# CHAPTER III

EXPERIMENTAL

## 3.1 Preparation of well dispersed CNTs

There are two kinds of carbon nanotubes(CNTs) in this research, virgin CNTs(Bayer MaterialScience, BET surface area of ca. = 340 m^2/g) and treated CNTs. Treated CNTs(TrCNTs) were prepared by mixed virgin CNTs 0.3 g with HNO_3 (Baker analysis 70%) 70 ml and sonicated them for 10 minute. They were washed by deionized water until neutralization and dried in the oven at 60 °C for 24 hr. This process was showed in Figure 3.1. The treated CNTs were characterized the functional group and surface area by FT-IR and BET, respectively.
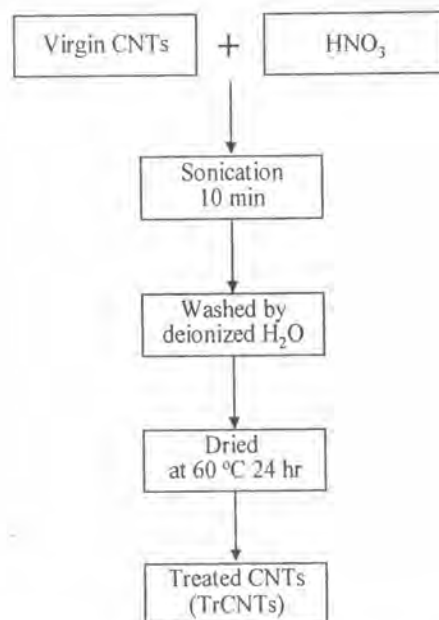
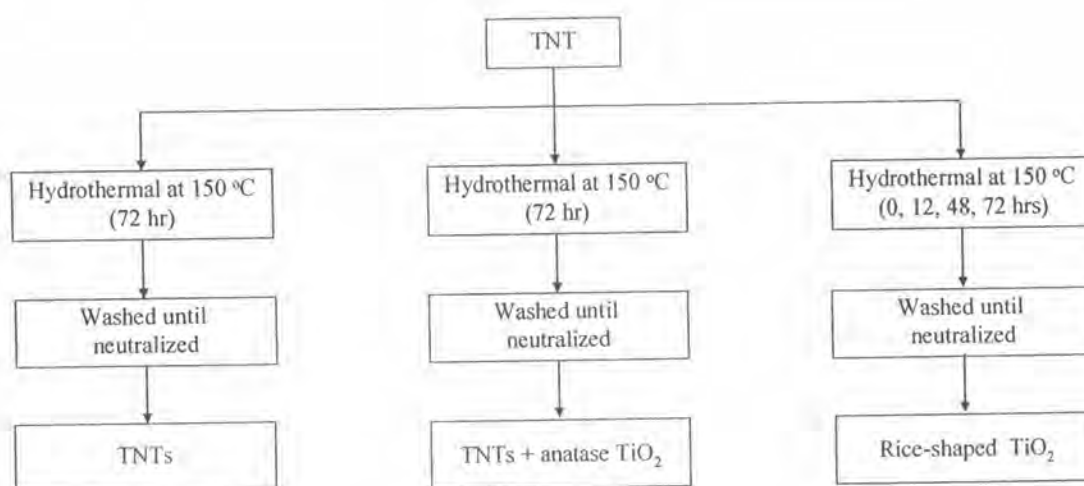**Figure 3.1** Schematic model for preparation of TrCNTs.

