CHAPTER I
INTRODUCTION

Nowadays, one of the most commonly found problems when using conventional energy resources, such as coal, fossil fuel, and natural gas, is environmental issues because a great number of carbon dioxide (CO_2) is released to atmosphere, causing global warming. Moreover, the consumption of oil is increasing very much while oil reservoirs are gradually decreasing, so the price of oil is increasing. One of possible solutions is usage of alternative energy resources, which are generated from renewable sources, such as solar energy, wind energy, tide power, and geothermal energy. Additionally, many research attempts have been focused on renewable hydrogen (H_2) production for the future need because hydrogen can serve directly as a fuel (e.g. for transportation or for the production of electricity in fuel cells) without producing pollutants upon combustion (Bard and Fox, 1995).

The key advantages of hydrogen are that (1) carbon dioxide is not produced when hydrogen is burnt, (2) 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, (3) hydrogen can be used in many potential applications, in place of fossil fuel, such as a fuel for furnaces, internal combustion engines, turbines and jet engines, automobiles, buses, and airplanes, and (4) hydrogen can be produced from water, which is an abundantly available, clean, and renewable energy source. Due to these advantages, hydrogen can be efficiently produced from a variety of sources, such as reforming of biomass and wastes, thermochemical process, high-temperature electrolysis, biological water splitting, photoelectrochemical water splitting (using semiconductor electrodes), and photocatalytic water splitting (using semiconductor powder). The photocatalytic water splitting is a promising process because it is an ideal method for producing energy. By this process, hydrogen would be a sustainable energy because it is produced from two major sources of renewable energy by using water as a feedstock and the solar light as energy, with a suitable photocatalyst for absorbing light to drive the water splitting to produce hydrogen. The hydrogen generation from the water splitting by using solar energy is also one of the fruitful ways for the conversion of solar energy into chemical energy.

Many research works have been extensively investigated about the water splitting to produce hydrogen by using many oxide semiconductor powders as light-absorbing material, called a photocatalyst. The oxide semiconductor photocatalyst is used in the form of solid phase, which is relatively inexpensive, safe for operation, and resistant to deactivation. Perovskite titanates, such as $MgTiO_3$, $CaTiO_3$, and $SrTiO_3$, are promising oxide semiconductor photocatalysts because they possess a layered structure, which leads to several advantages, such as high dielectric constant, enhanced charge separation, excellent thermal stability, and high chemical stability. However, it is difficult in applying these semiconductors with a wide band gap energy ($E_g > 3.2$ eV) for the photocatalytic water splitting, which can only be utilized for hydrogen production under ultraviolet irradiation ($\lambda < 400$ nm). As a matter of fact, UV light accounts for only 4% of the coming solar energy compared with 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 system capable of using the visible light region of the solar spectrum can be achieved by modifying photocatalyst in many ways, such as metal ion doping, metal ion implantation, anion doping, mixture of semiconductor with large and small band gap, and addition of electron donors (hole scavengers) and sensitizers. The dye 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. Some dye sensitizers, such as $[Ru(dcpy)_2(dpq)]^{2+}$ (Dhanalakshmi *et al.*, 2000), and $Ru(bpy)_3^{2+}$ or Eosin Y (Abe *et al.*, 2000), are able to absorb visible light and produce electrons as reducing agent strong enough to produce hydrogen. In order to regenerate the sensitizer, electron donors or sacrificial agents, such as diethanolamine (DEA), triethanolamine (TEA), and ethylenediaminetetraacetic acid (EDTA), are usually added to the solution to sustain the photoreaction cycle.

The purposes of this work were to study the use of a sol-gel process with the aid of a structure-directing surfactant for synthesis of mesoporous-assembled perovskite titanate nanocrystals and to comparatively investigate their photocatalytic activity for hydrogen production from sensitizer (Eosin Y)-containing system under visible light irradiation in the presence of diethanolamine (DEA) or triethanolamine (TEA). The effects of various synthesis conditions of perovskite titanate photocatalysts on their physical properties and photocatalytic H_2 production activity, as well as the effects of various reaction conditions, were investigated.