We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

A New Generation of Energy Harvesting Devices

Byunghong Lee and Robert Bob Chang

Abstract

This chapter has been mainly focused on the development and fabrication of various nanostructured materials for electrochemical energy conversion, specially, third generation (3rd) thin film photovoltaic system such as organic dye or perovskite-sensitized Solar Cells. Enormous efforts have been dedicated to the development of a variety of clean energy, capable of harvesting energy of various forms. Among the various energy forms, electrochemical devices that produce electric energy from chemical energy have received the most attention as the most promising power sources. In the majority of cases, researchers who come from the different background could engage on certain aspects of the components to improve the photovoltaic performances from different disciplines: (i) chemists to design and synthesize suitable donor-acceptor dyes and study structure-property relationships; (ii) physicists to build solar cell devices with the novel materials, to characterize and optimize their performances, and to understand the fundamental photophysical processes; and (iii) engineers to develop new device architectures. The synergy between all the disciplines will play a major role for future advancements in this area. However, the simultaneous development of all components such as photosensitizers, hole transport layer, photoanodes and cost effective cathode, combined with further investigation of transport dynamics, will lead to Photovoltaic cells, 30%. Herein, in this book, with taking optimized processing recipe as the standard cell fabrication procedure, important breakthrough for each components is achieved by developing or designing new materials, concepts, and fabrication technique. This book report the following studies: (i) a brief introduction of the working principle, (ii) the detailed study of the each component materials, mainly including TiO₂ photoanode under the category of 0D and 3D structures, strategies for co-sensitization with porphyrin and organic photosensitizers, and carbon catalytic material via controlled fabrication protocols and fundamental understanding of the working principles of electrochemical photovoltaic cell has been gained by means of electrical and optical modelling and advanced characterization techniques and (iii) new designed strategies such as the optimization of photon confinement (iv) future prospects and survival strategies for sensitizer assisted solar cell (especially, DSSC).

Keywords: photovoltaic cell, DSSC, perovskite, TiO₂, photosensitizer, carbon, photonic crystal

1. Introduction

The search for green sources of energy is considered one of the priorities in today's societies and occupies many policy makers' agendas. Excitonic Solar cell

such as organic dye or perovskite -sensitized solar cells (DSSC or PSC) is showing up as a promising solar harvesting technology that has bright future. Unlike conventional silicon p-n junction solar cell, an excitonic solar cell (ESC) can be modeled as a unipolar-junction cell and made from low-cost materials that do not need to be highly purified but still work well using simple manufacturing processes [1]. For example, similar to the photosynthetic process in plants where chlorophyll absorbs photons but does not participate in charge transfer, the photoreceptor and charge carrier are implemented by different components in solar cell. This separation of functions leads to lower purity demands on raw materials and consequently makes excitonic solar cell a low-cost alternative. Nevertheless, to compete with the future PV market, ESC should focus on the “Golden Triangle” issues, i.e., increasing light-to-electric energy conversion efficiency, enhancing long-term stability, and decreasing device cost [2].

Since the last third decades, scientists have devoted a great deal of effort on DSSCs’ four important components: photosensitizer, photoanodes, electrolytes, and counter electrodes; some significant processes have been achieved. The sensitization of semiconductors using dyes dates back to 19th century. It showed that the photosensitivity can be extended to longer wavelengths by adding a dye to silver halide emulsions [3, 4]. Grätzel has then extended the concept to the DSSC by adsorption of dye molecules on the nanocrystalline TiO_2 electrodes [5]. This breakthrough was due to large surface area of the mesoporous TiO_2 that allowed anchoring significantly high amount of dye molecules ($\sim 0.13 \text{ mmol/cm}^2$) onto it; thereby increasing the absorption cross-section. Since the first successful demonstration of DSSC over three decades ago, a wealth of DSSC components have been investigated for enhancing energy conversion efficiency. State of the art DSSCs achieve more than 11% energy efficiency allied to good performance under any atmospheric condition and low irradiance. Moreover, the possibilities of transparency and multi-colored cells are truly a competitive advantages of DSSCs. However, for stimulating industrial market, performance of DSSCs must be improved close to the efficiency values of the conventional silicon solar cells.

Since 2012, organic-inorganic perovskites solar have attracted considerable research attention for photovoltaic device due to its superb light-harvesting characteristics and electrical properties. Within relatively a short time, this organic-inorganic lead halide perovskite has yielded photovoltaic efficiencies of 25.5%, being the highest-performing solution-processed solar cell on record and displacing technologies such as DSSCs and organic photovoltaics (OPVs) [6]. In addition, the use of perovskite materials as light absorbers and hole transporting material (HTM) in solid-state sensitized solar cells has opened up a new direction for the high-efficiency thin-film solar cells. Despite the best candidate at satisfying the need for high efficiencies, concerns surrounding the long-term stability in an ambient atmosphere as well as the water-soluble toxic lead components in the archetypal perovskite, APbX_3 ($\text{A} = \text{methylammonium, formamidium, cesium}$, $\text{X} = \text{I}^-, \text{Br}^-, \text{Cl}^-$), have the potential risk for the environment issue. After around 10 years of intense PSC researches, several physical chemistry still have questions for the basic mechanism. In this aspect, the physical and chemical operation of DSSC has become more clear and a good example of a ESC system where the function of the overall device is better than predicted from the sum of the properties of its components. Therefore, this book address important breakthroughs our laboratory research for DSSC with taking optimized processing recipe as the standard cell fabrication procedure.

