INVESTIGATION ON TITANIUM DIOXIDE NANOTUBES PHOTOANODE FOR DYE SENSITIZED SOLAR CELL APPLICATION

by

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LIST OF ABBREVIATIONS

A	Anatase
ACN	Acetonitrile
AFM	Atomic force microscopy
AV	Alternating voltage
BET	*Brunauer–Emmett–Teller*
DI	Distilled water
DC	Direct current
DSSC	Dye-sensitized solar cell
EDTA-NTs	Nanotubes grown via fast method which anodized in electrolyte $Na_2[H_2EDTA]$
EG	Ethylene glycol
FE-SEM	Field emission scanning electron microscope
FF	Fill factor
FTO	Fluorine-doped tin oxide
GuNCS	Guanidinium thiocyanate
HOMO	Highest occupied molecular orbital
ITO	Indium tin oxide
J-V	Current density-voltage
LUMO	Lowest unoccupied molecular orbital
MOCVD	Metal organic chemical vapor deposition
NMBI	N-methylbenzimidazole
NT	Nanotube
N3	Cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato

	ruthenium(II)
N-719	Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)
PEDOT	Poly(3,4-ethylenedioxythiophene)
R	Rutile
SM315	Porphyrin dye
TBP	4-tert-butylpyridine
TCO	Transparent conducting oxide
UV	Ultraviolet
UV-Vis	Ultraviolet-visible
XRD	X-ray diffraction
YD2-o-C8	5,15-bis(2,6-dioctoxyphenyl)-10-(bis(4-hexylphenyl)amino-20-4-carboxyphenylethynyl)porphyrinato]zinc(II)

LIST OF SYMBOLS

B	Absorption constant
D	Mean crystallite size
E_g	Energy band gap
F(R)	Kubelka- Munk absorption coefficient function
h	Planck's constant
k	Boltzmann constant
k_{et}	Rate constant for the reduction of I_3^- by the conduction band electrons
K_1	Dimensionless constant
I_o	Intensity of the incident light
I_{mp}	Maximum current
I_{sc}	Short-circuit current
J_{mp}	Maximum current density
J_{sc}	Short-circuit current density
k_{et}	Rate constant for the reduction of I_3^-
n	Band gap transition
n_o	Concentration of electrons
P	Output power
P_{mp}	Maximum output power
Q	Magnitude of the electron charge
R	Reflectance
R_S	Series resistance
R_{SH}	Shunt resistance
T	Absolute temperature

V_{mp}	Maximum voltage
V_{oc}	Open-circuit voltage
Z	Atoms per unit cell
β	Full width half maximum of the diffraction peak
ϕ	Charge flux
n	Quantum yield for photogenerated electrons
η	Photovoltaic conversion efficiency
v	Frequency of photon
λ	Cu $K\alpha_1$ wavelength
θ	Diffraction angle

KAJIAN TENTANG FOTOANOD TITANIUM DIOKSIDA NANOTIUB BAGI APLIKASI PEWARNA SENSITIF SEL SOLAR

ABSTRAK

Kajian ini terutamanya fokus pada sintesis titanium dioksida (TiO_2) nanotiub (NT) dan penambahbaikan TiO_2-asas pewarna sel solar sensitive (DSSC) dengan pengoptimuman komponen. Titanium foil lepas rawatan permukaaan dengan penggilapan kertas pasir telah dipilih untuk tumbuh NTs disebabkan keringkasan kaedah ini dan permukaan yang rata telah dihasilkan untuk sintesis NT. TiO_2 NT telah ditumbuhkan melalui pelbagai jenis kaedah elektrokimia anodik seperti anodik satu-langkah, dua-langkah, alternative voltan dan cepat. Bagi anodik satu-langkah dan dua-langkah, diameter dan kepanjangan NT meningkat secara linear dengan voltan gunaan. Bagaimanapun, sampel anodik melalui dua kaedah ini mempunyai morfologi pandangan atas yang berbeza. Selain itu, kepanjangan NT didapati tak akan meningkat secara bosan dengan tempoh anodik proses. Tatasusunan nanotiub buluh-serupa berjaya ditumbuhkan melalui proses anodic dengan alternative voltan. Namun begitu, kadar pertumbuhan nanotiub bentuk melalui cara ini adalah paling rendah. Walaupun banyak penambahbaikan sudah dilaksanakan untuk menumbuh NT yang sangat teratur sepanjang beberapa tahun ini, kadar penumbuhan formasi NT masih tidak mencukupi, yang mana di sekitar 10 μm/jam sahaja. Kadar pertumbuhan NT yang ultra-cepat sehingga 71 μm/jam telah dicapai dalam kajian ini. Kadar pertumbuhan NT didapati amat bergantung kepada kehadiran ethylenediamine tetra-asetik asid garam dinatrium ($Na_2[H_2EDTA]$). Seterusnya, pengoptimuman komponen DSSC bebas dari cecair ionic dan tambahan telah dijalankan untuk menilai pengaruh oleh setiap komponen terhadap prestasi DSSC. Langkah pengoptimuman termasuk pelarut dan kepekatan

nisbah elektrolit redok; anodik voltan, tempoh dan jenis anodik proses bagi fotoanod; dan akhirnya, tempoh platinum deposit pada elektrod kaunter. Sebelum ini, kecekapan tertinggi yang dilapor dalam kesusasteraan dicapai oleh DSSC tanpa mengguna sebarang ionik cecair dan tambahan organic adalah 1.60%. Selepas pelbagai pengoptimuman, kecekapan DSSC yang terbaik dicapai oleh 18 μm EDTA-NTs fotoanod yang anneal pada suhu 500 ^{o}C; 0.05 M iodin (I_2) and 0.5 M natrium iodide (NaI) dalam elektrolit redok acetonitrile (ACN); dan FTO elektrod kaunter yang dideposit 0.25 nm lapisan platinum. Kecekapan fotokonversi yang terbaik diperolehi dalam projek ini adalah 2.27 %, yang mana sepadan dengan nilai ketumpatan arus litar pintas (J_{sc}), voltan litar terbuka (V_{oc}) and faktor isi (FF) masing-masing adalah 12.88 mA/cm^2, 0.48 V and 0.36. Sebagai perbandingan kepada karya-karya sastera yang serupa, kecekapan fotokonversi 2.27% yang dicapai dalam kajian ini adalah kecekapan tertinggi yang dilaporkan untuk DSSC berasaskan NT tanpa mengguna sebarang ionik cecair dan tambahan organic semasa pembinaan. Kajian ini menunjukkan pembinaan DSSC yang cekap dengan cara yang ringkas dan murah dalam masa yang berkesan boleh dilaksanakan tanpa mengguna sebarang ionik cecair dan tambahan organik yang mahal.

