Chapter 3
Methodology

In this study, TiO_2 NRs were synthesized with lower amount of HCl in hydrothermal solution compared to previous studies [6, 19]. This usability reduction of HCl not only contributes to decrease harmfulness of high acidity but also to decrease the manufacturing cost of NRs synthesis. TiO_2 NRs on a transparent conductive fluorine-doped tin oxide (FTO) glass substrate with seed layer were synthesized by a two-step method. TiO_2 thin films were first precoated by spin coating and annealing, followed by the growth of TiO_2 nanorods with a hydrothermal method. These experiments were performed, as followed.

3.1. Preparation of seed layers

As show in Figure 3.1 before the hydrothermal synthesis, FTO substrates were ultrasonically cleaned in 2% solution of alconox cleaning detergent and distilled water, de-ionized (DI) water, acetone and isopropanol for 30 min, sequentially. Next, the FTO substrates were dried in nitrogen gas flow and cleaned with ultraviolet-ozone process for 30 min. The cleaned FTO substrates were coated with a TiO_2 condensed layer, which were prepared by spin coating of 0.15 M titanium diisopropoxide bis(acetylacetonate) (TDB) in 1-butanal solvent at 3000 rpm for 30 s. The coated substrates were annealed at 125°C for 5 min, right after the films were coated by 0.30 M TDB solution and annealed at 125°C for 5 min. Then, the second coating process was repeated twice. Finally, as-seeded substrates were treated at 500°C for 30 min. According to Kulkarni A et al [37], The first 0.15 M TBO layer was used to improve substrate surface then the two 0.30 M TBO layers were coated after causing seed layers dense and firm. In this study, the spin coating was produced at 3000 rpm in prospect to increase diameter of initial TiO_2 NRs because high density of TiO_2 NRs could provide more electron transport and penetration of Perovskite layer. Owing to preliminary results, the higher spin coating round revealed denser NRs. Hence, seed layers were selected to spin at 3000 rpm which was the highest and the safest condition.

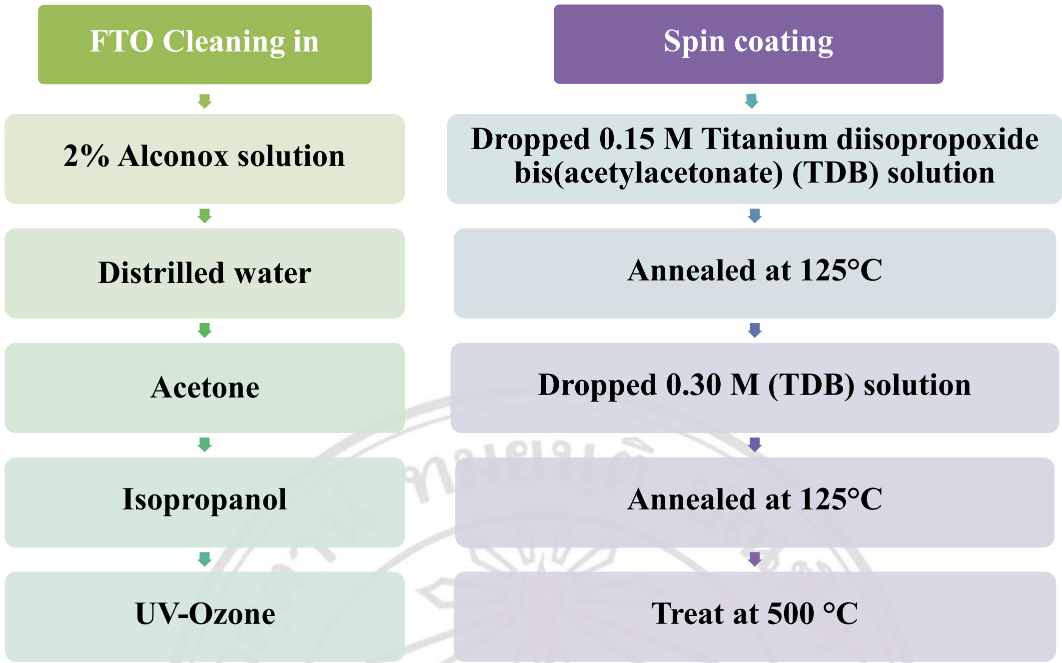

Figure 3.1 The Schematic of preparation of TiO_2 seed layer preparation

3.2. Hydrothermal synthesis of TiO_2 NRs

As shown in Figure 3.2, the hydrothermal synthesis was proceeded in a polytetrafluoroethylene (PTFE) or Teflon liner (50 ml volume) contained in a stainless autoclave. A 12 ml solution of deionized water and hydrochloric acid (HCl) (37% by weight) were mixed with volume ratios of 63:37 under magnetic stirring for 5 min. Then, titanium (IV) butoxide (TBO) (97 % Aldrich) as a precursor was added into the mixture and stirred for another 5 min (pH of the solution is 1-2). After that, the FTO substrates with TiO_2 seed layers were leaned against the wall of PTFE-liners with TiO_2 surface facing down. The autoclaves were heated at 150°C for various hydrothermal times before they were flown with water for cooling down to room temperature. Then the FTO films were brought out and quenched with distilled water following by drying at ambient conditions. The detailed of experimental conditions of hydrothermal process are listed in Table 3.1-3.3.