In order to meet this requirement, it will be necessary to alter at least two of the three major components simultaneously. In the majority of cases, however, researchers who come from the different background could engage on certain aspects of the components to improve the photovoltaic performances from

different disciplines: (1) chemists or material scientists worked for developing photosensitizer and charge transport materials; (2) physicists to elucidate photovoltaic properties and working mechanism; and (3) engineers to develop process and device structure for module level production. However, the simultaneous development of all components such as new photosensitizer or new classed structural perovskite materials with intrinsic stability and beneficial optoelectronic properties, solid state HTM and photoanodes, combined with further investigation of transport dynamics, will lead to ESCs with efficiencies exceeding 30%.

This report the following studies: (i) a brief introduction of the working principle, (ii) the detailed study of the each component materials, mainly including TiO₂ photoanode under the category of 0D and 3D structures, strategies for co-sensitization with porphyrin and organic photosensitizers, and carbon catalytic material via controlled fabrication protocols and fundamental understanding of the working principles of electrochemical photovoltaic cell has been gained by means of electrical and optical modeling and advanced characterization techniques and (iii) new designed strategies such as the optimization of photon confinement (iv) future prospects and survival strategies for sensitizer assisted solar cell (especially, DSSC).

2. Fundamentals of dye-sensitized solar cells

2.1 Operation principle

The principle of operation of a DSSC is well documented in the literature [7]. The simplified principle of the thin layer DSSC is shown in **Figure 1**. A light-harvesting Ru complex photosensitizers adsorbed on the surface of a porous nanocrystalline film composed of a wide bandgap metal oxide such as TiO₂, ZnO or SnO₂ absorb incident photon flux. The photosensitizers are excited from the ground state (D) to the excited state (D*) owing to the metal to ligand charge transfer (MLCT) transition (Eq. (1)). The excited electrons are injected into the conduction band of the TiO₂ electrode, resulting in the oxidation of the photosensitizer (Eq. (2)).

Injected electrons in the conduction band of TiO₂ are transported between TiO₂ nanoparticles with diffusion toward the back contact (TCO) and consequently reach the counter electrode through the external load and wiring. The oxidized photosensitizer (D⁺) accepts electrons from the I⁻ ion redox mediator, regenerating the ground state (D), and I⁻ is oxidized to the oxidized state, I₃⁻ (Eq. (3)). The injected electrons may recombine either with oxidized sensitizer at the TiO₂ (Eq. (4)).

The oxidized redox mediator, I₃⁻, diffuses toward the counter electrode and is rereduced to I⁻ ions.

The primary energy conversion process in DSSCs is a photoinduced charge separation at the metal oxide/dye/electrolyte interface.

Figure 1. Schematic diagram and principle of operation of proto-typed dye sensitized solar cells (inserted in the nanocrystalline TiO_2 film).

In order to elucidate DSSC working phenomenon, the physical kinetics and dynamics of charge transfer motion have been investigated in detail by many researchers, both experimentally and via computational modeling. Here, the electron transfer dynamics taking place at the oxide/dye/electrolyte interface for DSSCs are presented in **Figure 2** [7–9]. This figure also contains the information for several competing loss pathways, shown as red arrows. These loss pathways include decay of the dye excited state to ground, and charge recombination of injected electrons which with dye cations and with the redox couple.

Figure 2. State diagram of kinetics and energetics of a traditional DSSC. The positive charge transfer processes are indicated by blue color. The competing loss pathways of recombination with TiO_2 trap sites and dye surface are shown in red. Reprinted from [8, 10].

2.2 Dye/metal oxide interface

A monolayer dye molecules attached to the surface of the nanocrystalline film. The high surface area of nanocrystalline film ensures a large concentration of the light absorber leading to good light harvesting are critical to be efficient DSSCs. In addition, how and where the photosensitizer bound to the surface of TiO_2 is another important issues since unexpected bonding between photosensitizer and the TiO_2 surface lead to degrade electron injection performance. In the case of Ru complex, one carboxylic ligand provides good anchoring to metal oxide surface (Long-term stability against moisture condition can be improved by using phosphonic acid) as well as good electronic coupling of the excited states of photosensitizer with TiO_2 conduction band states [11].

