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Original Paper

Application and Challenge of Cadmium Sulfide Photocatalytic Hydrogen Production in Artificial Photosynthesis

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Abstract

Cadmium sulfide (CdS), as an important photocatalyst, has high photocarrier separation efficiency and quantum efficiency, which makes cadmium sulfide have significant advantages and wide application prospects in the field of photocatalytic hydrogen production. This paper will explore the properties of cadmium sulfide (CdS), the mechanism of photocatalytic hydrogen production, and its application in artificial light synthesis, and discuss current challenges such as photocorrosion, quantum efficiency, and propose possible solutions.

Keywords

Cadmium sulfide (CdS), photocatalytic hydrogen production, artificial light synthesis

With the rapid development of global economy, the energy crisis caused by industrialization and urbanization has seriously restricted the development. (Liu, Iocozzia, Wang et al., 2017) of human beings. Adhering to the road of sustainable development is the main development concept at present, so solar energy and hydrogen energy are environmentally friendly energy that meet the needs of future development. Solar energy is a kind of renewable and inexhaustible energy, and the technology of rational utilization of solar energy has broad prospects, and has made an indispensable contribution to alleviating the energy supply problem of human society. As a clean energy carrier with high fuel value, hydrogen is considered to be one of the most promising ways to solve energy problems in the future. Since Fujishima and Honda pioneered the use of Pt/TiO_2 electrode photoelectrochemical water decomposition to produce H_2 in 1972, solar hydrogen production through artificial photosynthesis has rapidly become a promising method for converting solar energy into hydrogen. (Fujishima & Honda, 1972) Since then, the development of semiconductor photocatalysts has become one of the important problems for researchers.

Among the many photocatalytic hydrogen evolution materials, metal sulfide has aroused people's interest in the field of photocatalysis due to its excellent optical, physical and chemical properties. Cadmium is a transition element with excellent electrical conductivity and good corrosion resistance. Nanometer cadmium sulfide (CdS), as an important classical II-VI semiconductor material, has been widely used in photochemical batteries and energy storage devices for its low cost, narrow band gap of about 2.4eV, abundant polycrystalline state and excellent electronic/optical properties, and has been widely studied in the fields of photoluminescence, electroluminescence, sensors, infrared window materials, photocatalysis and so on. However, it is still severely hindered by its inherent drawbacks. One of the biggest limitations is the instability of CdS, which results from photocorrosion during the reaction. Typically, S^{2-}in CdS are vulnerable to attack by photoexcited holes, leading to instability in CdS and the release of Cd^{+}. Another fatal disadvantage is rapid charge recombination, which results in low quantum efficiency. In addition, insufficient surface active sites and poor light absorption also limit the application of CdS in solar energy conversion.

1. Photocatalyst for Cadmium Sulfide

1.1 The Basic Characteristics of Cadmium Sulfide

Cadmium sulfide is a common semiconductor material, with high stability, easy synthesis and other advantages. The bandgap width of cadmium sulfide is about 2.4 eV, which makes it have high photoelectric conversion efficiency in the ultraviolet and visible range. Cadmium sulfide has good chemical and thermal stability, which makes it have a wide application prospect in the field of photocatalysis.[8] However, because cadmium sulfide is a direct band-gap semiconductor, electrons that transition from valence band to conduction band will quickly recombine with holes in a very short time, so the carrier utilization rate is low. In addition, CdS and CDs-based catalysts have disadvantages such as low photocatalytic activity and poor photostability due to serious photocorrosion and rapid recombination of charge carriers. Cds-based photocatalysts are prone to photocorrosion under light irradiation, because sulfur ions (S^{2-}) oxidize to sulfate ($SO_4^{\ 2-}$) or sulfur (S^0), resulting in the inactivation of the photocatalyst, resulting in the stability of the catalyst is greatly affected.

1.2 The Mechanism of Photocatalytic Hydrogen Production

Photocatalytic hydrogen production refers to the use of photon energy to split water into hydrogen and oxygen. This process involves the interaction of semiconductor materials, water molecules, and electrons. When light hits the semiconductor material, it absorbs photon energy, creating an electron-hole pair. The electron hole pairs recombine on or near the surface of the semiconductor material, releasing energy and producing hydrogen. The energy of the photons is absorbed by the semiconductor material and converted into electrical energy, thus achieving photoelectric conversion.Cadmium sulfide plays an important role in photocatalytic hydrogen production, mainly because cadmium sulfide has good photogenerated carrier separation efficiency and stability. The photogenerated electrons and holes of cadmium sulfide can be effectively separated in the semiconductor material, avoiding the electron-hole pair recombination, and improving the hydrogen yield.

