

CHAPTER 1

Introduction to Dye-sensitized Solar Cells and Surface Modification

Solar cell is an interesting alternative energy technology that can directly convert clean and renewable solar energy into electricity. Solar cells have ability to solve the limitation of energy source and environmental pollution problem from conventional fossil fuel. A development in solar cells has been started from silicon solar cells. Silicon shows the best material for high efficient material due to it can be easily doped to form p-type or n-type. Thus, mechanism of these cells is based about a p-n junction idea [1] [2]. However, high purifying crystalline is required to enhance power conversion efficiency (PCE) which leading a high cost fabrication. Therefore, many kind of solar cells are studied such as single-junction, multi-junction, thin film and emerging solar cells [3-6]. Dye-sensitized solar cells (DSSCs), one kind of emerging solar cells, have been introduced with a simple fabrication and low cost [7]. DSSCs is the one of an attractive kind of solar cells due to a simple production, an effective low cost material, non-vacuum system requirement and being environmental friendly [7-9] . In addition, differences of DSSCs products can offer opportunities of commercial large-scale production such as possibilities to design solar cell with a large flexibility in shape, light-weight products, color, and transparency [10,11].

Since O'Regan and Gratzel [12] pioneered a DSSCs carry on a mesoporous TiO_2 (m- TiO_2) photoelectrode with PCE around 7%. This solar cell technology still attracted growing interest for both of the scientific researches and commercial communities. The technology exhibit appealing properties such as transparency, colorful, simple integration into building, short energy payback time, potentially low cost production, etc [10].

1.1 Dye-sensitized solar cells

Basic components of conventional DSSCs include a photoelectrode (PE), a counterelectrode (CE), and an electrolyte solution (EL) [8] as shown in figure 1.1. The PE is a dye-sensitized semiconductor based on a transparent conducting oxide (TCO) substrate. The CE is a platinum (Pt) coated TCO, and the electrolyte solution containing a redox mediator (I_3^-/I^-).

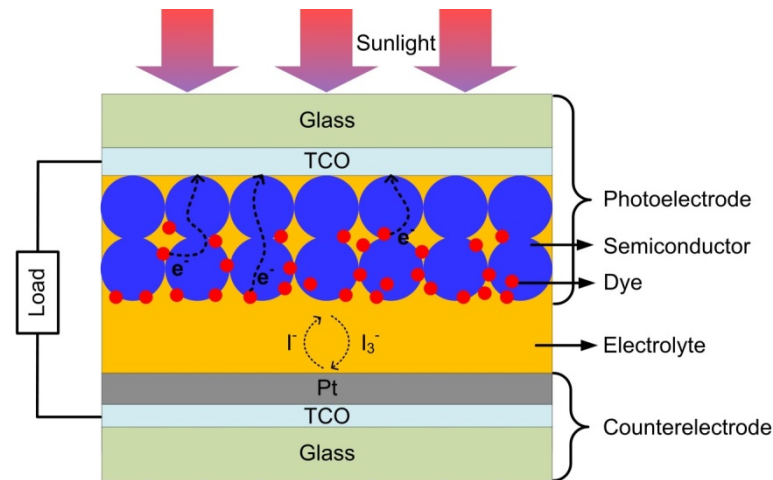


Figure 1.1 Schematics structure of a conventional dye-sensitized solar cells.

An essential mechanism in DSSCs upon sunlight is presented in figure 1.2 [13]. The major processes can briefly describe with 4 steps include electron generation, electron injection, transportation and regeneration. [7,14].

- (i) Electron generation. After dye molecules in ground state (S) adsorb solar energy ($E = h\nu$) from the incident photon, the molecules are excited (S^*); electrons are rising up in energy level from ground state (the highest occupied molecular orbital; HOMO) to excited state (the lowest unoccupied molecular orbital; LUMO).
- (ii) Electron injection. The generated electrons (e^-) are injected from the excited state dye molecules to the conduction band (CB) of semiconductor.
- (iii) Transportation. The injected electrons are continuously transported from the CB of semiconductor through an external load to the CE. Amount of electrons transport through the external load is related to short-circuit current density (J_{sc}).

- (iv) Regeneration. Dye molecules are oxidized (S^+) after the electron injection, and it regenerates by receiving electrons from redox couple present in a surrounding electrolyte (I^-) and back to its ground state. Finally, the oxidized electrolyte (I_3^-) are diffused to the CE and regenerated with returning electrons from the load. The regeneration rate is directly resulted to fill factor (FF) and cell performance, and the difference between redox potential and Fermi level of semiconductor is approximated to open-circuit voltage (V_{oc}).

