齐鲁工业大学（山东省科学院）
QILU UNIVERSITY OF TECHNOLOGY SHANDONG ACADEMY OF SCIENCES

本科毕业设计（论文）

题目 Study on the effect of reaction temperature to photocatalytic hydrogen production activity 反应温度对光催化产氢活性的影响研究

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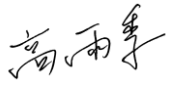
指导教师签名：  　　毕业设计（论文）作者签名： 

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Contents

Abstract in English

Energy is vital to humanity, and the problems of energy shortage and environmental protection have become increasingly severe in recent years. To solve these problems, the development of new energy sources is receiving more and more attention. Quantum dots have been widely studied as photocatalysts capable of harnessing solar energy. Still, the current quantum dots have the drawbacks of low efficiency of photocatalytic hydrogen production and low efficiency of visible light utilization. To find the factors affecting photocatalysis, especially the effect of temperature on photocatalytic activity, Ag-$ZnIn_2S_4$ photocatalysts were synthesized, and varying temperatures in this experiment characterized their photocatalytic activity. The electron sacrifices and concentrations used for testing were also determined by adding different electron sacrifices and concentrations of Ag-$ZnIn_2S_4$ photocatalysts.

The photocatalytic hydrogen production experiments at different temperatures revealed that the photocatalytic activity of Ag-$ZnIn_2S_4$ photocatalyst decreased after 30 °C while the photocatalytic activity of InP/ZnS photocatalyst increased consistently from 10 °C to 50 °C. This result is probably due to the ability of Ag-$ZnIn_2S_4$ to tolerate high temperatures, which is less stable than InP/ZnS. When constructing a photocatalytic hydrogen production system, studying the stability of the photocatalyst used in advance can improve the efficiency of photocatalytic hydrogen production.

Key words： Photocatalyst, Quantum Dots, Temperature, Concentration

Abstract in Chinese

摘 要

能源对于人类至关重要，近年来能源短缺和环保的问题日益严重。为解决这些问题，新能源的发展越来越受到关注。量子点作为能利用太阳能的光催化剂被广泛研究，但是目前的量子点存在，光催化制氢效率低，对可见光利用效率低的缺点。为了找到影响光催化的因素，特别是温度对于光催化产氢活性的影响，本实验通过水热法合成了 Ag-$ZnIn_2S_4$ 光催化剂并进行表征。通过加入不同的电子牺牲体以及不同浓度的 Ag-$ZnIn_2S_4$ 光催化剂来确定测试所使用的电子牺牲体和浓度。

通过不同温度的光催化产氢实验，发现 Ag-$ZnIn_2S_4$ 光催化剂在 30℃之后光催化活性降低而 InP/ZnS 光催化剂在 10℃至 50℃光催化活性一直增加。这是由于 Ag-$ZnIn_2S_4$ 对高温的耐受能力，稳定性不如 InP/ZnS 好。在构建光催化产氢体系的过程中，能够提前研究所使用的光催化剂的稳定性，可以提高体系整体的光催化产氢活性。

关键词：光催化剂　量子点　温度　浓度

Chapter 1 Introduction

1.1 Research background on photocatalytic hydrogen production

Energy is vital to the development of societies and countries. In recent decades, the acceleration of economic growth in developing countries has led to a rapid increase in energy consumption.[1] Fossil fuels produce carbon dioxide, and global energy demand exceeds 12 billion tons of oil equivalent per year, resulting in 39.5 gigatons of carbon dioxide emissions.[2] Carbon dioxide can harm the earth's environment and human life as a greenhouse gas. Fossil fuels are likely to continue to be used as traditional energy sources for decades to come. However, as economic and social demand for energy grows and a low-carbon society emerges, a major shift from conventional fossil fuels to non-fossil energy sources will become inevitable.[3]

Due to climate change and environmental pollution, new clean energy sources are being developed and gradually increasing their share in the energy mix. With technology and new materials, new clean energy sources have emerged, such as nuclear energy, fuel cells, biomass, shale gas, ocean energy, etc.[4] Solar energy is an abundant, clean and renewable source of energy, with an average of more energy hitting the earth every hour than the annual global energy consumption. Still, due to the low energy density of sunlight, it is difficult to be used directly.[5,6] Therefore, borrowing from photosynthesis in nature and converting solar energy into a green and clean energy storage utilising photocatalysis is an effective way to reduce dependence on fossil fuels and damage to the environment. Figure 1.1 shows China's primary energy consumption from 1980 – 2015, and the demand for new energy increased.

