



CHAPTER I INTRODUCTION

At present, all conventionally available energy resources, especially coal and fossil fuels, produce a large amount of carbon dioxide (CO₂), causing the global warming. The consumption of fossil fuels such as oil is rapidly increasing while oil reservoirs are decreasing. Therefore, renewable energy resources, including wind energy, tide power, and geothermal energy have been studied and used. In addition, many attempts have focused on hydrogen as an alternative and renewable energy for future demands (Jung and Park, 2004).

Hydrogen is an ideal energy source for the future due to its versatile application and environmentally friendly properties. In particular, no harmful products are emitted to the environment (Sreethawong *et al.*, 2009). Hydrogen can be efficiently produced from a variety of sources, such as reforming of biomass and wastes, thermochemical process, high-temperature electrolysis, photoelectrochemical water splitting, and photocatalytic water splitting (using semiconductor powder). The photocatalytic water splitting is an ideal method for producing hydrogen.

Photocatalytic water splitting is a chemical reaction for producing hydrogen by using two major renewable sources, i.e. water and solar energy (Sreethawong *et al.*, 2008). The use of a semiconductor photocatalyst is a promising technique because the photocatalyst is in a solid phase form. Titanium dioxide (titania, TiO₂) is commercialized as the most powerful photocatalyst because it is highly photoactive for most photocatalytic reactions, non-expensive, non-toxic, clean and environmentally friendly (Meng *et al.*, 2005). In addition, TiO₂ has been considered as the most promising photocatalyst owing to its strong oxidizing power 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 TiO₂) (Aita *et al.*, 2004). As a matter of fact, the UV light accounts for only 4 % of the coming solar energy compared to the 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) so as to reduce charge recombination, and composite design with porous materials (Fu *et al.*, 1995). Additionally, silicon oxide (silica, SiO₂) doping/addition can be used to improve the thermal stability and photocatalytic activity of TiO₂. Recently, the TiO₂-SiO₂ mixed oxide is reported to be more active than pure TiO₂ photocatalyst (Jung and Park, 2004). Moreover, zirconium dioxide (zirconia, ZrO₂) doping can improve the thermal stability and photocatalytic activity of the host TiO₂ for hydrogen production (Onsuratoom *et al.*, 2011). Besides, Zr-doped SrTiO₃ shows the high photocatalytic activity for degradation of methylene blue due to the defects of perovskite crystal lattice (Chen *et al.*, 2009).

The use of metal cocatalysts, in particular Pt and Ag, has been investigated by deposition/loading on the support surface, functioning as hydrogen evolution actives sites (Bamwenda *et al.*, 2005; Onsuratoom *et al.*, 2011). However, the use of bimetallic Pt-Ag cocatalyst to enhance the photocatalytic hydrogen production activity of the TiO₂-SiO₂, TiO₂-ZrO₂ and SrTi_xZr_{1-x}O₃ nanocrystal photocatalysts has never been investigated.

The objective of this research was to improve the hydrogen production activity from the sensitized water splitting under visible light irradiation of mesoporous-assembled TiO₂-SiO₂, TiO₂-ZrO₂, and SrTi_xZr_{1-x}O₃ nanocrystal photocatalysts by metallic Pt-Ag loading. The mesoporous-assembled nanocrystal photocatalysts were prepared by a sol-gel method with the aid of a structure-directing surfactant at the Ti-to-Si molar ratio of 97:3 and Ti-to-Zr molar ratio of 93:7 at the same ratio for SrTi_xZr_{1-x}O₃. The bimetallic Pt-Ag cocatalysts were loaded on a mesoporous-assembled nanocrystal photocatalysts with various Pt-to-Ag ratios by photochemical deposition method. The synthesized photocatalysts were then used for photocatalytic hydrogen production under visible light irradiation from a system containing Eosin Y sensitizer and diethanolamine electron donor.