2. The application of Photocatalysis in Artificial Photosynthesis

2.1 Photocatalytic Water Splitting

Photocatalytic water splitting for hydrogen production is an ideal sustainable energy solution, and the use of solar energy as an abundant, clean and almost cost-free energy source to produce hydrogen is widely regarded as an important development direction in the future energy field. For the photocatalytic decomposition of aquatic hydrogen technology, semiconductor photocatalysts play a central role in this process. By absorbing sunlight, they excite electrons to jump from the valence band to the conduction band, creating electron-hole pairs that are key to the subsequent water-splitting reaction. The more negative the conduction band position of the semiconductor photocatalytic material is, the more favorable it is to catalyze the reduction reaction of water and produce hydrogen. The location of the conduction band directly affects the catalytic activity and efficiency of the semiconductor material. In addition to the conduction band position, the band gap of the semiconductor material is also very important, and the appropriate band gap can ensure that the photocatalyst absorbs more light, especially visible light, thereby improving the overall photocatalytic efficiency.

2.2 Photocatalytic Degradation

With population growth and increased industrialization, pure and clean water resources are becoming increasingly scarce. Water body pollution involves not only organic pollutants, but also harmful microorganisms, posing a serious threat to human health and ecosystems. Traditional methods of wastewater treatment are often cumbersome and costly. Therefore, the development of simple, green and low-cost water treatment methods has become a top priority. Photocatalysis technology offers a new solution. By using sunlight, especially in its maximum wavelength range, photocatalysts can effectively inactivate harmful microorganisms in water and degrade organic pollutants. The mechanism of photocatalytic reaction to degrade organic pollutants follows the following steps: Under the action of photocatalyst, when the absorbed photon energy is greater than its band gap, photogenerated electrons and holes will be produced. These photogenerated holes can trap water molecules or hydroxyl groups and generate hydroxyl radicals ($\cdot OH$) with strong oxidizing properties. Photogenerated electrons can produce oxygen free radicals (O^{2-}) on the surface of the catalyst. These free radicals are the main active substances as well as powerful oxidants that can effectively break down organic pollutants Photocatalytic treatment can not only effectively degrade organic pollutants, but also deal with microbial contamination in water. (Nida, Bilal, Khalid et al., 2016) As a green and cost-effective technology, photocatalysis has shown great potential in the field of water treatment, and has therefore received extensive research attention.

2.3 Photocatalytic CO_2 Reduction

The strategy of photocatalyzing CO_2 into a useful fuel is very promising, and it can not only help reduce carbon dioxide in the atmosphere, but also produce valuable chemicals such as methane, methanol, carbon monoxide, ethanol, and formic acid, among this process mimics photosynthesis in many ways in green plants, and has important implications for solving the energy crisis and climate change. (Xiong, Song, Di et al., 2019) In photocatalysis, the photocatalytic material absorbs sunlight and excites electrons to jump from the valence band to the conduction band, producing photogenerated electrons and holes that can reduce CO_2 to form CO, methane or other multi-carbon products. The application of this technology can help reduce the concentration of CO_2 in the atmosphere while producing carbon-based compounds that can be used as fuels or chemical feedstocks, thus both reducing greenhouse gas emissions and providing a renewable source of energy. Although the concept of photocatalytic CO_2 reduction is attractive, there are currently challenges in terms of yield, selectivity and catalyst stability, with inefficiency and lack of stability being the main obstacles preventing the industrialization of this technology. To bring the photocatalytic CO_2 reduction technology to the level of industrial application, further research is needed to optimize the design of the catalyst and improve the photocatalytic efficiency and stability, while also improving the selectivity and yield of the product.

3. Challenges and Solutions

CdS are widely used in the study of photocatalytic cracking of water driven by visible light due to their unique properties, but their performance is still severely hampered by inherent drawbacks. One of the biggest limitations is the instability of CdS, which stems from photocorrosion during the reaction. Typically, S^{2-} in CdS are vulnerable to attack by photoexcited holes, leading to instability in CdS and the release of Cd ions. Another fatal disadvantage is rapid charge recombination, which results in low quantum efficiency. In addition, insufficient surface active sites and poor light absorption also limit the application of CdS in solar energy conversion.

