Synthesis and Application in Photocatalytic Hydrogen Production of Layered MoS$_2$

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Abstract. With the consumption of energy and the destruction of the environment by mankind, mankind is now facing a serious energy and environmental crisis. In order to solve this situation, photocatalytic hydrogen production from water will become an effective way. MoS$_2$ shows a good potential for photocatalytic hydrogen production, and the research in this paper will help to develop efficient photovoltaic hydrogen production materials. Two-dimensional MoS$_2$ is a layered transition metal compound similar to graphene. For its advantages, such as large specific surface area, suitable band gap, high catalytic activity of hydrogen evolution by edge suspension bond and strong photocorrosion resistance, it shows good application potential in photocatalytic hydrogen production. This paper summarizes the research progress of layered MoS$_2$ in photocatalytic hydrogen production in recent years. The preparation method of two-dimensional layered MoS$_2$, the structure and properties of MoS$_2$, and the application of the composite system formed by MoS$_2$ and other semiconductor materials in photocatalytic hydrogen production are introduced. Besides, the author discussed the development prospects of MoS$_2$.

1. Introduction
The main production and living energy of human beings comes from the burning of fossil fuels, and excessive burning of fossil fuels will face the problem of energy depletion and pollution discharge, these problems will cause great damage to the resources and environment. Solar energy is a kind of inexhaustible energy. Catalytic preparation of clean hydrogen energy through solar energy is an effective method to alleviate the current energy and environmental crisis. In order to facilitate the development of efficient photovoltaic hydrogen production materials, this article studies the synthesis of layered MoS$_2$, which shows good photovoltaic potential for hydrogen production, and its application in photocatalytic hydrogen production. The Gibbs free energy exchange current density function of MoS$_2$ absorbing hydrogen atoms is very close to that of catalysts such as Pt and Pd, and has a small over-potential of hydrogen evolution. The band gap width increases with the reduction of the number of layers, and becomes 1.9eV when reduces it to a single layer, and the corresponding absorption wavelength is 652nm, which belongs to visible light range. In addition, MoS$_2$ has a large yield and low price, which can realize large-scale production of photocatalytic hydrogen production.

2. Synthesis of two layers of MoS$_2$

2.1. Mechanical stripping method
The mechanical stripping method overcomes the intermolecular Van der Waals force by stripping the layered structural block materials with special Scotch tape, and finally obtains single-layer or multi-layer nanomaterials, which is a relatively mature 2D layered material preparation method at
present. The MoS\textsubscript{2} layered material prepared by the mechanical peeling method has a complete crystal structure and high purity. This method is also simple and easy to operate. However, due to its poor reproducibility and difficulty in large-scale preparation, the yield is very low, so it is generally used for laboratory research. Gacem et al. proposed an improved mechanical stripping method using wafer bonding to increase production and control the number of layers [1]. A piece of MoS\textsubscript{2} crystal is placed on the heat-resistant glass, and an anode electrode is connected to the MoS\textsubscript{2} crystal, and a cathode electrode is connected to the heat-resistant glass. A voltage of 200–1500 V is loaded between the two electrodes to a temperature of 130–200 °C to promote anode bonding. Finally, the bonded crystals are mechanically peeled off by adhesive tape to obtain MoS\textsubscript{2} flakes on the glass substrate.

2.2. Chemical method
Chemical methods include lithium ion intercalation and liquid phase exfoliation. The process of lithium ion intercalation is illustrated in figure 1. The lithium ion intercalation method dissolves the MoS\textsubscript{2} powder into the intercalation agent such as n-butyl lithium, and produces hydrogen gas between the crystal layers. The distance between the MoS\textsubscript{2} layers is increased to reduce the van der Waals force. Then the two-dimensional layered molybdenum disulfide with few layers to single layers is obtained by ultrasonic treatment. The advantage of this method is that the quality of 2D layered molybdenum disulfide obtained is better and the stripping degree is higher [2]. Liquid stripping method is the ultrasonic dissection of MoS\textsubscript{2} powder solution, in order to break the van der Waals forces inside the material and obtain the thin layer structure of the material. Larger particles are then removed from the solution by centrifugation, after the thin layer is obtained. The area and thickness of the thin layer structure is of high controllability. This method is easy to operate and the product is suitable for terahertz speckle measurement, but the product sheet form is easy to be broken in the process of ultrasonic processing. The quality of the thin layer is not high, and the product is made up of many tiny pieces of layer structure disorderly stack together.

