VISIBLE LIGHT ACTIVE METAL SULFIDES PHOTOCATALYST FOR HYDROGEN EVOLUTION IN AQUEOUS SOLUTION

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A thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy (Chemistry)

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I declare that this thesis entitled "Visible light active metal sulfides photocatalyst for hydrogen evolution in aqueous solution" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ........................................

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Date : ... 14 June 2012.........
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ABSTRACT

This research focuses on the development of multicomponent sulfides based-ZnS material \( \textit{i.e.}, \ M(x)\)-doped \( \text{Cd}_{0.1}\text{Zn}_{0.9}\text{S, In}(0.1)\text{-ZnS and Ga}(0.1)\text{-ZnS} \) \( (M = \text{Sn, Cu, or Ag, } x = 0.01, 0.03, 0.05) \) for photocatalytic hydrogen production under visible light irradiation. The role of dopant or co-dopants on the physical chemical properties of the photocatalyst and the effects on photocatalytic activity were investigated. The comparison studies on the effects of preparation methods, namely co-precipitation and hydrothermal method, on the physical chemical properties of the photocatalyst were investigated. High crystallinity which is beneficial for photocatalytic hydrogen production was obtained on the samples prepared by hydrothermal route. \( \text{Cd}_{0.1}\text{Zn}_{0.9}\text{S} \) solid solution combining both benefits of CdS and ZnS was further enhanced with the addition of dopants Sn, Cu or Ag in optimum amount. Cu and Ag improved the crystallinity and visible light absorption of \( \text{Cd}_{0.1}\text{Zn}_{0.9}\text{S} \) with Cu\((0.03)\)-doped \( \text{Cd}_{0.1}\text{Zn}_{0.9}\text{S} \) hydrogen production rate at 3.86 mmol/h and Ag\((0.01)\)-doped \( \text{Cd}_{0.1}\text{Zn}_{0.9}\text{S} \) at 3.91 mmol/h. Sn\((0.01)\)-doped \( \text{Cd}_{0.1}\text{Zn}_{0.9}\text{S} \) produced hydrogen at 3.52 mmol/h which benefited from higher conduction band level. When Cd was replaced by In, the photocatalytic activity of In\((0.1)\)-ZnS was small due to the low absorption in the visible region. The absorption was enhanced with doping of Sn, Cu or Ag. These photocatalysts benefited from the small crystallite size and the improved visible light absorption. For Ga co-doped with Sn, Cu or Ag, only Ga and Cu co-doped ZnS showed efficient photocatalytic activity with hydrogen production rate of 114 \( \mu \text{mol/h} \). This is due to the synergistic effect of Ga and Cu. The photocatalytic activity of Ga\((0.1)\),Cu\((0.01)\)-ZnS was improved greatly with the addition of 0.5 wt% Ru with hydrogen production rate at 744 \( \mu \text{mol/h} \). From this study, development of multi component sulfides successfully provides a route for the development of visible light active photocatalyst with high photocatalytic activity when suitable dopants at optimum amount are added.
ABSTRAK

