

**SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC STUDIES  
OF CdS INCORPORATED TITANOSILICATE FOR HYDROGEN  
GENERATION**

**NG YEW CHOO**

**UNIVERSITI TEKNOLOGI MALAYSIA**

SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC STUDIES OF  
CdS INCORPORATED TITANOSILICATE FOR HYDROGEN GENERATION

NG YEW CHOO

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Specially dedicated to my family members, my supervisor, co-workers,  
friends and anybody always by my side.....

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## PREFACE

This thesis is the result of my work carried out in the Department of Chemistry; Universiti Teknologi Malaysia between July 2006 to December 2008 under supervision of Prof. Dr. Mustaffa Shamsuddin. Part of my work described in this thesis has been submitted in the following exhibition, publication and presentations:

1. Yew-Choo Ng, Ching-Yih Jei and Mustaffa Shamsuddin. Titanosilicate ETS-10 Derived from Rice Husk Ash. *Microporous. Mesoporous Materials* 122 (2009) 195-200.
2. Bronze Medal Award. Nanostructured CdS on ETS-10 for In-Situ Hydrogen Generation. *10<sup>th</sup> Industrial Art and Technology Exhibition (INATEX)*. UTM skudai. 2008.
3. Gold Medal Award. Nanostructured CdS on ETS-10 for In-Situ Hydrogen Generation. *8<sup>th</sup> Malaysian Technology Expo (MTE)*. PWTC Kuala Lumpur. 2009.
4. Ng Yew Choo and Mustaffa Shamsuddin. Physicochemical Studied of CdS Nanoparticles-Titanosilicate Hybrid. *Regional Annual Fundamental Science Seminar (RAFSS)*. Poster Presentation. UTM Skudai. 2007.
5. Ng Yew Choo and Mustaffa Shamsuddin. Analysis of Titanosilicate Supported CdS Photocatalyst for Water Splitting Reaction. *21<sup>th</sup> Symposium Kimia Analysis Malaysia (SKAM-21)*. Oral Presentation. UMS Sabah. 2008.
6. Yew-Choo Ng and Mustaffa Shamsuddin. Solid State Morphology and Band Gap Studied of ETS-10 Supported CdS Nanoparticles. *Journal of Iranian Chemical Society*. Manuscript No.: PS-08-240-08.

## ABSTRACT

This study relates to a development of heterogeneous solid catalyst, Engelhard titanasilicate (ETS-10) supported cadmium sulfide (CdS) for water splitting reaction to generate hydrogen under visible light irradiation. Highly crystalline truncated bipyramid shape of ETS-10 was successfully synthesized with the molar composition of  $\text{TiO}_2:3.75\text{SiO}_2:1.5\text{NaOH}:0.54\text{KF}:21.25\text{H}_2\text{O}$  at  $220^\circ\text{C}$  for 52 hours. The as-synthesized CdS crystallized at the size of approximately 8 nm in the cubic structure with the lattice constant  $a=0.5818$  nm and reflection peaks of (111), (220) and (331) lattice planes. The effect of the synthesis route of CdS, the effect of percentage loading of CdS and reusability of the catalysts towards water splitting were also reported. The conduction edge of the photocatalyst was found to be more negative than  $\text{H}^+/\text{H}_2$  redox potential. The highly crystalline phases of photocatalyst were able to prevent a charge recombination leading to enhancement in the hydrogen production yield. The existence of co-catalyst (ETS-10) in the catalytic system induces reduction of water and increases the efficiency of charge separation. The hybrid photocatalyst was found to be more stable and do not undergo photo-corrosion. CdS derived from in-situ sulphur reduction method (CdS-IS) performed better than CdS derived from reverse micelle method (CdS-RM). For 0.1 g of catalyst, the average rate of reaction for the first 5 hours was found to be  $68.69 \mu\text{mol/hr}$  and  $49.05 \mu\text{mol/hr}$  for CdS-IS and CdS-RM respectively. Besides, the results showed that the higher the percentage of CdS loaded on ETS-10, the higher amount of hydrogen gas liberated. The reusability of the photocatalysts was demonstrated in three cycles and the hydrogen gas evolved slightly decreased with the number of the reusability.