To be the effective electron transfer, the lowest unoccupied molecular orbital (LUMO) level of excited dye molecules is appropriately lower than the highest unoccupied molecular orbital (HUMO) level of the metal oxide. Under illumination, the photoexcited sensitizers are injected into the metal oxide and diffused from the dye/metal oxide interface to substrate. In an efficient DSSC, a time scale of femtoseconds to picoseconds nanoseconds of injection process is witnessed on the strong electronic coupling between photoexcited sensitizer and metal oxide. The injected electrons experience fast recombination process and thermalisation down to at the electron Fermi level of the electrode [12].

2.3 Dye/electrolyte interface

After ultrafast electron injection from the photoexcited dye into the conduction band of TiO_2 , the dye is in its oxidized state and must be reduced by an electron donor in the electrolyte for regeneration. The standard electron donor is iodide. For many typed dye, high value of regeneration efficiency, which give the probability that an oxidized dye is regenerated by an electron donor in the electrolyte rather than by recombination with an electron in the TiO_2 , have been estimated in iodide. The reaction mechanism from reduction of oxidized sensitizer (D^+) by iodide follows:

Eq. (6) is most likely a one-electron transfer reaction between D^+ and I^- . ($\epsilon(\text{I}^\bullet/\text{I}^-) = +1.33$ V vs. NHE in aqueous solution.) The dye regeneration is firstly occurred from the formation of a $(\text{D} \cdots \text{I})$ complex since the redox potential (ϵ) of the iodine radical reacted to the sensitizer ($\epsilon(\text{D} \cdots \text{I}) = +1.23$ V vs. NHE in acetonitrile) shows a relatively lower potential of 0.1 V. The dye regeneration is firstly occurred from the formation of a $(\text{D} \cdots \text{I})$ complex since the redox potential (ϵ) of the iodine radical reacted to the sensitizer ($\epsilon(\text{D} \cdots \text{I}) = +1.23$ V vs. NHE in acetonitrile) shows a lower potential of 0.1 V. Dissociation of ground-state dye D and $\text{I}_2 - \bullet$ is secondly occurred from the formation of a $(\text{D} \cdots \text{I}_2 - \bullet)$ complex. Finally, $\text{I}_2 - \bullet$ is by the composition of triiodide and iodide. The second-order rate constant for this reaction is about $2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile.

The oxidized sensitizer (specially, the most commonly reported Ru complex dye, named as N719) is regenerated by the iodide/iodine redox couple in the liquid

electrolyte in the range of 100 ns to 10 μ s. The different regeneration time can be explained by iodide concentration, the presence of additives such as identity of cation salt (lithium ions) and tertbutylpyridine (tBP). To be the effective DSSC, the recombination process of electrons with either oxidized dye molecules or acceptors in the electrolyte must be minimized compared with regeneration process, which usually happens on a time scale of about 1 μ s [7, 13–15].

2.4 TiO₂ interface for electron transport

Unlike the typical the electron transport mechanism in bulk semiconductors, the electron transport mechanism of TiO₂ in DSSC need to be extend from the properties of the individual nanoparticles to the particle connectivity or electronic coupling between the particles, and the geometrical configuration of the assembly. Interestingly, the mesoporous nanocrystalline TiO₂ layer exhibit the highly efficient charge transport through the nanocrystalline TiO₂ layer, while the low inherent conductivity of the film ca. bulk mobility of TiO₂ (1cm²/Vs), ZnO (200cm²/Vs), and SnO₂ (250cm²/Vs) as well as the presence of disorder from randomly arranged metal [16]. The main consequence of disorder in the electronic structure of the material is the appearance of localized states. This puzzling phenomenon has been explained by multiple-trapping model, in which the diffusion of conduction band electrons is affected by the trapping-detrapping events [17–20]. Electron transport in nanostructured oxide films impregnated with a highly concentrated electrolyte is believed to occur mainly by diffusion. It is generally accepted that this diffusional transport is influenced by the existence of electron localized states or traps in the semiconductor.

In the TiO₂ nanoparticles, electrons undergo a number of processes. A main process is the transport of electrons in the extended states of the conduction band (CB), where the concentration of free electrons n_c is defined as

$$n_c = n_0 e^{qV/k_B T} \quad (10)$$

here n_0 is an equilibrium concentration in the effective density of states of the CB and k_B is the Boltzmann constant, q denotes elementary charge and T is the temperature ununit. In a steady state, transport process is under the control of displacing electrons in the TiO₂ CB with the trap in equilibrium occupation.

TiO₂ nanoparticles exhibit numerous localized states in bandgap, which can capture and release electrons to the transport level. The position of Fermi level (E_{Fn}) plays an important role in calculating the probability of electron capture since trapping events below E_{Fn} are quiescent from almost fully occupied traps, while empty traps above the E_{Fn} happens in reverse.

