine the performance of CO_2 photoreduction to some extent.

Many kinds of catalysts have been explored in CO_2 photoreduction, but it's also needed to explore some novel photocatalytic materials with earth abundant, non-toxic, low-cost and high photocatalytic activity. TiO_2-based photocatalysts and graphitic carbon nitride (g-C_3N_4) are especially potential and recommendable in the future. Firstly, TiO_2 is the widely used photocatalyst because of its photo and chemical stability, inexpensive and nontoxicity. However, the large band gap and low visible light utilization limited its application. Doping with metal, non-metal and metal oxides can improve light utilization efficiency and reduce the recombination of photogenerated electrons and holes [12]. Recently, graphitic carbon nitride (g-C_3N_4) has also received a great deal of attention from researchers in CO_2 photoreduction, for its abundance, cheap and easy to get, physicochemical stability and nonmetal composition. While g-C_3N_4 has some weaknesses, as the high recombination rate of photogenerated electron-hole pairs, small specific surface area and low photocatalytic activity limited its use in CO_2 photoreduction. The design of the electronic structure and heterostructure of g-C_3N_4, such as metal doping, non-metal doping and the formation of composites, would greatly inhibit the recombination rate of photogenerated electron-hole pairs and promote visible-light responsive and photocatalytic performance.

The production of renewable solar fuel through CO_2 photocatalytic reduction, namely artificial photosynthesis, has the reaction features of natural photosynthesis to achieve solar-driven CO_2 reduction [13–16]. Actually, photocatalytic CO_2 conversion is a "kill two birds with one stone" approach. The use of CO_2 can help with the cuts of carbon emission, while the products can serve as green and renewable solar fuels. In addition, CO_2 feedstock could be supplied from the capture and storage strategy (CCS) [17]. The strategy of CCS is a more economical and attractive solution, in addition to solving the CO_2 storage problem, and the produced fuels have potential to replace the fossil fuels using the available instruments [18].

In general, the photocatalytic process is the oxidation-reduction coupled reactions, which involves the use of solar energy as driving force for the excitation and transfer of the holes and electrons. Therefore, in a photocatalytic reaction process, to excite and separate the electron-hole pairs, the energy of incident light must be equal or greater than the band gap of the photocatalysts, and the energy of these photogenerated carriers depends on the position of the conduction band and the valence band of the photocatalysts. Fig. 1 shows the basic principle of the photocatalytic CO_2 reduction. Firstly, under light illumination, a flux of photons absorbed by the semiconductor

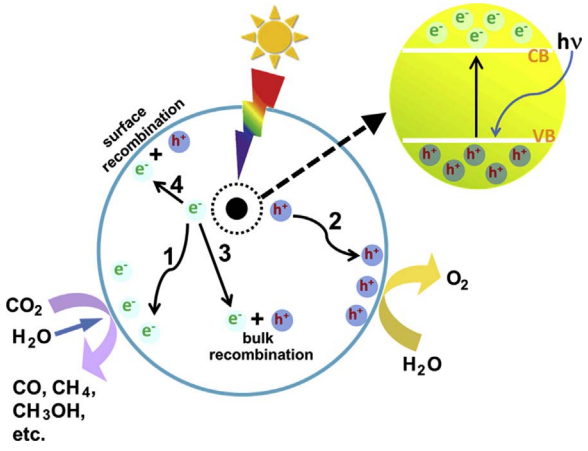

Fig. 1. Schematic principle of photocatalytic reduction of CO_2. The processes involved in CO_2 photoreduction with H_2O on the semiconductor surface.

photocatalysts excite electrons from the valence band (VB) to the conduction band (CB), leaving an equal number of holes in the VB. Then, the excited electrons and holes separate from each other and migrate to the photocatalyst surface (path ***1***, ***2***). Finally, the electrons reduce CO_2 into hydrocarbon fuels such as CO, CH_3OH, and CH_4 in the presence of H_2O, while the holes oxidize H_2O. Nevertheless, there are also bulk and surface recombination for electrons and holes (path ***3***, ***4***). The overall efficiency of photocatalytic reduction of CO_2 is determined by the balance of thermodynamics and kinetics of these processes [19].

To achieve overall CO_2 photoreduction, the energy requires that the bottom of the CB must be positioned at a more negative potential than CO_2 reduction potential, while the top of the VB must be positioned at a more positive potential than H_2O oxidation potential. Table 1 lists the CO_2 reduction potentials versus the NHE at pH = 7 to generate CO, HCHO, CH_3OH, CH_4 and C_2H_5OH, respectively. Obviously, a series of different products could be formed over various photocatalysts, which is determined by the number of electrons and protons (e^-/H^+) involved in reactions. For example, two protons and two electrons are needed in CO formation, while C_2H_5OH formation occurs by reaction with twelve electrons and twelve protons. The selectivity of product is one of the significant problems in CO_2 photoreduction process, which may be influenced by reaction conditions and thermodynamic reduction potentials.

With the continuous development of CO_2 photocatalytic reduction technology in recent years, many research achievements in various fields have been emerged, which make people have a more in-depth understanding of the process and mechanism of photocatalytic reduction of CO_2. Based on the brief introduction of the basic principle of photocatalytic CO_2 reduction, this review summarizes the latest research results in the field of CO_2 photocatalytic reduction in the last five years. The novel and important photocatalyst materials for CO_2 reduction are exampled and emphasized, and recent studies on the related reaction mechanisms are also presented. On the basis of the

Table 1
The reduction potentials for CO_2 photoreduction with H_2O to various products with reference to NHE at pH = 7.

Reaction (pH = 7)	E^o_{redox}/(V vs. NHE)
$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$	0.82
$2H^+ + 2e^- \rightarrow H_2$	−0.41
$CO_2 + H^+ + 2e^- \rightarrow HCO_2\cdot$	−0.49
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.53
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.48
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−0.38
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	−0.24
$CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	−0.33