Penyelidikan ini tertumpu kepada perkembangan sulfida pelbagai komponen berdasarkan ZnS iaitu \( M(x)\)-dop \( Cd_{0.1}Zn_{0.9}\)S, \( In(0.1)\) \( M(x)\)-ZnS dan \( Ga(0.1)\) \( M(x)\)-ZnS (\( M = Sn, Cu, atau Ag, x = 0.01, 0.03, 0.05\)) untuk penghasilan hidrogen melalui fotopemangkinan. Peranan yang dimainkan oleh dopan atau ko-dopan terhadap ciri fizikal dan ciri kimia fotomangkin serta kesan terhadap aktiviti pemangkin telah dikaji. Perbandingan antara kaedah penyediaan melalui ko-mendakan dan hidrotherma kepada ciri fizikal dan ciri kimia fotomangkin telah dilakukan. Kehabluran yang tinggi adalah bermanfaat kepada fotopemangkinan untuk penghasilan hidrogen telah diperolehi dengan sampel yang disediakan melalui kaedah hidrotherma.  Aktiviti fotopemangkinan larutan pepejal \( Cd_{0.1}Zn_{0.9}\)S menggabungkan faedah kedua-dua CdS dan ZnS kemudiannya ditingkatkan dengan penambahan dopan Sn, Cu atau Ag dalam jumlah yang optimum. Cu dan Ag meningkatkan kehabluran dan penyerapan cahaya nampak oleh \( Cd_{0.1}Zn_{0.9}\)S dengan \( Cu(0.03)\)-dop \( Cd_{0.1}Zn_{0.9}\)S mempunyai kadar penghasilan hidrogen pada 3.86 mmol/jam dan \( Ag(0.01)\)-dop \( Cd_{0.1}Zn_{0.9}\)S pada 3.91 mmol/jam. \( Sn(0.01)\)-dop \( Cd_{0.1}Zn_{0.9}\)S menghasilkan hidrogen pada 3.52 mmol/jam dengan peningkatan aktiviti adalah disebabkan oleh tahap jalur konduksi yang lebih tinggi. Apabila Cd diganti dengan In, aktiviti pemangkinan \( In(0.1)\)-ZnS adalah rendah disebabkan penyerapan cahaya nampak yang rendah. Penyerapan cahaya ditingkatkan dengan penambahan dopan Sn, Cu atau Ag. Fotomangkin yang didopkan ini memanfaatkan saiz hablur yang lebih kecil dan peningkatan penyerapan cahaya nampak. Untuk Ga ko-dop dengan Sn, Cu atau Ag, hanya Ga dan Cu ko-dop ZnS menunjukkan kecekapan aktiviti fotopemangkinan dengan kadar penghasilan hidrogen 114 µmol/jam. Keadaan ini disebabkan oleh kesan sinergi antara Ga dan Cu. Aktiviti pemangkinan ditingkatkan lagi dengan penambahan 0.5 wt% Ru dengan kadar penghasilan hidrogen pada 744 µmol/jam. Daripada kajian ini, sulfida pelbagai komponen berjaya menyediakan kaedah bagi perkembangan fotomangkin yang aktif dalam cahaya nampak dengan aktiviti pemangkinan yang tinggi apabila dopan yang sesuai pada jumlah optimum ditambahkan.
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<tr>
<td>Å</td>
<td>Dimension unit, Amstrongs (x10^{-10}m)</td>
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<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
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<td>CdS</td>
<td>Cadmium sulfide</td>
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<td>CB</td>
<td>Conduction band</td>
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<td>DR-UV</td>
<td>Diffuse reflectance UV-Visible Spectroscopy</td>
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<td>EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
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<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
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<tr>
<td>GC-TCD</td>
<td>Gas Chromatography Thermal Conductivity Detector</td>
</tr>
<tr>
<td>H$_2$</td>
<td>Hydrogen gas</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer (x10^{-9}m)</td>
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<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>S$_2^-$</td>
<td>Sulfide ion</td>
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<tr>
<td>SO$_3^{2-}$</td>
<td>Sulfite ion</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Titanium dioxide</td>
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<tr>
<td>UV</td>
<td>Ultra violet</td>
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<tr>
<td>VB</td>
<td>Valence band</td>
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<tr>
<td>XPS</td>
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CHAPTER 1

INTRODUCTION

1.1 Hydrogen Gas as Future Energy

The world’s primary source of energy now is petroleum-based fuels. As the world’s demand for energy increases, high usage of fossil fuels contributes to the increase in carbon dioxide emission in the atmosphere which causes global warming [1]. As petroleum is a limited source which might become more expensive by days, the finding of new energy source is crucial. On the other hand, hydrogen energy promises a better environment and sustainability by being one of the most promising alternative energy. Hydrogen, like electricity, is a secondary form of energy that does not exist freely in nature [2-5].

The combustion of hydrogen does not emit carbon dioxide, this makes it a clean fuel and can be utilized to generate electricity by using fuel cells. Energy yield of hydrogen (122 kJ/g) is almost 3 times higher than fossil fuels [6]. The uses of hydrogen now are being expanded for combustion engines and electric-powered vehicles using fuel cell. When the H-H bond in hydrogen combines with oxygen, it releases chemical energy and produces water as by-product. This makes hydrogen fuel a clean energy. Hydrogen is stored as solid or liquids in compounds like metal hydrides, metane, methanol and hydrocarbons [7].

Hydrogen at present has a market of roughly fifty billion US$ for 40 Mt annual production. However, hydrogen is mostly used as chemical substance rather
than as fuel. Hydrogen is mostly used as processing agent in oil refineries and chemicals production processes [8].

Further increase in populations will result in increase demand for food and commodities that lead to the increasing demand for hydrogen for fuels and chemical processes. The increase in food and energy demand lead to the raise of greenhouse gases. Thus, it is viable for hydrogen to be produced from sustainable energy sources.

1.2 Hydrogen Production Methods

Fossil based natural gas and coal is currently the main source for industrial hydrogen production. Hydrogen production using natural gas by steam-methane reforming process has led to tremendously amount of CO₂ emission, typically 5 kg CO₂/kg H₂ [9]. Steam-reforming process is endothermic with nickel catalyst and temperature range 970-1100 K and pressure up to 3.5 Mpa [10]. The steps are shown in Equation 1.1 and 1.2. Purification steps to remove carbon dioxide and other contaminants are needed [11].