INVESTIGATION ON TITANIUM DIOXIDE NANOTUBES PHOTOANODE FOR DYE SENSITIZED SOLAR CELL APPLICATION

ABSTRACT

This study primarily focused on the synthesis of titanium dioxide (TiO_2) nanotubes (NTs) and the improvement of the TiO_2-based dye-sensitized solar cell (DSSC) by components optimization. Titanium foil with sandpolish surface treatment was chosen to grow NTs due to its simplicity and even surface for the synthesis of NTs. TiO_2 NTs were grown via various types of electrochemical anodization methods such as one-step, two-step, alternating voltage and fast anodization methods. For one and two-step anodizations, diameter and length of NT increased linearly with the applied voltage. However, the top view morphology of samples anodized by these methods was differed. In addition to that, NT length was not increased monotonously with anodization duration. Bamboo-like NT arrays were successfully grown via alternating voltage anodization. Nevertheless, the growth rate of NT formed via alternating voltage anodization method was lowest**.** Although lots of enhancements had been done to fabricate highly-ordered NTs through all these years, the growth rate of the basic NT formation is still highly insufficient, which at around 10 μm/hour only. However, a fast growth rate of NTs up to 71 μm/hour had been achieved in this study. The growth rate of NT was found to be strongly dependent on the presence of ethylenediamine tetra-acetic acid disodium salt ($Na_2[H_2EDTA]$). Next, components optimization of the ionic liquid and additive-free DSSC was carried out to evaluate the influence of each component on the performance of DSSCs. The optimization steps including solvent and concentration ratio of redox electrolyte; voltage, duration and type of anodization method of photoanode; and lastly, platinum sputtered durations of counter electrode.

The previous highest efficiency achieved by DSSC without ionic liquid and additive reported in literature for similar work is 1.60 %. After several optimizations, the best efficiency DSSC was achieved by 18 μm EDTA-NTs photoanode with annealing temperature at 500 °C; 0.05 M iodine (I_2) and 0.5 M sodium iodide (NaI) in acetonitrile-based (ACN) redox electrolyte; and platinized FTO with 0.25 nm platinum thin layer as counter electrode. The best photoconversion efficiency obtained in this project was 2.27%, in which the corresponding values of short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}) and fill factor (FF) were 12.88 mA/cm^2, 0.48 V and 0.36, respectively. As a comparison to those similar literature work, the 2.27% photoconversion efficiency achieved in this project is the highest efficiency reported for NT based DSSC without presence of ionic liquid and additive during fabrication. This study demonstrated that simple, time effective and inexpensive method to fabricate DSSC with considerable efficiency without using any costly ionic liquid or organic additive is feasible.

CHAPTER 1: INTRODUCTION

1.1 Overview

Nanotechnology is defined as the study of functional systems at atomic and molecular scale [1]. In short, it is a kind of technology which at least one of its dimension is on the nanometer scale (1 to 100 nm). Advancement in nanotechnology entails to the upgrowth of various nanostructures which further developed as applications.

The properties of solids depend on size, chemical composition, atomic and electronic structure. Hence, nanostructured materials also exhibit new properties due to the change in dimensionality of the system and atomic structure [2]. With the advancement of technology, nanostructured materials with various morphological forms such as nanopores, NTs, nanoparticles, nanowires, nanorods and other forms can be fabricated.

TiO_2 is one of the metal oxides that has been intensively studied. TiO_2 is popular due to its high chemical stability, excellent photoelectrochemical, optical and electronic properties [3, 4]. Nanostructured TiO_2 can be synthesized by various methods such as electrochemical anodization, sol-gel and hydrothermal methods. Besides that, the applications of TiO_2 nanostructures are mainly divided into four fields: photovoltaic, photocatalysis, gas sensing and biological applications [5-11].

In this project, DSSC (photovoltaic application) will be extensively studied. DSSC was discovered by O'Regan and Gratzel in 1991 [12]. DSSC has been intensively investigated by researchers due to low production cost, as well as high productivity and energy conversion efficiency [13]. In addition, the fabrication method is simple. DSSC can be considered as one of the important development of new

generation of solar cell in harvesting the solar energy.

The effect of NT geometry to the performance of DSSC is reviewed in this project. The NT geometry such as length, tube diameter and morphology property does significantly affects the photovoltaic properties of the DSSCs. Longer NT length is desirable as its offer more surface for dye loading. However, once the NT length close to or exceeded photoelectron diffusion length, the electrons recombination increase and thus results in low short circuit current density, J_{sc}. The tube diameter affects the performance of DSSC through effective surface area. Smaller tube diameter enable to pack more NTs in a standard active area which increase the effective surface area for dye loading. However, air might trapped in the tube and open circuit voltage, V_{oc} decayed, if the tube diameter is too small. Highly ordered NTs have to obtain for high efficiency DSSC. Highly ordered NTs minimize the electrons recombination and hence improve the efficiency of DSSC by enhance the V_{oc}.

1.2 Problem Statement

Since the development of TiO_2 anodization from non-ordered porous structure to the highly controllable self-ordered NTs, electrochemical anodization method becomes one of the most studied methods. Although lots of enhancements had been done to fabricate highly-ordered NTs through all these years, the growth rate of the basic NT formation is still highly insufficient, i.e. the growth rate at around 10 μm/hour only [14].

With the achievement of highly controlled NT, most of the researchers on the anodization of Ti have shifted their focus from the improvement of the formation of NTs to the application of the anodized TiO_2 NTs as water splitter, DSSC and sensors [6-8, 10, 15, 16]. DSSC is one of the most studied TiO_2 applications as TiO_2 shows a

promising results as one of the potential DSSC photoanode, which is 13.0 and 7.0 % for front and backside-illuminated, respectively [17, 18]. Although the efficiency of TiO_2-based DSSC still much lower as compared to the silicon-based solar cells efficiency (25.6 %), however, TiO_2-based DSSC still has its market and worth for further research owing to its cost-to-efficiency or price-to-performance ratio as compared to other types of solar cells [13, 19].

To improve the performance of DSSC, extensive research activities have been focusing on the selection of gel electrolytes, ionic liquids, and various additives such as dialkyl imidazolium iodides, hexaalkyl-substituted guanidinium iodides, 4-tert-butylpyridine (TBP), N-methylbenzimidazole (NMBI) and guanidinium thiocyanate (GuNCS) to push up the performance [20-24]. The addition of organic additives and ionic liquids in the fabrication process will enhance the performance of DSSC. However, the presence of those ionic liquids and additives will significantly increase the production cost of DSSC at the same time.

The previous highest efficiency achieved by DSSC without ionic liquid and additive reported in literature for similar work is 1.60 % [25, 26]. Besides that, the DSSC with sodium iodide based redox electrolyte that achieved 1.60 % mentioned is fabricated by using nanoparticle based photoanode. As a comparison to those similar literature work, the 2.27% photoconversion efficiency achieved in this project is the highest efficiency reported for NT based DSSC without presence of ionic liquid and additive during fabrication.

Basically, there are very less emphasis has been given to improve the efficiency of the DSSC by modifying the TiO_2 NTs morphological properties through various types of anodization methods. This project is focusing on the improvement of the efficiency of the solar cells by manipulating the morphologies of TiO_2 nanotubes while

trying to keep the low fabrication cost by using simple pure redox electrolyte with the absence of ionic liquid and additive.

1.3 Research Objectives

The main objectives of this study are:

1. To investigate the morphological changes of TiO_2 NTs under various types of electrochemical anodization methods (i.e. one-step, two-step, alternating voltage and fast anodization). The nanotubes characteristic features aimed to synthesize in this project are highly ordered NTs with larger effective surface area nanotubes.
2. To improve the growth rate TiO_2 NTs by presence of complexing agent during electrochemical anodization.
3. To fabricate high efficiency low cost TiO_2 NT-based DSSC without using of costly ionic liquid and additives.
4. To evaluate, analyze the photovoltaic properties of DSSC by optimizing the components of DSSC (i.e. photoanode, redox electrolyte and platinized counter electrode).

