# CHAPTER I
# INTRODUCTION

The consumption of petroleum has fluctuated during the 20th century, at least partially because of the rise of the automobile industry. Today, fossil fuels, such as coal, oil and natural gas, provide more than three quarters of the world's energy consumption, which causes global warming because fossil fuels can produce a great amount of carbon dioxide ($CO_2$) (Yakovlev *et al.*, 2009). At present, various concerns about environmental protection lead to renewable energy, which comes from natural resources, such as sunlight, wind, rain, tides, and geothermal heat. Additionally, hydrogen has received great attention to use as alternative and renewable energy for internal combustion-engine and fuel cell because of making zero pollutant emission to environment (Seo *et al.*, 2009) and having high energy density by weight (2.5 times than hydrocarbon fuels and nearly 5 times than methanol and ethanol) (Ashokkumar, 1998).

The potential sources of hydrogen include fossil fuels (i.e. coal, oil, and natural gas), a variety of chemical intermediates (e.g. refinery products, ammonia, and methanol), and alternative resources (e.g. bio-mass, bio-gas, and waste materials). Especially, hydrogen can be produced by water splitting reaction, which is an ideal process because it is clean with plenty energy resources of water and solar energy (Sreethawong *et al.*, 2005). The use of a semiconductor photocatalyst is a promising technique because the photocatalyst is in a solid phase form. Titanium dioxide (titania, $TiO_2$) is the most effective photocatalyst and has been widely used owing to low commercial cost, nontoxicity, high photostability, high chemical stability over a wide pH range, etc. (Cristante *et al.*, 2008). However, it still provides low photocatalytic efficiency, which is limited by three main causes, including the recombination reaction between photo-generated electrons and holes, the backward reaction between hydrogen and oxygen to reproduce water (Patsoura *et al.*, 2007), and the limited light harvesting ability of photocatalysts (Anpo M. 2004). The improvement of its photocatalytic water splitting performance can be achieved by many ways, such as doping with metals to narrow its band gap energy, addition of electron donors (hole scavengers) to the reaction system, and establishment of

semiconductor-semiconductor mixed oxide in order to reduce the charge carrier recombination (Yang *et al.*, 2006). In particular, incorporating $TiO_2$ (band gap energy of ~3.2 eV) by other semiconductors with larger band gap energy, especially $ZrO_2$ (band gap energy of ~5 eV) (Emeline *et al.*, 1998) to obtain $TiO_2$-$ZrO_2$ binary mixed metal oxides or $Ti_xZr_{1-x}O_2$ solid solutions, has shown higher photocatalytic activity than pure $TiO_2$ due to the improvement of the thermal stability and photocatalytic activity of the host $TiO_2$. With an appropriate incorporated $ZrO_2$ content, the increase in specific surface area of the mixed oxide at a proper calcination temperature, the retardation of anatase-to-rutile phase transformation, and the increase in number of active sites on the $TiO_2$ surface for water reduction have been proved to be the principal causes of this physical property and photocatalytic activity improvement (Yu *et al.*, 1998). The addition of silica to $TiO_2$ also brings about an increase in the photocatalytic activity because $TiO_2$-$SiO_2$ mixed oxides normally have higher thermal stability by suppressing the phase transition from anatase to rutile (Kim *et al., 2006*), larger surface area, greater band gap energy, and smaller crystallite size (Mahyar *et al.*, 2010). Moreover, several research works have reported that the loading of a precious noble metal, such as Pt, Au, Pd, etc., on a semiconductor surface is beneficial for greatly enhancing the efficiency of photocatalytic water splitting reaction (Sreethawong *et al.*, 2005, Yan *et al.*, 2008, Puangpetch *et al.*, 2011). However, such metals are very expensive, while some effective non-precious transition metals, especially Cu, are less expensive and can still be employed for the photocatalytic activity enhancement. According to our knowledge, the use of $SrTi_xZr_{1-x}O_3$ and $SrTi_xSi_{1-x}O_3$ nanocrystals with mesoporous-assembled structure and with Cu loading for the photocatalytic water splitting has never been investigated.

Therefore, the purpose of this work was to investigate, for the first time, the effect of composition of mesoporous-assembled $SrTi_xZr_{1-x}O_3$ and $SrTi_xSi_{1-x}O_3$ nanocrystals on the photocatalytic activity for hydrogen production from the water splitting under UV light irradiation. The mesoporous-assembled $SrTi_xZr_{1-x}O_3$ and $SrTi_xSi_{1-x}O_3$ nanocrystal photocatalysts with various Ti-to-Zr and Ti-to-Si molar ratios were synthesized by a sol-gel process with the aid of a structure-directing surfactant and systematically characterized by various techniques. The synthesized

photocatalysts were then employed for the photocatalytic water splitting using methanol as a hole scavenger. The effect of Cu cocatalyst loading by a photochemical deposition method on the photocatalyst characteristics and subsequent hydrogen production activity were also examined.