CHAPTER I
INTRODUCTION

Nowadays, energy is a key input to drive and improve the human life. The energy consumption is directly proportional to the population growth, the improvement of the living standard of humanity, and the industrialization of the developing countries. The global demand for energy is expected to increase rather significantly in the near future. The primary source of currently consumed energy is fossil fuels, coal, and gas; however, the limitation of fossil fuel reserves and large-scale environmental degradation, particularly global warming, air pollution, and acid rain, strongly suggest that renewable and environmentally friendly energy resources are vital for the global energy supplies. Renewable energy resources, such as wind, water, and sun, can be used without greenhouse gas emission, and they are unlimitedly available (Omer, 2008). Using renewable energy resources means to use natural cycles to produce energy. It also means to produce energy without destroying the environment, without causing cancer through atomic radiation or asthma through emissions, and without exploiting natural resources (Balat, 2008). Therefore, many research works have been focused on renewable hydrogen production as an alternative energy resource for the future needs because hydrogen is considered to be an ideal resource of renewable energy owing to the following viewpoints:

- Hydrogen can be produced from a variety of sources, including from water, which is known to be abundantly available in the world, so it will be sufficient all the time,
- When hydrogen is burnt with air, the main product is water, which can safely return to nature, without carbon dioxide (CO_2) produced,
- Hydrogen has higher energy content by weight than any common fuels (about three times more than gasoline), and the heat of combustion of hydrogen is much higher than that of hydrocarbon fuels (about 2.5 times and nearly 5 times more than methanol and ethanol),
- Like electricity, hydrogen is an energy carrier and will have great potential in the future. It can also be used in places where it is hard to use electricity since it can be stored and transported to where it is needed,

- Hydrogen can be used in many potential applications, in place of fossil fuels, such as a fuel for furnâces, internal combustion engines, turbines and jet engines, automobiles, buses, and airplanes, and

Hydrogen can be readily produced from a variety of sources, such as reforming of biomass and wastes, thermochemical process, high-temperature electrolysis, photoelectrochemical water splitting (using semiconductor electrodes), and photocatalytic water splitting (using semiconductor powder). Nevertheless, finding a method to produce hydrogen cheaply and efficiently from a renewable resource is the first step in developing a safe and non-polluting energy resource.

From the viewpoint of conversion of solar energy into chemical fuel, direct production of hydrogen from photocatalytic splitting of water over various kinds of oxide semiconductors has gained much attention aiming to search a sustainable source of hydrogen energy supply. Photocatalytic water splitting is one of the promising processes for hydrogen production since two renewable resources, i.e. water and sunlight, are used. This process is termed for the production of hydrogen (H_2) and oxygen (O_2) from water by directly utilizing the energy from sunlight with a suitable photocatalyst for absorbing light to drive the water splitting to produce hydrogen. Although several research works on this process are still undergoing, it offers the potential to provide clean hydrogen energy for the near future.

Many research works have been extensively investigated about the photocatalytic water splitting to produce hydrogen by using many kinds of 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, resistant to deactivation, highly chemically stable, and environmentally friendly. Among them, titanium dioxide (TiO_2) has been considered as the most promising photocatalyst owing to its inexpensiveness, strong oxidizing power, non-toxicity, and long-term photostability (Chen and Mao, 2007). However, it can be activated only under UV light irradiation ($\lambda < 400$ nm) because of its large energy band gap (3.2 eV for anatase TiO_2) (Aita *et al.,* 2004). As a matter of fact, UV light accounts for only 4% of the coming solar energy as compared to visible light, which occupies the most part of solar light (45%). For further improvement of effective utilization of the solar energy, considerable efforts have been made to shift its photocatalytic activity to the visible light region.

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 doping with metals or ions to narrow the band gap energy, addition of electron donors (hole scavengers) and sensitizers, establishing junctions between different phases (metal-semiconductor or semiconductor-semiconductor) in order to reduce charge recombination (Fu *et al.,* 1995), and composite design with porous materials. In particular, incorporating TiO_2 by other semiconductors with larger band gap energy, such as La_2O_3, SnO_2, SiO_2, and ZrO_2 (Anderson *et al.,* 1997, Kawahara *et al.,* 2001, Reddy *et al.,* 2002, and Wang *et al.,* 2006) has been proved to be an effective route to improve the thermal stability and photocatalytic activity of TiO_2. Among them, a mixed oxide system with TiO_2 and ZrO_2 has been widely investigated in the photocatalysis field since TiO_2-ZrO_2 photocatalysts with suitable TiO_2 and ZrO_2 compositions are more efficient than pure TiO_2 photocatalysts for photocatalytic reaction activity. The increase in surface area with respect to TiO_2 at a given calcination temperature, the inhibition of rutile formation, the rise in surface acidity, and the creation of active defects on the TiO_2 surface have been proposed as possible causes of this improvement (Yu *et al.,* 1998).

The aim of this work was to optimize the composition of TiO_2-ZrO_2 binary metal oxides for achieving the highest photocatalytic activity for hydrogen production from the sensitized water splitting under visible light irradiation. The mesoporous-assembled TiO_2-ZrO_2 nanocrystal photocatalysts with various Ti and Zr molar concentrations were synthesized by a sol-gel process with the aid of structure-directing surfactant. The synthesized photocatalysts were then used for the photocatalytic hydrogen production under visible light irradiation from a system containing Eosin Y sensitizer and diethanolamine electron donor. The effects of calcination conditions and Pt loading by two different methods (i.e. single-step sol-gel and photochemical deposition) on the photocatalyst properties and hydrogen production activity were mainly investigated.