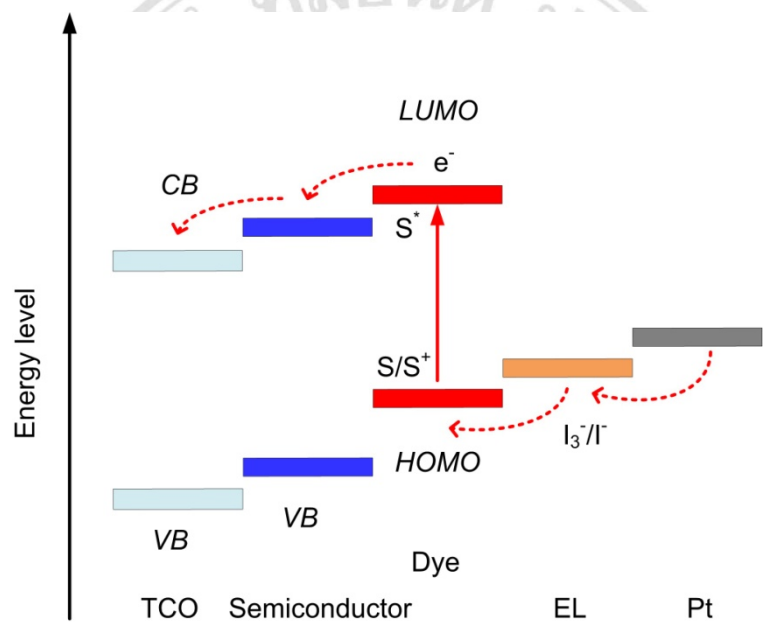


Figure 1.2 An essential schematics diagram of DSSCs mechanism.

To evaluate PCE performance, current density (J) versus voltage (V) curve is measured as can be seen in figure 1.3. The PCE is defined in equation (1.1).

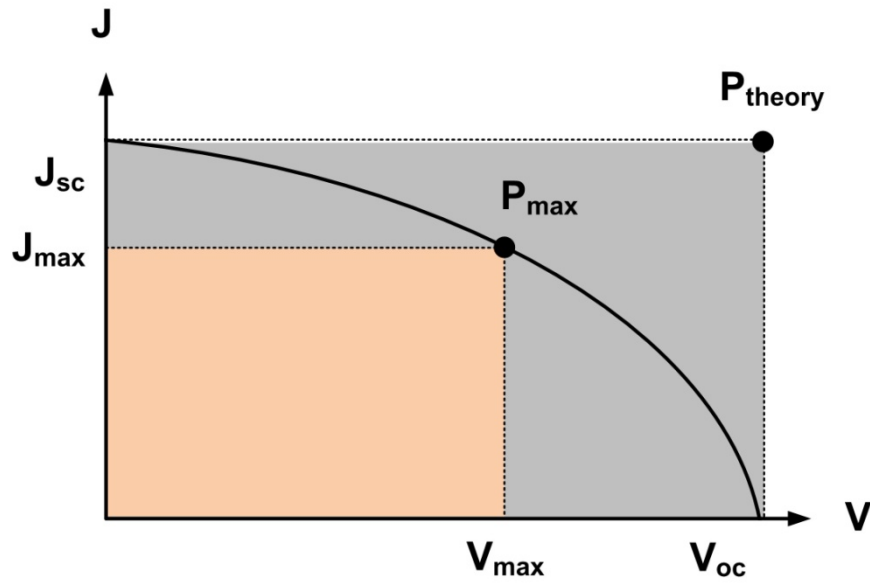


Figure 1.3 General J-V curve of DSSCs.

$$\text{PCE}(\%) = \frac{J_{sc} V_{oc} \text{FF}}{P_{in}} \times 100 \quad (1.1)$$

P_{in} is a power of incident solar spectrum which is general using of 100 mw/cm^2 for standard measurement, called “AM 1.5”. The solar spectrum is the amount of radiant energy received from the sun per unit area per unit time, and the spectral distribution of AM 1.5 is the most spectral through into the earth have wavelengths from 300 to 3,000 nm.

The FF is defined as a ratio of the maximum power ($P_{max} = J_{max} V_{max}$) of the cell to theoretical power ($P_{theory} = J_{sc} V_{oc}$). So, FF value is varying between 0 and 1.

$$\text{FF} = \frac{P_{max}}{P_{theory}} = \frac{J_{max} V_{max}}{J_{sc} V_{oc}} \quad (1.2)$$

1.1.1 Reviews of photoelectrodes

Conventional photoelectrodes is a coated-semiconductor onto transparent conducting oxide film (TCO) substrate. Typical materials are TiO_2 , ZnO and ZnO [13], due to their appropriation in optical and electrical properties. Among the wide band gap materials, ZnO is one of the interesting metal oxides for DSSCs application [15]. ZnO presents higher electron mobility in comparison to TiO_2 that result to fast charge

separation and electron transportation [16]. Besides, there is a variety of preparations and nanostructures as can be seen in table 1.1.