3.2 Preparing TNTs, (rice-shape)TiO$_2$

Rutile commercial TiO$_2$ (Aldrich 99%, BET surface area of ca. 2 m^2/g) was worked as precursor to fabricate Titanate nanotubes(TNTs) in hydrothermal process 0.5 g of TiO$_2$ precursor with 50 ml of 10-M NaOH aqueous solution in Teflon vessel were hydrothermal at 150 ^{o}C 72 hr. After finished the process, they were rinsed by HCl 0.1 M 500 ml for elimination of Na$^+$ and neutralized process by deionized water 300 ml. Eventually, They were dried in oven at 60 ^{o}C for 24 hr. These processes were showed in Figure 3.2. The powder of TNTs was characterized morphology, phase crystallinity and surface area.
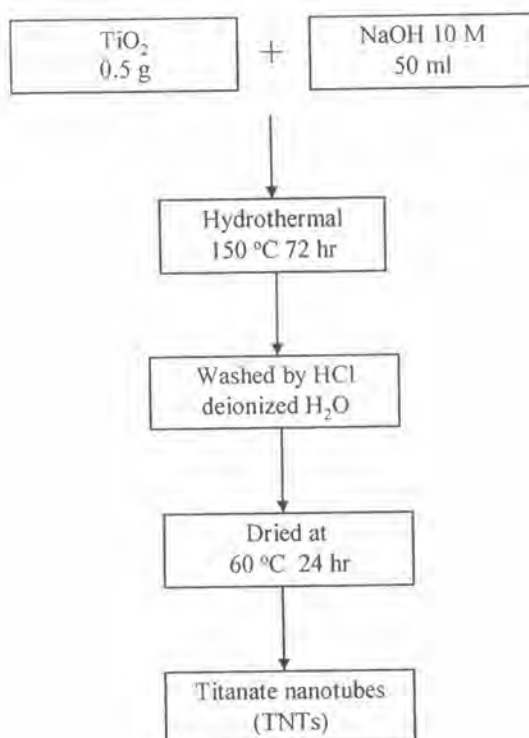
Figure 3.2 Schematic model of preparation TNTs.

For the second step hydrothermal, TNTs were introduced to prepare (rice-shape) TiO$_2$. There are three types of media which were investigated, NaOH, water with oxygen anion and deionized water. TNTs as precursor 0.5 g were hydrothermal in each media at 150°C 72 hr. After finished hydrothermal process, they were washed until neutralized by deionized water and dried at 60 $^{\circ}$C for 24 hr.The product of each media was characterized by TEM, XRD and BET. After the suitable media were gained, the suitable time were examined within 72 hr. These process were showed in Figure 3.3.

Figure 3.3 Schematic model of preparation rice-shaped TiO$_2$.

3.3 Preparation of the composites

From previous experimental, the suitable condition for preparing TNTs and(rice-shape)TiO_2 were investigated. Those experiment conditions were obtained to prepare the composites between titanium or titanium derivative with CNTs. First part of our experiment, we have two kinds of CNT, virgin CNTs and TrCNTs. They were mixed with TiO_2 by sonication power in NaOH 10-M solution 30 min for well mixed of reactant and bring it to autoclave to hydrothermal at 150 ^{o}C for 72 hr. TrCNT-TNT and CNT-TNT were obtained by this process. These processes were showed in Figure 3.4.

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                    │   Virgin CNTs    │
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                      │              ▼
                      │      ┌──────────────────┐
                      │      │   HNO₃ 70%       │
                      │      │ sonicated 10 min │
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          ┌──────────────────────────────────────┐
          │ ┌──────────┐   +   ┌──────────┐       │
          │ │  TiO₂    │       │   NaOH   │       │
          │ │rutile 99.99%│    │   10 M   │       │
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                 │  Hydrothermal    │
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                 │  Washed by HCl   │
                 │ Deionized H₂O    │
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                 │ Dried at 60 °C   │
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          │   CNT-TNT    │ │  TrCNT-TNT   │
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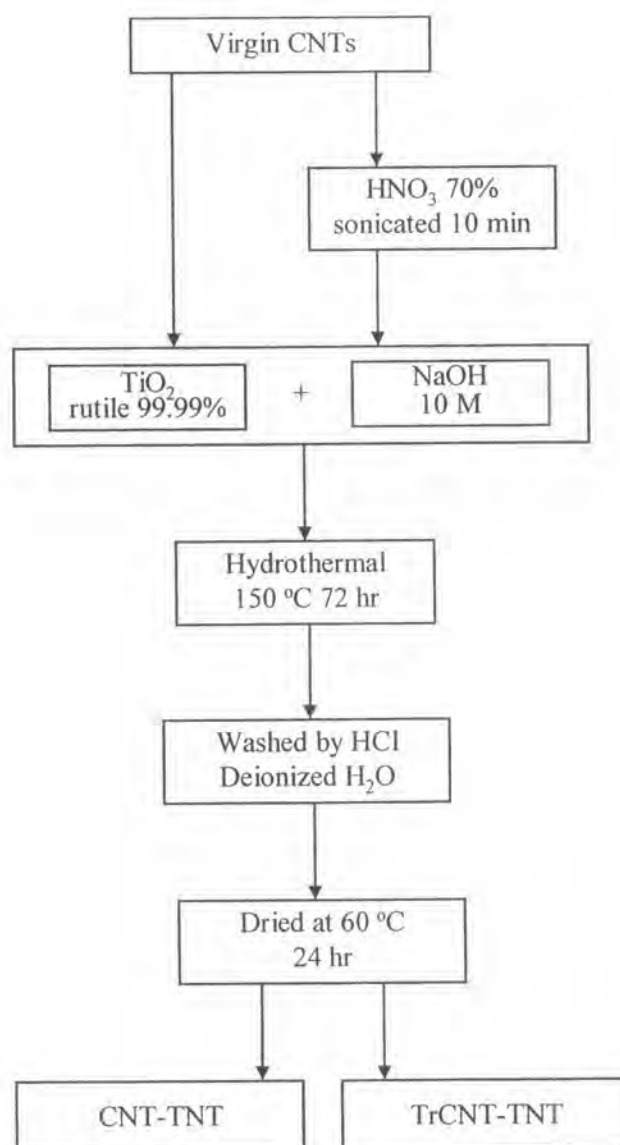
Figure 3.4 Schematic model of preparation composites