## ABSTRAK

Kajian ini berkaitan dengan pembangunan pepejal mangkin heterogen titanasilikat, kadmium sulfida (CdS) berpenyokong Engelhard titanasilikat (ETS-10) dalam tindak balas pemecahan air bagi penghasilan gas hidrogen di bawah pancaran cahaya nampak. Hablur ETS-10 yang berbentuk dwipiramid terpotong telah disintesis dengan komposisi molar  $\text{TiO}_2:3.75\text{SiO}_2:1.5\text{NaOH}:0.54\text{KF}:21.25\text{H}_2\text{O}$  pada suhu  $220^\circ\text{C}$  selama 52 jam. CdS yang disintesis menghablur pada saiz 8 nm dalam struktur kiub dengan pemalar kekisi  $a = 0.5818$  nm dan jalur pemantulan pada satah kekisi (111), (220) and (331). Kesan cara sintesis CdS, kesan peratusan pertambahan CdS dan penggunaan semula mangkin terhadap tindak balas pemecahan air juga dilaporkan. Jalur konduksi foto-mangkin ini didapati bersifat lebih negatif daripada keupayaan redoks  $\text{H}^+/\text{H}_2$ . Fasa berhablur foto-mangkin mampu mengelakkan gabungan semula cas justeru meningkatkan penghasilan gas hidrogen. Kewujudan ko-mangkin (ETS-10) di dalam sistem pemangkinan menggalakkan penurunan air dan meningkatkan keberkesanan pemisahan cas. Foto-mangkin hibrid ini didapati lebih stabil dan tidak mengalami pengurangan foto. CdS yang disediakan daripada cara penurunan *in-situ* sulfur (CdS-IS), berfungsi lebih baik berbanding dengan CdS yang disediakan daripada cara misel berbalik (CdS-RM). Dengan 0.1 g mangkin, purata kadar tindak balas bagi 5 jam pertama adalah  $68.69 \mu\text{mol/jam}$  and  $49.05 \mu\text{mol/jam}$  bagi CdS-IS and CdS-RM masing-masing. Selain itu, pemerhatian menunjukkan semakin tinggi peratusan CdS yang disokong di atas ETS-10, semakin tinggi jumlah gas hidrogen yang dibebaskan. Penggunaan semula foto-mangkin juga dikaji sebanyak tiga kitaran, di mana pembebasan gas hidrogen semakin berkurang dengan bilangan penggunaan semula.

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## LIST OF ABBREVIATIONS

HHV	-	Higher heating value
CdS	-	Cadmium sulfide
ETS-4	-	Engelhard titanosilicate-4
ETS-10	-	Engelhard titanosilicate-10
UV	-	Ultra violet
Vis	-	Visible
RHA	-	Rice husk ash
KF	-	Potassium fluoride
NaOH	-	Sodium hydroxide
H <sub>2</sub> O <sub>2</sub>	-	Hydrogen peroxide
GC-TCD	-	Gas chromatography thermal conductivity detector
Å	-	Dimension unit, Amstrongs ( $\times 10^{-10}$ m)
TiO <sub>2</sub>	-	Titanium dioxide
ASTM	-	American Society for Testing and Materials
CB	-	Conduction band
VB	-	Valence band
ccm/g	-	Cubic centimeter per gram
nm	-	Nanometer ( $\times 10^{-9}$ m)
ZnO	-	Zinc(II) oxide
Fe <sub>2</sub> O <sub>3</sub>	-	Iron(III) oxide
ZnS	-	Zinc(II) sulfide
H <sub>2</sub>	-	Hydrogen gas
E <sub>G</sub>	-	Energy gap
fcc	-	Face-centered-cubic
hcp	-	Hexagonal close-packed
CdS/ETS-10	-	Cadmium Sulfide supported on ETS-10
Si/Ti	-	Silicon to titanium ratio