1.4 Originalities of Research

The originalities of this research lie on the following aspects:

1. Significant enhancement of TiO_2 NT growth rate by the presence of EDTA. The NT growth rate in this project is significantly higher than those reported in literature. Fast TiO_2 NT growth rate was achieved by controlling applied voltage and concentration of EDTA.
2. Fabrication and step by step optimization quantitative study of TiO_2 NT-based DSSC without using costly ionic liquid and additives. The optimization studies

done were merely depends on the effects of manipulated parameters, instead of achieve high DSSC efficiency.

3. The comparative studies of ionic liquid and additive free DSSCs' performance with manipulation of TiO_2 NT morphological properties synthesized via various types of anodization methods was done as it is scarcely studied.
4. Enhancement of ionic liquid and additive free nanotube-based DSSC's performance by optimization the sodium iodide concentration which has not been investigated so far. Photoconversion efficiency was enhanced as compared to those pure sodium-based electrolytes DSSC reported in literature.

1.5 Outline of Thesis

Chapter 2 encompasses the literature review of TiO_2 NTs, including the overview of TiO_2, preparation methods of TiO_2 and the formation mechanism of NTs. Besides that, literature reviews of DSSC are also included. The literature review of DSSC covers with historical background of solar cells, operation principle, components and characterization of TiO_2-based DSSC.

Chapter 3 describes the growth conditions of TiO_2 NTs and the fabrication of DSSCs. Apart from that, the experimental setup and principle operation of instrumentations involved in this project are also covered.

Chapter 4 presents the characterization results and discussions of the synthesized TiO_2 NTs under various types of electrochemical anodization conditions. The anodization parameters including anodization voltage, durations and concentration of electrolyte.

Chapter 5 depicts the characterization results of the DSSC components. The components studied include redox electrolyte, photoanode and counter electrode of

DSSC. Further analysis and discussion of the characterization results are also done in the same chapter.

Chapter 6 summarizes the project as a conclusion and provides some ideas for future work that the efficiency of TiO_2-based DSSCs can be further improved.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter presents the relevant literature review of TiO_2 nanostructures and DSSC. Fundamental properties, growth techniques and growth mechanism of TiO_2 are presented.

Next, historical background of solar cells will be reviewed. Operation principle and components of DSSC will be briefly discussed. The performance evaluation of DSSC is then listed out in the last section of this chapter.

2.2 Synthesis of Titanium Dioxide (TiO_2) Nanotubes

2.2.1 Fundamental Properties of TiO_2

Titanium dioxide (TiO_2) is also known as titania and titanium (IV) oxide. It is discovered by Martin H. Klaproth. TiO_2 has attracted much attention owing to its high chemical stability and excellent photochemical, optical and electronic properties [3, 4]. TiO_2 has been widely used as water splitters, DSSCs and sensors [6-8, 10, 15, 16]. TiO_2 exists in nature as a mineral and the most well-known mineral forms are rutile, anatase, and brookite [27, 28]. Anatase and brookite phases are metastable meanwhile the most stable crystal form of TiO_2 is rutile phase [29]. Crystallization of the anatase phase TiO_2 occurred at 400 ^oC while rutile formed at 700 ^oC and higher [30].

TiO_2 is an n-type photosemiconductor with wide band gap. The band gap energy of TiO_2 is around 3.02 eV for rutile and 3.23 eV for anatase, and is only activated under ultraviolet (UV) light where the wavelength is smaller than 380 nm [31, 32]. The fundamental properties of anatase, rutile and brookite are listed in Table 2.1. Besides that, unit cell, crystal structure and crystal image of the crystal phases

were presented in Figure 2.1.

Table 2.1: Fundamental properties of crystal phases TiO_2.

Properties	Anatase	Rutile	Brookite	Ref.
Molecular weight (g/mol)	79.88	79.88	79.88	[12]
Crystal structure	Tetragonal	Tetragonal	Orthorhombic	[33, 34]
Lattice constant (Å)	a = 3.784 c = 9.515	a = 4.594 c = 2.959	a = 9.184 b = 5.447	[33, 34]
Atoms per unit cell (Z)	4	2	8	[33, 34]
Volume of elementary cell (nm^3)	0.136	0.062	0.257	
Density (g/cm^3)	3.79	4.13	3.99	[33, 34]
Bandgap (eV)	3.23	3.02	3.20	[35-37]
Light absorption (nm)	< 390	< 415	< 387	
Ti – O band length (Å)	1.937 (4) 1.965 (2)	1.949 (4) 1.980 (2)	1.87 – 2.04	[33, 34]
O – Ti – O angle	77.7° 92.6°	81.2° 90.0°	77.0° - 105°	[33, 34]
Melting point	Transform to rutile	1830 - 1850°C	Transform to rutile	[38]
Hardness (Mohs)	5.5 – 6.0	6.0 – 6.5	5.5 – 6.0	[38]
Specific gravity	4.0	4.2	4.0	[39]
Refractive index	2.488 – 2.561	2.605 – 2.616	2.583 – 2.700	[40]

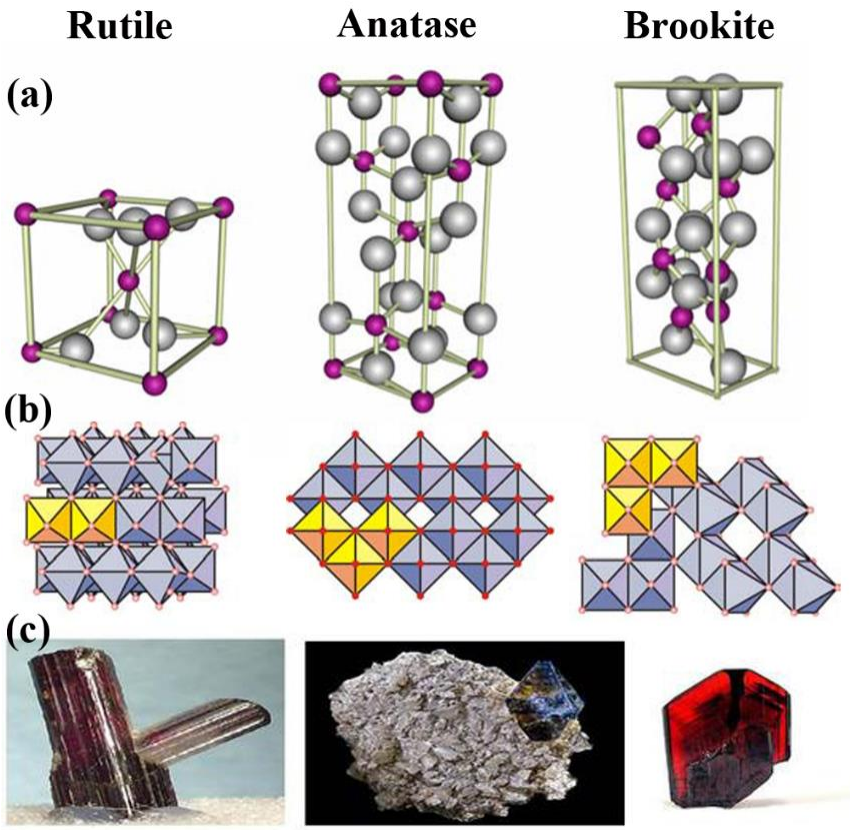

Figure 2.1: (a) Unit cell, (b) crystal structure and (c) crystal image of TiO_2 rutile, anatase and brookite [41, 42].