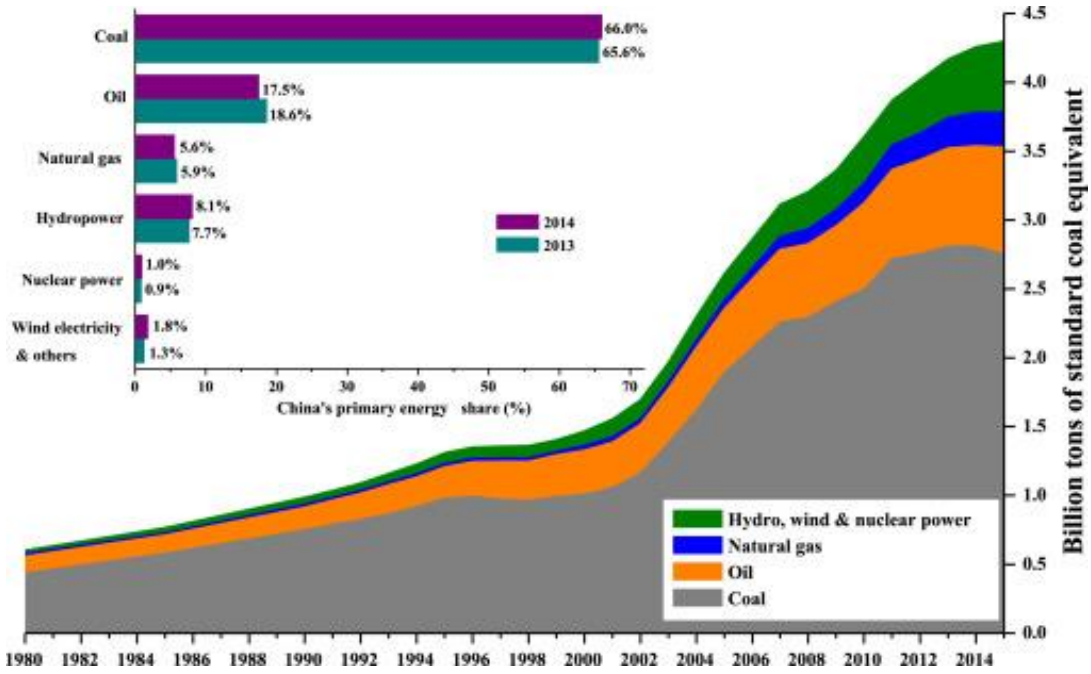


Figure 1.1 China's primary energy consumption from 1980 - 2015[7]

Hydrogen energy is a secondary energy source actively developed in the world's new and renewable energy sector, among the solar fuels generated using the photocatalytic process. Hydrogen does not produce atmospheric pollutants such as carbon dioxide, sulfur dioxide, and soot during combustion. It has relatively strong storability compared to solar and wind energy, so hydrogen energy has been seen as one of the most desirable clean energy sources in the future.[8] Therefore, using semiconductor photocatalysts to convert solar energy into clean and renewable hydrogen energy effectively solves today's energy consumption problems and environmental degradation.

The photocatalytic hydrogen production system constructed using current photocatalyst materials has poor responsiveness to visible light. The conversion rate of solar energy to hydrogen is still low, which cannot meet the requirements for wide application. Therefore, through research and exploration in photocatalytic hydrogen production, we can design and prepare efficient photocatalyst materials and construct efficient hydrogen production systems. This is important to promote rational energy use, energy structure adjustment, and environmental protection. This will play an essential role in promoting reasonable energy use, energy restructuring and ecological protection.

1.2 Principle of photocatalytic hydrogen production

The energy band structure comprises a low-energy valence band (VB) filled with electrons and an empty high-energy conduction band (CB). Semiconductors absorb ultraviolet, visible and near-infrared light, producing holes (h^+) and electrons (e^-), which the electrons are transferred to the conduction band (CB) and leave holes in the valence band (VB). In the presence of an electric field, the electrons and holes are separated and migrate to different positions on the particle surface. The protons from H_2O receive photogenerated electrons and are reduced to hydrogen, while the combination between holes and H_2O leads to oxygen production.[9]

To drive the photocatalytic reaction, the E_{CB} of the photocatalyst is more negative than that of the H^+/H_2 (0 V vs. NHE) potential. The E_{VB} is more positive than O_2/H_2O (1.23 V vs. NHE), which requires the photocatalyst's bandgap to be at least higher than 1.23 eV. Due to the large kinetic overpotential required for hydrogen production and half-reaction processes, the photocatalyst band gap value for photocatalytic decomposition of water to H_2 and O_2 should be more excellent than 1.23 eV.

The reaction process of photocatalytic splitting of water to produce H_2 and O_2 is also summarized as follows:

$$Photocatalyst \overset{hv}{\Rightarrow} e_{VB}^- + h_{VB}^+ \quad (1)$$

$$2H^+ + 2e_{CB}^- \longrightarrow H_2\ (g) \quad (2)$$

$$2H_2O\ (l) + 4h_{VB}^+ \longrightarrow O_2(g) + 4H^+ \quad (3)$$

$$2H_2O\ (l) \overset{hv}{\Rightarrow} 2H_2\ (g) + O_2\ (g) \quad (4)$$

(1) shows the reaction of photon absorption by the catalyst, (2) shows the reduction semi-reaction, (3) shows the oxidation half-reaction and (4) shows the whole reaction.

The photocatalyst can absorb visible light and transfer electrons to the surface to reduce the proton. By accepting electrons from the oxygen/sacrificial agent, the excited photosensitizer returns to the ground state. The sacrificial agent provides electrons to prevent the photogenerated electrons from compounding with holes, thus producing highly efficient hydrogen. The synergistic effect of the above three components can effectively facilitate hydrolysis's photocatalytic hydrogen production reaction.[10]

1.3 Hydrogen-producing photocatalyst

Japanese scientists Fujishima and Hondaz reported a photoelectrochemical cell for the production of multiphase photocatalytic H_2 by water decomposition in 1972[11], which demonstrated the feasibility of hydrogen production by photolysis of water. Various semiconductor photocatalysts, such as chalcogenides, metal oxides and carbonaceous materials, have been studied.[12]

1.3.1 Chalcogenides

Chalcogenides have attracted much attention because of their suitable bandgap structure, abundant active sites and good photostability. So far, many Chalcogenides have been used for photocatalytic hydrogen production studies.[13] There are two types of chalcogenides, one is monochalcogenides (ZnS, CdS, CdSe) and the other is dichalcogenides ($Cd_{1-x}Zn_xS$, Zn-In-S). Among the known catalysts, CdS is widely used for solar photocatalytic hydrolysis reactions because of its suitable energy band position, excellent visible light response and controlled morphology for hydrogen production with a low bandgap (2.44 eV).[14] The photogenerated charges of CdS are easily compounded, and CdS is susceptible to its photo corrosion after a long reaction time, which makes the photocatalytic hydrogen production activity and stability of CdS poor.

