Chapter 1
Introduction

1.1 Rational

As the need of new materials for facing new applications in energy and environment areas, wide band gap semiconductors become very promising materials due to outstanding properties such as large band gap, high electron mobility, and reasonably good thermal conductivity. Among semiconducting wide band-gap oxide materials, titanium dioxide (TiO_2) and zinc oxide (ZnO) are alternative materials as electron transporting layer (ETL) with suitable energy levels relative to Perovskite. Due to their prominent electron transfer which as crucial factor for Perovskite solar cells (PSCs) performance, many approach have been found that both of them can enhance the overall power conversion efficiency (PCE). Even though ZnO exhibits higher electron mobility compare to TiO_2, PSCs based on ZnO have a serious problem such as the poor stability. Perovskite (composted of methyl ammonium ($CH_3NH_3^+$) and lead triiodide PbI_3^-) deposited on ZnO is easy to decompose during thermal treatment but this effect cannot be found between Perovskite and TiO_2 interfaces. Since TiO_2 has acidic surface while ZnO surface shows basic property which has high adsorption of positive charge. When Perovskite is exposed on ZnO, deprotonation reaction with $CH_3NH_3^+$ occurs which could break the ionic interaction between $CH_3NH_3^+$ and PbI_3^- and obstruct the crystal formation of the Perovskite [1]. Therefore, TiO_2 is the better choice and overwhelmingly interesting in the fundamental aspects and applications as well as the main motivation of this work.

TiO_2, due to its high efficient photoactivity, stability and non-toxicity, is the prime candidate for manufacturing chemicals on a large scale [2]. Achievements in recent years have widely focused on solar cell research. However, the functionality for native TiO_2 forms can be excited only by ultraviolet (UV) light, $\lambda < 387$ nm, that only constitutes less than 5% of solar irradiance because of the wide band gaps (3.0 eV for rutile and 3.4 eV for anatase). As a result, only UV light or higher-energy photons can be absorbed by native TiO_2 forms, while a large portion of the visible and near infrared photons (longer-wavelength photons) cannot [3]. Therefore, extensive efforts have been

made to develop the native TiO_2 forms into broaden light absorption and suppress charge recombination toward efficient solar energy conversion. Especially, employed in efficient PSCs, TiO_2 plays a key role as ETL or hole blocking layer receiving injected electrons from photogeneration in a Perovskite layer and transferring to collecting electrode [4]. ETL is established between fluorine-doped tin oxide (FTO) conductive glass and Perovskite active layer. Traditional ETL is constructed from a native thin TiO_2 mesoporous arrangement or TiO_2 compact layer. However, they contribute to avoid direct contact between FTO and Perovskite [5]. Various observations report that TiO_2 nanorods (NRs) have capability more than conventional TiO_2 nanoparticles (NPs).

The mesoporous layers (MSLs) consist of a great number of 20 nm-sized nanoparticles. Their small sizes produce many grain boundaries that obstruct electron flow by trapping electrons at grain boundary, leading to degradation of charge transfer. Moreover, MSLs do not provide a direct pathway to electron, which results in energy loss because of electrons scattering in grain boundary regions [6-8]. Furthermore, the electron transport and electron diffusion length can enhance in solar cell with TiO_2 NRs. Because long lifetime electrons in TiO_2 NRs attribute to the increment of charge carriers, leading to photo conversion efficiency increase from 6.17% (for NPs) to 9.12% (for NRs) [9]. In addition, energy conversion efficiency of solar cells using spherical TiO_2 NRs is 46.1% higher than those using TiO_2 NPs [10]. The lower lifetimes of TiO_2 NPs might be due to the improvement of electron-hole recombination rate. The average of electron diffusion length of TiO_2 NPs is much lower than that of the TiO_2 NRs. This indicates that the electrons of the TiO_2 NPs spend a long transitive time at the intraband trap sites [7, 11].

Nowadays, one-dimensional (1D) TiO_2 nanostructures have been considered as a significant material to develop solar conversion efficiencies because they provide abundant surface areas. This will enhance the number of active sites that contribute to improve the electron percolation and increase charge transport. Earlier study on self-organizing electrochemical anodization TiO_2 nanotubes (TiO_2 NTs), hydrothermally grown TiO_2 nanotubes (TiO_2 HNTs) and hydrothermally grown TiO_2 nanorods (TiO_2 NRs) revealed that TiO_2 NRs exhibited about three times photoelectrochemical (PEC) performance higher than that of TiO_2 NTs and almost six times higher than that of hydrothermally TiO_2 HNTs. Moreover, the electron lifetime of TiO_2 NRs was higher

than both of TiO_2 NTs about 10^4 times [12]. PEC performance of TiO_2 NRs has taken into account for these reasons. The lower intrinsic resistance of the rutile TiO_2 NRs can improve photoelectrocatalytic activity up to 3.5 higher than that of the anatase TiO_2 NRs, indicating the preferable electron transport property of the rutile TiO_2 [13]. Interestingly, the chloride on the rutile TiO_2 NR surfaces may trap the photogenerated holes, resulting in increasing of the charge separation and the photoactivity for PEC [14]. Moreover, nanowires (NWs) generally have diameters in order of tens nanometers with aspect ratio about 1000 while NRs have diameters in 1-100 nm range and the proportional relationship between width and height is about 5-100. Morphology control of NWs is difficult because of their extremely high aspect ratio and wide inter-wire spacing. The significantly small and long architectures are not well-established can causing NWs to collapse and hit with each other. Previous study revealed that NWs obtained from hydrothermal approach appeared like the long fibers lying down overlap to each other in horizon direction parallel to substrate surface [15]. Theses irregular orientation may promote random walk and provide more scattering site of electron in NW structures causing a high probability of charge recombination. Therefore, NRs are more interesting because the easier size, shape, and crystallographic orientation can be tuned in vertical orientation. Recently, a high performance of PSCs at 17.6% efficiency using single-crystalline TiO_2 NRs as ETL has been reported, supporting that the TiO_2 NR architectures are dominating and interesting [6].

