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# Research progress in reduction of carbon dioxide by TiO<sub>2</sub>-based photocatalytic materials

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**Abstract.** From the current global energy consumption distribution, traditional fossil fuels still occupy a dominant position, and their share will remain high for some time to come. However, limited non-renewable traditional resources cannot always be used by humans. When they are finally consumed, the consumption of traditional fossil fuels such as oil, natural gas, coal, etc. will generate a lot of greenhouse gases, and the massive emissions of CO<sub>2</sub> will cause a series of unfavorable chain reactions. Photocatalytic reduction of CO<sub>2</sub> as a hydrocarbon fuel not only reduces the CO<sub>2</sub> content in the atmosphere, but also solves the environmental problems brought about by the greenhouse effect, and can provide energy fuel with considerable economic effects. The research progress of photocatalytic reduction of CO<sub>2</sub> is reviewed. Some common TiO<sub>2</sub>-based photocatalytic materials are introduced, and the characteristics of various materials are compared. Finally, the research on TiO<sub>2</sub>-based photocatalytic materials is prospected

## 1. Introduction

With the continuous development of industry, human beings have more and more demand for energy, which leads to the consumption of fossil energy is increasing, and the emission of CO<sub>2</sub> is increasing day by day. According to the International Energy Agency (IEA), global CO<sub>2</sub> emissions in 2014 were 32.3 billion tons. Aiming at the current energy utilization status and the characteristics of CO<sub>2</sub>, photoreduction of CO<sub>2</sub> is a good way to solve the greenhouse effect and energy problems. CO<sub>2</sub> photocatalytic technology uses photogenerated electrons generated by photocatalytic materials to restore CO<sub>2</sub> to some organic substances with practical use value, such as methanol and methane. Compared with other CO<sub>2</sub> treatment technologies, photocatalysis has the advantages of low environmental pollution, mild reaction conditions and low energy consumption. Therefore, CO<sub>2</sub> photocatalytic technology has potential use value and broad development prospects in the field of governance and its applications. With the deepening of research, photocatalytic materials are mainly divided into titanium dioxide, other metal oxides and inorganic semiconductor materials. Anpo's research team will investigate the effects of carrier, particle dispersion, reaction temperature, ratio of CO<sub>2</sub> and H<sub>2</sub>O on photocatalytic reduction of CO<sub>2</sub> by photocatalytic reduction of CO<sub>2</sub> in different sizes of anatase TiO<sub>2</sub>. Exploratory studies using an electron spin resonator revealed that the reaction between CO<sub>2</sub> and H<sub>2</sub>O was achieved by electron transfer between and [1]. This paper mainly introduces the characteristics of several TiO<sub>2</sub>-based photocatalytic materials.



## 2. Photocatalytic reduction mechanism

CO<sub>2</sub> is a typical linear symmetrical triatomic molecule. The electrons are concentrated on the oxygen atoms on both sides. The molecular structure is very stable and difficult to activate. This determines that the CO<sub>2</sub> molecule is a weak electron donor and a strong electron acceptor. And can 3.8 eV [2]. The photocatalytic reduction mechanism of CO<sub>2</sub> simulates the process of plant photosynthesis. Green plants fix CO<sub>2</sub> through photosynthesis. Based on this process, researchers artificially simulate photosynthesis to fix CO<sub>2</sub> in the atmosphere. The photosynthetic reaction to reduce CO<sub>2</sub> is essentially an oxidation-reduction process under the action of photons. It consists of the following basic processes:

- 1) reactants such as CO<sub>2</sub> and H<sub>2</sub>O are adsorbed on the surface of the photocatalytic material;
- 2) The photocatalytic material generates electron-hole pairs under the action of light;
- 3) uncomplexed electrons and holes are respectively moved to the surface of the photocatalytic material;
- 4) reacting between electrons and holes and reactants such as CO<sub>2</sub>;
- 5) The product is desorbed on the surface of the photocatalytic material.

## 3. Introduction to TiO<sub>2</sub>-based photocatalytic materials

The photocatalyst mainly includes TiO<sub>2</sub>[4], ZnO[5], Fe<sub>2</sub>O<sub>3</sub>[6], etc. TiO<sub>2</sub> is a well-recognized semiconductor catalyst with excellent properties, which is non-toxic, non-polluting, low in cost and wide in band gap. It is widely used not only in photocatalysis, but also in dye sensitized batteries and sensors. The micro-morphology and particle size of TiO<sub>2</sub> are the key factors affecting its performance. Compared with powdered TiO<sub>2</sub>, TiO<sub>2</sub> nano-array has its unique advantages. Nano-array can provide effective transmission channel for rapid migration of electrons due to its special structure, and nano-array grows on the surface of electrode, which is stable in structure and easy to recycle. [7].