1.3.2 Metal oxides

The standard metal oxide photocatalysts are TiO_2、ZnO、SnO_2、VO_x、MoO_x, etc. TiO_2 has been widely studied and applied in various photocatalysts as the most commonly used photocatalyst due to its chemical stability, non-toxicity and low cost.[15] TiO_2 is an n-type semiconductor that shows $\lambda < 400$ nm absorption in the UV region and exhibits excellent photocatalytic properties under ultraviolet (UV) and VL irradiation.[16] ZnO has broad UV absorption, high photostability, a bandgap of 3.37 eV and an immense excitation binding energy (60 meV).[17] Both ZnO and TiO_2 are wide bandgap semiconductors.[18]

1.3.3 Carbonaceous materials

In addition to metal oxides and Chalcogenides, g-C_3N_4 is also a hydrogen-producing photocatalyst. It has attracted worldwide attention due to its visible light activity, easy synthesis of low-cost materials, chemical stability, and unique layered structure. [19] With a moderate bandgap of 2.7 eV, corresponding to a wavelength of 460 nm, g-C_3N_4

can be active in visible light, while g-C_3N_4 can be easily prepared at a low cost. Most importantly, g-C_3N_4 is non-toxic and has good stability. However, g-C_3N_4 has the same drawbacks. g-C_3N_4 has poor light absorption in the visible region and has a low surface area.[20] The combination of carbon materials and semiconductors is reported to improve photocatalytic activity.[21]

1.4 Factors affecting photocatalytic efficiency

According to equation (1) of the photocatalytic hydrogen production principle, the first step is that the semiconductor absorbs ultraviolet, visible and near-infrared light to produce holes (h^+) and electrons (e^-). The bandgap affects the efficiency of photocatalytic hydrogen production, and as mentioned above, ZnO and TiO_2 are wide bandgap semiconductors, so their utilization and conversion of sunlight are low. Acar et al. also summarized the influence of the properties of redox reactions on the photocatalyst surface on the efficiency of photocatalytic hydrogen production, such as surface morphology, crystal structure and particle size, and the resistance to photo corrosion also affects the efficiency of photocatalytic hydrogen production.[22] The reaction kinetics of the oxidation and reduction half-reactions have an essential effect on the hydrogen production activity.

1.4.1 Effect of temperature on photocatalytic hydrogen production

Since hydrolysis is a heat-absorbing reaction, the reaction temperature will affect the reaction. Semiconductor photocatalysts use solar energy to decompose water to produce hydrogen via oxidation-reaction. Ma et al. found that the different temperature-dependent behavior of redox potential is an essential feature of photocatalytic half-reactions.[23] Meng et al. found a positive effect of solution temperature on the photocatalytic activity of g-C_3N_4, TiO_2 and ZnO catalysts. They explained the mechanism of the impact in terms of kinetics and thermodynamics. An increase in solution temperature leads to a faster rate of radical generation, thus increasing the photocatalytic activity.[24] Also, the increase in solution temperature affects different types of semiconductor photocatalysts differently. However, the rise in temperature is detrimental to the photocatalytic process: i) it promotes the complexation of photogenerated electrons and holes, and ii) it promotes the desorption of adsorbed reactants.[25]

1.5 The significance of the topic and the research content of this thesis

Photocatalytic hydrogen production is an effective way to prepare clean energy from solar energy. However, the current efficiency of photocatalytic hydrogen production is still low. It cannot be applied on a large scale, so the study of the reaction conditions of photocatalytic hydrogen production is sought to help improve the efficiency of photocatalytic hydrogen production and thus alleviate the energy shortage problem. As an essential reaction condition for photocatalytic hydrogen production, the effect of temperature on the efficiency of photocatalytic hydrogen production still needs to be studied in depth. To investigate the effect of temperature on photocatalytic efficiency, the following study was done in this thesis.:

(1) The Ag-$ZnIn_2S_4$ photocatalysts were prepared by a one-step hydrothermal method, and the success of the synthesis was verified by an X-ray powder diffractometer, UV-vis NIR spectrophotometer and fluorescence spectrometer. The physicochemical properties of the photocatalysts were characterized.

(2) To determine the appropriate concentration for investigating the effect of concentrations on the efficiency of photocatalytic hydrogen production by adding different concentrations of Ag-$ZnIn_2S_4$ photocatalysts and studying the efficiency of photocatalytic hydrogen production under visible light irradiation.

(3) To determine the suitable electron sacrifices for investigating the efficiency of photocatalytic hydrogen production by adding different types of electron sacrifices and studying the efficiency of photocatalytic hydrogen production under visible light irradiation.

(4) The photocatalytic hydrogen production was carried out at different temperatures under visible light irradiation using Ag-$ZnIn_2S_4$ as the catalyst and isopropanol as the electron sacrifices and comparing the different photocatalytic reaction efficiencies.

Chapter 2 Experiment Section

2.1 Reagents and instruments

The reagents and instruments used in this experiment are shown below in table 2.1 and table 2.2.

Table 2.1 Reagents

Name	Purity	Manufacturer
Silver nitrate ($AgNO_3$)	AR	SINOPHARM
Zinc acetate ($Zn(OAc)_2$)	AR	3AChem
Indium acetate ($In(OAc)_3$)	AR	3AChem
Sodium sulfite (Na_2SO_3)	AR	3AChem
Disodium sulfide nonahydrate (Na_2S9H_2O)	60%	3AChem
Triethanolamine (TEOA)	AR	ALADDIN
Sodium ascorbate ($C_6H_7N_aO_6$)	AR	MACKLIN
Sodium hydroxide (NaOH)	AR	SINOPHARM
Sulfuric acid (H_2SO_4)	AR	SINOPHARM
Triethylamine (TEA)	AR	SINOPHARM
International Phonetic Alphabet (IPA)	AR	SINOPHARM
Nitrogen (N_2)	99.99%	DEYANG
Methane (CH_4)	99.99%	DEYANG

Table 2.2 Instruments

Name	Model	Manufacturer
Centrifuge	H1850	XIANGYI
Gas Chromatograph	GC-2014	SHIMADZU CORPORATION
UV-Visible Near Infrared Spectroscopy Photometer	UV-1800PC	Agilent Technologies, Inc.
Photocatalytic reactor	460nm	Homemade
Fluorescence spectrometer	F97Pro	Lengguang Technology
pH meter	FE28	Mettler Toledo
X-ray powder diffractometer	D8-ADVANCE	Bruker AXS