Table 1.1 Photovoltaic parameters of some ZnO DSSCs.

Nanostructures	Dye	J_{sc} (mA/cm²)	V_{oc} (V)	FF	PCE (%)
Nanorod [17]	N719	2.08	0.74	0.43	0.66
Nanorod [18]	N719	3.31	0.64	0.40	0.84
Nanorod [19]	N719	6.1	0.58	0.38	1.38
Nono-porous film [20]	D205	9.87	0.58	0.54	3.08
Nanoparticle [21]	N719	10.68	0.73	0.58	4.45
Nanoparticle [22]	D194	12.7	0.55	0.67	4.66
Nanoparticle [23]	N3	9.5	0.61	0.45	2.6
Nanowire/ nanoparticle [24]	N719	8.48	0.73	0.61	3.8
Nanorod/nanoparticle [25]	N719	7.00	0.60	0.52	2.19
Nanoshell [26]	Y123	8.1	0.90	0.57	4.2

Photoelectrodes is the most important component that has significant affecting to the PCE. Because it has many key roles for improving photovoltaic performance such as dye adsorption, light scattering, charge separation and electron transportation [27,28]. Therefore, photoelectrodes is an attractive consideration for developing with different methods. A composite materials of GaN-TiO₂ is presented for improving a charge transport in photoelectrodes [29]. The composite material provides more pathways for electron transport because a higher conduction band of GaN offers injected electrons and transfers through a lower conduction band of TiO₂. Moreover, a

recombination is suppressed because most of generated electrons are in better separation and transportation. A scattering layer is proposed to improve light harvesting efficiency (LHE) as can be seen in figure 1.4 [28,30], and higher electron generation rate is expected to increase due to an increase in the light harvesting efficiency.

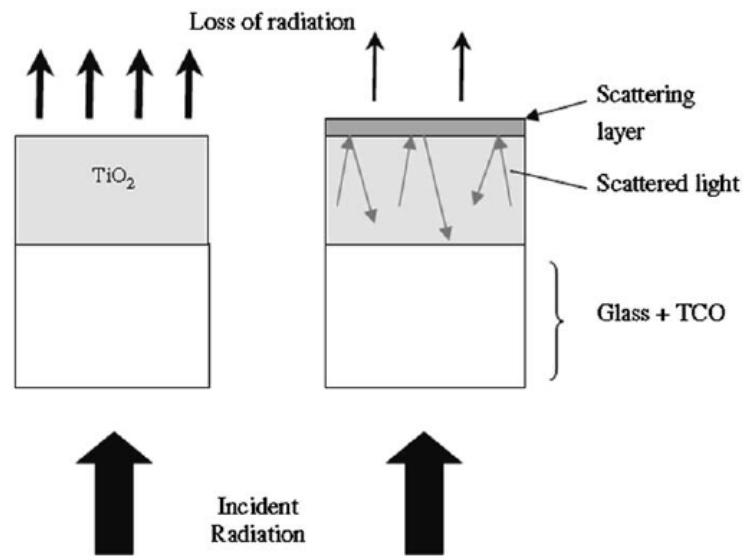


Figure 1.4 Schematic diagram of scattering layer strategy. Reproduced with permission from ref [30]. Copyright (2014) The Royal Society of Chemistry.

Surprisingly, an application of nanostructure for improving photoelectrodes demonstrates many effects [8,20,21]. Nanoparticle photoelectrodes is one efficient candidate structure can provide a high surface-to-volume ratio for dye adsorption and light scattering. However, there are still disadvantage due to very small particles affecting an aggregation at the surface, reducing electron transfer and fill factor. Therefore, surface modification of photoelectrodes proposes an improvement in DSSCs performance [31]. Among surface modification, the chemical texturing process is most attractive due to the advantages such as effective low cost, simplicity and short-time process [32,33]. Chemical reaction has potential to remove aggregate particles and create porous structure for achieving dye adsorption and light scattering [34]. In addition, most of chemical etchants have potential in the texturing process such as HCl, HF, HNO₃, KOH, NaOH and NH₄Cl [34-37].