CNT-TNT and TrCNT-TNT.

For preparation of the composite in anatase phase, TNTs were worked as precursors in same condition of preparation rice-shaped TiO_2 anatase phase. TNTs were mixed with virgin CNTs or treated CNTs in deionized H_2O at 150 °C for 24 hr. CNTs-(rice-shape)TiO_2 and TrCNT - rice-shaped TiO_2 were obtained from this process.

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                    ┌─────────────────────┐
                    │     Virgin CNTs     │
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                                  ▼
                        ┌────────────────────┐
                        │     HNO₃ 70%       │
                        │  sonicated 10 min  │
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         │  │   TNTs   │    +     │  Deionized H₂O   │ │
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                        │   Hydrothermal     │
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                        │   Dried at 60 °C   │
                        │       24 hr        │
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              │ CNT-rice-shaped TiO₂│  │ TrCNT - rice-shaped TiO₂ │
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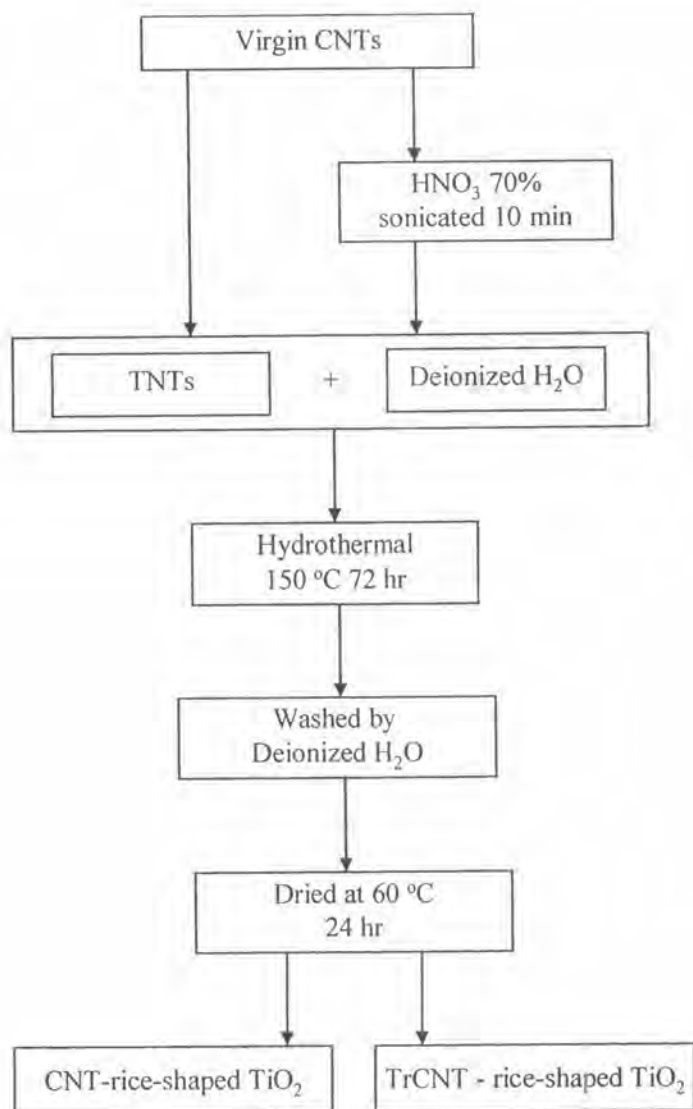
Figure 3.5 Schematic model of preparation composites CNT - rice-shaped TiO_2 and TrCNT- rice-shaped TiO_2.