OR type	-	Strong oxidation and reduction power
O type	-	Strong oxidation power
R type	-	Strong reduction power
X type	-	Weak oxidation and reduction
KBr	-	Potassium bromide
H <sup>+</sup> /H <sub>2</sub>	-	Reduction of hydrogen ion to hydrogen gas
D	-	Electron donor / hole scavenger
A	-	Electron acceptor
EDTA	-	Ethylenediaminetetraacetic acid
TEOA	-	Triethanolamine
SO <sub>3</sub> <sup>2-</sup>	-	Sulfite ion
H <sub>2</sub> PO <sub>2</sub> <sup>-</sup>	-	Hypophosphite ion
XRD	-	X-ray diffraction
FTIR	-	Fourier Transform Infrared spectroscopy
DR-UV	-	Diffuse reflectance UV-Vis Spectroscopy
FESEM	-	Field Emission Scanning Electron Microscopy
TEM	-	Transmission Electron Microscopy
EDAX	-	Energy Dispersive Spectroscopy
W	-	Watt

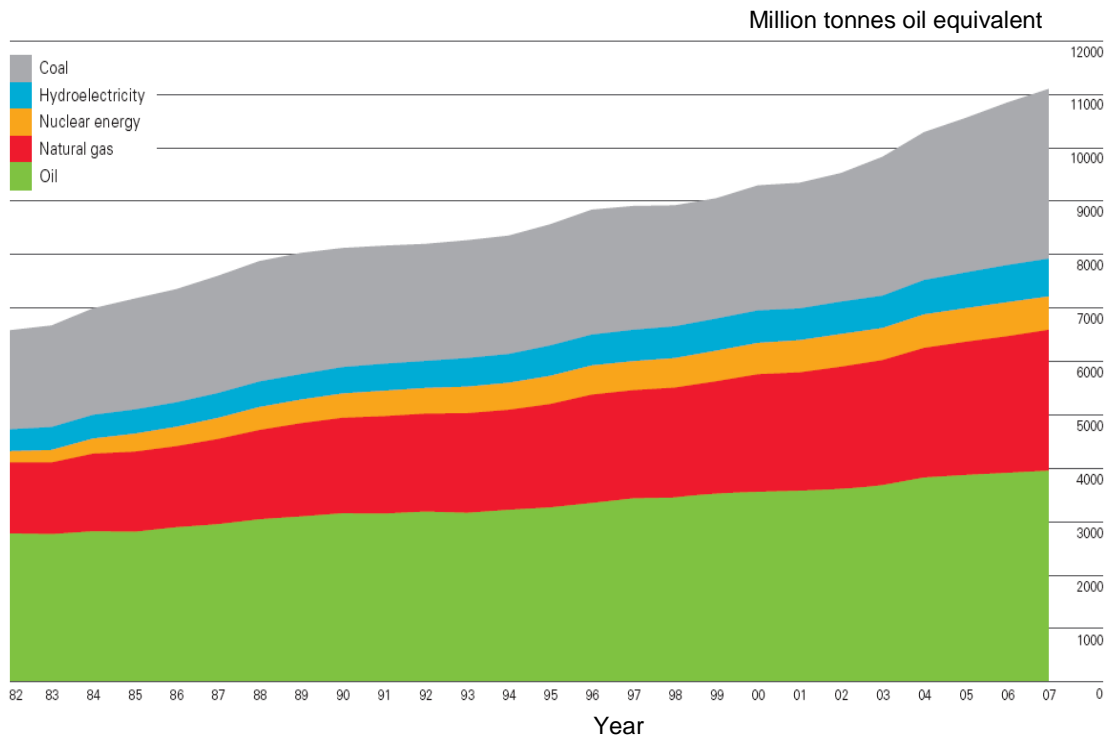
## **CHAPTER 1**

### **INTRODUCTION**

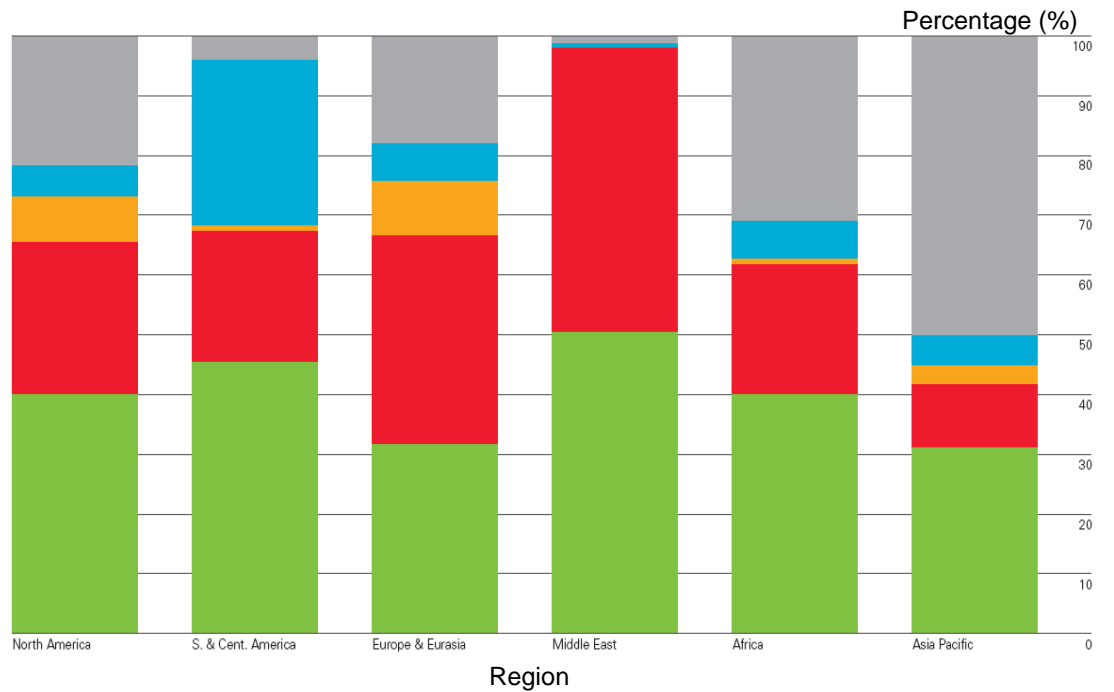
#### **1.1 Research Background**

Recently, one of the biggest issues that capture most of our concern is the fuel's market value. It has been the all-time front page news in the newspaper for the last several months. Everyone is talking about the tremendous increase in prices of the petrol and diesel around the world. It draws a huge attention because the fuel's market value