TiO_2 NRs can serve as medium in highly efficient Perovskite solar cell**.** The Perovskite structure is defined as ABX_3 compound consisting of corner-sharing BX_6 octahedral, where X is an anion or halogen (generally iodine) with A and B are cations of different sizes (A being larger than B). The larger cation A is usually an organic methylammonium ($CH_3NH_3^+$) ion. Pb has been extensively use as cation B because it is effectively durability against oxidation. For $CH_3NH_3PbI_3$ Perovskite, the cubic phase forms only at average high temperatures (>330 K) and band gap energy is 1.55 eV with effectively absorption in the visible range [16, 17]. Perovskite is an intrinsic

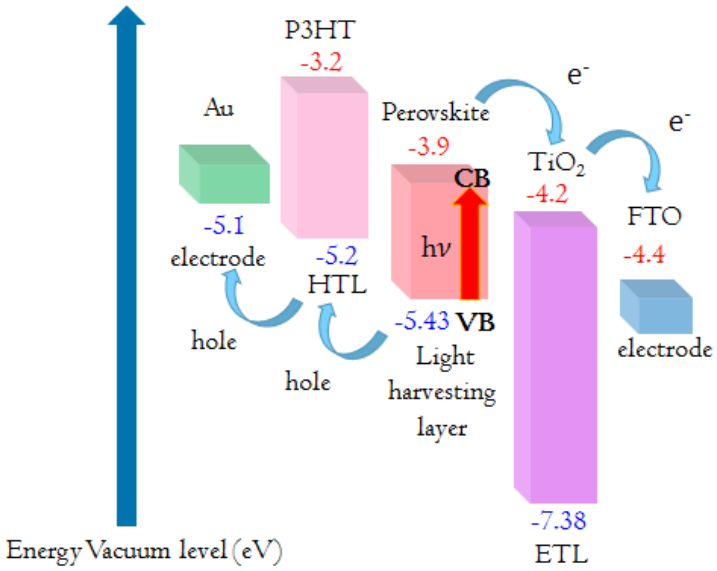

Figure 1.1 Band diagram of perovskite solar cell

semiconductor that converts light energy to electron-hole pair. The excited electrons receive energy from photon and change energy level from valance band to conduction band. The motion of electron in conduction band results in collection of charge carriers at an electrode. In normal structure of Perovskite solar cell, Perovskites are placed between electron transporting layers (ETLs) which usually are TiO_2, and hole transporting layers (HTLs) that generally use Poly(3-hexylthiophene) (P3HT). Because conduction band of TiO_2 is lower than the conduction band of Perovskite, it transfers electrons from conduction band of Perovskite to the FTO anode [18]. Valence band of P3HT is above the valence band of perovskite, holes transfer through the metal electrode as shown in Figure 1.1. With electrons on the anode and holes on the cathode, the solar cell can supply power to an external system. For high performance solar cells, good ETLs should have good electron mobility, the energy levels of ETMs should agree with those in Perovskite materials that improve the electron transfer and block holes, last but not least ETLs should have high transparency in visible light region which reduces absorption of visible light before traveling to Perovskite active layer [1]. Therefore, this work aims to achieve highly crystallinity and crystallographic orientation of TiO_2 NRs which could promote high transmittance of TiO_2 film by hydrothermal method because this procedure is preferential compared to other techniques. For the system involved high pressure in autoclave, then a single- and poly-

crystalline can be produced at low temperature (<250°C) , which do not require a sintering process at high temperature. Furthermore, the equipment and methodologies are simple and proper for low cost manufacturing [4 ,1 9] . The synthesis will be conducted in minimal amount of harmful chemical such as hydrochloric acid (HCl) with the attribution of TiO_2 seed layers. Several factors affect the development of TiO_2 NRs such as precursor concentrations, calcination and reaction times that will be studied to control the growth of TiO_2 NRs. Moreover, growth mechanism of TiO_2 NRs in each condition will be used to explain the phenomena that occur during hydrothermal reaction. The prepared TiO_2 NRs that exhibit would dominant structural and optical properties that would suit to employ as ETLs in perovskite solar cell.

1.2 Research objectives

1.2.1 To synthesis TiO_2 nanorods by hydrothermal method on fluorine-doped tin oxide glass substrate assisted by a seeding layer.

1.2.2 To characterize structural and optical properties of the obtained TiO_2 NRs.

1.3 Research scope

This research concentrates on synthesis and characterization of TiO_2 NRs by hydrothermal procedure under 200ºC in HCl solution using Ti(IV)-butoxide (TBO) as a precursor. The hydrothermal synthesis occurs in Teflon liners (50 ml volume) contained in stainless autoclaves. Various techniques, including field emission scanning electron microscopy (FE-SEM) , Transmission electron microscopy (TEM) and X-ray diffraction (XRD) , will be employed to investigate the morphology and crystalline structure of the prepared TiO_2. The optical properties will be analyzed by UV–VIS spectroscopy. The basis of crystal structure that have high possibility to formulate under our hydrothermal condition such as rutile and anatase is also studied. Moreover, growth mechanism of rutile and anatase TiO_2 during hydrothermal process will be explained.

1.4 Research location

Applied physics research laboratory, Department of Physics and Materials Science, Faculty of Science, Chiang Mai University

1.5 Usefulness and application of the research

TiO_2 NRs can be obtained by low acid hydrothermal solution. Moreover, the TiO_2 NRs prepared from this research can be pursued as ETL layer in Perovskite solar cell