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (1.1)
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (1.2)
\]

Similar to hydrogen production from natural gas, coal gasification to produce hydrogen also resulted in large quantities of CO₂ emission. Hydrogen production from coal is carried out by synthane process or CO₂ acceptor process [10]. For synthane process, coal and steam are reacted together at high temperature and pressure which produces CO, CO₂ and H₂ as well as requires further washing steps.

To reduce the environmental impact of CO₂ emissions from fossil fuels based H₂ industry, renewable energy precursors are highly required to develop carbon-free
production of H₂. Nuclear energy gained energy from atoms by nuclear reactions. Nuclear energy can be used to produce hydrogen by water electrolysis process or decomposition of water using thermal energy generated by nuclear reactor [12]. There are several drawbacks in using nuclear energy for hydrogen production. Firstly is due to the lack of official support and limited supplies of uranium. Moreover, the reactivity of coolant, high power density and high operating temperatures make it difficult to operate safely [13]. In addition to them, nuclear generation creates waste that must be disposed off.

Biomass consists of biological materials such as plants, wood or waste that can be used for industrial purposes. Pure hydrogen can be produced from the biomass gasification by steam reforming. During reaction, CO and H₂O react in a 1:1 molar ratio on a catalytically active metal site to form CO₂ and H₂[14]. This makes hydrogen generated from biomass not totally carbon free. Moreover, people are keener to use biomass directly as fuel instead of using biomass to generate hydrogen. Biomass for energy plantations also faces great competition from agricultural systems to meet world’s food demand. Agricultural wastes are often left in their original places for soil fertility. Biomass energy needs a large land area to grow energy crops and uses great energy input especially water.

Wind energy produces electricity by rotating turbines. The electricity is used for electrolyzing water for hydrogen production. Wind energy for hydrogen production is relatively cheap with 3.50$/kg in 2007. However, there were several protests concerns about wind farm effect on wildlife and turbine noise with its location in remote and high altitude area. It will be necessary for it to be converted and store into hydrogen energy [15].

Hydroelectric power is generated by water pushing the turbines. The usage of hydroelectric power is declining probably because large forest area would be inundated. As trees die, their decay released CO₂. Wildlife habitat could be destroyed too. Hydroelectric power sites would impact the climate by altering river flow rates.
For geothermal production of hydrogen, it can be done by geothermal steam, water electrolysis by electricity generated from geothermal, geothermal heat for high temperature electrolysis or geothermal heat for thermochemical processes to dissociate water [16]. Like hydroelectric power, geothermal energy releases CO₂ during its operation.

Hydrogen generation without involving carbon can be obtained by using solar energy. Not only is it abundant, solar energy can be converted to various form whether in the form of heat, light or electricity [17]. However, faced with the intermittency characteristic of solar radiation, it is crucial that solar energy is captured and converted or stored in the form of usable energy like hydrogen. Solar energy in the form of light is seen as the most efficient path of production of hydrogen as when in the form of electricity [18] or heat, it is either expensive or require large mirror or tower as concentrator [19]. Solar energy in the form of light to hydrogen in photo conversion system includes semiconductor photocatalysts for water splitting process. A semiconductor stored electronic energy in the form of electrons and holes can be used to split water molecules into H₂ and O₂. This reaction is done in near-ambient conditions. The properties of the semiconductor used as photocatalyst strongly affect the energy conversion efficiency of water splitting process. Development of efficient photocatalyst by studying the properties of the semiconductors working under visible light irradiation should be emphasized. Our current research focus is to synthesize high efficiency and stability semiconductor based on metal sulfides photocatalyst for hydrogen production.

1.3 Problem Statement

Hydrogen energy is seen to be the most appropriate substitute to the current energy supply. While various methods have been highlighted earlier, the most attractive solution is the use of solar energy. Solar energy is one of the most plentiful renewable sources. Although photovoltaic panels are currently used as solar energy panel, it requires large amount of area and high cost for the production of crystalline
silicon. Alternative method to harvest solar energy and convert it to hydrogen energy is by using semiconductor photocatalyst.

Currently, metal sulfides semiconductor used as photocatalyst has been gaining wide interest due to its high photocatalytic activity for hydrogen production [20-31]. Compared to their metal oxides counterpart, metal sulfides generally possess ideal conduction and valence band which meet the requirements for photocatalytic hydrogen production. However, metal sulfides often suffer from photocorrosion during photocatalytic reaction because sulfides are prone to oxidation. ZnS is one of the effective metal sulfides for hydrogen production due to its high conduction band level. The large band gap of ZnS prohibits full utilization of the broad spectrum of solar energy as most of the solar energy comprises of visible light energy. Therefore, many attempts have been done to modify this photocatalyst so that it becomes visible light responsive but still maintain the high conduction band. By forming solid solution with narrow band gap CdS, ZnS was able to function under visible light irradiation. However, the efficiency and stability can be further enhanced by doping with suitable metal ions. This inspired the utilization of multi component metal sulfides photocatalysts. In this study, the focus is on Sn, Cu and Ag metal ions. Multicomponent sulfides enhanced the photocatalytic activity through the benefits and role of each metal ion comprising the photocatalyst, similar to co-doping principles. Two or more metal ions provide synergistic effects that are not available for single metal ion doped photocatalyst. The development of new, efficient and stable metal sulfides photocatalyst through this multicomponent sulfides or co-doping is needed in order to utilize visible light which comprises large part of the solar spectrum to produce hydrogen.