3.4   Preparation of titanium precursor for electrode

3.4.1 Preparation of titanium slurry

First, the solvent were prepare by 49.75 g of terpineol (Fluka, M. 154.25, $C_{10}H_{18}O$) and 0.25 g. of sodium dodecyl sulfate (SDS, Merck shuchardt, $C_{12}H_{25}NaO_4S$). They were stirred for 30 min. for homogeneous phase.

The above prepared composite, TNT and rice-shaped TiO_2 were added to anatase TiO_2 (Aldrich 99%, BET surface of ca. 273 m^2/g) which proportioned in the range of 0, 0.21, 1.06, 2.1 and 21 %wt. These proportions related to the amount of CNTs were 0, 0.01, 0.05, 0.1 and 1 %wt., in titanium slurry, respectively. These powder was added to the prepared solvent. Then, they were sonicated and stirred for 1 hr. before adding ethyl cellulose (EC, Fluka biochemical) which worked as binder. After that, they were stirred and heated at 80 °C for homogeneous phase. The titanium precursor was prepared from this process. The amount of each precursor was cleary shown in Table 3.1.

Table 3.1 showed the amount of each precursor.

%Addition Chemicals(g)	0	0.21	1.06	2.1	21
TiO_2	1.075	1.0698	1.0524	1.0314	0.8519
TNT or rice-shaped TiO_2 or The prepared composites	0	0.0052	0.0226	0.0436	0.2231
EC	1.075	1.075	1.075	1.075	1.075
Solvent	6	6	6	6	6

3.4.2 Preparation of electrode and counter electrode

First, the conductive glass (FTO, sheet resistance $15 \ \Omega/m^2$ Asahi glass CO.,Ltd,) were cut in area of 2×3 cm. The block and rubber were used to screen print titanium precursor and platinum precursor (Solartec, Thailand) on conductive glass. The thin film were sintering at 500 °C for 1 hr.

3.4.3 Fabrication DSSCs

The electrode thin film were immersed in dye(N719, DyesSol, Australia) solution for 1 hr at 65 °C. After that, electrode and counter electrode were joined by serlyn. The electrolyte were injected before measurement their efficiency.

3.5 Analytical instruments

Fourier Transform Infrared Spectroscopy(FT-IR)

The fuctional groups on surface of CNTs were determined using infrared spectroscopy as shown in Figure 3.6. Before measurement, each sample was mixed with KBr at a ratio of sample to KBr of 1:100 and then was pressed to form a thin wafer. The equipment used was a Nicolet impact 400. IR spectra were record from an accumulation of 32 scans in 400-3800 cm^{-1} range with a resolution of 4 cm^{-1}.
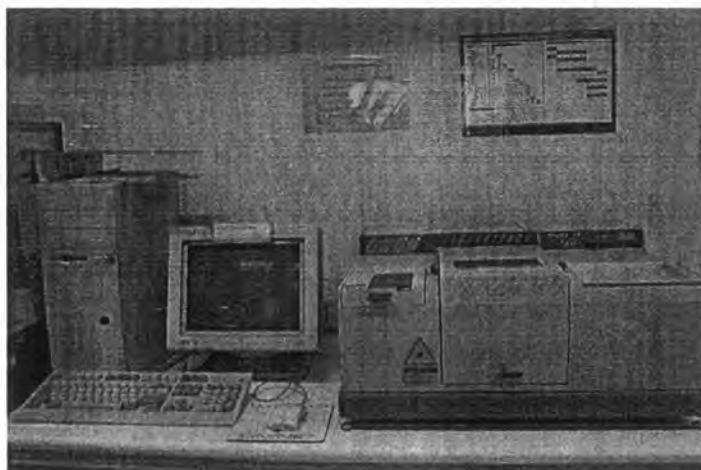
Figure 3.6 Fourier Transform Infrared Spectoscopy.