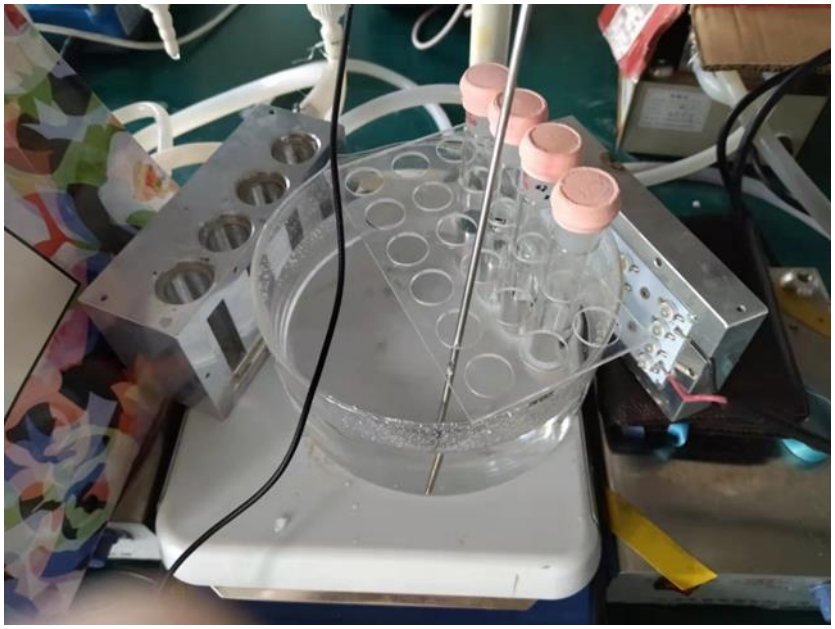
2.2 Synthesis of Ag-$ZnIn_2S_4$ quantum dots

78 mg (0.425 mol) $Zn(OAc)_2$ and 248 mg (0.85 mol) $In(OAc)_2$ should be added to a 50 ml centrifuge tube with 16 ml Ultrapure water. The solution needs to be homogeneously dispersed by ultrasound. After that, the solution needed to be transferred to the PTFE liner, 0.68 ml of $AgNO_3$ solution (0.25 mol/L) was added, and water was made up to 17 ml. After the solution is mixed well, aqueous L-Cysteine solution (1.62 mmol) should be added (196 mg of L-Cysteine solution in 3 ml of ultrapure water), and 10 M of NaOH solution has used the pH of the solution is adjusted to 10.0. Finally, 122 mg of C_2H_5NS should be added to the solution and stirred for five minutes, after which the solution appeared yellow. The PTFE liner is closed and heated to 110°C for 4 hours.

The PTFE-lined solution is cooled to room temperature and transferred to a 50 ml centrifuge tube for centrifugation (8000 r/min, 4 min), after which the residual solids are removed. 20 ml of IPA should be added to the solution and centrifuged (8000 r/min, 4 min), and the solid in the centrifuge tube is dispersed in 10 ml of ultrapure water.

2.3 Photocatalytic hydrogen production experimental

This section will investigate the effect of different electron sacrifices of Ag-$ZnIn_2S_4$ and the concentration of quantum dots on the photocatalytic hydrogen production efficiency. The appropriate concentration and electron sacrifices will be selected to investigate the effect of temperature on the photocatalytic hydrogen production efficiency of Ag-$ZnIn_2S_4$ quantum dots. Picture 2.1 illustrates the photocatalytic hydrogen production device.



Picture 2.1. Photocatalytic hydrogen production device

2.3.1 Photocatalytic hydrogen production experiments with different electron sacrifices

The fact that processes using pure water are usually inefficient or not operable is an important reason for limiting the efficiency of photocatalytic hydrogen production. The use of sacrificial molecules as electron sacrifices can significantly improve the efficiency of H_2 production.[26] Electron sacrifices trap photogenerated holes and promote the reaction. In this thesis, a comparison of photocatalytic hydrogen production

performance is performed by using five different electron sacrifices. The specific practical steps are as follows:

Five 15 mL glass reaction tubes labelled 1, 2, 3, 4 and 5 are used to add a magnetic rotor and 0.2 ml of Ag-$ZnIn_2S_4$ quantum dots and 4.8 ml of ultrapure water. 1 ml of IPA and 200 μL of saturated NaOH solution is added to test tube 1. 0.5M Na $_2SO_3$, Na_2S mixture is added to into test tube 2, 2ml of 200mg/ml Na_2A (Vitamin C sodium) is added to into test tube 3 (To control the total volume of the solution to be the same, the 4.8 ml of ultrapure water initially added to the test tube was adjusted to 3.8 ml.) and change the pH to 5.0-5.3, 1ml TEOA is added to into test tube 4, 1ml TEA is added to into test tube 5, all the tubes should be sealed, and air should be removed from the test tube with N_2. After that, 1.0 ml of CH_4 was injected and sealed with wax, and the tubes were exposed to 460 nm LED light, and the hydrogen gas produced was detected by gas chromatography after two hours of reaction.

2.3.2 Effect of different concentrations of semiconductor catalysts on the efficiency of photocatalytic hydrogen production

Six 15 ml glass reaction tubes labelled 1, 2, 3, 4, 5 and 6 are used to add the magnetic rotor. 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 ml of Ag-$ZnIn_2S_4$ quantum dots are added to glass reaction tubes 1 through 5, respectively, and supplemented with ultrapure water to 5 ml. 1 ml of TEA is added to all-glass reaction tubes, respectively, and then seal all the tubes, and remove the air from the tubes with N_2. After that, 1.0 ml of CH_4 is injected into the tubes, sealed with wax, and the test tubes are exposed to a 460 nm LED lamp, and the hydrogen gas produced is detected by gas chromatography after two hours of reaction.