The procedure for characterization was employed to investigate morphology, crystalline structure, and optical properties of the prepared TiO_2, using field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and UV–VIS spectroscopy, respectively.

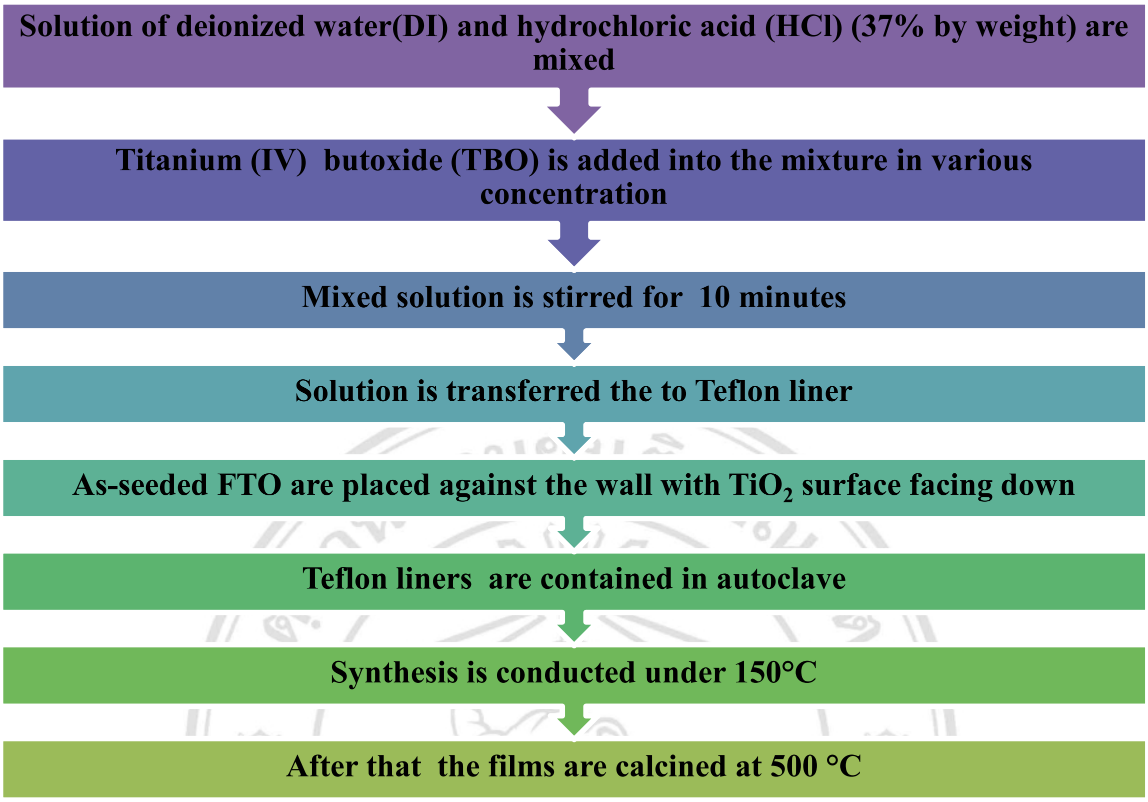

Figure 3.2 Phase diagram of hydrothermal synthesis

The experiments were performed to investigate the factors effect on TiO_2 NRs growth including seed effect, precursor concentrations, calcination and reaction times.

Table 3.1 Effect of TiO_2 seed layer on the growth of TiO_2 NRs

Sample	Hydrothermal at 150°C for 1.5 h
FTO	-
Seed /FTO	-
TiO_2 NRs/FTO	1.0 % TBO
TiO_2 NRs/ Seed/FTO	1.0 % TBO

In order to study effect of seed layers, feature of bare FTO and seeded FTO will be compared. Then morphology of 1.0 % TBO TiO_2 NRs grown on FTO and seeded FTO will be also compared as shown in Table 3.1

Table 3.2 Effect of calcination treatment at high temperature on morphology and size of TiO_2 NRs

Sample	Hydrothermal at 150 °C for 1.5 h	Calcined at 500 °C
TiO_2 NRs/ Seed/FTO	0.7 % TBO	-
TiO_2 NRs/ Seed/FTO	0.7 % TBO	✓
TiO_2 NRs/ Seed/FTO	1.0 % TBO	-
TiO_2 NRs/ Seed/FTO	1.0 % TBO	✓

For effect of calcination treatment at high temperature, two sets of 0.7 % and 1.0 % TBO TiO_2 NRs were hydrothermal grown on seed layers as details in Table 3.2. Then the morphology and size of calcined NRs and non calcined NRs will be compared.

To study effect of precursor concentration, TiO_2 NRs were hydrothermal grown on seed layers at 150°C for 1.5 h at various in TBO concentration of 0.3%, 0.5%, 0.7% and 1.0 % .

Table 3.3 Hydrothermal synthesis of TiO_2 NRs at different hydrothermal times

TBO concentration	Hydrothermal time (h)		
	1	1.5	2
0.7 %	✓	✓	✓
1.0 %	✓	✓	✓

In order to study effect of hydrothermal reaction times, 0.7 % and 1.0 % TiO_2 NRs were hydrothermal grown on seed layers at 150°C for different reaction times at 1h, 1.5h, and 2h