1.1.2 Reviews of counterelectrodes

A counterelectrode is a catalytic material used for returning an electron from an external load into devices. This part requires a high reaction rate material for rapid regenerating oxidized electrolyte with high acceleration. A high surface area is demonstrated as one of strategy to increase interface contact for efficient catalytic process as can be seen in figure 1.5 [38]. An atomic layer deposition is used to prepare an inverse opal Pt to form high surface area Pt counterelectrodes. The surface area showed an excellent increase by 50-fold compare to conventional flat counterelectrodes. The high surface areas lead an improvement of electron transfer rate which is resulted to a doubles of FF, and PCE shows a significant gain from 1.0% to 1.8%.

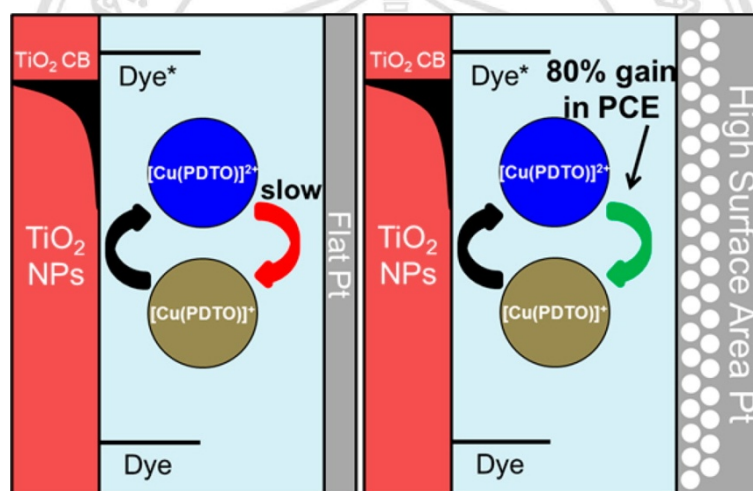


Figure 1.5 Surface modification of high surface area Pt counterelectrodes. Reproduced with permission from ref [38]. Copyright (2014) American Chemical Society.

Beside, porous structure of counterelectrodes is a challenge for increasing catalytic process [39]. A simple sequential deposition of porous NiO (PNO) and Pt was used to prepare porous counterelectrodes and the process was illustrated in figure 1.6. PCE exhibited an enhancement of 8.17% for porous counterelectrodes which is better than the conventional Pt counterelectrodes (7.23%). This is caused by achieving electrocatalytic activities confirmed by cyclic voltammograms as can be seen in figure 1.7, which is a direct result from an increase in high active areas.

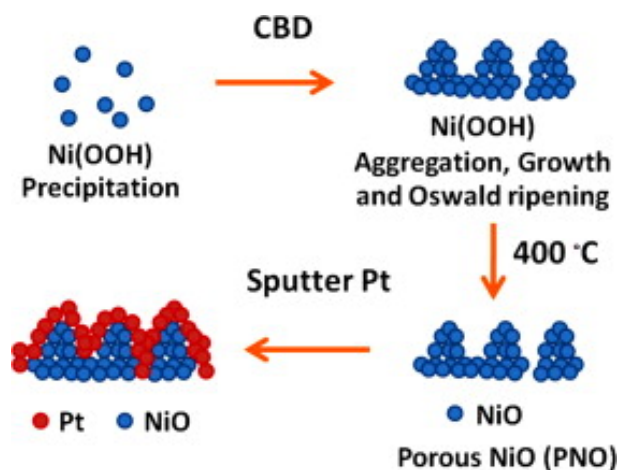


Figure 1.6 Illustration of porous counterelectrodes preparation. Reproduced with permission from ref [39]. Copyright (2014) Elsevier.

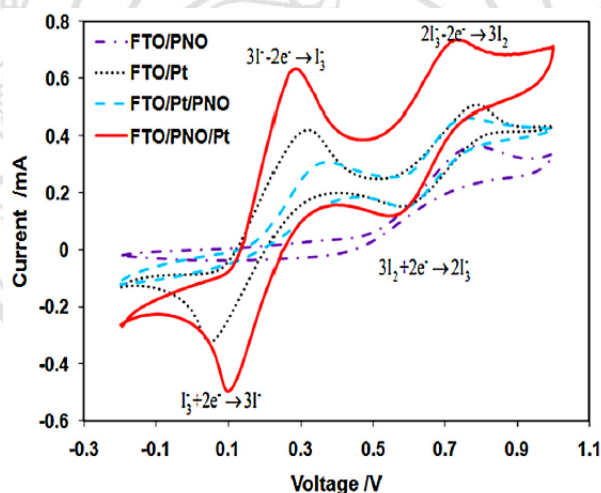


Figure 1.7 Cyclic voltammograms of porous counterelectrodes based DSSCs. Reproduced with permission from ref [39]. Copyright (2014) Elsevier.