![Figure 1. Schematic view of lithium ion intercalation method](image)

2.3. Chemical vapor deposition
The basic principle of chemical method is to peel the multi-layer MoS\textsubscript{2} into a single layer or a few layers, while the principle of chemical vapor deposition is to use gaseous substances to carry out chemical reactions on the solid surface and directly generate MoS\textsubscript{2} films. The chemical vapor deposition device is shown in figure 2 (a). The source in the quartz tube is heated by a thermostatic electric furnace and volatilized. The volatile source initiates a biochemical reaction at high temperature and is transported to the downstream of the quartz tube under the action of inert gas. The temperature drop in the downstream of the quartz tube results in the deposition of the products after the chemical reaction and then falls onto the pre-placed substrate. The optical microscope image of the synthesized MoS\textsubscript{2} is shown in figure 2 (b). In the process of chemical vapor deposition, gas flow rate, pressure and temperature have important effects on deposition rate, film thickness and uniformity. The sample synthesized by this method has a large area, which is conducive to measurement and
characterization, but usually some impurities will be introduced to affect the study of its layered structure [3].

![Figure 2](image)

**Figure 2.** Fig. 2 (a) Device diagram of CVD method for synthesizing single-layer MOS2; (b) Optical microscope images of monolayers of MoS2 synthesized on SiO2/Si substrates by CVD method.

3. Structure and properties of MoS2

Layered MoS2 was prepared by many methods for research precisely because layered MoS2 has large specific surface area and suitable band gap width, which shows good application potential of MoS2 in photocatalytic hydrogen production.

3.1. Crystal structure of layered MoS2

Layered MoS2 is similar to the graphene layer structure, each layer is electrically neutral and, with similar lamellar structure of "sandwich". As shown in figure 3, Mo atomic layer sandwiched between two layers of S atoms, and the Mo-S atomic layer through covalent bond links, layered MoS2 "sandwich layer" connect by weak van der Waals force, between each layer spacing of MoS2 is about 0.65 nm, easy to slip along the layer surface [4].

![Figure 3](image)

**Figure 3.** Sandwich structure of 2D layered molybdenum disulfide

MoS2 has three crystal structures, 1T, 2H and 3R structures. The three structures are shown in figure 4. 1T-MoS2 is metastable, and a phase transition from 1T to 2H occurs at high temperature. A single cell is octahedral coordination, and each "sandwich" layer acts as a stacked repeating unit. 2H-MoS2 is a stable state, the most common, with two "sandwich" layers as repeating units, and each layer of metal atom has tourism coordination. 3R-MoS2 is a metastable state with three "sandwiches" as repeating units, and the coordination of each layer of metal atoms is also tri-prism, usually associated with the chemically synthesized 2H structure transition metal thionides.
3.2 Energy band structure of layered MoS$_2$

The electronic band structure of MoS$_2$ is closely related to the number of layers. The band gap of block MoS$_2$ is indirect band gap with a bandwidth of 1.2eV, and the band gap of single layer MoS$_2$ is direct band gap with a bandwidth of 1.9eV. As the number of layers of block MoS$_2$ decreases, the quantum size effect appears, and the quasi-continuous energy level changes into discrete energy level. Figure 5 shows that the electronic structure of MoS$_2$ changes, and the band gap widens gradually with the reduction of the number of layers. When the number of layers is single layer, due to the hybridization of the Pz orbital of S atom and the d orbital of Mo atom, the transition mode of the electron is changed to vertical transition, and the band gap is transformed from indirect band gap to direct band gap [5].

4. Application of four MoS$_2$ and its complex in catalytic hydrogen production

4.1. Photocatalytic hydrogen production

4.1.1. Principle of photocatalytic hydrogen production. The basic conditions for photoluminescence water catalyst must be: H+/H$_2$ and O$_2$/H$_2$O oxide-reduction potential falls between the valence band maximum (VBM) and the BandMinimum (CBM) of the material. The process of photogenerated electrons and holes on the surface of semiconductor catalyst by light irradiation is summarized in figure 6. After the material absorbs photons, the electrons transition from valence band (VB) to the luminous band (CB), and the luminous holes are generated in VB [6]. The electrical potential of CBM is higher than the redox potential of H+/H$_2$, so the luminous electrons can reduce H$^+$ to H$_2$ in the...
water. The potential of VBM is lower than the REDOX potential of O$_2$/H$_2$O, so the photogenerated holes can oxidize water molecules to O$_2$.

![Figure 6](image.jpg)

**Figure 6.** Diagram of the process of photogenerated electrons and holes produced by light irradiation on the surface of a semiconductor catalyst.