2.3.3 Photocatalytic hydrogen production experiments with different temperatures

After the above experiments, TEA and Na_2A (Vitamin C sodium) were finally identified as the electron sacrificial bodies used to test the effect of temperature on the efficiency of photocatalytic hydrogen production and the volume of Ag-$ZnIn_2S_4$ used for the test was 0.2 ml. In this section, the experiments consisted of three sets of control experiments. Each group of experiments consisted of hydrogen production experiments with solution temperatures at 10 ℃, 20 ℃, 30 ℃, 40 ℃, and 50 ℃. The experimental procedure for control experiment I was as follows:

Each 15 ml glass reaction tube marked as 1 and 2 was used to add magnetic rotors and 0.2 ml of Ag-$ZnIn_2S_4$ quantum dots, and 4.8 ml of ultrapure water, followed by 1 ml of TEA. all tubes were sealed, and the air in the tubes was removed with N_2. After that, 1.0 ml of CH_4 was injected and sealed with wax, and the solution temperature was maintained at 10 ℃ in a constant temperature water bath. The test tubes were exposed to a 460 nm LED lamp, and the hydrogen gas produced after two and four hours of reaction was detected by gas chromatography. Afterwards, the same reaction system was re-prepared, and the reaction temperature was changed to 20 ℃, 30 ℃, 40 ℃ and 50 ℃ to repeat the above experiments and determine the hydrogen gas produced after two and four hours of reaction at different temperatures.

The second group of experiments changed the electron sacrificial body of the reaction system to Na_2A (Vitamin C sodium) by adding 0.2 ml of Ag-$ZnIn_2S_4$ quantum dots and 3.8 ml of ultrapure water to each tube followed by adding 2 ml of Na_2A (Vitamin C sodium) and adjusting the pH to 5.0-5.3. The other reaction conditions were in the same order as the first group of experiments. The third group of experiments changed the quantum of the reaction system to InP/ZnS by adding 0.2 ml of InP/ZnS quantum dots and 3.8 ml of ultrapure water, followed by adding 2 ml of Na_2A (Vitamin C sodium) and adjusting the pH to 5.0-5.3. The other reaction conditions were the same as in the first group of experiments. Experiments determine the hydrogen gas produced after two and four hours of reaction at different temperatures.

Chapter 3 Results and Discussion

3.1 Characterization

In this section, the characterisation of Ag-$ZnIn_2S_4$ will be detected by XRD, UV-Vis diffuse reflectance spectroscopy and photochemical testing.

3.1.1 XRD Characterization

The crystal structure of Ag-$ZnIn_2S_4$ photocatalyst can be characterised by X-ray powder diffractometry (XRD). As shown in Figure 3.1, there are three distinct diffraction peaks at 2Θ = 27.7°, 55.0°and 56.5°, which correspond to the (102), (110) and (200) crystal planes of the hexagonal Ag-$ZnIn_2S_4$. While the three broad peaks also imply the nanocrystals are tiny in size in three dimensions. The results are identical to the diffraction peaks of Zhang et al. and prove that the synthesised photocatalyst is Ag-$ZnIn_2S_4$. [27] Which demonstrates the successful preparation of Ag- $ZnIn_2S_4$ quantum dots.

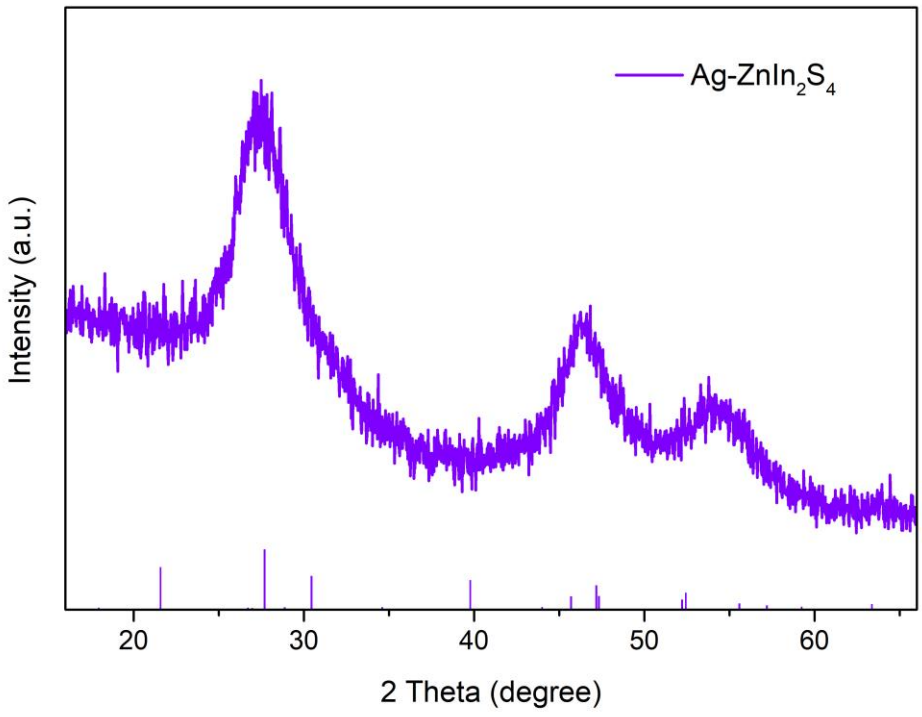


Figure 3.1 Ag-$ZnIn_2S_4$ XRD pattern

3.1.2 Optical characteristics of Ag-$ZnIn_2S_4$

The light absorption properties of photocatalysts can be detected by UV-visible diffuse reflectance spectroscopy. As shown in Figure 3.2 (a), the absorption of Ag-$ZnIn_2S_4$ quantum dots starts from near 500 nm, and the absorbing property increases rapidly, proving that the quantum dots have good absorption properties in the visible region. The fluorescence spectrum can also show the optical characteristics of Ag-$ZnIn_2S_4$. Figure 3.2 (b) shows. The quantum dot has a mighty luminescence peak near 630 nm, which has a significant wavelength difference with the absorption of the quantum dot, indicating that the quantum dot is an indirect bandgap semiconductor.