1.1.3 Reviews of electrolytes

Electrolyte is a liquid redox mediator for interchanging charge between the electrodes in the devices. It has the role to regenerate oxidized dye by transferring electrons to the dye, and it receives the returning electron from the counterelectrode for regenerating its self [40]. The electrolytes are commonly used of I^-/I_3^- redox couples because its usefulness such as a simple preparation, high conductivity, low viscosity,

and better inner interfacial contact between electrodes. An essential redox process of the electrolyte in DSSCs can be described as the follows;

- (i) Dye regeneration: The electrolyte regenerates an oxidized dye (S^+) and become an oxidized electrolyte as the relation; $S^+ + I^- \rightarrow S + 3I^-$.
- (ii) Electrolyte regeneration. The oxidized dye diffuses to the counterelectrode and regenerates its self by accepting the returning electron from the external load; $3I^- + 2e^- \rightarrow I_3^-$.

According to the sequential electrochemical redox reactions in the equation (1.3) and (1.4) [41], some of alternative electrolytes such as Br^-/Br_3^- , $(I^-, Br^-)/(I_2Br^-)$ and $(I^-, Br^-)/(I_3^-, I_2Br^-)$ were introduced to achieve an V_{oc} as can be seen in figure 1.8. These electrolytes can extend V_{oc} because the standard electrochemical potential is more positive than that of I^-/I_3^- .



For longer operation, liquid electrolyte containing iodine might be an inappropriate material for stability because it will degrade the solar cell performance. The iodine, high corrosive material, might be reacts with Pt metal to form PtI_4 and aggregate at the surface of counterelectrodes [42]. This effect suppresses the regeneration process and result to a lower performance. Therefore, alternative electrolytes were introduced to avoid this effect. An organic electrolyte thiolate/disulfide (T^-/T_2) was introduced (T^-/T_2) [42]. However, the T^-/T_2 electrolyte based DSSCs showed lower PCE than conventional I^-/I_3^- electrolyte. To achieve PCE, quasi-solid-state electrolytes and solid-state solid-state transport materials were introduced [40].

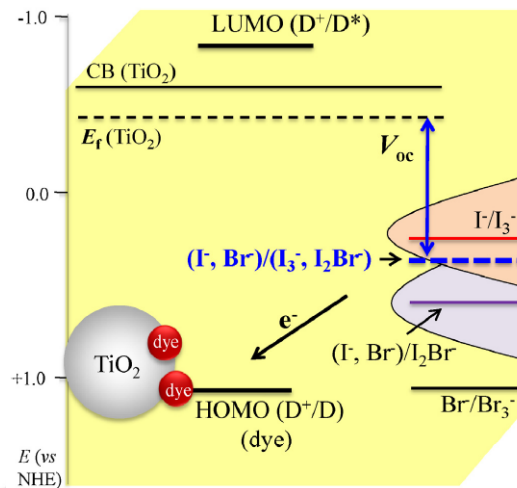


Figure 1.8 Energy diagram of some electrolytes. Reproduced with permission from ref [41]. Copyright (2013) Elsevier.

1.2 Surface modification

A surface modification is a relatively simple method for treating photoelectrodes surface. Various approaches are performed using the surface modification such as improvement of light harvesting, increment of dye adsorption, reduction of dye aggregation and electron recombination [31]. There are differences in modification methods and approaches as seen in table 1.2.

Popular techniques included laser, plasma and texturing have been investigated in several reports due to controllability, simplicity and efficiency. For examples, a laser beam treatment is introduced to texture porous photoelectrodes [43]. A demonstration of laser treatment using KrF laser showed appropriate nanoporous structures for improving light trapping and dye absorption as seen in figure 1.9. PCE showed a major increase related to J_{sc} which is a result from increase in dye adsorption.

Table 1.2 Photovoltaic parameters of some DSSCs fabricated with modified ZnO.

Modification	Dye	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
Ga-doped [17]	N719	3.96	0.76	0.41	1.23
I-doped [23]	N3	15.0	0.65	0.47	4.6
Eu ³⁺ , Tb ³⁺ -doped [44]	N719	10.13	0.76	0.67	5.13
Thermal treatment [45]	N3	15.66	0.55	0.35	3.01
TiF ₆ treatment [46]	N719	15.16	0.60	0.65	5.94
TiCl ₄ treatment [47]	D149	4.96	0.70	0.67	2.33

Plasma jet shows an efficient method for modifying surface with large-area process, size-controllable, various material process, rapid process and inexpensive vacuum system [48-50]. Figure 1.10 shows a simple diagram of plasma jet system. A sample is placed on the movable stage and modified under generated plasma jet with specific condition. The plasma was generated between two electrodes by applying voltage. A plasma jet of Ar/O₂ gases was demonstrated to modify TiO₂ surface [50]. After the modification, the TiO₂ surface showed a not significantly changed but changed in chemical composition was observed. For DSSCs application, PCE was enhanced directly related to short-circuit current density in comparison to the non-modified TiO₂ based.

