CHAPTER I
INTRODUCTION

The purpose of this chapter is to point out the need for developing efficient photocatalysts for both photodegradation of organic pollutants and photocatalytic hydrogen production.

1.1 Rationale and Problems

As the increase in the global energy-source problems and the global environment problems, one of promising technologies for the future that can solve these problems is photocatalysis because it is environmentally friendly, which utilizes the clean and abundant energy resource of solar energy, to perform the reactions. The photocatalysis can be applied in both organic pollutant elimination and hydrogen production, as claimed in several researches. The photocatalytic process has been demonstrated as a potential means for complete photodegradation of organic pollutants at a low cost and with simplicity in operation as it can be operated at ambient conditions. Moreover, it does not utilize any toxic materials. In addition, the photodegradation of most organic pollutants generally produces CO_2 and H_2O. The final product of H_2 is also produced from the water splitting reaction. The attractive features of hydrogen are as follows: hydrogen can be produced from clean and renewable sources as water and solar energy, leading to the clean and renewable life cycle of hydrogen; hydrogen has an excellent energy density by weight, its heating value is much higher than any other fuels (2.5 times higher than hydrocarbon fuels and nearly 5 times higher than methanol and ethanol); and hydrogen is an environmentally friendly fuel without release of pollutants (such as greenhouse gasses).

The drawback of the organic pollutant photodegradation is its slow reaction rate that makes this process not to be widely applied for wastewater treatment. Similarly in hydrogen production application, the solar-to-hydrogen energy conversion efficiency is too low for the technology to be economically sound. The slow rates of all photocatalysts mainly result from the rapid recombination of photo-

generated electrons and photo-generated holes, as well as the backward reactions and the poor activity of photocatalysts themselves, especially under visible light irradiation. In response to these deficiencies, many groups have been conducting researches with an emphasis on effective remedy methods. One of interesting approaches is to use sacrificial reagents and carbonate salts to prohibit the rapid recombination of electron-hole pairs and backward reactions (Avudaithai and Kutty, 1987; Sayama and Arakawa, 1992, 1994, 2000; Takata *et al.*, 1998; Li *et al.*, 2003). Other approaches are metal loading, metal ion doping, dye sensitization, composite semiconductor, anion doping and metal ion-implantation (Asahi *et al.*, 2001; Ishii *et al.*, 2004; Konta *et al.*, 2004; Ohno *et al.*, 2004, 2005; Kudo, 2006; Subramanian *et al.*, 2006).

One of promising photocatalysts is strontium titanate ($SrTiO_3$) because of its superior physical and chemical properties, such as its excellent thermal stability, photocorrosion resistibility, and good structure stability as the host for metal doping (Ohno *et al.*, 2004, 2005). Especially, $SrTiO_3$ can be used as an electrode for photoelectrolysis of water (Kumar *et al.*, 1992) and used as a photocatalyst for H_2 and O_2 production though the water splitting by light irradiation, because its redox potential of electrons and holes that are induced by UV irradiation is powerful enough to decompose water into H_2 and O_2 (Wang *et al.*, 2005). However, $SrTiO_3$ has a large band gap of about 3.2 eV, and it can utilize only the UV radiation, which is the small fraction in the solar radiation (accounts for only 4% of the incoming solar energy) (Zou *et al.*, 2001; Ni *et al.*, 2007), leading to the low photocatalytic activity of $SrTiO_3$ in the visible region. Due to the low photocatalytic activity in the visible region, the visible-light harvesting potential has been induced into $SrTiO_3$ by doping with various elements, such as lanthanum and nitrogen co-doped $SrTiO_3$ (Wang *et al.*, 2005), chromium doped $SrTiO_3$ (Chang and Shen, 2006), sulfur and carbon co-doped $SrTiO_3$ (Ohno *et al.*, 2005), and NiO-$SrTiO_3$ (Ashokkumar, 1998). Other techniques, such as dye sensitization and composite photocatalyst, have been also used to enhance the photocatalytic activity under visible light irradiation. In addition, the photocatalytic activity does not depend only on light harvesting property, but also the structure of the photocatalysts (Moumen *et al.*, 1995; Motte and Pileni, 2000; Pileni, 2003; Liao and Liao, 2007). Some research groups reported

