CHAPTER I
INTRODUCTION

At present, all conventionally available energy resources, especially coal and fossil fuels, produce a large amount of carbon dioxide (CO_2), causing the global warming. In addition, the consumption of oil is rapidly increasing while oil reservoirs are decreasing. Consequently, renewable energy resources, such as wind energy, tide power, and geothermal energy, are very important. Additionally, many attempts have focused on hydrogen as an alternative and renewable energy for future demands (Jung and Park, 2004).

Hydrogen is now being recognized as an ideal energy source for the future due to its versatile application, environmentally friendly properties, and several other acceptable standpoints. In particular, no harmful products (e.g. CO_2, smog, and particulates) are generated or 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 (using semiconductor electrodes), and photocatalytic water splitting (using semiconductor powder). The photocatalytic water splitting is ideal method for producing hydrogen. Nevertheless, finding a method to produce hydrogen cheaply and efficiently from renewable resources is the first step in developing a safe and non-polluting energy resource.

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 promising technique because the photocatalyst is in a solid phase form. Titanium dioxide (titania, TiO_2) is recognized as the most powerful photocatalyst because it is highly photoactive for most photocatalytic reactions, non-expensive, non-toxic, clean and environmentally friendly (Ni *et al.*, 2005). In addition, TiO_2 is 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 TiO_2) (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) in order to reduce charge recombination, and composite design with porous materials (Fu *et al.*, 1995). Additionally, silica (SiO_2) doping/addition can be used to improve the thermal stability and photocatalytic activity of TiO_2. Recently, the TiO_2-SiO_2 mixed oxide was reported to be more active than pure TiO_2 photocatalyst (Jung and Park, 2004). Moreover, the use of metal cocatalysts, in particular Pt and Au, has been simultaneously investigated by deposition/loading on the support surface, functioning as hydrogen evolution actives sites (Bamwenda *et al.*, 2005; Sreethawong *et al.*, 2005).

The purpose of this research was to optimize the composition of TiO_2-SiO_2 binary metal oxides and Pt-Au bimetallic cocatalysts for achieving the highest photocatalytic activity for hydrogen production from the sensitized water splitting under visible light irradiation. The mesoporous-assembled TiO_2-SiO_2 mixed oxide nanocrystal photocatalysts with various TiO_2-to-SiO_2 molar ratios were synthesized by a sol-gel process with the aid of a structure-directing surfactant. The Pt and/or Au loading on a mesoporous-assembled TiO_2-SiO_2 mixed oxide nanocrystal photocatalyst with various Pt-to-Au weight ratios was performed by a photochemical deposition method. The prepared photocatalysts were then used for photocatalytic hydrogen production under visible light irradiation from a system containing Eosin Y sensitizer and diethanolamine electron donor. The effects of mixed oxide composition, calcination temperature, and Pt and/or Au loading on the photocatalyst properties and hydrogen production activity were mainly investigated.