is directly affecting the prices of goods, or even the economy of countries. In addition to transportation and power generation, mass quantities of petroleum and petroleum derived chemicals are required as raw materials and fuels in many industries such as manufacturing, food processing and pharmaceutical industries.

The world energy consumption obtained from BP Statistical Review is shown in Figure 1.1 (BP, 2008). Fossil fuels such as petroleum, coal and natural gas are still remain as the most important energy resources. Petroleum is still the world's leading fuel, but has lost its global share of the market for six consecutive years while coal remained as the fastest growing fuel and has gained the share of the market for six years. Petroleum remains as the dominant fuel in all regions except Europe and Eurasia and Asia Pacific. Coal dominates in the Asia Pacific region primarily because it meets 70% of China's energy needs. The regional energy consumption pattern in year 2007 is shown in Figure 1.2 (BP, 2008).



**Figure 1.1:** The world energy consumption from year 1982 to 2007 (BP, 2008)



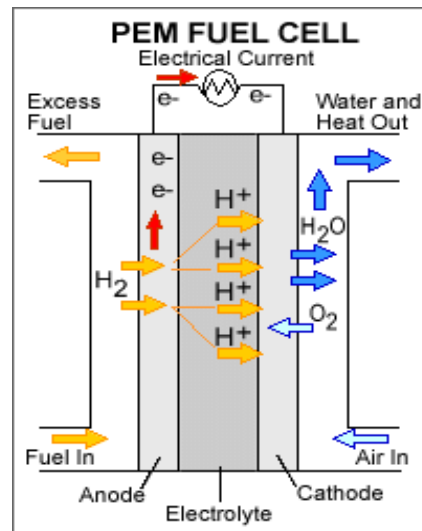
**Figure 1.2:** The regional energy consumption pattern in year 2007 (BP, 2008)