(a) (b)

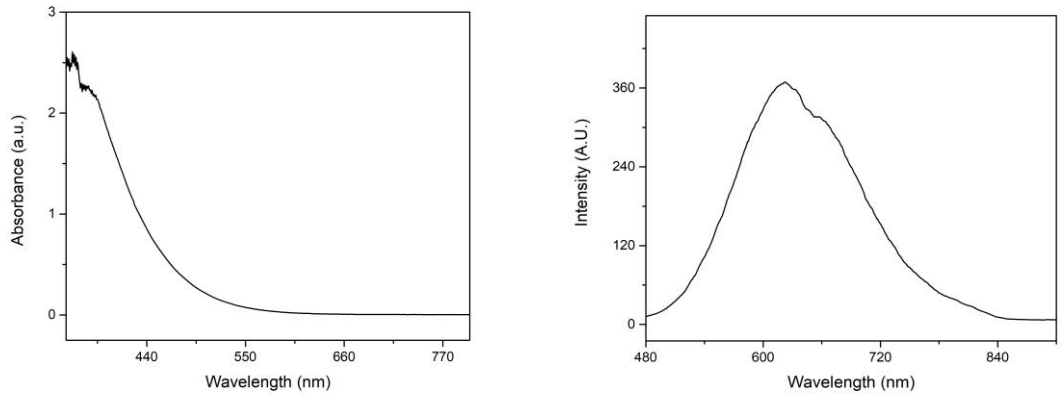


Figure 3.2 (a) UV-Vis diffuse reflectance spectroscopy, (b) Fluorescence spectrum.

The Tauc curve can further investigate the energy band position information of Ag-$ZnIn_2S_4$. Figure 3.3 exhibits that the bandgap of the synthesised Ag-$ZnIn_2S_4$ photocatalyst is 2.60 eV， which proves it has a suitable bandgap to absorb visible light and catalyse the reduction of protons to produce hydrogen gas.

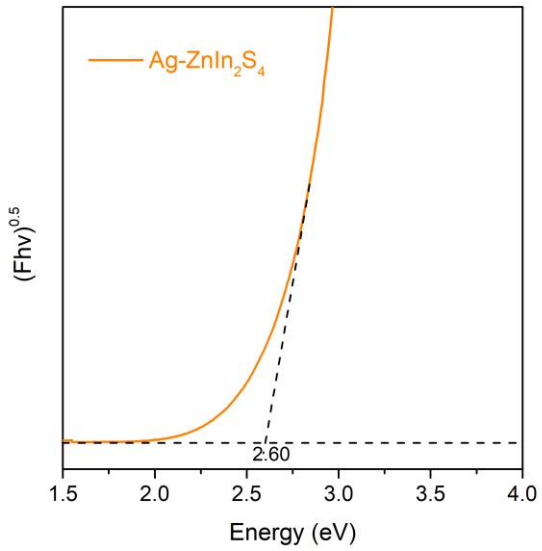


Figure 3.3 Tauc curve of Ag-$ZnIn_2S_4$

3.2 Results of hydrogen production

3.2.1 Different concentrations of Ag-$ZnIn_2S_4$

The first thing to determine when conducting a photocatalytic hydrogen production experiment is the concentration of the photocatalyst (volume of photocatalyst). From figure 3.4, the hydrogen production efficiency per mg decreases with the addition of the photocatalyst, which may be due to the masking effect of the quantum dots. Too low a concentration of photocatalysis can lead to unsatisfactory results. At the same time, too high a concentration can increase the complexity of the experiment (better sealing of the photocatalytic system is required, and increased complexity of the gas chromatograph detection). 2.23 g (2 ml) of Ag-$ZnIn_2S_4$ will be used to screen electron sacrifices and test the effect of temperature on photocatalytic efficiency.

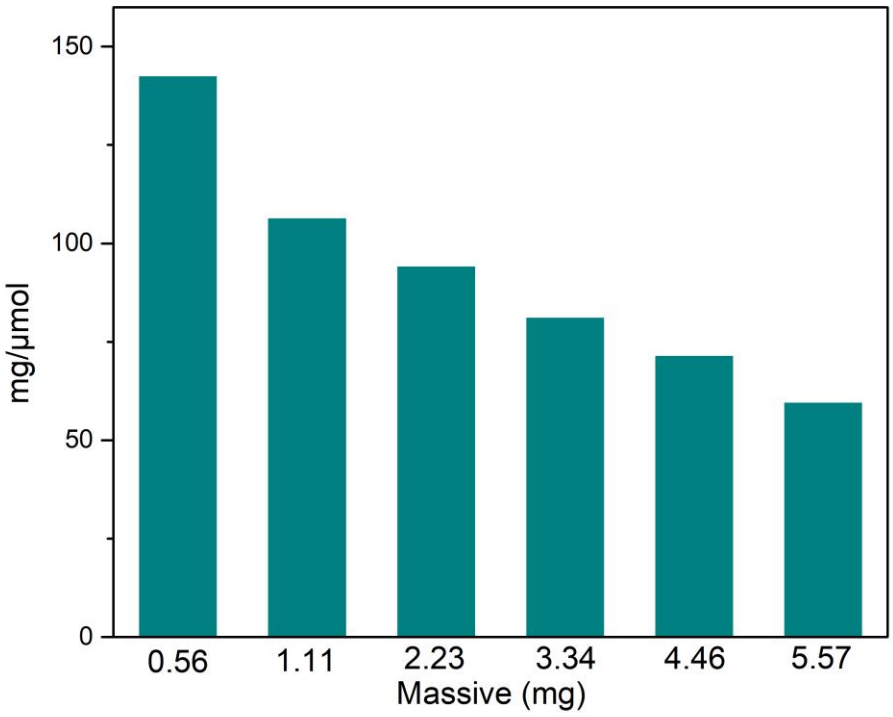


Figure 3.4 Results of hydrogen production with different concentrations

3.2.2 Different electron sacrifices

Figure 3.5 shows the results of hydrogen production with different electron sacrifices. TEA and Na_2A have the highest hydrogen production efficiency, so TEA and Na_2A were chosen as electron sacrificial bodies to study the hydrogen production rate of Ag-$ZnIn_2S_4$ at different temperatures. Different electron sacrifices may cause this phenomenon with varying potentials of redox and adsorption capacities of electron sacrifices and photocatalysts.