A localized state at energy E_t sets free electrons at a rate;

$$\tau_t^{-1} = \beta_n N_c e^{\frac{E_t - E_c}{k_B T}} \quad (11)$$

where β_n is the time constant for electron capture (which is independent of trap depth). Since τ_t increases exponentially with the depth of the state in the bandgap, the slowest trap is the deepest unoccupied trap. The effect of traps is dominant whenever a transient effect is induced, in which the position of the Fermi level is modified, with the correspondent need for traps release. Therefore, traps also become a dominant aspect of the recombination of electrons in a DSSC, that is a charge transfer to the electrolyte or hole conductor. The specific density of localized states (DOS) in the bandgap of TiO₂, named as $g(E)$, can be also established by capacitance techniques that provide the chemical capacitance, that is defined as follows:

$$g(E) = \frac{N_L}{k_B T_0} \exp\left(\frac{E - E_c}{k_B T_0}\right) \quad (12)$$

Here N_L is the total DOS, and T_0 is a parameter with temperature units that determines the depth of the distribution, that is alternatively expressed as a coefficient $\alpha = T/T_0$. If we consider that electrons can only be transported via the CB, then we need to consider how the density of electrons in the CB.

The carrier mobility is associated with random motion of free carriers, which is directed linked to the conductivity and resistivity. The expression of the electron conductivity σ_n associated to free carrier transport is [21].

$$\sigma_n = \frac{q^2 D_0}{k_B T} n_c \quad (13)$$

Here D_0 is the free electron diffusion coefficient. The conductivity can be expressed by the temperature-dependent features using the framework of multiple trapping where electron displacement occurs via extended states at the CB edge with the free electron diffusion coefficient. This result has been measured by the common techniques such as intensity modulated photocurrent spectroscopy (IMPS), transient photocurrent under a small perturbation of the illumination, or transport resistance of impedance spectroscopy [22–24].

2.5 Electrolyte/counter electrode interface

In theory, the maximum photovoltage of the DSSC is determined by the energy difference between the redox potential and the Fermi level of the metal oxide semiconductor. However, the output voltage under load is usually less than the open circuit voltage the theoretical expected. This voltage loss is mainly attributed to the overall overpotential of electrolyte and counter electrode (CE) interface. The mass-transfer overpotential is largely affected by the ionic conductivity of electrolytes and the transportation of mediator species from the CE to the photoanode. The kinetic overpotential or charge-transfer overpotential can be determined by electrocatalytic properties of the CE surface toward mediator reduction [25]. To be effective CE, it should exhibit excellent conductivity and inhibit high electrocatalytic activity for reduction of the redox couple. The effect of electric field and transport by ionic migration can be negligible because of high ionic conductivity and ionic strength of liquid electrolyte. With increasing viscosity such as gel, quasi-solid and solid state electrolyte, an inadequate flux of redox components leads to sacrifice the photocurrent of the DSSC. In the case of the iodide/triiodide electrolyte, charge transport corresponds to formation and cleavage of chemical bonds:

The CE must exhibit catalytically fast reaction and low overpotential because the counter electrode reduces the redox species. (triiodide $\rightarrow$ iodide) Platinum (Pt) materials is widely used as a suitable catalyst for reaction 1.14 to replenish the reduced species in the redox electrolyte. However, Pt is very expensive and rare so they have limited potential for commercial use. Therefore substantial researches are under way to develop inexpensive alternative materials for larger commercialisation prospects. The charge transfer reaction between the counter electrode surface and the electrolyte occurs the charge-transfer resistance (R_{CT}) in the DSSCs. The small R_{CT} will give a higher fill factor (FF), which leads to a high conversion efficiency.

3. Optimizing material and configuration for typical DSSCs

Numerous publications and review articles on DSSC have appeared in the literature for certain aspects of the DSSC fabrication or performance during the past three decades [26–30]. Proto-type module cells for manufacturing are actively under development [31–35]. This book reviews systematical parameters via controlled experiments (such as materials preparation, processing, device fabrication and assembly, measurements and device modeling) and the interfacial properties introduced by electrochemical impedance spectroscopy (EIS) for making better solar performance [36–38]. The inherent material properties such as impurity, surface properties in the DSSC are studied from this powerful tool for studying the kinetics of charge transport and electron–hole recombination. Furthermore, this book suggests other ways to improve cell efficiency externally from the photon confinement.

3.1 Understanding DSSC operation model by EIS

As mentioned in Section 1, diverse electrochemical processes take place in a DSSC during the cell operation. The I-V curves provide the information on the basic parameters such as short-circuit current (I_{SC}), open-circuit potential (V_{OC}), Fill factor (FF), and cell efficiency (η). The impedance spectroscopy measurements are widely used for investigating the properties of a broad class of material system and device. It provides essential information on carrier transport and recombination. In EIS measurement, a direct current (DC) signal is applied to the cell by a small sinusoidal alternating current (AC) perturbation under steady light illumination. From the measured current response, the magnitude of the impedance for amplitude and phase shift is determined as a function of modulation frequency. From the relevant equivalent circuit, the measured data are fitted by some software (such as Zview or Gamry Echem Analyst etc) and the charge transfer kinetics in a DSSC can be estimated.