2.2.2 Preparation Methods of TiO_2

To fabricate TiO_2 nanostructures, various growth techniques have been discovered. These include electrochemical anodization method [5, 9, 43-48], sol-gel method [49-54], hydrothermal method [55-57], direct current magnetron sputtering method[58-60], microwave hydrothermal method [61] and metal organic chemical vapor deposition (MOCVD) [62, 63].

Electrochemical anodization is the most promising method that favoured by researchers since it offers superior control over the dimensions that none other technique can compare with [5]. Besides that, it also offers many advantages such as simple setup and fabrication process, low costs, special geometrical structures and highly ordered arrays can be fabricated easily [47, 48] . As a consequence,

electrochemical anodization method was applied in this project to synthesize TiO_2 nanostructures which further used as photoanode of DSSC.

Electrochemical anodization is an electrolytic passivation process where an oxide film can be grown on certain metals. Under specific condition, a thin and dense barrier oxide of uniform thickness is able to grow on metals. Parameters such as electrolyte, temperature, applied voltage, anodization duration, etc had been reported as important factors to affect the growth of the nanostructures [5, 43, 64-68].

The typical electrochemical cell is shown in Figure 2.2. In an anodization cell, the conducting material (in this case, titanium) be treated is called anode and connected to the positive terminal of a power supply. Typically, inert conductor such as, platinum, carbon or copper rod is used as cathode and connected to the negative terminal of a power supply. Both anode and cathode are dipped in an electrolyte bath.

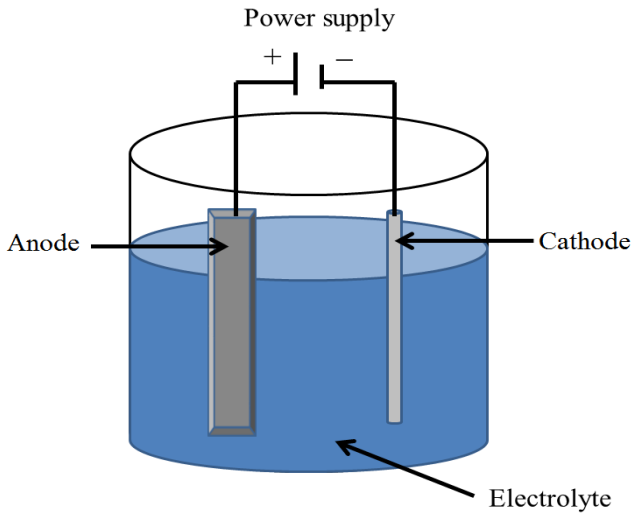

Figure 2.2: Electrochemical anodization cell.

The study of the growth of TiO_2 nanostructures via electrochemical anodization technique had been reported by many researchers. Figure 2.3A shows the typical morphology of first generation TiO_2 NT arrays. First generation NTs were synthesized in hydrofluoric (HF) electrolytes and its thickness was less than 600nm [43, 44]. The second generation of NT arrays was anodized by using sodium fluoride (NaF) or NH_4F

buffered neutral electrolytes to replace the HF electrolyte [45, 46]. Highly-ordered NT arrays with greater length were successfully grown in this generation by controlling the pH electrolyte [45]. Meanwhile, third generation of NT arrays were synthesized in electrolytes with almost water free condition by using non-aqueous, polar electrolyte such as glycerol, ethylene glycol, diethylene glycol, formamide, etc. Figure 2.3B revealsthe image of NT arrays grown by glycerol and fluoride-based electrolytes and the smooth NT arrays grown was around 7 μm [69]. Besides that, NTs with hexagonal arrangement were grown by replaced glycerol with ethylene glycol, as shown in Figure 2.3C [70]. Recently, rapid breakdown anodization method was discovered to grow long NTs in a very short duration (Figure 2.3D). Typically, chloride-based or perchlorate-based electrolyte was used in rapid breakdown anodization, instead of fluoride-based electrolyte [68, 71, 72]. However, it requires a high applied voltage which sufficiently high to create a local breakdown of the oxide film that NT bundles will be grown at the breakdown site further on. Self-organized NTs were failed to form via this approach although it offers a rapid growth rate of NTs.

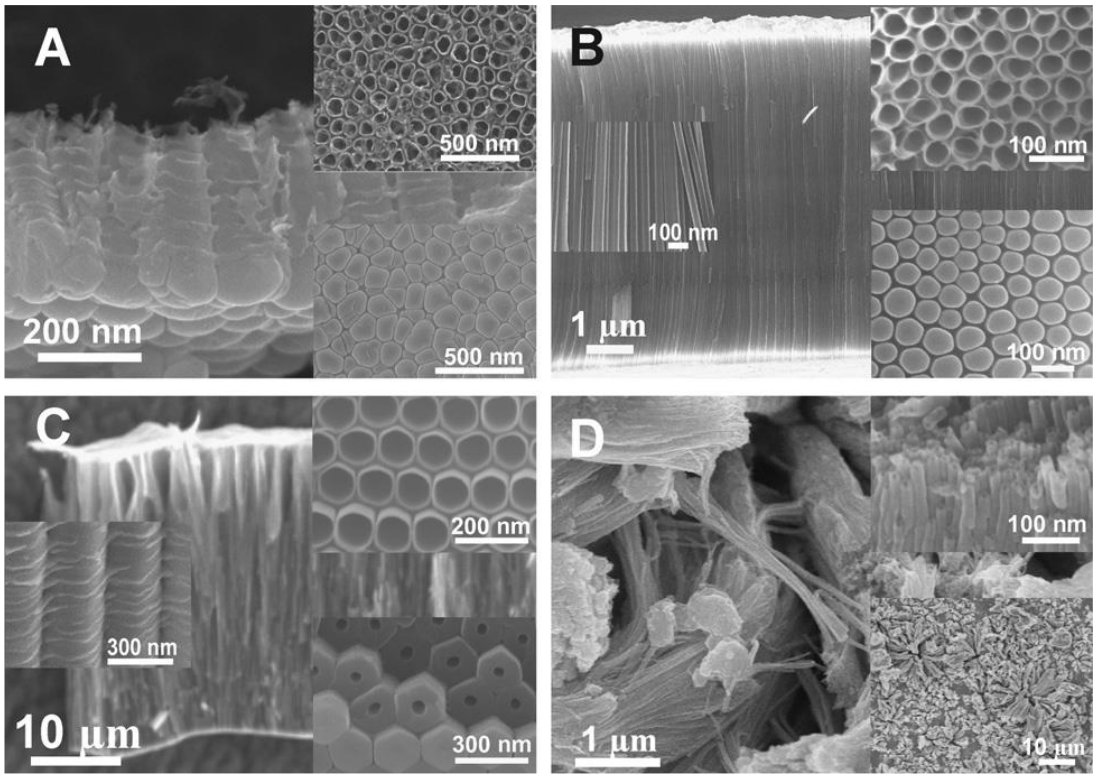

Figure 2.3: SEM images of TiO_2 NT arrays synthesized via various anodization approaches. TiO_2 NT arrays grown by using (A) hydrofluoric electrolyte, (B) glycerol and fluoride-based electrolyte, (C) ethylene glycol and fluoride-based electrolyte. The insets show high magnification top, bottom and cross section view of the corresponding TiO_2 NT arrays. (D) TiO_2 NT arrays synthesized via rapid breakdown anodization method. The insets show cross section and top view (low magnification) of the NT arrays [73].