3.1 Energy Band Regulation

The regulation of semiconductor band structure is a very important field, which directly affects the electronic and optical properties of semiconductor materials. Doping and constructing solid solutions are two important means of regulating band structure. Doping refers to the introduction of foreign atoms (dopants) into the semiconductor lattice. Dopants can be either donors of electrons (N-type doping) or recipients (P-type doping). Dopants adjust a material's band structure by changing its conductivity and introducing new energy levels. This method is essential for improving the light absorption properties of the material and adjusting the carrier concentration and mobility, among other things. Chen et al. (Shi, Ye, Liang et al., 2018) created an effective electron trap level by doping phosphorus (P) into CdS (Cadmium Sulfide) and utilizing the sulfur vacancy. This change not only extends the lifetime of photogenerated electrons, but also enhances their performance in photocatalytic reactions, especially in the process of photocatalytic hydrogen evolution. In addition, the band structure can also be controlled by constructing solid solutions. A solid solution is a material made by mixing the atoms of two or more compounds in a certain proportion in the same lattice. By constructing a solid solution, the energy band structure can be adjusted and optimized on the basis of the original material, thus affecting its light absorption characteristics and carrier dynamics. Huang et al. (Huang, Fang, Yu et al., 2020) prepared $Cd_XZn_{1-X}S$ nanocrystalline solid solution by hydrothermal method, which showed excellent photocatalytic hydrogen evolution performance. The combination of twin structure, sulfur-rich vacancy and wurtzite sphalerite phase not only promotes the effective separation of photogenerated electrons and holes, but also improves the utilization rate of photogenerated electrons for hydrogen production reaction.

3.2 Morphologic Control

The morphology of photocatalyst has a significant impact on its photocatalytic performance, which is directly related to the number and accessibility of surface active sites and the transport characteristics of charge carriers. In recent years, many morphologies of CdS have been explored, including 0D, 1D, 2D and 3D structures, and the corresponding synthesis mechanism has been proposed, and the relationship between CdS and photocatalytic activity has been analyzed. For example, Xiang et al. found that 2D ultra-thin CdS nanosheets obtained by calcination at 300°C for 4 h showed excellent photocatalytic activity, and the photocatalytic hydrogen production rate at 450 nm reached 149.67 μmol h^{-1}, and the corresponding apparent quantum efficiency was 36.7%. The high crystallinity of CdS and the ultra-thin two-dimensional nanosheet structure provide a high surface-to-volume ratio and an abundance of active adsorption sites, thus achieving enhanced photocatalytic activity and excellent photocatalytic stability. The two-dimensional ultrathin nanosheet structure prevents surface sulfide ions from being oxidized due to the extremely short interfacial distance and photocatalytic carrier transport, resulting in effective photocorrosion inhibition.

3.3 Defect Engineering

Materials in the synthesis process is inevitably accompanied by the existence of defects, in the material discipline, defects are divided into point defects, line defects, surface defects and body defects. (Bai, Zhang, Gao et al., 2018) Point defects can significantly change the electronic properties of materials, affecting the conductivity and optical properties of materials by acting as electron acceptor or donor. Line and surface defects involve larger scale structural incompletions, such as dislocations (line defects) and grain boundaries (surface defects), which can affect the mechanical, electronic, and thermal properties of the material. Bulk defects are large scale defects within the material, such as holes or cracks. They typically affect the structural integrity and macroscopic properties of the material. In semiconductor materials, the presence and regulation of defects is particularly important for their electronic properties. A moderate amount of surface defects can enhance photocatalytic efficiency, while in vivo defects usually have a negative impact on photocatalytic performance. Chen et al. demonstrated a strategy to control sulfur vacancy (VS) concentration in CdS nanorods by changing the molar ratio of the chemical precursor, and successfully improved the efficiency of electrocatalytic CO_2 reduction. At a Cd/S ratio of 2:1, the concentration of sulfur vacancy reached 9%. As a defect, the sulfur vacancy provides an additional active site on the surface of the CdS nanorods, which helps to electrocatalyze the CO_2 reduction reaction.

3.4 Support Cocatalyst

Cocatalyst is considered to be one of the most effective ways to improve the photocatalytic hydrogen production performance of CdS water decomposition. On the one hand, the cocatalyst can act as the reduction or oxidation active site of water and catalyze the surface reaction by reducing the activation energy. On the other hand, the junction or interface formed between the cocatalyst and CdS facilitates charge separation and transport, thus inhibiting the recombination of photogenerated electrons and holes. In order to realize the rational design of cocatalyst, it is necessary to coordinate the energy level and electronic structure of cocatalyst and CdS. That is to say, the co-catalyst and CdS should have compatible lattice and electronic structures with suitable Fermi level or band level so that the transfer of charge occurs in the correct direction between the semiconductor and the co-catalyst driven by the built-in electric field at the interface. Zhang (Zhang, Yang, He et al., 2022) et al. prepared a Pt nanoparticle decorated CdS nanorods (CdS/Pt) photocatalyst and demonstrated that there are three main electron quenching pathways in CdS, including shallow electron capture, recombination of free electrons and trapped holes, and interband recombination of electron-hole pairs. The latter two processes consume most of the light-generated charge carriers. For CdS/Pt, the deposition of Pt NPs not only weakens the surface defects of CdS and inhibits electron capture, but also builds an efficient electron transfer channel at the CdS/Pt interface. Non-precious metals, due to their unique advantages such as low cost, easy availability and superior transport performance, become an ideal substitute for co-catalysts of CdS photocatalysts.

