Research progress in reduction of carbon dioxide by TiO$_2$-based photocatalytic materials

Haijun Feng$^1$, Fangqin Li$^2$, Jianxing Ren, Xiaotong Zhang, Chuang Ma and Xin Hou

$^1$Department, University, City, Province, ZIP code, Country
$^2$Department, University, City, Province, ZIP code, Country
$^3$Corresponding author’s e-mail: 724897515@qq.com

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$_2$ will cause a series of unfavorable chain reactions. Photocatalytic reduction of CO$_2$ as a hydrocarbon fuel not only reduces the CO$_2$ 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$_2$ is reviewed. Some common TiO$_2$-based photocatalytic materials are introduced, and the characteristics of various materials are compared. Finally, the research on TiO$_2$-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$_2$ is increasing day by day. According to the International Energy Agency (IEA), global CO$_2$ emissions in 2014 were 32.3 billion tons. Aiming at the current energy utilization status and the characteristics of CO$_2$, photoreduction of CO$_2$ is a good way to solve the greenhouse effect and energy problems. CO$_2$ photocatalytic technology uses photogenerated electrons generated by photocatalytic materials to restore CO$_2$ to some organic substances with practical use value, such as methanol and methane. Compared with other CO$_2$ treatment technologies, photocatalysis has the advantages of low environmental pollution, mild reaction conditions and low energy consumption. Therefore, CO$_2$ 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$_2$ and H$_2$O on photocatalytic reduction of CO$_2$ by photocatalytic reduction of CO$_2$ in different sizes of anatase TiO$_2$. Exploratory studies using an electron spin resonator revealed that the reaction between CO$_2$ and H$_2$O was achieved by electron transfer between and [1]. This paper mainly introduces the characteristics of several TiO$_2$-based photocatalytic materials.
2. **Photocatalytic reduction mechanism**

CO₂ 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 CO₂ molecule is a weak electron donor and a strong electron acceptor. And can 3.8 eV [2]. The photocatalytic reduction mechanism of CO₂ simulates the process of plant photosynthesis. Green plants fix CO₂ through photosynthesis. Based on this process, researchers artificially simulate photosynthesis to fix CO₂ in the atmosphere. The photosynthetic reaction to reduce CO₂ is essentially an oxidation-reduction process under the action of photons. It consists of the following basic processes:

1) reactants such as CO₂ and H₂O 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 CO₂;
5) The product is desorbed on the surface of the photocatalytic material.

3. **Introduction to TiO₂-based photocatalytic materials**

The photocatalyst mainly includes TiO₂[4], ZnO[5], Fe₂O₃[6], etc. TiO₂ 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 TiO₂ are the key factors affecting its performance. Compared with powdered TiO₂, TiO₂ 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 TiO₂ and doped TiO₂**

In a single TiO₂ research experiment, TiO₂ 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 TiO₂. The forbidden band width of anatase TiO₂ 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 TiO₂ generally have a large forbidden band width (For example, the anatase TiO₂ 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, TiO₂ is mainly used for N-doping, other halogen elements such as C, B and S. However, there are still some problems with doped TiO₂, 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 TiO₂ and doped TiO₂, the expected targets cannot be achieved in both experimental and practical applications. This also limits the practical application of single TiO₂ and doped TiO₂. Jian et al [9] used the microemulsion method to prepare lanthanum-doped and cerium-doped nano-TiO₂. Sanchez-Dominguez [10] also prepared Zn-doped TiO₂ 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 TiO₂ 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 photomerge 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 TiO₂ nanotubes (TNTs). Promotes the migration of photogenerated carriers and promotes the separation of charges. The TNTs are then modified by Cu₂O nanoparticles to promote visible light absorption. Higher photogenerated carrier recombination inhibits the photocatalytic efficiency of TNTs. Zhao H et al [12] used Al₂O₃ chemical deposition method to construct surface defects. Experimental data show that when v layer is very thin, the surface passivation ability of Al₂O₃ on TiO₂ can enhance photocatalytic activity, but the Al₂O₃ layer as insulator Thickness hinders the transfer of electrons to the surface, thereby reducing the photocatalytic conversion of CO₂.

6. Conclusion
Researchers use photocatalytic materials to photocatalytically reduce CO₂ 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 CO₂ 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].

References
[1] Anpo M., Yamashita H., Ichihashi Y., et al. Photocata-lytic reduction of CO₂ with H₂O on various titanium-ox-ide catalysts (1995). Journal of Electroanalytical Chemis-try, (1995), 396(1 /2) : 21－26
[2] X. Chen, S.S. Mao. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications (2007). Chemical Reviews, 107(7): 2891.
[3] L.Liu,X.Chen. Titanium dioxide nanomaterials: self-structural modifications (2010). Chemical Reviews, 114(19): 9890-9918.
[4] [Kay A, Cesar I, Grätzel M. New benchmark for water photooxidation by nanostructured alpha-Fe₂O₃ films(2010). Cheminform, 38(11):459-468
[5] Zhou Q, Fang Z, Li J, et al. Applications of TiO₂ nanotube arrays in environmental and energy fields: A review(2015). Microporous and Mesoporous Materials, 202: 22-35.
[6] Sanchez-Dominguez M, Morales-Mendoza G, Rodriguez-Vargas M J, et al. Synthesis of Zn-doped TiO₂, nanoparticles by the novel oil-in-water (O/W) microemulsion method
and their use for the photocatalytic degradation of phenol (2015). Journal of Environmental Chemical Engineering, 3(4):3037-3047.

[7] Roza L, Umar A A, Rahman M Y A, et al. Seed-Mediated Liquid Phase Deposition Method for TiO$_2$ Nanostructure Growth on ITO Substrate: Effect of Surfactant (2017). Advanced Materials Research, 364:393-397.

[8] Li Y, Zhang W, Shen X, et al. Octahedral Cu$_2$O-modified TiO$_2$ nanotube arrays for efficient photocatalytic reduction of CO$_2$ (2015). Chinese Journal of Catalysis, 36(12):2229-2236.

[9] Zhao H, Chen J, Rao G, et al. Enhancing photocatalytic CO$_2$ reduction by coating an ultrathin Al$_2$O$_3$ layer on oxygen deficient TiO$_2$ nanorods through atomic layer deposition (2017). Applied Surface Science, 404.

[10] Sato K, Li J G, Kamiya H, et al. Ultrasonic Dispersion of TiO$_2$ Nanoparticles in Aqueous Suspension (2010). Journal of the American Ceramic Society, 91(8):2481-2487.

[11] Mutuma B K, Shao G N, Kim W D, et al. Sol-gel synthesis of mesoporous anatase-brookite and anatase-brookite-rutile TiO$_2$ nanoparticles and their photocatalytic properties. Journal of Colloid & Interface Science, 2015, 442:1-7.

[12] Wang L, Nie Z, Cao C, et al. Chrysanthemum-like TiO$_2$ nanostructures with exceptional reversible capacity and high coulombic efficiency for lithium storage. Journal of Materials Chemistry A, 2015, 3(12):6402-6407.