In this book, for a deep comprehensive understanding of the device operation, Adachi model are employed to figure out the key parameters that control the efficiency of a DSSC [39–42]. **Figure 1** shows the schematic diagram of DSSC structure. In this system, the light comes from the indium or fluorine doped tin oxide (ITO or FTO) coated transparent conductive glass, the sheet resistance as small as 10 $\Omega/\text{sq.}$ is required, as an anode electrode (left) [43]. An insulating blocking layer and mesoporous metal oxide film (TiO_2 , ZnO , SnO_2 etc.) is deposited on top of bottom electrode. Next, dye molecules are covered by the surface of mesoporous metal oxide and iodine electrolyte is interpenetrated into metal oxide/dye layer. The platinum coated FTO substrate is used as a catalyst for iodide reduction as the counter electrode (right).

The kinetic behavior of charge trap and de-trap mechanism from electrochemical and photoelectrochemical processes affects the different capacitive and resistive element of faradaic impedance. EIS data generally shows Nyquist and Bode plots. An general plot shows x-axis the real impedance (Z') versus the y-axis the imaginary impedance (Z'') in the complex plane. From EIS analysis, the complex impedance (Z) of each component express Z_0 , Z_1 , Z_2 , and Z_3 , respectively. (i.e. Z_0 is the contact impedance of conductive glass; Z_1 is the Pt-catalyzed counter electrode impedance; Z_2 is the complex impedance for the interfacial resistivity among metal oxide, dye molecule, and the iodine electrolyte; Z_3 is the Warburg impedance for diffusion of tri-iodide ions). The resulting data from impedance is directly linked to the information on materials quality, internal, interfacial properties of the DSSC.

Suppose the complex impedance is the same as its resistance. ($Z = R$) R_o represents the ohmic contact resistance from the FTO and the metal. The impedance of the electron transfer at the Pt counter electrode (Z_1) can be modeled as an RC parallel circuit, and simply expressed as:

$$Z_1 = \frac{1}{\frac{1}{r_{p1}} + i\omega C_{p1}} \quad (15)$$

where, r_{p1} , C_{p1} describes the resistance and capacitance at the Pt coated CE, respectively.

Z_3 represents the finite Warburg impedance contributes to the diffusion impedance for the diffusion of tri-iodide ions in the electrolyte at the low frequency region with a frequency maxima of ω_{z3} [40, 44].

$$Z_3 = R_D \frac{1}{\sqrt{\frac{i\omega}{D_1/\delta^2}}} \tanh \sqrt{\frac{i\omega}{(D_1/\delta^2)}} \text{ where } R_D = \frac{k_B T}{m^2 q^2 A \nu C^* D_1 \delta} \quad (16)$$

D_1 and δ represent the diffusion coefficient of I_3^- and the thickness of the liquid film respectively. R_D is the DC resistance of impedance of diffusion of tri-iodide. The number of electrons transferred in each reaction, m , is 2 in this case. A_ν and C^* are the Avogadro number and the concentration of I_3^- in the bulk, respectively.

The impedance Z_2 of the charge transport through diffusion into the mesoporous TiO_2 and recombination at the TiO_2 /dye/electrolyte interface shows in the middle semicircle of the EIS graph. As seen in **Figure 2**, photoexcited electrons in the CB will decay and excite at rate k_1 and k_2 into surface trap states of the TiO_2 as well as the back reaction in the iodine electrolyte at a rate of (k_r). The charge transfer kinetics for injection, diffusion, collection, trapping, de-trapping and recombination of electrons in the TiO_2 of the DSSC can be calculated by [39, 40]:

$$\frac{\partial n(x,t)}{\partial t} = D_{cb} \frac{\partial^2 n(x,t)}{\partial x^2} - k_1 n(x,t) + k_2(x,t) + G(x,t) \quad (17)$$

$$\frac{\partial N(x,t)}{\partial t} = -k_2 N(x,t) - k_r N^2 + k_1 n \quad (18)$$

Here n is the excess electron density in the CB of the TiO_2 under illumination, N is the excess electron density of the trap sites, D_{cb} describes the diffusion coefficient of an electron in the CB and the function G is the generation rate of electrons injected into the TiO_2 [40]. By varying the potentials, the excess CB electron density $n(x,t)$ will be expressed as followed [39].

$$n(x,t) = n_s(x,t) + \Delta n(x) e^{i\omega t} \quad (19)$$

$$N(x,t) = N_s(x,t) + \Delta N(x) e^{i(\omega t + \varphi)} \quad (20)$$

Here, n_s and N_s describe the steady state electron densities (Δn and ΔN are the amplitudes of the modulated component) in the CB and the trap state, respectively. Defining,

$$D_{eff} = D_{cb} \frac{k_2}{k_2} \quad (21)$$

$$k_{eff} = 2N_s k_r \quad (22)$$

$$\gamma^2 = \frac{k_{\text{eff}}}{D_{\text{eff}}} + \frac{i\omega}{D_{\text{eff}}} \quad (23)$$

and using the following boundary conditions at

$$x = 0, qD_{\text{eff}} \left(\frac{\partial \Delta n}{\partial x} \right) = \frac{\Delta I}{A} = \Delta J \quad (24)$$

$$x = L, \frac{\partial \Delta n}{\partial x} = 0 \quad (25)$$

the impedance Z_2 is obtained by Kern et al. as [39].