2.2.3 Formation Mechanism of TiO_2 Nanotubes

Schematic diagram of TiO_2 NTs formation is shown in Figure 2.4. The detail description of formation mechanism is as below [5, 74-77]:

(a) A thin layer of amorphous TiO_2 was formed on the Ti surface due to the interaction between titanium with O^{2-} or OH^- ions from the electrolyte. The formation was described as the equation below:

Anode: $Ti \rightarrow Ti^{4+} + 4\ e^-$ (2.1)

$Ti^{4+} + 4\ OH^- \rightarrow Ti(OH)_4$ (2.2)

$Ti^{4+} + 2\ O^{2-} \rightarrow TiO_2$ (2.3)

$$Ti(OH)_4 \rightarrow TiO_2 + 2\ H_2O \quad (2.4)$$

Cathode: $4\ H^+ + 4\ e^- \rightarrow 2\ H_2$ (2.5)

Overall: $Ti^{4+} + 2\ H_2O \rightarrow TiO_2 + 4\ H^+$ (2.6)

(b) By supplying potential, electric field created leads to the reaction between amorphous TiO_2 and fluorine ions. The reaction formed $[TiF_6]^{2-}$ complex which dissolves the TiO_2 layer and resulting in random tiny pits and cracks on the TiO_2 layer.

$$TiO_2 + 6\ F^- + 4\ H^+ \rightarrow TiF_6^{2-} + 2\ H_2O \quad (2.7)$$

(c) As anodization goes on, the tiny pits were then grows larger and become pores which further evolved into TiO_2 NT structure, as shown in Figure 2.8c, d and e.

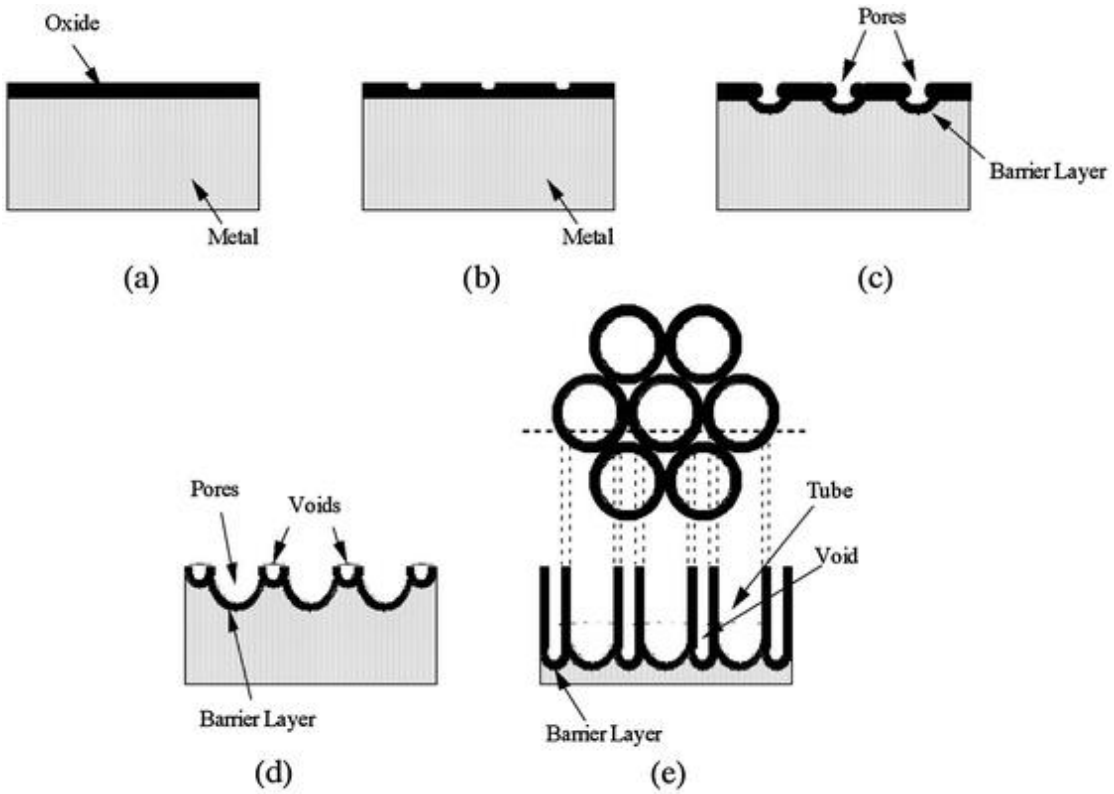

Figure 2.4: Schematic diagram of TiO_2 NTs formation. (a) Formation of oxide layer; (b) formation of corrosion pits and cracks; (c) expansion of pits to nanopores; (d) further chemical dissolution of nanopores; (e) formation of NT arrays [78].

Basically, the growth of NT depends on three simultaneous processes, which is (i) field-assisted oxidation at Ti metal to form metal oxide, (ii) field-assisted dissolution of Ti metal ions in the electrolyte and (iii) the chemical etch of Ti and TiO_2 [5, 44, 77]. These processes strongly affect the electrochemical etching and chemical dissolution rate, which leads to different growth rate of NTs. Note that the formation of NTs actually is a competition between chemical etching and oxidation process. The electrochemical etching rate was determined by field-assisted oxidation and dissolution process. Meanwhile, the etching speed of NTs determines the chemical dissolution rate [5, 77]. If the electrochemical etching rate is faster than the other one, longer NTs are grown. Otherwise, shorter NTs are attainable.

2.3 Dye-Sensitized Solar Cell

2.3.1 Historical Background of Solar Cells

Solar energy is one of the most intensively subjects studied by many scientists. Solar cell is an electrical device designed to directly convert sunlight into electricity by using the photovoltaic effect. Basically, there are three generations of solar cell, which is wafer based, conventional thin layer and emerging thin film solar cells, as shown in Figure 2.5 below.

