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Application of MOFs in the Field of Photocatalysis

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Abstract: MOFs is the abbreviation of Metal organic Framework. Compared with the traditional inorganic metal materials, MOFs materials have the advantages of larger surface area, more diverse structure and function, and have been widely used in the field of photocatalysis. From the perspective of photocatalysis, this paper summarizes the application research process of MOFs material in the field of photocatalysis in the recent years, including photocatalytic decomposition of water to hydrogen production, photocatalytic decomposition of carbon dioxide, degradation of pollutants and so on. The application prospect of MOFs materials is prospected.

Keywords: Metal Organic Frameworks; Photocatalysis; Degradation of Pollutants; Hydrogen Production; Catalytic Reduction of CO_2

1. The role that mofs materials can play in the field of photocatalysis in the current era context

In 1995, a team led by Professor Omar M. Yaghi from the University of California, Berkeley, reported in the journal Nature the synthesis of a two-dimensional coordinated compound with rigid organic ligand benzene-1, 3, 5-tricarboxylic acid (BTC) and transition metal Co, which was called MOF (metal-organic framework). The theory of metal-organic frameworks was formally proposed based on this discovery. Due to its advantages such as high porosity, low density, large specific surface area, adjustable pore size, and diverse topology structure compared to traditional inorganic porous materials, MOFs materials have achieved a staggering development in the following two decades. MOFs materials are a type of hybrid material formed by self-assembly of organic ligands and metal ions or clusters through coordination bonds, with molecular voids within. Many MOFs materials can exhibit semiconductor properties. Under light conditions, MOFs materials will produce photoelectrons and holes, which can then be separated, allowing the electrons and holes to migrate to the surface of the material to facilitate photocatalytic reactions or redox reactions.

Today, the biggest challenges facing humanity as it enters a new era of development are mainly energy shortages and environmental pollution. Developing new energy sources, especially using clean energy such as wind energy and solar energy, and actively treating pollutants are the generally recognized main ways to address these two problems. Photocatalytic materials are currently one of the important tools that humanity uses to respond to the global energy crisis and environmental pollution using solar energy. Photocatalytic materials are materials that undergo no chemical changes under the action of light, but can promote chemical reactions. They can effectively utilize the natural light energy to convert it into the energy needed for chemical reactions and generate catalytic effects, making the surrounding oxygen and water molecules excited into highly oxidizing free negative ions. The photocatalytic activity is closely related to the porous structure of the photocatalyst, and the porous structure means that as many reaction active sites as possible will be exposed, the distance between the photo-generated electrons and holes will be greatly shortened, and the utilization rate of the photo-generated electrons and holes will be improved, thereby effectively improving the catalytic performance of the photocatalyst. Among the materials studied in the materials field in recent years, MOFs materials have many advantages over traditional inorganic metal materials and have gradually become an important research object in the field of photocatalysis research. Therefore, in the practical application of MOFs materials, photocatalysis has become one of the rapidly developing fields in recent years.

This article starts from the photocatalytic reactions that MOFs materials can undergo, and mainly summarizes the research progress in the three major areas of photocatalytic water splitting for hydrogen production, photocatalytic reduction of carbon dioxide, and degradation of pollutants using MOFs materials. Finally, a brief outlook is given on the future development of MOFs materials in the field of photocatalysis.

2. Application of mofs materials in photocatalysis field

2.1 MOF materials photocatalytic water splitting for hydrogen production.

Hydrogen is a renewable green energy source that has long been considered one of the ideal energy sources for human use due to its much higher energy density than traditional chemical dyes. And because there is an abundance of water on Earth, the decomposition of water to produce hydrogen is undoubtedly one of the best solutions for producing hydrogen, providing the possibility for humans to utilize energy with even higher energy density.

Since 1972, when Japanese scientists Fujishima Akira and his teacher Honda discovered the phenomenon of continuous hydrogen production on titanium dioxide electrodes (anatase type) under ultraviolet light, the field of photocatalytic water splitting has been opened up, and solar photocatalysis is expected to become the best solution for mass production of hydrogen from water due to its green, clean, and wide-ranging raw material sources. Compared to other traditional solutions for hydrogen production such as electrolysis of water, solar photocatalytic water splitting for hydrogen production has stronger competitiveness.

MOFs materials have significant advantages over traditional inorganic metal materials, such as large specific surface area, adjustable pore size, and flexibility in design. However, the photo-generated electrons and holes in pure MOFs materials are prone to recombination, resulting in a significant drop in the catalytic performance of MOFs materials. As a result, there are very few related studies on using pure MOFs materials for photo-catalytic water splitting to produce hydrogen. The main research trend is to add MOFs materials, some photo-sensitizers, and other co-catalysts to the reaction system for photo-catalytic water splitting to produce hydrogen.

Due to poor catalytic performance of pure MOFs materials, we usually add a small amount of noble metal nanoparticles as co-catalysts to guide electrons and promote the separation of photogenerated electrons and holes, thereby achieving the goal of improving the utilization of electrons to improve the photocatalytic performance of MOFs materials.

MOFs materials can also be combined with semiconductor materials to form composite materials. This is mainly due to the fact that the currently popular method of using semiconductor materials such as titanium dioxide to catalyze the decomposition of water to produce hydrogen also faces problems such as easy recombination of photoelectrons and holes, and limited utilization of solar energy. However, by combining the two, the MOFs material that does not possess photo-catalytic ability itself can serve as a good photosensitizer to improve the light absorption of semiconductor photo-catalytic materials and, to a certain extent, alleviate the above problems and improve the catalytic performance.