### 1.1.1 Renewable Resources

Due to the depletion of petroleum and the rising demand for alternative resources, several approaches must be carried out in order to overcome this obstacle especially in the development of renewable resources to replace the unstable and diminishing natural fuel. A number of renewable resources technologies are now commercially available, the most notable being wind power, photovoltaics, solar thermal systems, biomass and the various forms of water power (Thring, 2004). Biomass is gaining high attention as it is one of the most available renewable energy resources that can be used to reduce the dependency on fossil resources (Williams and Nugranad, 2000). Biomass refers to living and recently dead biological material that can be used as fuel or for industrial production. Some of the agricultural wastes that consist of carbon could be utilized as raw materials to generate the heat and electricity for milling processes. Since enormous numbers of agriculture activities are conducted locally, therefore this method could be applied in energy recovery scheme. However, the utilization of biomass for energy conversion through combustion is still limited due to its poor fuel properties such as high moisture and ash contents, low bulk density, low energy content (William and Nugranad, 2000).

One of the alternatives for energy generation is the usage of hydrogen fuel cell. Several researches have been developed in order to obtain a highly efficient and effective hydrogen fuel cell (James and Michael, 2005). A hydrogen fuel cell converts chemical energy directly into electricity by combining oxygen from the air with hydrogen gas. However, unlike a battery, a fuel cell does not run down or require recharging. It will produce electricity as long as fuel, in the form of hydrogen, is supplied. No pollution is produced and the only byproducts are water and heat. Figure 1.3 shows the functional principle of the Proton Exchange Membrane (PEM) fuel cell.





**Figure 1.3:** Principle of the PEM fuel cell (Strasser and Siemens, 1995)

### 1.1.2 Hydrogen Economy

Hydrogen, the first element on the periodic table, is the least complex and the most abundant element in the universe (Mohammad and Chen, 2005). However, not much is available in pure form on earth and is available either as water (when combined with oxygen) or as a hydrocarbon (when combined with carbon). For this reason, hydrogen is only an energy carrier and not a primary energy source. Extraction of hydrogen from its compounds was studied with the presence (Lindström *et.al.*, 2003; Chang *et.al.*, 2005; Hu and Lu, 2007; Wang *et.al.*, 2007) or absence of catalysts (Marty and Grouset, 2003).

A hydrogen economy has been proposed as a way to reduce global greenhouse gas emission due to its properties as a very clean fuel and burning it results in no greenhouse emissions or undesirable carbon compounds (James and Michael 2005). Hydrogen contains the highest energy density on a mass basis of all chemical fuels which can be quantified by its higher heating value (HHV) of 141.9 MJ/kg. The higher heating value is the amount of energy released during the oxidation reaction of a fuel with air at a starting and finishing temperature of 25°C.

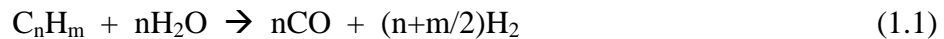
Heating values of hydrogen and other fossil fuels are tabulated in Table 1.1, which clearly indicates that hydrogen has the highest energy density (Lo *et.al.*, 2006).

**Table 1.1:** Heating value for selected fuels (Lo *et.al.*, 2006)

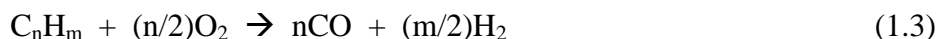
<b>Fuel</b>	<b>HHV (MJ/kg)</b>
Coal	34.1
Methane	55.5
Natural gas	42.5
Propane	48.9
Gasoline	46.7
Diesel	45.9
Hydrogen	141.9

### 1.1.3 Hydrogen Production

The production of hydrogen is more costly than any other fuel. Hydrogen can be produced by reforming hydrocarbons, in which the steam reforming of methane being the most efficient method (Christofoletti *et.al.*, 2005; Lo *et.al.*, 2006). Steam reforming is a very established technology and is used to generate large quantities of hydrogen in industrial processes. This reaction is an endothermic process; slow to start-up and relatively inflexible with regard to non-steady state operation. The mechanism of the steam reforming is shown in equations below (Thring, 2004).