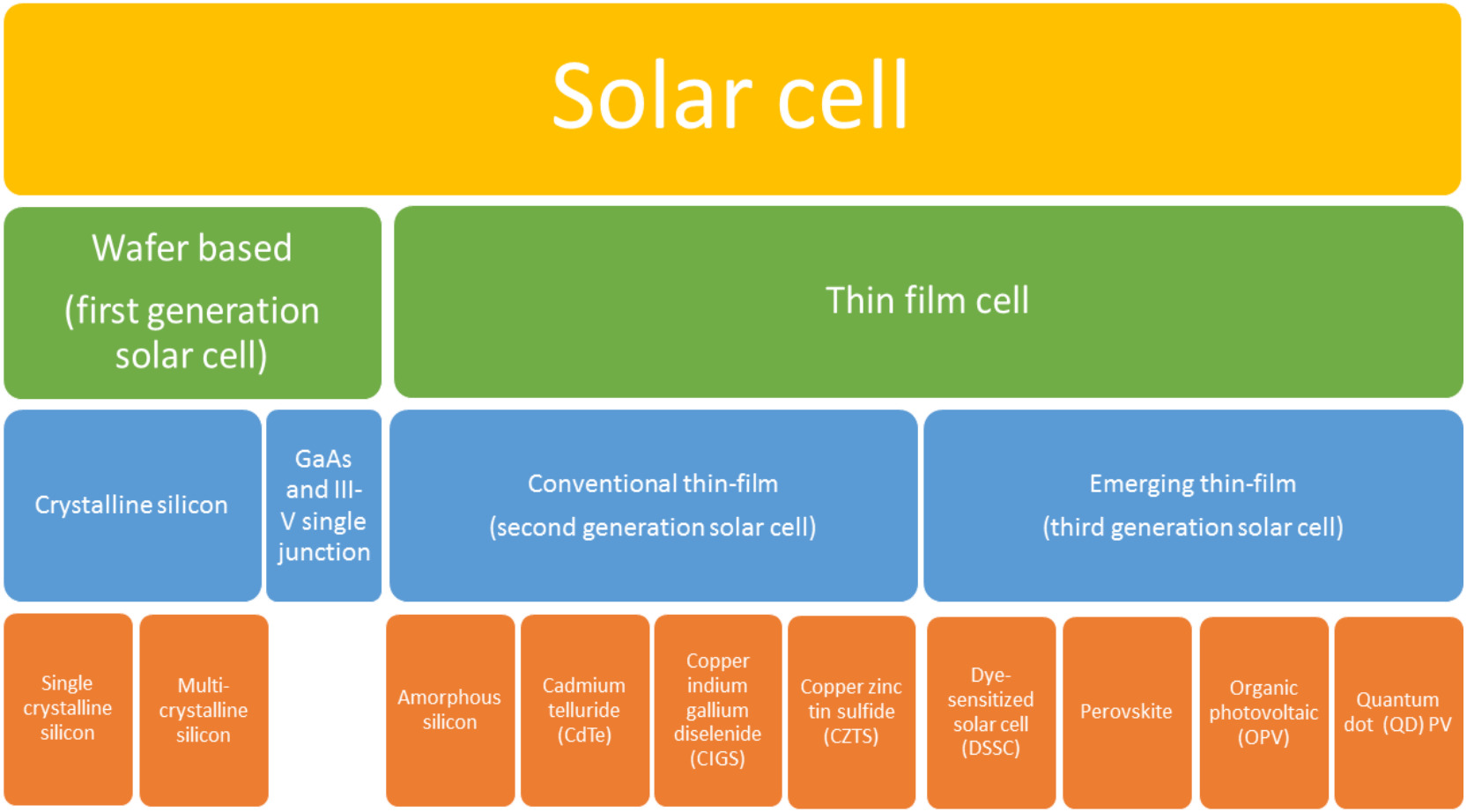

Figure 2.5: Basic generations of solar cell [79].

Crystalline silicon-based solar cell is the first generation of solar cell which designed in 1954. These cells are broadly classified into monocrystalline cell, polycrystalline cells, polycrystalline thin line cells, polycrystalline band cells, and polycrystalline power cells [79, 80]. Silicon-based solar cells working based on diffused p-n junction technology. The joint of n-type (excess electrons) and p-type (excess holes) semiconductor material forms a p-n junction. Diffusion of electrons and holes at the joint interface causes electric field is generated and forming depletion region. Besides that, electric potential difference called "built-in voltage" is formed across the interface. The schematic of a p-n junction of silicon-based solar cell is illustrated in Figure 2.6. The high conversion efficiency of silicon-based solar cells up to 25.6 % is main reason that this type of solar cells have dominated the PV market for the past 50 years [19]. However, the requirements of high materials cost, highly purified silicon, highly controlled conditions and use of toxic chemicals for production has hindered the extensive production of the first generation silicon-based solar cells [81, 82].

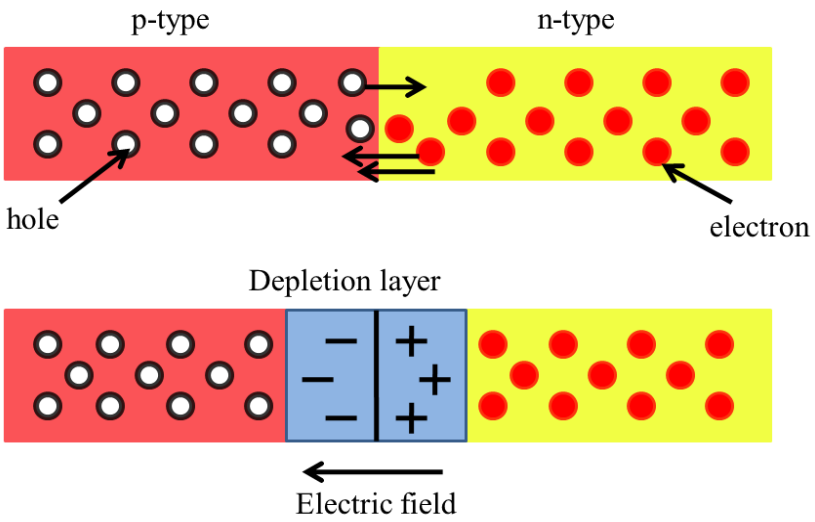

Figure 2.6: Schematic diagram of a p-n junction of silicon-based solar cell.

The second generation of solar cells are referred to those thin layer cells which normally can be classified into copper-indium diselenide (CIS), Cadmium Telluride cells (CdTe), amorphous silicon cells, micro-amorphous cells, dye cells and microcrystalline cells [79]. Thin layer solar cells working by thin film deposition of purely inorganic materials on a glass, plastic or metal substrate. Production of this type of solar cells is ease and flexible. Besides that, the production cost is significantly reduced due to less materials required [83]. However, efficiency of thin layer solar cells is lower than the crystalline silicon-based solar cells. Moreover, thin layer solar cell offers shorter warranty and tends to degrade faster than the first generation silicon solar cell.

Third generation of solar cells are emerging solar cells which based on nanostructured materials. Third generation of solar cells classified into polymer based solar cells, concentrated solar cells, nanocrystal based solar cells and dye-sensitized solar cells [79]. The first two generation solar cells are fabricated by opaque materials and require front illumination which needs to move by following the position of the sun. In contrast to the first two generations solar cells, the mesoscopic nature of the third generation solar cells allows the production of transparent photovoltaic window cells [84]. Transparent cells enable both front and back illumination. Dye-sensitized solar cell (DSSC) is the most promising efficient solar cells among the third generation solar cells. DSSC, also known as Grätzel cell, which developed by Brian O'Reagan and Micheal Grätzel in 1991 [12].

Figure 2.7 and Table 2.2 provide the trend and comparison of the best efficiency cell among various types of solar cells measured under light intensity 100 W/m^2 at room temperature. Highest efficiency had been recorded by multi-junction cell, which around 46.0 % [85]. In contrast, the best efficiency achieved by crystalline

silicon solar cell is 25.6 % [19]. So far, the best efficiency of DSSC up to 13.0 % (frontside illuminated), as listed in Table 2.2 [17]. The frontside illuminated DSSC always offers a higher efficiency. In contrast, the highest efficiency recorded by backside illuminated DSSC was 7.0 and 8.8 % for nanotube and nanotube/nanoparticles structure, respectively [18, 86]. Incident light undergoing a 30 % losses due to the reflection by platinum sputtered counter electrode and absorbance of redox electrolyte for the backside illuminated DSSC [87].