$$Z = -S \frac{1}{qA} \frac{1}{D_{\text{eff}} \gamma} \frac{1 + e^{2\gamma L}}{\sqrt{\frac{1}{k_{\text{eff}}}} \frac{1 - e^{2\gamma L}}{1 - e^{2\gamma L}}} \quad (26)$$

$$S = \frac{K_B T}{qn_s} \sqrt{\frac{1}{k_{\text{eff}}}} \quad (27)$$

By defining

$$\omega_d = \frac{D_{\text{eff}}}{L^2}, \omega_k = k_{\text{eff}} \text{ and } \gamma L = \sqrt{\frac{\omega_k}{\omega_d} + \frac{i\omega}{\omega_d}} \quad (28)$$

The equivalent impedance Z_2 of Bisquert [39] is obtained as follows:

$$Z_2 = R_\omega \left(\frac{1}{(\omega_k/\omega_d)(1 + i\omega/\omega_k)} \right)^{1/2} \coth[(\omega_k/\omega_d)(1 + i\omega/\omega_k)]^{1/2} \quad (29)$$

$$R_\omega = \frac{k_B T}{q^2 A n_s} \frac{L}{D_{\text{eff}}} = \text{Con} \frac{L}{D_{\text{eff}}}, R_k = \frac{\omega_d}{\omega_k} \times R_\omega = \text{Con} \frac{1}{L k_{\text{eff}}} \quad (30)$$

Here, ω is modulation frequency (s^{-1}) (with $\omega_k = k_{\text{eff}}$), R_ω is the electron transport resistance, and R_k is the charge transfer resistance related to recombination of electrons at the $\text{TiO}_2/\text{electrolyte}$ interface. The relation can be expressed by $R_k = (\omega_d/\omega_k) \cdot R_\omega$.

The total impedance (Z_s) of the DSSC can be calculated by the summation of Z_1 , Z_2 , Z_3 , and the external resistance, Z_0 ,

$$Z_s = Z_0 + Z_1 + Z_2 + Z_3. \quad (31)$$

From experimental (L , A , δ) and EIS data (the maxima values of ω_{Z1} , ω_{Z2} , ω_{Z3} of the semi-circle diameters along the Z' axis), necessary information on charge transport kinetics can be determined (**Figure 3**).

3.2 Materials preparation

3.2.1 TiO_2 nanoparticle

The highly crystalline anatase TiO_2 nanoparticles (NPs) was synthesized by 2-step autoclaving technique (**Figure 4(a)**). A pH controlled TiO_2 suspension was prepared by commercial TiO_2 power. (P25, Degussa) The TiO_2 suspension is placed in a total volume of 60 mL in a Teflon-lined stainless steel autoclave (125 mL

Figure 3.
(a) A electrical equivalent and (b) an illustrative Nyquist plot of a DSSC with R_0 , R_1 , R_2 , and R_3 , and each peak frequency maxima of ω_{Z1} , ω_{Z2} , and ω_{Z3} , respectively. Reprinted from [26, 51].

volume, Parr Instrument Co.) and heated at 240°C for 12 h. The resulting powders are dried at ~80°C in a conventional drying oven for 24 hour (**Figure 4(b)**). The pure Anatase colloidal TiO_2 nanoparticle was obtained by autoclaving the low-pH titanate suspension at 240°C for 12h (**Figure (4c)**) [45].

3.2.2 Photosensitizer (purified N719 dye)

For photosensitization studies, the calcined TiO_2 nanoparticle electrode were immersed in the ethanol solution containing purified 3×10^{-4} M cis-di(thiocynato)-N,N'-bis(2,2'-bipyridyl-4-carboxylic acid-4'-tetrabutylammonium carboxy late) ruthenium (II) (N719, Solaronix) for 18 h at room temperature [46]. Commercial N719 dye may not produce high efficiency because of impurities. Therefore, purification is required. The N719 complex is firstly dissolved in water with

Figure 4.
Scheme showing a typical procedure for highly crystalline TiO_2 nanoparticle based DSSC. Reprinted from [26].

tertrabutylammonium hydroxide and then purified three times with chromatography. (Sephadex LH-20) The pH values below 4.5 is controlled by 0.02 M HNO_3 . The titration is carried out slowly over a period of three hours. Then, the solution is kept at -20°C for 15 hours. After allowing the flask to warm to 25°C , the precipitated complex is collected on a glass frit and air dried.