In contrast, partial oxidation reforming is an exothermic process and work faster and more responsive if compared to steam reforming. However, it produces relatively higher levels of carbon monoxide and lower concentration of hydrogen. The third system which involves a combination of these two processes is known as autothermal reforming. The mechanism of the partial oxidation reforming is shown in equations below (Thring, 2004).



Hydrogen also can be produced via coal gasification. However, formation of carbon monoxide and carbon dioxide from hydrocarbon reformation and coal gasification is inevitable. Moreover, the yield collected is not 100 % pure (Zhu *et.al.*, 2005; Praveen and Alan 2005; Praveen and William 2006). Hydrogen gas derived from biomass and biogas was found to contain impurities (Osamu, 2006; Hadi and Tomohiro, 2006).

Another method of producing hydrogen is by water splitting using electricity generated from renewable resources such as solar, wind, hydro and biomass. In addition, water splitting can be conducted in thermochemical cycles when operating at high temperatures (Panini and Srinivas 2006). Hydrogen production based on the type of fuel is shown in Table 1.2.

**Table 1.2:** Hydrogen production based on the types of fuel (Panini and Srinivas 2006)

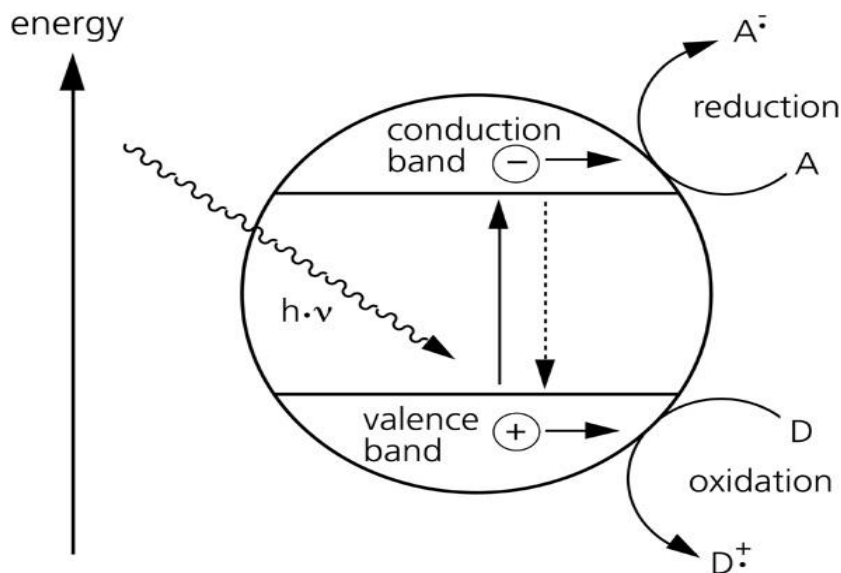
<b>Fuel</b>	<b>Amount (billions of Nm<sup>3</sup>/year)</b>	<b>Percentage</b>	<b>Method of production</b>
Natural gas	240	48%	Steam reforming
Oil	150	30%	Partial oxidation reforming
Coal	90	18%	Coal gasification
water	20	4%	Electrolysis

Methane or natural gas is the fuel of choice and almost 50% of industrial hydrogen production uses methane as a fuel. For higher hydrocarbons like gasoline or diesel partial oxidation reforming is generally used. During recent years, autothermal reforming is increasingly being employed (Praveen and Alan, 2005).

Hydrogen obtained from gasification of coal currently contributes 18% of the world hydrogen consumption. Among those commercial techniques, hydrogen production from electrolysis of water is the only method that produces hydrogen gas in high purity. However, only 4% of the total world hydrogen production is produced via this method. In general, hydrogen production from renewable sources is economically impractical due to the current technical constraint. The storage of the hydrogen for consumer applications has proved to be a difficult challenge as well (Lo *et.al.*, 2006).