Although the efficiency recorded by silicon based solar cells is higher than the third DSSCs (third generation solar cell), the cost-to-efficiency or price-to-performance ratio of DSSCs is always better than the former one, as shown in Figure 2.8 [13]. The third generation solar cells are able to be fabricated at a cost of less than $ 0.50/W, potentially $ 0.20/W or better, which equals to one-fifth of the silicon solar cells. While significantly decrease the fabrication costs, it does offer better efficiencies. Apart from that, DSSCs offer additionally advantageous in light weight, low production cost, ease of fabrication, transparency of cells, insensitive to temperature changes, light capture from all angles [88-91].

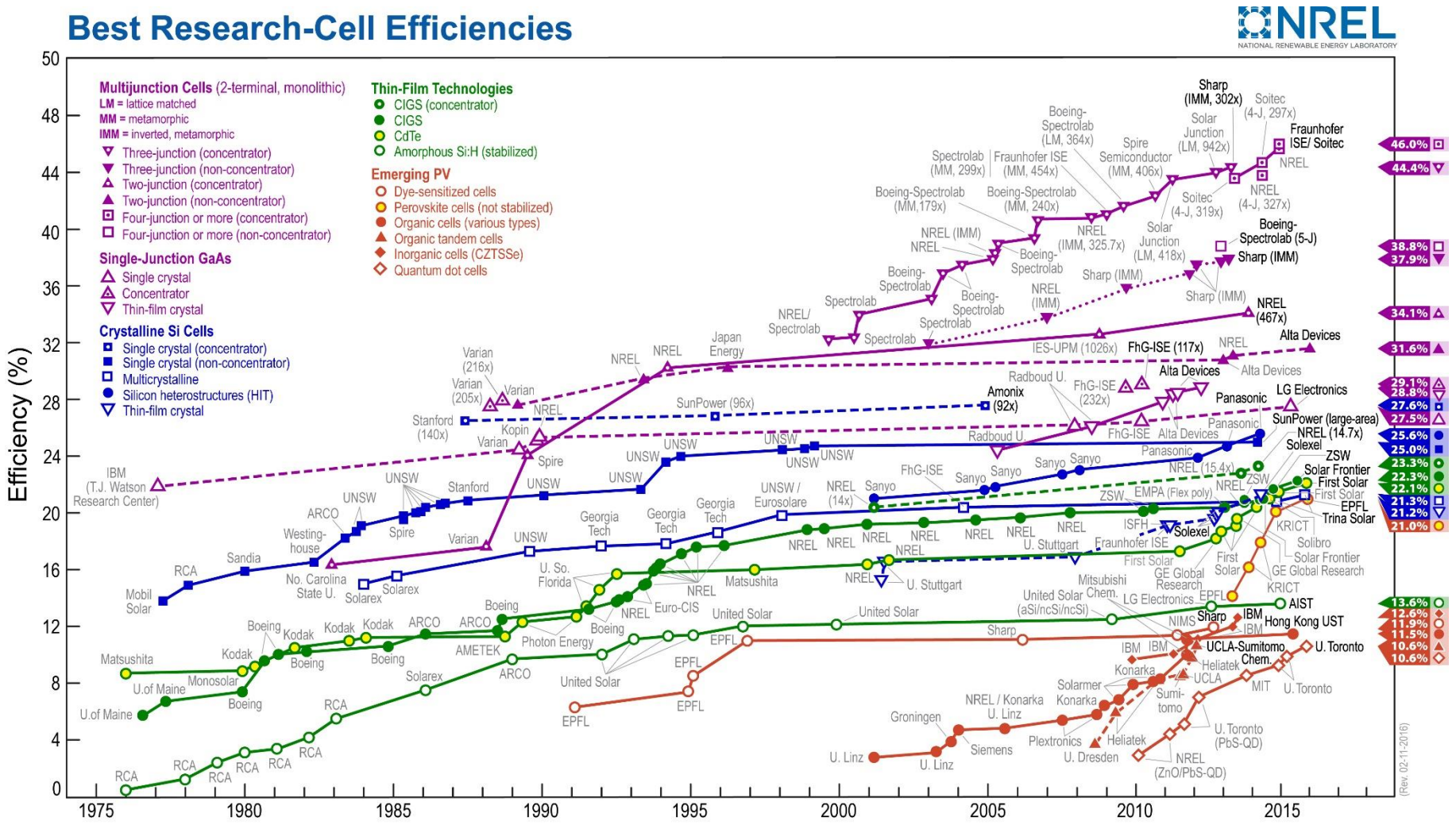

Figure 2.7: The trend of best research solar cell efficiencies throughout 30 years [92].

Table 2.2: Solar cell best research efficiencies table.

Classification	Area (cm^2)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	Efficiency (%)	Ref.
Multijunction cells						
Four junction cell	0.050	337.9	4.23	0.851	46.0	[93]
Five junction cell	1.021	9.564	4.77	0.852	38.8 ± 1.2	[94]
InGaP/GaAs/InGaAs	1.047	14.27	3.07	0.867	37.9 ± 1.2	[95]
Two junction Si cell	1.000	13.45	1.34	0.702	12.7 ± 0.4	[96]
Three junction Si cell	1.043	9.920	1.90	0.721	13.6 ± 0.4	[97]
Crystalline silicon						
Single Crystal	143.7	41.80	0.74	0.827	25.6 ± 0.5	[19]
Multicrystalline	242.7	39.80	0.67	0.800	21.3 ± 0.4	[98]
Thin film module	239.7	38.50	0.69	0.803	21.2 ± 0.4	[99]
Thin film technologies						
CIGS (cell)	0.993	35.70	0.76	0.776	21.0 ± 0.6	[100]
CIGS (minimodule)	15.89	35.29	0.70	0.756	18.7 ± 0.6	[101]
CdTe (cell)	1.062	30.25	0.88	0.794	21.0 ± 0.4	[102]
Amorphous Si	1.001	16.36	0.90	0.698	10.2 ± 0.3	[103]
Emerging Photovoltaic						
DSSC	1.000	18.10	0.91	0.780	13.0	[17]
Organic thin film	0.993	19.40	0.79	0.714	11.0 ± 0.3	[104]
Perovskite thin film	1.020	19.29	1.07	0.751	15.6 ± 0.6*	[105]
Inorganic (CZTSSe)	1.000	35.20	0.51	0.698	12.6	[106]
Quantum dot cell	1.000	21.60	0.61	0.710	10.6	[107]

*not stabilised, initial efficiency

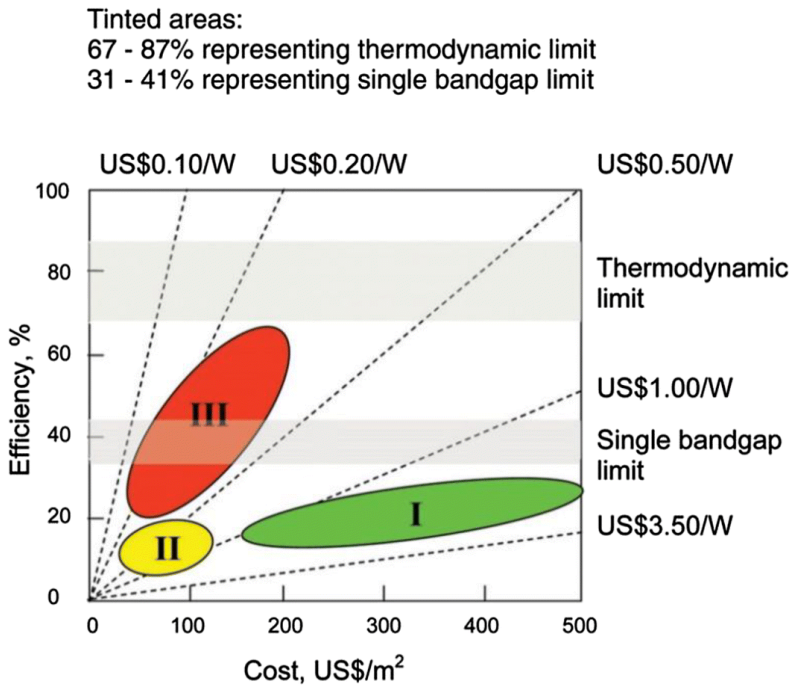

Figure 2.8: The corresponding efficiency and fabrication cost of the first (I), second (II) and third (III) generation of solar cells [13].