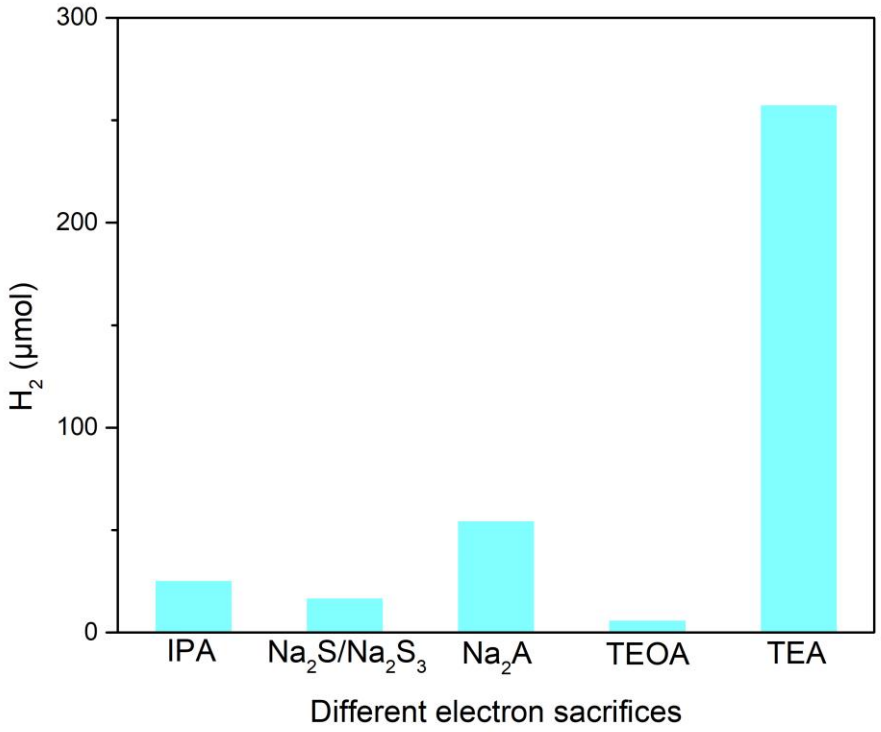


Figure 3.5 Results of hydrogen production with different electron sacrifices

3.2.3 Effect of temperature on photocatalytic efficiency

The photocatalytic hydrogen production activity of Ag-$ZnIn_2S_4$ quantum dots at different temperatures was investigated. Figure 3.6 shows that the photocatalytic activity of Ag-$ZnIn_2S_4$ increases with increasing temperature and reaches the highest photocatalytic activity at 30 ℃. However, the photocatalytic activity d ecreases after temperatures higher than 30 ℃. Under the optimal temperature condition, the hydrogen production activity of this catalyst is about 2.5 times that of 10 ℃, which proves that the temperature has a powerful influence on the photocatalytic hydrogen production activity; the hydrogen production activity increases with increasing temperature, which is since the higher the temperature, the faster the molecules move, and more reacting molecules have more energy than needed for practical collision, it can be expected that increasing the temperature will increase the reaction rate (Arrhenius equation); however, with the further temperature increases, its hydrogen-producing activity decreases, which may be due to the poor stability of Ag-$ZnIn_2S_4$ and the high temperature destroys the structure of Ag-$ZnIn_2S_4$.

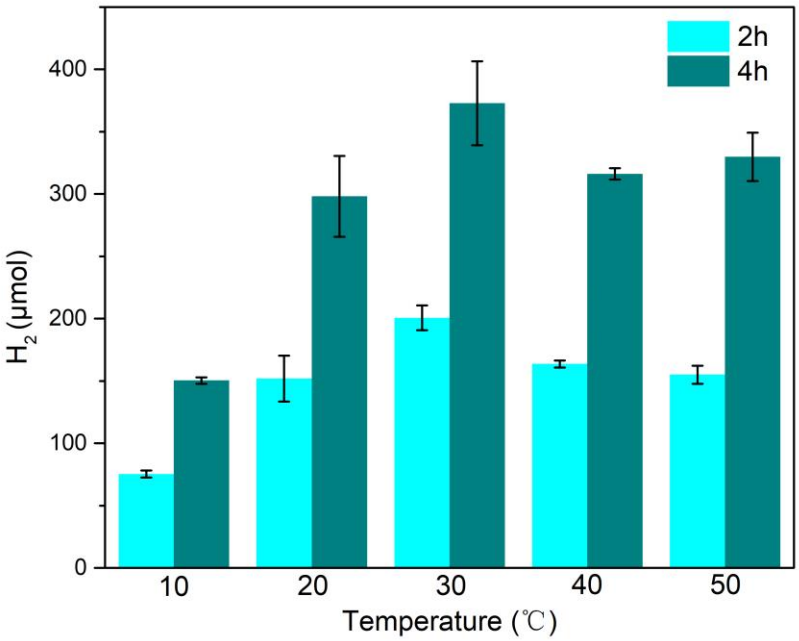


Figure 3.6 Results of hydrogen production of Ag-$ZnIn_2S_4$ and TEA

To investigate the effect of different electron sacrifices on the photocatalytic activity, experiments on the photocatalytic hydrogen production of Ag-$ZnIn_2S_4$ and Na_2A at different temperatures also have been done and found that the hydrogen production results were similar to the first set of experiments. Ag-$ZnIn_2S_4$ had the highest hydrogen production efficiency at 30 ℃, about 2.1 times higher than at 10 ℃, while the photocatalytic activity weakened when the temperature was above 30 ℃. The results indicate that different electron sacrifices did not affect the effect of temperature on photocatalytic activity.