that mesoporous-structured photocatalysts can offer higher photocatalytic activity and better light-induced hydrophilicity than non-porous-structured photocatalysts. A new solution-based approach that has been developed to achieve mesoporous-structured materials is the sol-gel process with self-assembly of the surfactant template. The porosity of mesoporous photocatalysts can be controlled when being synthesized by using a surfactant-assisted templating sol-gel method (Cassiers *et al.*, 2003; Yusuf *et al.*, 2003; Sakulkhaemaruethai *et al.*, 2004; Sreethawong *et al.*, 2005a, b).

Due to the excellent properties of $SrTiO_3$ and the high photocatalytic activity from better light-induction and higher hydrophilicity of mesoporous-structured materials (Bacsa and Kiwi, 1998; Dai *et al.*, 1999; Sreethawong *et al.*, 2005c, d, e, 2006), this study aims to investigate the use of sol-gel method with the aid of structure-directing surfactant for the synthesis of mesoporous-assembled $SrTiO_3$ nanocrystals under mild conditions and to investigate the use of the synthesized $SrTiO_3$ for the photodegradation of organic pollutants and for the photoproduction of hydrogen from the decomposition of water.

1.2 Objectives

1.2.1 To investigate the use of a sol-gel method with the aid of structure-directing surfactants for the synthesis of mesoporous-assembled $SrTiO_3$ nanocrystals and metals-loaded mesoporous-assembled $SrTiO_3$ nanocrystals.

1.2.2 To study the photocatalytic activity of the synthesized $SrTiO_3$ (pristine $SrTiO_3$) photocatalysts for the photodegradation of model organic pollutants.

1.2.3 To assess the photocatalytic activity of the pristine and metals-loaded $SrTiO_3$ photocatalysts for photocatalytic hydrogen production.

1.3 Scope of Research Work

The sol-gel method with the aid of structure-directing surfactants was used to synthesize $SrTiO_3$ photocatalysts with three different surfactants: laurylamine hydrochloride (LAHC), cetyltrimethylammonium bromide (CTAB), and

cetyltrimethylammonium chloride (CTAC), and four different solvents: water (H_2O), ethyl alcohol (EtOH), ethylene glycol (EG), and mixed solvent between EtOH and EG. The calcination temperature was varied in the range of 600°C to 750°C with different heating rates. The photocatalytic activity of the synthesized $SrTiO_3$ photocatalysts for methyl orange degradation was tested to find out the best synthesis conditions. Then, the $SrTiO_3$ photocatalyst prepared at the optimum conditions was loaded with various metals for the enhancement of their photocatalytic activities towards both organic pollutant degradation and hydrogen production.

The ultimate goal of this research was to find out the best synthesis approach for $SrTiO_3$-based photocatalysts, which provide the highest photocatalytic activity in both organic pollutant degradation and photoproduction of hydrogen. Literature reviews and applications of photocatalysts/photocatalysis will be presented in Chapter II. Chapter III will describe the synthesis method of $SrTiO_3$ photocatalysts with different metal loading and the photocatalytic testing. The investigation in the synthesis approach and the photocatalytic activity for methyl orange degradation of the synthesized $SrTiO_3$ photocatalysts will be presented in Chapter IV. Chapter V will present the effects of hole scavenger, Pt co-catalyst loading, and reaction temperature on the photocatalytic activity for hydrogen production via water splitting reaction of the synthesized $SrTiO_3$ photocatalysts. The effects of metal type and loading on the photocatalytic activity for hydrogen production via water splitting reaction of the synthesized $SrTiO_3$ photocatalysts will be discussed in Chapter VI. The effect of chemical structure and properties of hole scavengers on the photocatalytic activity for hydrogen production via water splitting reaction of the synthesized $SrTiO_3$ photocatalysts will be presented in Chapter VII. Chapter VIII will include the conclusions of the research and the recommendations.

1.4 References

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