2.3.2 Operation Principle of the DSSC

The absorption of light followed by the generation and transport of charge carriers to the electrodes are the principal functions of any photovoltaic cell. In contrast to the conventional solar cells, the possibility of premature electrons and holes recombination is prevented in DSSCs. The photon absorption and charge carrier transport processes were took place separately in DSSCs. The photon absorption process was achieved by the dye molecules. However, the charge carrier transport process takes place at the conduction band edge of the semiconductor [108]. Owing to separation of the fundamental processes, the demand of high-purity materials are then becomes inessential for DSSCs fabrication [109].

DSSC are normally composed of four major components, which are semiconductor photoanode, dye sensitizer, redox electrolyte and counter electrode. Figure 2.9 illustrates the operation principle of a typical sandwich structure DSSC. The

fundamental operation principle of DSSC consists of the following processes [110-113]:

1. Dye molecule is excited from ground state to the excited state upon absorption of incident light.

   Excitation: $TiO_2 \mid Dye + light \rightarrow TiO_2 \mid Dye^*$ (2.8)

2. Electron injected to the conduction band of the semiconductor, owing to the difference in energy levels of the electronic states. The electron injection process causes the dye becomes oxidized.

   Injection: $TiO_2 \mid Dye^* \rightarrow TiO_2 \mid Dye^+ + e^-$ (2.9)

3. The electron is then transport to the TCO working electrode.
4. Electron creates external current while migrates to the counter electrode through external circuit.
5. Oxidized dye is regenerated to its initial state by donation of electron from iodide in the redox electrolyte.

   Regeneration: $TiO_2 \mid 2\ Dye^+ + 3\ I^- \rightarrow TiO_2 \mid 2\ Dye + I_3^-$ (2.10)

6. Hole diffuses to the platinized counter electrode.
7. Reduction reaction of the triiodide performed by accepting electrons from the external circuit. As a result, oxidized iodide is stored to its original state.

   Reduction: $I_3^- + 2\ e^- \rightarrow 3\ I^-$ (2.11)

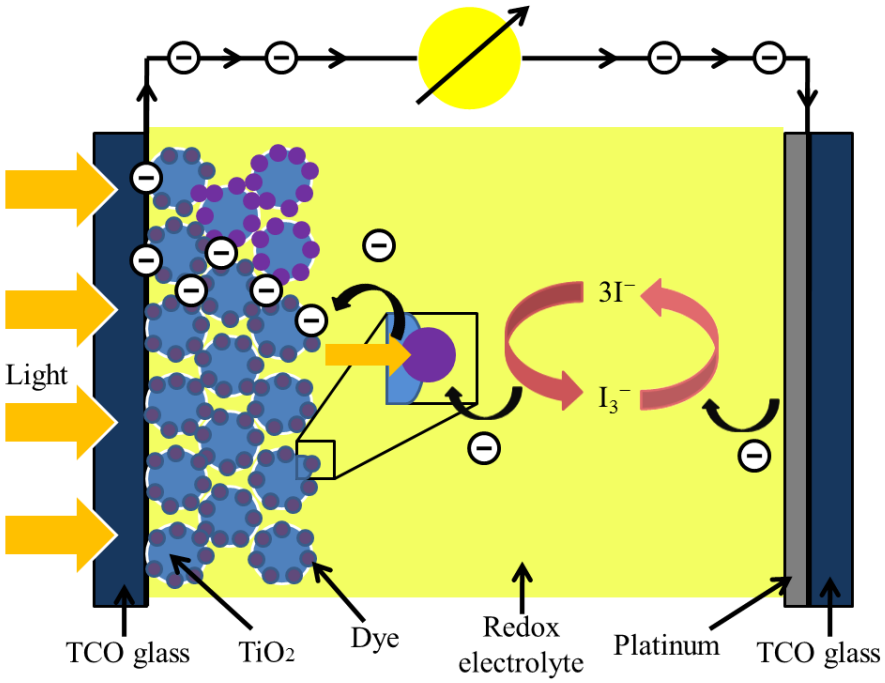

Figure 2.9: Operation principle of a typical sandwich structure DSSC [114].

The reversible redox cycles between platinized counter electrode and dyes, allows the electron injection process from dye to semiconductor to be repeatable. In consequence, electric power is generated from the DSSC without suffering from permanent chemical transformation [113]. However, backward charge transfer processes also performed in the same time when the forward charge transfer processes mentioned as above take place. The backward charge transfer processes including:

- Regeneration of the oxidized dye by back transfer electrons from the semiconductor [115]. The dark reaction recombination is as below:

  $TiO_2 \mid Dye^+ + e^-$ (semiconductor) $\rightarrow TiO_2 \mid Dye$ (2.12)

- Regeneration of the oxidized dye due to excited-state decay of the dye [116].
- Recombination of injected electrons with the oxidized species in the redox electrolyte [117, 118]. The corresponding recombination is as below:

  $I_3^- + 2\ e^-$ (semiconductor) $\rightarrow 3\ I^-$ (2.13)

The complete backward charge transfer or charge recombination processes will reduce the performance of DSSC. Electron lifetime is a crucial parameter to control

the possibility of charge recombination process. A shorter electron lifetime leads to a faster recombination. In order to avoid backward electron transfer, the excited-state decay rate of dye should be lower than the electron injection rate of dye to the semiconductor. Besides that, the electron injection rate should be performed within a quantum yield [119].

2.3.3 Components of DSSC

A DSSC generally composed by four components, which is photoanode, dye sensitizer, redox electrolyte and counter electrode.

2.3.3(a) Photoanode

In a DSSC, the photoanode is responsible to become a stand for dye loading and transports the excited electrons injected from dye to external circuit. Semiconductors with wide bad-gap such as TiO_2, zinc oxide (ZnO) and niobium pentoxide (Nb_2O_5) are always selected as photoanode [77, 120-125]. The semiconductor mentioned above offers the aspects below which causing them behave as an ideal photoanode [110, 126]:

(i) High surface area to ensure high percentage of dye loading.

(ii) High electron transfer rate to ensure high charge collection efficiency.

(iii) High chemical stability to ensure cell's resistance to photocorrosion.

(iv) Good structural arrangement.

(v) Low cost and environment friendly**.**

In literature, the porosities, morphologies and film thickness of the semiconductor nanostructures were studied to obtain a DSSC with better efficiency. At the beginning, TiO_2 DSSCs were in the form of anatase phase nanoparticles. TiO_2