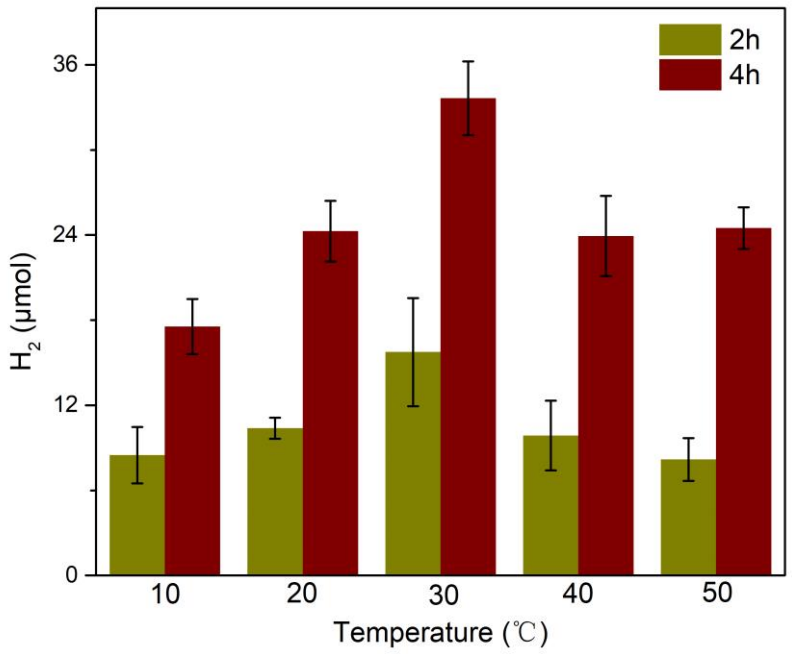


Figure 3.7 Results of hydrogen production of Ag-$ZnIn_2S_4$ and Na_2A

To further investigate whether the conclusions drawn are generalisable, the photocatalyst InP/ZnS and the electron sacrifices Na_2A will be used to test the effect of temperature on photocatalytic activity. Concerning Narayanaswamy's method, InP/ZnS photocatalysts were successfully synthesised.[28] However, the experimental results differ from those of Ag-$ZnIn_2S_4$. Figure 3.8 shows that the photocatalytic activity of InP/ZnS increases continuously from 10 ℃ to 50 ℃, while the photocatalytic activity of InP/ZnS at 50 ℃ is about four times higher tha n that at 10 ℃. This may be due to the better stability of InP/ZnS and better tolerance to high temperatures.

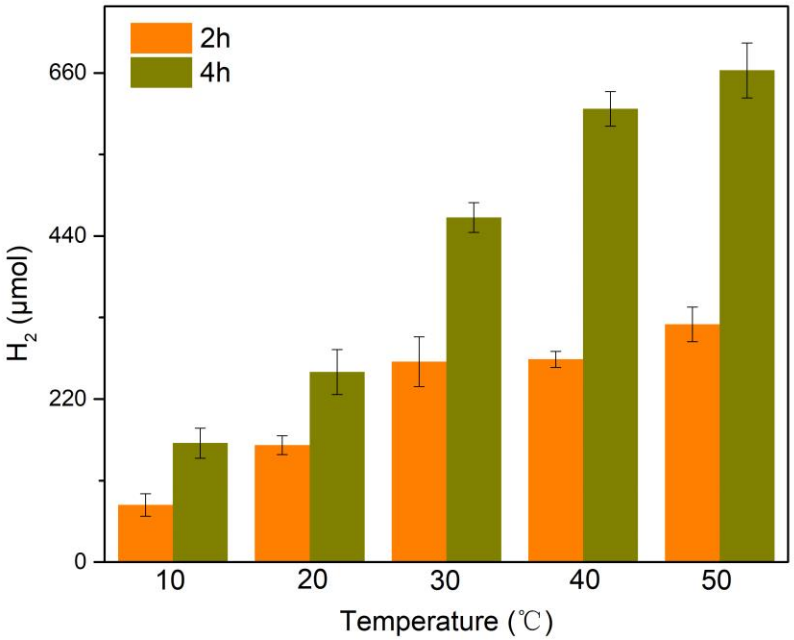


Figure 3.8 Results of hydrogen production of InP/ZnS and Na_2A

Chapter 4 Conclusion

Ag-$ZnIn_2S_4$ photocatalyst was successfully synthesised by the hydrothermal method. The synthesised Ag-$ZnIn_2S_4$ was characterised using XRD Characterization, UV-Vis diffuse reflectance spectroscopy and Fluorescence spectrum. The results demonstrated the successful synthesis of Ag-$ZnIn_2S_4$, and the UV-Vis absorption peak of the synthesised Ag-$ZnIn_2S_4$ was found to start decaying rapidly at 510 nm with a bandgap of 2.60 eV for Ag-$ZnIn_2S_4$. The electron sacrifices (TEA, Na_2A) for analysing the effect of temperature on hydrogen production efficiency were determined by photocatalytic hydrogen production experiments and the bandgap for the testing volume of photocatalyst (0.2 ml). Through three sets of photocatalytic experiments at different temperatures, it was found that the photocatalytic activity of Ag-$ZnIn_2S_4$ decreased after 30 °C. In contrast, the photocatalytic activity of InP/ZnS continued to increase from 10 °C to 50 °C. This phenomenon may be caused by the different tolerance of different photocatalysts to high temperatures already the stability of photocatalysts.

In future studies, attention needs to be paid to the effect of temperature on the photocatalytic system, primarily to study the tolerance temperature of the desired photocatalyst in advance. Analysing the high-temperature tolerance and stability of different photocatalysts can help enhance and improve the current phenomenon of low efficiency of photocatalysts, which can help realize the large-scale application at an early date.

However, due to the epidemic, many more in-depth studies and comparative experiments could not be conducted properly, and the investigations are still inadequate. In the future, tests such as XPS or XRD will be needed to verify if the catalyst is deactivated at high temperatures.

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