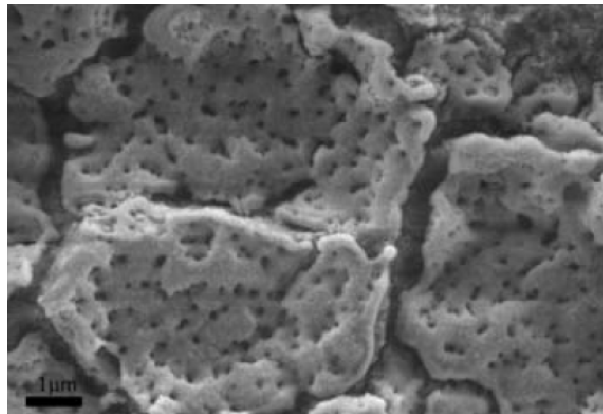


Figure 1.9 Nanoporous photoelectrode modified by KrF laser beam. Reproduced with permission from ref [43]. Copyright (2013) Elsevier.

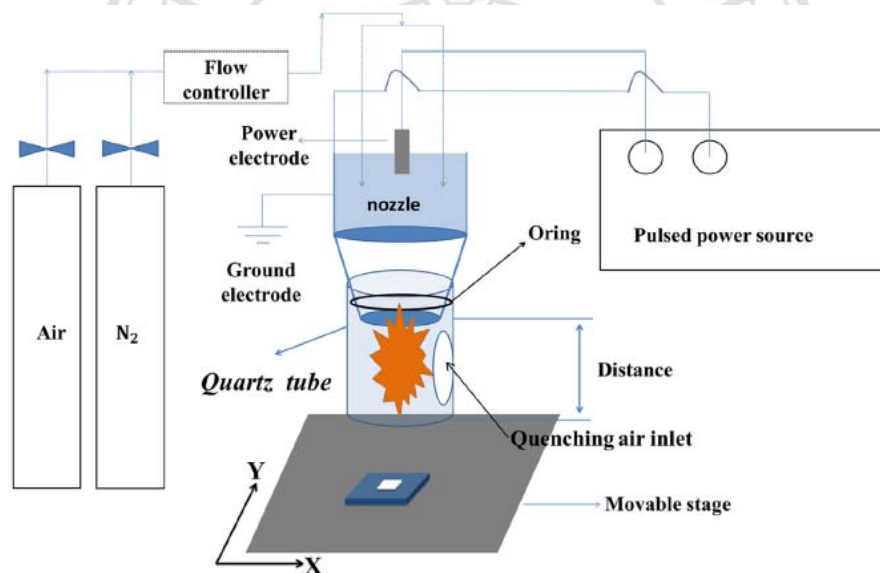


Figure 1.10 A simple diagram of plasma jet system. Reproduced with permission from ref [48]. Copyright (2014) Elsevier.

Finally, texturing process is presented an efficient method for modifying surface with simple and effective low cost process [32]. It can be used for texturing an appropriate surface by using a suitable for positive and negative ions. Generally, a strong acid solution carried with hydronium (H_3O^+) ion is frequently used for texturing process. HCl solution was reported to modify Al-doped ZnO (AZO) surface [51]. Grain boundary is attacked by H_3O^+ resulted to a formation of porous films and an improvement of light scattering property. On the other hand, an application of base

solution was presented to texture ZnO nanorods photoelectrodes using KOH solution [34]. Specific surface area (SSA) of the photoelectrodes increased after the texturing process with optimal condition as shown in figure 1.11. The increased specific surface area achieved the dye adsorption and light-harvesting efficiency, leading to enhanced power conversion efficiency. Nevertheless, alternative chemical such as Na_2SO_4 showed an efficient reagent to modify TiO_2 photoelectrodes [52]. The SO_4^{2-} groups provided an energy barrier between the TiO_2 and electrolytes in DSSCs as can be seen in figure 1.12. The optimal modifying condition of the TiO_2 photoelectrodes result to a dominate improvement in short-circuit current density and power conversion efficiency.