Apart from visible light response, other factors affecting the photocatalytic efficiencies, especially the physical properties of a photocatalyst should be taken into account. The physical properties are largely dependent on the synthesis route. High crystallinity of photocatalysts is often desired for photocatalytic hydrogen process. A detail comparison between two most simple photocatalysts synthesis method, \textit{i.e.},
co-precipitation and hydrothermal method is needed to access the influence of synthesis route to the photocatalytic activity.

1.4 Objective

In this study, in order to synthesize a highly effective and stable photocatalyst with visible light response and having suitable band edges for hydrogen production, several objectives need to be accomplished.

(a) To synthesize the following metal sulfides photocatalysts, Cd$_{0.1}$Zn$_{0.9}$S, $M(x)$-doped Cd$_{0.1}$Zn$_{0.9}$S by co-precipitation and hydrothermal method, In($0.1$)-ZnS, In($0.1$),$M(x)$-ZnS, Ga($0.1$)-ZnS and Ga($0.1$),$M(x)$-ZnS ($M = $ Sn, Cu, Ag, $x = 0.01, 0.03, 0.05$) through hydrothermal method.

(b) To characterize the physical-chemical properties of the photocatalyst.

(c) To evaluate the performance of the photocatalyst for hydrogen evolution from water under visible light irradiation.

1.5 Scope

This present study is devoted to the improvement of ZnS as a photocatalyst for visible light hydrogen evolution from water with sacrificial agent. While typically high efficiency and stability photocatalyst was not obtained in the course of this study, new multicomponent sulfides photocatalyst with considerable hydrogen yield and fundamental concepts were developed that provide foundation and possible route for future work. This indeed is expected to be able to meet the hydrogen energy demand in the future.
1.6 Approach

CdS [20-28] and ZnS [29-31] are most commonly used metal sulfides photocatalyst for hydrogen production. CdS is active for photocatalytic hydrogen production under visible light due to its appropriate position of band potentials. However, CdS is susceptible to photocorrosion producing Cd$^{2+}$ [32-35]. ZnS on the other hand has high conduction band which is essential for reducing water to hydrogen, but unfortunately ZnS has wide band gap that makes it inactive under visible light irradiation. Combining CdS and ZnS together as one photocatalyst provides an efficient photocatalyst with high conduction band and visible light active properties [32-35]. $M(x)$-doped Cd$(0.1)$-ZnS series discusses the 2 simple methods (co-precipitation and hydrothermal) for preparing this efficient photocatalyst. The products were characterized and tested for photocatalytic hydrogen production. This efficient photocatalyst was further enhanced by doping with metal ions, Sn, Cu or Ag and are discussed in details in Chapter 4. Doping of these metal ions changes the physical properties and photocatalytic activities. As hydrothermal method was found to be a better method for synthesizing these multicomponent sulfides photocatalyst, only this method was employed in latter chapters.

Although CdS is one of the most widely used metal sulfides photocatalyst for hydrogen production, the toxicity of Cd metal ions inhibit the wide usage of this photocatalyst. Researchers are finding other options by using other narrow band gap metal sulfides photocatalyst to combine with ZnS. Until recently, In$_2$S$_3$ with narrow band gap was found to be active for photocatalytic hydrogen production [36]. Combining In$_2$S$_3$ with ZnS produces a visible light active photocatalyst [37]. Indium metal ion doping was also reported to enhance the photocatalytic activity of CdS [38]. Doping metal ions like Sn, Cu or Ag into In-ZnS was proposed to enhance the light absorption and also photocatalytic activity. The physical properties and photocatalytic activities were discussed in detail in Chapter 5.

In Chapter 6, the combination of Ga metal ions with Sn, Cu or Ag metal ions with ZnS were discussed. Elements associated with d$^{10}$ electronic configurations,
such as Ga$^{3+}$ are attractive because their conduction and valence bands are formed by hybridized sp orbitals with large band dispersion that would lead to high charge mobility hence, high photocatalytic performance [39,40]. Here, Ga acts as a co-dopant together with Sn, Cu or Ag metal ions. The role of Ga metal ions here was not as visible light absorption enhancer but introducing oxygen vacancies for efficient electron-hole separation [41,42]. The physical properties and photocatalytic activities were also investigated.