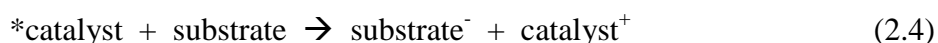
#### 1.1.4 Photocatalysis

Photocatalysis is a division of chemistry studying catalytic reactions proceeding under the action of light. In photocatalytic process, the surface reaction involved is redox reaction (Serpone, 1989). The basic of the photocatalysis process is shown in Figure 2.2. The initial step of photocatalysis is the adsorption of photons by a molecule to produce highly reactive electronically excited states. The photon needs to have energy of  $h\nu$  equal to or more than the band gap energy of the semiconductor. The energy absorbed will cause an electron to be excited from the valence band to the conduction band, leaving a positive hole in the valence band. This movement of electrons forms  $e^-/h^+$  or negatively charged electron/positively charged hole pairs (Serpone, 1989). The positively charged holes in valence band are powerful oxidants, whereas the negatively charged electrons in conduction band are good reductants. The void region which extends from the top of the filled valence band to the bottom of the vacant conduction band is called the bandgap (Serpone, 1989).



**Figure 1.4:** Photocatalytic process.

Photocatalysis can be defined as acceleration of a photoreaction by the presence of a catalyst. The catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/ or with a primary photoproduct, depending on the mechanism of the photoreaction (Bard, 1979). According to Serpone (1989), when the light is absorbed by the catalyst (Equation 2.1), the system represents a sensitized photoreaction which may occur either via energy transfer (Equations 2.2 and 2.3) or via electron transfer (Equations 2.4 to 2.6).



The very first photoinduced redox reaction was discovered by Fujishima and Honda in 1972 (Fujishima and Honda, 1972). They used an n-type titanium dioxide ( $\text{TiO}_2$ ) semiconductor electrode, which was connected through an electrical load to a platinum black counter electrode and exposed to near UV light. The extensive

research was conducted on producing hydrogen from water as a means of solar energy conversion. Later, this redox reaction was utilized in the decomposition of organic and inorganic compounds for environment protection.

Most of the organic and inorganic substances decomposition involves the formation of intermediate in a form of radical. Irradiation of semiconductor with light of energy higher than the band gap results in creation of holes in the semiconductor valence band (VB) and electrons in the conduction band (CB) followed by trapping of separated charges shallow traps (tr) at the solid-solution interface (Izumi *et. al.*, 1981). These traps carriers can be recombine or react with the substrates to form various groups of radicals such as hydroxyl radicals and hydrogen radicals as shown in the following equations.



Semiconductors such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CdS}$  and  $\text{ZnS}$  can act as sensitizers for light-induced redox processes due to their electronic structure, which is characterized by a filled valence band and empty conduction band. These characteristics enable them to generate  $e^-/h^+$  or negatively charged electron/positively charged hole pairs when they received a photon with sufficient energy.

The excited electrons and created holes can recombine and scatter the input energy as heat or get trapped in meta-stable surface states. The excited electrons and created holes can also react with electron donors and acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. The reactants, reaction intermediates and products are transported between the semiconductor surface and the bulk solution all the time (Fox and

Dulay, 1993). The rate of photocatalysis is proportional to the adsorption and desorption rate (Maldotti et. al, 2002).

## 1.2 Problem Statement

From the literature review, cadmium sulfide (CdS) nanoparticles prepared by reverse micelle method showed photocatalytic activity for hydrogen generation from water under visible light irradiation (Guan *et. al.*, 2005). However, the way of preparing CdS nanoparticles by these methods are complicated, wasting a lot of solvents and surfactants (create disposal problem) and time consuming. At present, there is still no report of the CdS nanoparticles being prepared by in-situ sulphur reduction method used in hydrogen generation. Since CdS nanoparticles prepared with this method is more feasible, nearly zero waste and economically practical, it becomes very suitable for low cost hydrogen generation.