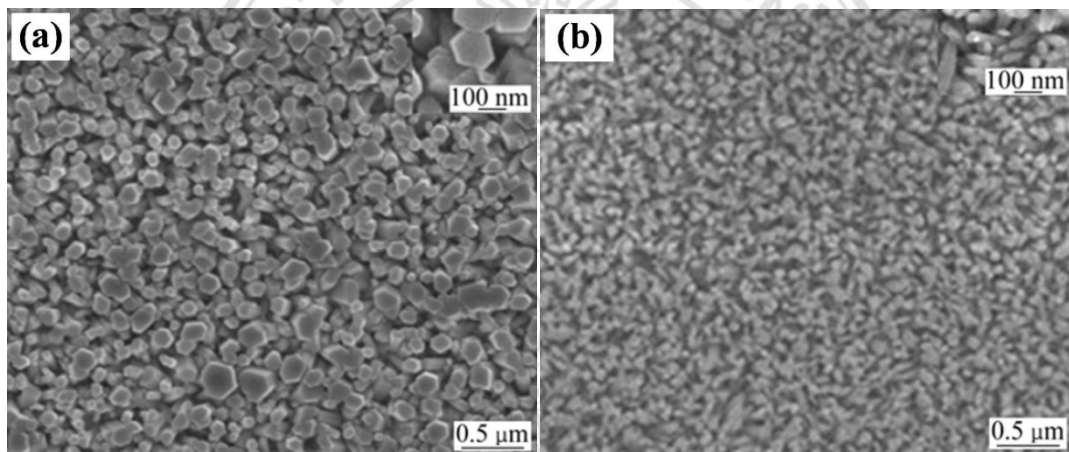


Figure 1.11 SEM images of (a) ZnO nanorods and (b) optimized texturing ZnO nanorods. Reproduced with permission from ref [34]. Copyright (2012) Elsevier.

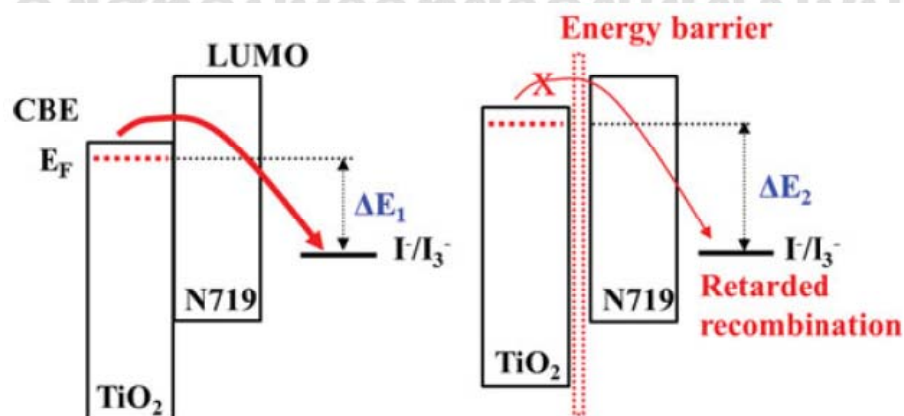


Figure 1.12 An energy barrier formation after Na_2SO_4 treatment. Reproduced with permission from ref [52]. Copyright (2014) Taylor & Francis.

1.3 Chemical texturing process

A chemical texturing process is investigated to modify surface of materials because it is the cheapest process with simplicity. A chemical wet texturing process is firstly introduced. It is widely used to texture surface of silicon wafers for silicon solar cell application. It demonstrated potentiality to reduce surface reflectance and improve light trapping. After the investigation of wet process, a vapor texturing process is developed to control texturing direction and rate.

1.3.1 Wet texturing process

The wet texturing process is an essential method using texturing solution. The surface is textured by a direct immersion of material into a bath of texturing solution with optimized condition as shown in figure 1.13. The process demonstrates an efficient texturization which can be provided low surface reflectance and high light trapping in silicon solar cell due to a pyramid-like structure formation. According to the most application for silicon wafer, a hybrid silicon-DSSCs is reported based on silicon wafer substrate as shown in figure 1.14 [53], and it is successfully demonstrated low-cost and high-performance production. A wafer substrate is textured with HF:H₂O:C₂H₅OH to form a homogeneous macro-porous silicon (PSi) layer. The DSSCs measurement shows a double in power conversion efficiency after texturing process compared with the non-textured wafer. The improved performance is clearly observed that due to a reduced surface reflectance and increased dye adsorption. Moreover, a textured ZnO films is also report with a controlling shape [33]. In addition, it is also seem for DSSCs application. ZnO films textured with a mixture solution of (NH₄)₂TiF₆ and H₃BO₃ is presented to enhance power conversion efficiency of DSSCs [46]. The DSSCs performance shows an excellent in optimal condition with surface stability, effective interfacial area and dye adsorption. Among the improved property, dye adsorption is the most challenge for the texturing process with appropriate porous films and chemical surfaces. Therefore, the demonstration is also suggested that the chemical wet texturing process is an effective strategy for surface modification.