The whole process of photocatalysis can be divided into three steps: photoexcitation produces electrons and holes, electrons and holes are separated and diffused to the surface of the catalyst, oxidation and reduction reactions occur on the surface of the catalyst. When electrons and holes are separated and diffused to the surface of the catalyst, venerated electrons and holes recombine through different mechanisms. Among them, the main mechanism of recombination is described above, that is, venerated electrons fall back into the valence band by means of interband recombination. At the same time, venerated electrons can also be captured by electron traps on the surface or inside the semiconductor, and then recombine. This recombination process can also occur in holes, which are captured by interband or surface state traps. Various possible recombination mechanisms are summarized in figure 7. In the catalytic hydrogen production process, these recombination processes should be inhibited to improve the efficiency of the photocatalytic reaction.

![Figure 7](image.jpg)

**Figure 7.** Diagram of the internal electron transfer process of TiO2/MOS/graphene composite structure as a catalyst for photocatalytic hydrogen production.

Two-dimensional materials have attracted much attention because of their large specific surface area, high carrier migration speed and excellent optical properties. In photo-splitting water hydrogen production areas, because of the differences in body material, the thickness of two-dimensional material is only a few atoms in a certain direction. After the photons are absorbed, it can form electrons and holes directly on the surface. The trip of the bright raw electrons and holes migrate to the material on the surface is far less than the body material, the rate of the electrons and holes to compound is reduced. In addition, the higher specific surface area of two-dimensional materials is also conducive to the catalytic reaction.
4.1.2. Application of MoS2 in photocatalytic hydrogen production. Latorre-Sanchez et al. prepared sheet MoS2-graphene heterostructural materials. The photocatalytic hydrogen production efficiency of this heterostructured material is twice times higher than that of pure MoS2 [7]. Chang deposited metal CdS on MoS2- graphene colINCIDENT film, and found that the mass fraction of CdS was 2.0%, and the hydrogen production rate was the highest when the mixture ratio of MoS2 and graphene was 1:2 [8]. Jia et al. dispersed CdS and MoS2 on the graphene nanosheets, and the hydrogen production rate reached 3.072mL/L, greatly improving the photocatalytic efficiency [9]. Moreover, it is found that the electron transfer rate between CdS and MoS2 on the two-dimensional graphite mesh structure is very fast, which can reduce the electron-hole pair recombination in CdS, thus enhancing the efficiency of photoelectric excitation catalytic hydrogen production at the edge site of MoS2.

Xiang et al. prepared TiO2-MoS2/Gr composites by two-step hydrothermal method [10]. The TiO2 nanoparticles are uniformly and tightly attached to the MoS2/Gr composite material, so the electrons can be transferred from TiO2 to MoS2/Gr rapidly, which can effectively promote charge separation and improve photocatalytic activity. They also found that by adjusting the ratio of Gr in the MoS2/Gr composite catalyst and the ratio of MoS2/Gr in the ternary catalyst. The ratio can realize the adjustment of the activity of ternary catalyst. The photocatalytic hydrogen evolution rate of the optimized TiO2-MoS2/Gr composites can reach 165.3μmol·h-1, and the quantum efficiency at 365nm is 9.7%.

The 2D porous g-C3N4 nanosheets/nitrogen-doped graphene/layered MoS2(CNNs/NrGO/MoS2) ternary nanomaterials prepared by Chen et al. [11] show good photocatalytic activity under visible light. Both g-C3N4 nanometer sheets with large specific surface area and layered two-dimensional MoS2 nanometer materials can absorb visible light to enhance the absorption of visible light and generate more venerated carriers. As an electron medium between two-dimensional MoS2 and CNNs in CNNs/NrGO/MoS2 composites, the charge separation and transfer ability of CNNs/MoS2 interface (chip to chip) is improved. This composite structure provides a wide optical window for light absorption, and effectively reduces the distance of charge transmission and diffusion. At the same time, the large contact area also facilitates the rapid separation of carriers. CNNS NRGO/MoS2 composite materials under simulated sunlight irradiation showed enhanced photocurrent density. At the same time, it is a good way to methylene oxidation and reduction of Cr (VI).

5. Conclusion

The preparation method of two-dimensional layered MoS2 is briefly described in this paper. The preparation cost of MoS2 is low and the technology is simple. The width of band gap and conduction band position of monolayer MoS2 make it theoretically able to directly catalyze hydrogen evolution under visible light. Two-dimensional MoS2 photocatalytic materials will play a great role in solving energy shortage and water pollution problems. However, many problems are still need to be solved, such as incomplete controllable preparation, the composite method with other materials to be optimized, the low utilization rate in the near infrared region, and the realization of large-scale production and use of MoS2 still need to be improved. It is necessary to conduct further studies in this field for more improvement.

6. References

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