3.2.3 Liquid electrolyte

The liquid electrolyte was prepared by dissolving 0.6 M of 1-butyl-3-methylimidazolium iodide (**BMII**), 0.03 M of iodine, 0.1 M of guanidinium thiocyanate (**GuSCN**) and 0.5 M of 4-tert-butylpyridine (**tBP**) in acetonitrile and valeronitrile (85:15 v/v). Most additives are understood at a fairly phenomenological level, and their effects are often attributed to modification of redox couple potential, band shifts of the semiconducting electrode material, effects of surface blocking, or surface dye organization. The study for additives have been reviewed extensively elsewhere [47, 48]. For example, it was found that smaller size Li^+ ions cause a shift in the TiO_2 conduction band edges toward more positive potentials than larger size 1,2-dimethyl-3-hexylimidazolium ions. As a result, an electrolyte containing Li^+ ions produced a lower photovoltage and at the same time higher photocurrent than that containing imidazolium cations because of an alteration of both the energy and number of excited state levels of the dye that participate in electron injection [46]. The effects of tBP were studied in more detail in DSSCs showing that both band edge shift and increased electron lifetime play a role [49].

Even if tBP and Li^+ ions play a different role for solar cell performance, both additives are widely used in liquid electrolyte. As another effective additive, adding GuSCN can be also good choice. It shifts the conduction band edge of TiO_2 toward lower energies, suggesting adsorption of the cation onto the TiO_2 surface. Coadsorbants, adsorbed onto the TiO_2 during the dye adsorption procedure, can have similar effects as additives in the electrolytes [50].

3.2.4 Catalytic layer

The cathode-electrode was produced by coating F:SnO₂ glass with a thin layer of a 5 mM solution of H_2PtCl_6 in isopropanol and was heated at 400°C for 20 min. Best performance and long-term stability has been achieved with very low Pt-loadings ($5 \mu\text{g cm}^{-2}$), so that the counter electrode remains transparent. Charge transfer resistances of less than $1 \Omega \text{ cm}^2$ can be achieved.

3.3 DSSC fabrication for conventional typed cell

A paste of anatase hydrothermal TiO_2 powder was made by stirring with the mixture 0.5 g of anatase- TiO_2 NPs, 100 μl of Triton X-100, 0.2 g of polyethylene glycol (PEG, Fluka, Mw = 20,000) into 3 ml acetic acid (0.1 M). The TiO_2 paste is coated on a FTO glass by doctor blade technique. The thickness of the TiO_2 film was measured by a surface profiler (TENCOR. P-10) [26, 51]. **Figure 4(d)** and **(e)** gives an illustrative sequence of steps that were used in the fabrication of our solar cells. The top and bottom electrodes were sandwiched together with thermal melt polymer film (**Figure 4e**).

3.3.1 TiO_2 Nanoparticles prepared by 2-step hydrothermal treatment

Anatase TiO_2 NPs were investigated by using a field-emission scanning electron microscope (SEM, S4800, Hitachi) and JEOL-2010 TEM (JEOL, Japan) equipped with an energy dispersive spectrometer (EDS) to investigate the TiO_2 NPs and determine

Figure 5.
 (a) X-ray diffraction patterns of hydrothermal TiO_2 nanoparticle after calcination at 500°C. Inset shows the SEM images of nanoparticle after calcination. (b) a. TEM, b. SEAD pattern, c. HR-TEM bright field images and d. EDX analysis of TiO_2 nanocrystals prepared by 2-step autoclaving technique scheme showing a typical procedure for highly crystalline TiO_2 nanoparticle based DSSC.

the compositions of the samples at 200 kV. The NPs were also characterized by x-ray diffraction (D/Max-A, Rigaku) measurements. **Figure 5(a)** shows a X-ray scan of the Anatase TiO_2 NPs before and after sintering as described below. The inset shows a typical SEM photo of the NPs used in the experiment. These results reveal broad diffraction peaks at 25.3° , 37.8° , 48.2° , 53.9° and 55.2° were observed, which can be indexed to the (101), (004), (200), (105) and (211) reflections of anatase TiO_2 . **Figure 5(b)** provides the high resolution transmission microscopic (TEM) images and selected area electron diffraction pattern of the TiO_2 NPs. It provides the corresponding electron diffraction pattern taken from the TiO_2 NPs showing that the NPs are crystalline Anatase TiO_2 . **Figure 5(b)** gives the high-resolution TEM (HRTEM) image of NPs indicating that the TiO_2 NPs are single-crystalline. Lattice of 0.189 nm and 0.243 nm corresponding to (200) and (103) planes of the tetragonal TiO_2 , respectively, have been resolved. The inset is the corresponding fast Fourier transform (IFFT) image of selected area in **Figure 5(b)c**. In **Figure 5(b)d** the EDS taken from TiO_2 NPs shows that the NPs are composed of Ti and O. The Cu peak comes from the grid. From these measurements, we concluded that our starting materials were pure Anatase.