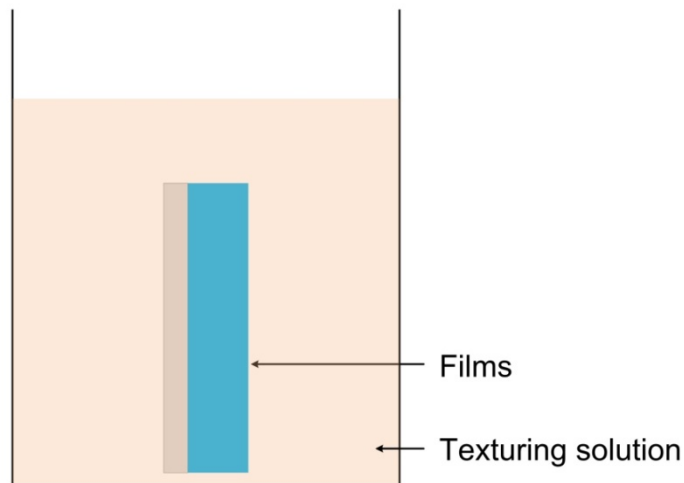


Figure 1.13 Illustrated scheme of a chemical wet texturing process.

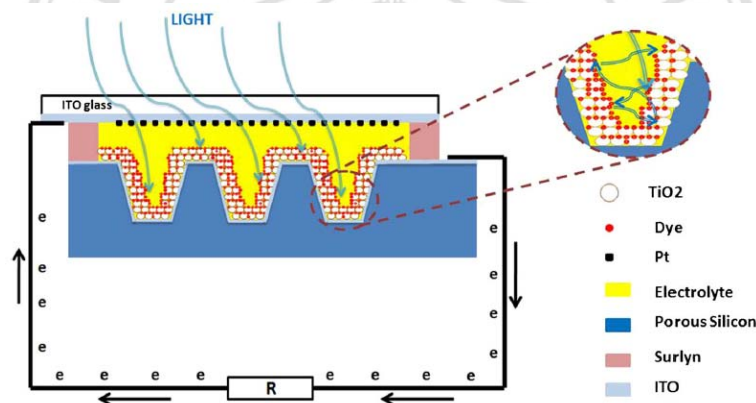


Figure 1.14 A hybrid silicon-DSSCs structure with textured macro-porous silicon photoelectrodes. Reproduced with permission from ref [53]. Copyright (2015) Springer.

1.3.2 Vapor texturing process

Due to some limitation of the wet process, the chemical vapor texturing process is developed with an idea of a vaporized bombardment as shown in figure 1.15. A chemical vapor is generated from texturing solution with a continuing stimulation. After the vapor generation, it is normally flowed in a vertical direction to attack the films surfaces. The textured films are performed after the reaction between generated vapor and particles at the surface. The process is investigated because it has several advantages such as a non-wanted formation avoiding, a relative small depth and a regular textured surface [54].

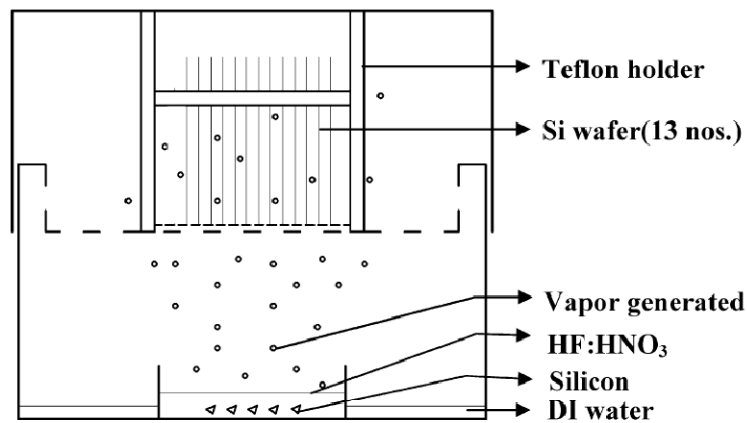


Figure 1.15 A schematics of a chemical vapor texturing process. Reproduced with permission from ref [54]. Copyright (2008) Elsevier.

1.4 Research objectives and usefulness

1.4.1 Research objectives

- 1) To synthesize and characterize carrier transport layers of photoelectrode and counterelectrode in DSSCs.
- 2) To improve power conversion efficiency of ZnO DSSCs by carrier transport layers.

1.4.2 Research usefulness

The carrier transport layers of photoelectrode and counterelectrode will be obtain and will be use in ZnO DSSCs for enhancing the power conversion efficiency.

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