2.2 MOFs materials for photocatalytic reduction of carbon dioxide.

Since the first industrial revolution was launched by Britain in the 1860s, human productivity has been greatly enhanced in a short period of time. However, at the same time, a huge amount of greenhouse gas carbon dioxide was emitted into the atmosphere due to the burning of fossil fuels for energy, which is also considered one of the main causes of the current greenhouse effect. In order to alleviate the greenhouse effect, it is necessary to find and develop suitable new materials to adsorb, transform or isolate carbon dioxide to reduce its emissions. One of the most promising ways to convert carbon dioxide is to use photocatalysts to catalyze the conversion of carbon dioxide into some small molecular chemical raw materials or fuels such as formic acid, carbon monoxide, and methanol.

However, it is not difficult to find that the bond energy of the carbon-oxygen double bond in carbon dioxide (750KJ/mol) is much higher than the bond energy of the carbon-oxygen bond and carbon-hydrogen bond in the converted substance (327KJ/mol and 411KJ/mol), respectively. This means that the key to efficiently reducing carbon dioxide lies in effectively capturing and activating it. And the MOFs material's good adsorption of carbon dioxide and its multi-active sites exposed to carbon dioxide due to its porous structure, which brings good activation ability to carbon dioxide, is gradually becoming a good material for carbon dioxide reduction applications and is studied more.

MOF materials have intrinsic semiconductor properties, so pure MOF materials can be used directly as photocatalysts for photocatalytic reduction of carbon dioxide. Since the amino group can effectively improve the interaction between the MOF material and carbon dioxide, the NH2-MIL-125(Ti) material synthesized using 2-aminoterephthalic acid (BDC-NH2) can exhibit better adsorption of carbon dioxide.

In addition, due to the widely recognized photocatalytic or homogeneous catalytic properties of metal complexes such as ruthenium and rhodium, MOFs materials can also utilize these metal complexes to sensitize the photocatalytic reduction of CO_2 through the use of metal complexes. However, it should be noted that when using this method, the metal complexes used as homogeneous catalysts are difficult to separate and tend to become unstable during the catalytic process, which can cause product contamination and render the catalyst inactive and unable to be recycled. If the metal complexes are fixed in situ to the MOFs material using a synthesis method, these problems can be effectively solved, and the synergistic catalysis between the two can be promoted to improve the overall photocatalytic performance.

2.3 MOFs materials degrade pollutants.

Currently, due to the rapid development of industry and improper treatment of pollutants, many regions around the world are facing serious water pollution problems, and among them, water pollution caused by organic dyes is particularly severe. Organic dyes generally have stable chemical properties and have a long natural degradation cycle in nature, and entering the water source can pose a great threat to human health if consumed. Therefore, it is now necessary to develop an effective and economical means of dealing with these pollutants. Photocatalysis, a method of utilizing renewable and gentle solar energy to effectively and economically treat pollutants, has received considerable attention.

MOFs, a new type of catalytic material, has been widely used in advanced oxidation technology and has shown great potential for the treatment of organic pollutants. A variety of MOFs materials with diverse structures and compositions have been developed, and researchers have continuously improved and modified classic MOFs materials to develop more functional photocatalytic materials, effectively degrading pollutants and better addressing the challenges posed by pollutants.

Essentially, the process of degrading pollutants using MOFs materials involves utilizing the strong oxidizing properties of hydroxyl radicals generated during the photocatalytic process to react with organic dye pollutants, ultimately breaking them down into carbon dioxide, water, and other pollution-free substances. In this reaction process, because the production of hydroxyl radicals on the surface of the photocatalyst during the lighting process is the key to degrading organic fuel pollutants, the catalytic activity of the MOFs material as a photocatalyst is related to factors such as the pH of the solution, the solvent, and others that affect the number of hydroxyl radicals in the solution. Research has shown that the vast majority of MOFs materials can be used as photocatalysts for degrading organic dye pollutants.

MOFs materials and other semiconductor materials can be used for the degradation of organic pollutants through photocatalysis. Some MOFs materials with a defined crystal structure can serve as photosensitizers, expanding the effective light capture and light contact area of the photocatalyst. Alternatively, MOFs can serve as the photocatalyst, with the photoelectrons easily transferred from the organic ligands in the MO material to the metal cluster (LCCT). Of course, MOFs materials and semiconductors can also be used separately as photocatalysts. In addition, the photocatalytic activity of MOFs materials can be improved by extending the light absorption region to the visible light region through the addition of amine, allowing the photocatalyst to better utilize solar energy and improve its catalytic activity. However, this method has not yet been widely applied, and can provide a direction for future improvements in catalyst catalytic activity.

3. Conclusion and prospects

This paper reviews the recent advances and applications of MOFs materials in the field of photocatalysis. As a novel and promising photocatalytic material, MOFs materials have received more attention and have attracted many researchers to conduct studies in recent years. Although the design, preparation, and application prospects of MOFs materials in the catalytic field seem promising, there are still some problems and challenges in the actual application of modified MOFs materials in the treatment of wastewater organic matter, photocatalytic hydrogen production by water splitting, and photocatalytic reduction of carbon dioxide. At present, there are still many unknowns in the systematic design of MOFs materials that need to be explored. How to choose the most promising catalyst from a large number of MOFs materials and complete the targeted chemical reaction specifically, and how to meet the higher standards of industrial application for catalytic materials, etc., require further research to solve these problems in the future.

In summary, MOFs materials have their own unique charm in the field of photocatalysis. The current in-depth research on MOFs materials is of great significance for expanding the practical application of MOFs materials and improving photocatalytic reactions. In the not-so-distant future, MOFs materials will experience faster development to meet the problems that society will face in the areas of energy and environment.

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