Transmission Electron Microscopy (TEM)

TEM analysis was studied using JEOL-1230 as shown in Figure 3.7. The sample was suspended in alcohol before ultrasonic treatment for (15 min) for ensuring its uniform dispersion. A drop of clearly solution was then dropped onto a copper-grid (Figure 3.8). The specimen was loaded into sample chamber and waiting for the vaccum condition and steady state inside the chamber for 30 min.
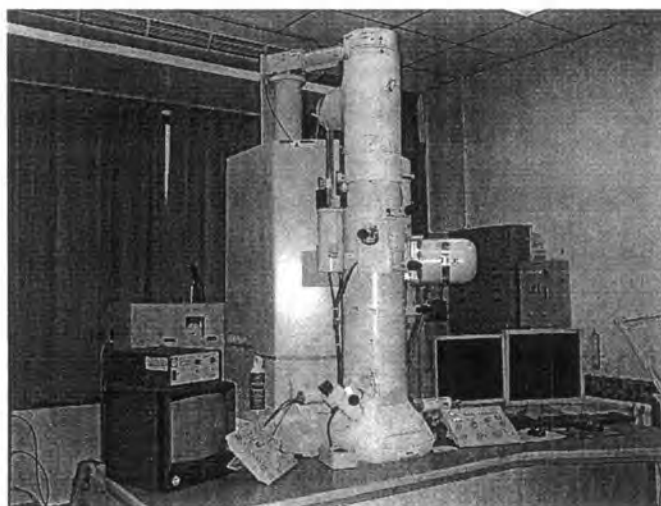

Figure 3.7 Transmission Electron Microscopy (TEM).
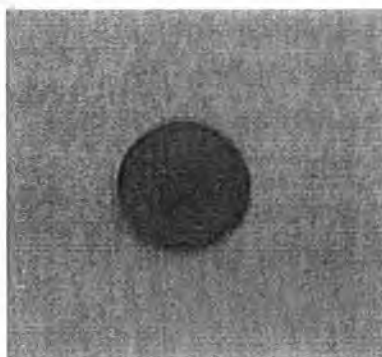
Figure 3.8 Copper grid for Transmission Electron Microscopy.

X-Ray Diffraction (XRD)

The XRD (Philips, PW3710) was used to analyze phase of the investigated sample. Figure 3.9 shows the XRD analysis system used in this work. The titania sample was spread on the glass slide and then set in the equipment which provide x-ray beam for the analysis.
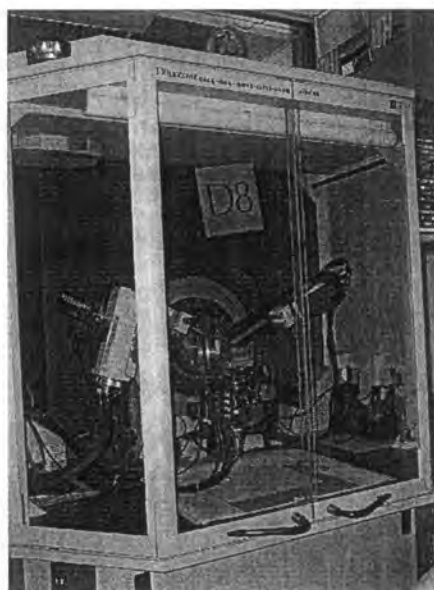
Figure 3.9 X-Ray Diffraction (XRD).

BET surface area analyzer

The BET surface area (Figure 3.10) S_{BET}, mesopore volume V_{meso}, micropore volume V_{micro}, and pore size distribution, of each samples were determined from N_2 adsorption-desorption isotherms measured at 77 K using the adsorption apparatus (BELSORP 28SA, BEL Japan Inc., Japan). Pore size distribution and V_{meso} were evaluated by applying the Dollimore-Heal method to the desorption isotherm, whereas the t-plot method was used to estimate V_{micro}.

Figure 3.10 BET surface area analyzer.

IV tester

The efficiency of DSSCs were characterized by IV tester as shown in Figure 3.11 (MVSystem Inc., Xenon short ARC (Osram XBO 1000 W/HS OFR)). Current voltage measurments using white light source measure, unit under air mass(AM) 1.5 G factor and can convert to efficiency of solar cell. In active area of solar cell was 0.36 cm^2.

Figure 3.11 IV Tester.