## 4. Single TiO<sub>2</sub> and doped TiO<sub>2</sub>

In a single TiO<sub>2</sub> research experiment, TiO<sub>2</sub> has three different crystal forms: rutile, anatase, and brookite, which are unstable in use due to the sillimanite type in use. There will be restrictions in the application. Therefore, the rutile type and anatase type are mainly studied for a single TiO<sub>2</sub>. The forbidden band width of anatase TiO<sub>2</sub> is 3.2 volts, which can only respond to light in the ultraviolet band. One of the main reasons is that a series of semiconductor photocatalysts represented by TiO<sub>2</sub> generally have a large forbidden band width (For example, the anatase TiO<sub>2</sub> has a forbidden band of =3.2 eV), which only responds in the ultraviolet range, while the ultraviolet light below 400 nm is less than 5% of the total solar energy, and about 43% of the total solar energy. Mainly concentrated in the 400 -700 nm band, which greatly limits their photocatalytic applications under visible light irradiation, so it is an effective method to change the corresponding range of the spectrum for the incorporation of non-metallic elements. At present, TiO<sub>2</sub> is mainly used for N-doping, other halogen elements such as C, B and S. However, there are still some problems with doped TiO<sub>2</sub>, mainly due to whether the reaction mechanism undergoes substantial changes and the stability of the improved photocatalyst. Due to the high recombination rate of photogenerated electron-hole pairs in single TiO<sub>2</sub> and doped TiO<sub>2</sub>, the expected targets cannot be achieved in both experimental and practical applications. This also limits the practical application of single TiO<sub>2</sub> and doped TiO<sub>2</sub>. Jian et al [9] used the microemulsion method to prepare lanthanum-doped and cerium-doped nano-TiO<sub>2</sub>. Sanchez-Dominguez [10] also prepared Zn-doped TiO<sub>2</sub> by microemulsion method, which showed high photocatalytic performance, which is considered as an effective way to prepare photocatalyst in O/W microemulsion method.

## 5. Semiconductor compounding

The forbidden band width of the semiconductor TiO<sub>2</sub> is generally from 2.2 to 3.0 eV and is a discontinuous region. The photocatalytic properties of a semiconductor are determined by its special band structure. When light is radiated with light having energy equal to or greater than the band gap

energy of the semiconductor, electrons on the valence band are excited onto the conduction band and migrate to the surface of the particle under the action of the electric field, thus forming holes in the valence band. Thereby a hole/electron pair with high activity is produced. The holes can capture electrons in the adsorbed substance or solvent of the semiconductor surface, so that the originally unabsorbed substance is activated and reduced by the oxidized electron acceptor through the electrons receiving the surface. In view of the high recombination rate of photogenerated electrons, the researchers will recombine with semiconductors, and by overlapping the different semiconductor levels, the carrier mobility will be improved, and the recombination rate of photogenerated electron hole pairs will be reduced. The disadvantage of high photocombine electron hole recombination rate. Thereby increasing the photocatalytic activity. Since the forbidden band width is wide, it is necessary to use a semiconductor having a narrow band gap for recombination. Liu et al studied the photocatalytic activity of /composite photocatalysts. The modified photocatalytic reduction products HCOOH and CO yields have been significantly improved. The semiconductor is modified with a narrow band gap semiconductor to extend into the visible light region to facilitate separation of photogenerated electrons. Li Y et al [11] firstly provided active sites for reactant adsorption through nanotubes through TiO<sub>2</sub> nanotubes (TNTs). Promotes the migration of photogenerated carriers and promotes the separation of charges. The TNTs are then modified by Cu<sub>2</sub>O nanoparticles to promote visible light absorption. Higher photogenerated carrier recombination inhibits the photocatalytic efficiency of TNTs. Zhao H et al [12] used Al<sub>2</sub>O<sub>3</sub> chemical deposition method to construct surface defects. Experimental data show that when v layer is very thin, the surface passivation ability of Al<sub>2</sub>O<sub>3</sub> on TiO<sub>2</sub> can enhance photocatalytic activity, but the Al<sub>2</sub>O<sub>3</sub> layer as insulator Thickness hinders the transfer of electrons to the surface, thereby reducing the photocatalytic conversion of CO<sub>2</sub>.

## 6. Conclusion

Researchers use photocatalytic materials to photocatalytically reduce CO<sub>2</sub> to hydrocarbons. Not only can it effectively control the negative effects of the greenhouse effect, but also can solve the social problems of insufficient energy. Photocatalytic technology has made some progress and breakthroughs in researchers in various countries, but at present, photocatalytic reduction of CO<sub>2</sub> still has a series of problems mainly: 1) Photocatalyst energy utilization is low. The conversion rate to solar energy is low. 2) Low quantum efficiency. The high recombination rate of photogenerated electron holes will result in a decrease in photocatalytic activity. 3) The reaction mechanism is not clear enough. Although there have been a lot of research on the intermediate products and kinetics in the reaction process, the entire photocatalytic reduction process has not been clearly revealed. 4) The reaction product is poorly controlled. Due to the limitation of the photocatalytic material and the unclear reaction mechanism, the expected reduction products are often not obtained[12].

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