Many researchers have reported preparation of Engelhard titanosilicates (ETS-10) using Ludox and water glass as silica sources showed photocatalytic activity for hydrogen generation from water under ultra violet (UV) irradiation (Guan *et. al.*, 2005; Sitharamam *et. al.*, 2004). In this research, rice husk ash was used as silica source due to its high percentage of silica and locally available in cheaper price. In addition, the ETS-10 that derived from rice husk ash (RHA) was found to be more crystalline and posses higher surface area up to 35.5% (Jei *et. al.*, 2008). The high crystallinity character of ETS-10 is very desirable in water splitting reaction. Therefore, ETS-10 is suggested as the support material to enhance the function of CdS in water splitting reaction. As-synthesized ETS-10 was further treated by hydrogen peroxide ( $H_2O_2$ ) to narrow down its band gap to enable it function under visible light irradiation.

The well known photocatalyst such as titanium dioxide only function well under UV light irradiation due to its wide band gap energy properties. Unfortunately, the usage of titanium dioxide is not desirable because only 3% of sun

energy reaches the earth in that UV region. Therefore, the development of visible light driven photocatalyst was gaining much more attention. CdS solely easily undergoes photocorrosion. In order to solve this problem, several approaches have been carried out to promote an efficient charge separation. As reported earlier, CdS nanoparticles prepared by precipitation in the zeolite matrix showed a significant result in water splitting reaction (Sathish *et. al.*, 2006). In this research, an in-situ hydrogen generation from water by CdS nanoparticles supported on pure ETS-10 is suggested as a photocatalyst. CdS nanoparticles supported on modified ETS-10 was also tested for comparison purposes.

### 1.3 Objectives of Research

The main aim of this research is to investigate the influence of synthesis and modification techniques on CdS/ETS-10 photocatalyst towards the hydrogen gas yield under visible light irradiation. This thesis extensively discusses the design of the continuous flow micro-reactor coupled with gas chromatography to thermal conductivity detector (GC-TCD) for the online detection of hydrogen gas. The details of the research objectives are as shown below:

- (i) To synthesize and modify nano-sized CdS and microporous titanosilicate ETS-10.
- (ii) To impregnate the CdS on ETS-10 by incipient wet technique.
- (iii) To characterize the physico-chemical properties of the as-synthesized samples.
- (iv) To set-up and calibrate the microreactor coupled with online GC-TCD for hydrogen detection.
- (v) To evaluate the performance of the samples in hydrogen generation from water under visible light irradiation.



- (vi) To optimize condition of the reaction including the catalysts preparation method, CdS to ETS-10 ratios, light sources used and the function of sacrificed agents in water.

#### **1.4 Scope of Research**

This research focuses on the synthesis and modification pathway of the CdS/ETS-10 hybrid photocatalyst and examines its physicochemical properties. Two methods were applied in the CdS preparation, including reverse micelle method and in-situ sulphur reduction method. ETS-10 used is generally prepared by hydrothermal synthesis route with Degussa P25 titanium dioxide as titanium source and RHA as silica source. ETS-10 derived from Ludox-30 as silica source was also prepared for comparison purposes. The effect H<sub>2</sub>O<sub>2</sub> treatment on ETS-10 was performed to evaluate the effectiveness of the charge separation effect compared with the original ETS-10. The photocatalyst prepared was tested in water splitting process under visible light irradiation. The volume of hydrogen gas generated was recorded by water displacement method whereas the purity of hydrogen gas being confirmed by online GC-TCD. The optimization condition of the reaction includes catalysts preparation method, CdS to ETS-10 ratios, light sources used and the presence and absence of sacrificed agents in water.

#### **1.5 Thesis Outline**

This thesis consists of 5 chapters and completed with a list of references. Chapter 1 has presented a brief introduction to the research background and some advantages or application of the output. It has also discussed the problem statement and summarizes the objectives of the research. Chapter 2 presents some fundamental concepts of photocatalyst, water photo-splitting, semiconductor and role of hole scavengers as electron donors. Additionally, chapter 2 includes some

previously relevant literature reviews on the hydrogen generation from other type of photocatalysts. Chapter 3 discusses the experimental steps including: synthesis, characterization, reactor set-up and catalytic testing of the samples. Chapter 4 shows the results and discussion of the finding, whereas the conclusion and suggestions of research was reported in chapter 5.