3.5 Construct a "Junction" Structure

The photogenerated electron-hole pair is easy to recombine during the transfer to the surface reaction site, which greatly reduces the photocatalytic activity of the catalyst. Through the difference of energy band structure of different photocatalysts, an internal electric field can be formed at the material interface, which helps to drive the photogenerated electrons and holes to migrate in different directions, improve their transport efficiency to the reaction site, and thus improve the photocatalytic activity. Scholars have indeed proposed the concept of many different types of "junctions", including heterojunctions, out-of-phase junctions and in-phase junctions, and the design and construction of these structures have played a key role in improving the efficiency of photocatalysis.

Firstly, three main types of heterojunction structures are introduced. A Type I heterojunction is made up of two semiconductor materials in which the conduction and valence bands of one material are located between the conduction and valence bands of the other material. This structure forms a "potential well" that helps increase the concentration of charge carriers, but may limit its migration between the two materials, and the electron-hole pair is not very efficient at separating. In a type II heterojunction, the conduction and valence bands of the two semiconductor materials are staggered, and as electrons transition from the conduction band of one semiconductor to the conduction band of the other, the holes move between the valence bands. This type of heterojunction provides a more efficient charge separation mechanism, facilitating the separation of electrons and holes and reducing the possibility of internal recombination. A Type III heterojunction is coupled by two semiconductors, one of which has lower conductance and lower valence and conduction band potential than the other. The Type III structure makes the separation of electrons and holes more difficult because they tend to migrate into the same material, potentially leading to rapid recombination of electron-hole pairs. In some cases, a type III semiconductor heterojunction can be applied in a Z-Scheme heterojunction to connect the two semiconductors by some type of bridge, paving the way for the bonding of the holes of semiconductor 2 and the electrons of semiconductor 1.

A heterojunction is indeed a special type of heterojunction in which different crystalline phases of the same semiconductor material form an interface that has a significant effect on charge separation and transfer. When semiconductor materials with different crystal phases form a heterojunction, due to their different band structures (conduction and valence band energy levels), an internal electric field will be formed at the contact interface, which helps to separate the electrons and holes generated by light excitation. The heterojunction of some semiconductor compounds with polycrystalline phases has been shown to improve the photocatalytic performance. P25 is a typical example, it is composed of anatase phase and rutile phase TiO_2. This structure is excellent at improving photocatalytic activity, outperforming TiO_2 with a single crystalline phase, because the interface between the anatase and rutile phases promotes more efficient charge separation. (Kevin, Paul, & Kimberly, 2010) A similar phenomenon was found in Ga_2O_3 (Wang, Xu, Li et al., 2012) and $CaTa_2O_6$ (Wang, Chen, Aleksander et al., 2013) with phase junctions. But the phase junction is not a simple mixture of different crystalline phases of a semiconductor. Since the interfacial charge transfer between different phases is key to facilitating electron-hole separation, establishing a clearly defined interface is essential for the design of the junction.

An in-phase junction is an interfacial region formed between the same semiconductor of the same crystalline phase. Bai (Bai, Zhou, Zhang et al., 2019) et al. found that the band structure of a semiconductor is closely related to the particle size of the material according to the quantum limiting effect. Semiconductors with different particle sizes have different degree of band bending, and then an internal electric field is formed on the same semiconductor interface with the same crystal phase and different particle sizes. The built-in electric field formed in the in-phase junction region will promote the transfer of photogenerated electrons from large semiconductor particles to small semiconductor nanoparticles, while the photogenerated holes will migrate in the opposite direction, which effectively inhibits the photogenerated electron-hole recombination and achieves efficient photocatalytic activity.

4. Conclusion

In order to overcome the challenges of stability and efficiency in photocatalytic hydrogen production of cadmium sulfide, the modification methods of cadmium sulfide are continuously studied. As a renewable energy production mode, in the design and optimization of cadmium sulfide photocatalytic hydrogen production system, it is necessary to avoid the use of harmful metals and organic solvents, select low-cost, renewable materials, and optimize reaction conditions to reduce energy consumption.

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