CHAPTER I
INTRODUCTION

Nowadays, conventional energy resources, such as coal, fossil fuel, and natural gas, are being extensively used due to the major world's energy requirements. While the price of these resources is increasing, their demands are still rapidly growing without concerning about environmental issues. A great number of carbon dioxide (CO_2) are generated from the conventional energy usage, which is the most dramatically significant for global warming as a subsequent result. Moreover, the raw materials for conventional fuel are being decreased. Therefore, many researches have been focused on renewable hydrogen production as an alternative energy resource for the future needs. Hydrogen is considered as an ideal resource of future energy owing to the following viewpoints:

- Hydrogen can be efficiently produced from a variety of sources, especially from water, which is an abundantly available, clean, and renewable energy source.
- There are no dangerous products emitted from the combustion of hydrogen, whereas the greenhouse gases (especially CO_2), which are the main cause of the global warming, as well as smog and harmful particulates in the air, are generated from the combustion of the fossil fuel by vehicles.
- Fuel cell powered by pure hydrogen emits no harmful pollutants.
- The heat of combustion of hydrogen is much higher than that of hydrocarbon fuel for 2.5 times and nearly 5 times that of methanol and ethanol.
- Hydrogen can be used in many potential applications, in place of fossil fuel, such as powering of non-polluting vehicles, domestic heating, and aircraft.
- Hydrogen and fuel cell technology have the potential to strengthen our national energy security by reducing our dependence on foreign oil.

Thus, alternatively safe, pollution-free, practical, and economically competitive hydrogen technologies should be developed to become a major energy resource in the future.

Since hydrogen is recognized as an environmentally friendly and a highly efficient fuel, as well as water is also a clean, renewable, and cheap resource, an important reaction responsible for hydrogen production is photocatalytic water

splitting reaction by using the major renewable energy resource (i.e. water). The feedstock, water, is available in virtually inexhaustible supply, and the resulting fuel, hydrogen, is attainable without polluted by-products. This is one of alternative potentials for future energy supply. However, the water splitting reaction is endothermic, so its energy requirement is rather high. Solar energy is the major source of renewable energy, and it is therefore the promising energy source for renewable hydrogen production. Solar energy in space is available continuously, independently of the diurnal cycle, and non-polluting. The hydrogen generation from the water splitting by using solar energy is one of the fruitful ways for the conversion of solar energy into chemical energy.

There have been extensive studies of the water splitting by light-absorbing material, called a photocatalyst, for production of hydrogen. The photocatalytic water splitting reaction for hydrogen production by using oxide semiconductor photocatalyst is one of the most promising techniques because the photocatalyst is used in the form of solid phase, which is relatively inexpensive, safe for using, resistant to deactivation, highly chemically stable, and environmentally friendly. Several investigations have been carried out by using many semiconductors. Among them, titanium dioxide (TiO_2) has been considered as the most promising photocatalyst because of its very high photocatalytic performance. However, the difficulty in applying this semiconductor for the photocatalytic water splitting is its large band gap energy (3.2 eV for anatase TiO_2), which can only be utilized for hydrogen production under ultraviolet radiation ($\lambda < 400$ nm). As a matter of fact, UV light accounts for only 4% of the coming solar energy compared to visible light, which occupies the most part of solar light (45%). In order to achieve efficient water splitting under abundant visible light irradiation, it is necessary to develop new photocatalytic system.

The development of photocatalytic systems capable of using the visible light region of the solar spectrum by TiO_2 semiconductor suspensions has been done in many ways, such as metal ion doping, metal ion implantation, anion doping, mixture of semiconductor with large and small band gap, and sensitization by sensitizer doping. The sensitization of semiconductor is very promising technique because it enables the use of semiconductors that do not intrinsically absorb visible light, and

does not suffer destructive photodecomposition. The visible light excites the sensitizer molecules adsorbed on the TiO_2 surface, and the electrons are subsequently injected into the conduction band (CB) of TiO_2 directly or through the loading metals indirectly. The CB and loading metals act either as a mediator for transferring electrons from the excited sensitizer or as a substrate of electron acceptors on the TiO_2 surface, whereas the valence band (VB) remains unaffected in a typical photosensitization. Some sensitizers having redox property and visible light sensitivity can be used in this photocatalytic system. In order to regenerate the sensitizer, electron donors or sacrificial agents, such as diethanolamine (DEA), triethanolamine (TEA), and ethylenediaminetetraacetic acid (EDTA), are usually added into the solution to sustain the photoreaction cycle. Sensitization of TiO_2 by various sensitizer compounds, such as $[Ru(dcpy)_2(dpq)]^{2+}$ (Dhanalakshmi *et al.*, 2000) and $Ru(bpy)_3^{2+}$, or Eosin Y, (Abe *et al.*, 2000), have been employed, and it was experimentally found that hydrogen production rate could be greatly enhanced by adding these sensitizer molecules into TiO_2-containing system.

The purpose of this research was to study the photocatalytic hydrogen production via water splitting by using titania photocatalyst suspension with a dissolved sensitizer (i.e. Eosin Y) under visible light irradiation in the presence of diethanolamine (DEA) as an electron donor. Mesoporous-assembled TiO_2 nanocrystal synthesized via a sol-gel process with the aid of a structure-directing surfactant was used for the photocatalytic activity test, compared with many commercially available non-mesoporous-assembled TiO_2 photocatalysts. Because the nanocrystalline mesoporous-assembled TiO_2 possesses very small physical dimensions, large surface area and pore volume for reactant accessibility, uniform pore size distribution, and high volume fraction of atom located at the surface, it is very interesting to apply this material for the sensitized hydrogen production system. Effects of various preparation conditions for the TiO_2 photocatalysts without and with Pt loading on their physical properties and photocatalytic H_2 production activity were investigated. Several reaction parameters, such as electron donor concentration, sensitizer concentration, photocatalyst dosage, and initial solution pH, were studied.