3.3.2 Study for the optimal TiO_2 film thickness

To find the optimized condition for hydrothermal treated TiO_2 film, the cell efficiency as a function of the TiO_2 film thicknesses is studied. In **Figure 6** (top), I give plots of V_{oc} , J_{sc} , FF , and η as functions of film thicknesses. The efficiency per NP increases almost linear with decreasing film thickness until about $2\ \mu\text{m}$. From these measurements, the optimal TiO_2 film thickness is around $11.5\ \mu\text{m}$ with our cell architect and fabrication procedures. It should also be noted that the highest open circuit voltage and fill factor are achieved at the thinnest active layer thickness, while the short circuit current density increases with increasing film thickness (for thickness below $15\ \mu\text{m}$). From this thickness study, we then varied other cell parameters to optimize the overall cell efficiency. In **Figure 6** (bottom) we plot cell efficiency times the number TiO_2 NP as a function of NP film thickness. it is shown that the efficiency per TiO_2 NP increases dramatically as the active NP layer decreases. This shows the large inherent loss of charges in these DSSCs.

In **Figure 7**, AC impedance measurements with best-fit model curves of the cell is used for analyzing function on the different TiO_2 NP film thicknesses. Form the Bode phase plots, the negative shift of the frequencies of the main peaks with an

Figure 6. Relationship of DSSC device performance (top) and efficiency per TiO_2 NP (bottom) depending on film thickness (top). Reprinted from [26, 52].

Figure 7. AC impedance measurement (a) bode, (b) Nyquist plots, (c) electron density (n_s) and (d) the relation between the electron recombination resistance (R_k) and the electron diffusion resistance (R_w) of cells with different TiO_2 NP film thicknesses. The solid curves are from a best fit model.

increase in the film thickness. In a simple equation, since ω_{max} is inversely associated with the life time of electron $\tau = 1/(2\pi f)$, the decrease in ω_{max} indicated a reduced rate for the charge-recombination process in DSSC. Hence, electrons with longer τ values were prevented from recombining, characterized by a larger charge transfer resistance. In the aspect of ω_{max} , about 6 μm thick film show the longest electron lifetime and relatively small total series resistance, leading to high V_{oc} and FF . However, in the case of N719 dye, the dye absorption at that thickness is not enough to reach the maximum performance. The more detailed phenomenon can be understood by the further consolidated impedance model we suggested.

All cases of samples were equal in the total cell thicknesses (L). Therefore, there is a tradeoff relation between cell gaps of dye coated TiO_2 film and electrolyte, for example, for the thicker thin films of TiO_2 film, the electrolyte spacing is smaller. The resulting data from our model shows specific characteristics worth noting; (1) In the case of ultra-thin TiO_2 film, two distinctive circles can be found and the impedance Z_3 is dominated rather than that of Z_1 and Z_2 in the low-frequency region. (2) For thicker TiO_2 layers, the contribution from Z_2 is more pronounced (3) The estimated the diffusion coefficient in the electrolyte (D_1) is the highest for the thinnest TiO_2 layer [26]. From this model, low k_{eff} , high R_k/R_w , high D_{eff} and high n_s are necessary condition to attain highly efficient DSSC. As seen in **Figure 7 (c,d)**, over $10\text{ }\mu\text{m}$ thick film exhibit the improved electron density (n_s) and high electron diffusion coefficient (D_{eff}), but the recombination time is shorter than the time for diffusion across the TiO_2 layer ($R_k < < R_w$, $w_d < < w_k$). As a result, we conclude about $11.5\text{ }\mu\text{m}$ is the optimized film thickness in my system. The detailed physical values are summarized in **Table 1**.

3.4 Interfacial modification

There are numerous efforts to improve cell performance from different modifications techniques such as different semiconductors, dyes, or ionic conductors or on changing its nanostructures [53, 54]. Most of modification works show a tradeoff relation between the short-circuit current and open-circuit voltage. This can be explained the the modification of components affect sensibility of charge-transport and recombination dynamics [55]. Therefore, this has been a big challenge in the field of DSSC design. In this book, effective surface passivation and treatment method provide on how it possible to contribute on the cell performance.

3.4.1 TiCl_4 treatment

The best-known techiqnue to improve the performance of the solar cells is a post-treatment of the TiO_2 film with a solution in TiCl_4 is grown onto an extra layer of TiO_2 nanoparticles constituting the film. The TiCl_4 treatment results in an improvement in photocurrent, normally between 10% and 30%. Depending on the quality of the TiO_2 used to make the initial film, the extrema of the improvement can be from $<5\%$ to $>200\%$ [35, 56]. The largest improvements come when using the poorest quality TiO_2 films. **Figure 8(a)** show the SEM images and XRD patterns for TiCl_4 treated TiO_2 film. When the TiCl_4 exposure condition is increased, the

Film Thickness (μm)	D_{eff} ($10^{-5}\text{ cm}^2\text{s}^{-1}$)	k_{eff} (Hz)	R_k/R_w	Con (Ωcms^{-1})	R_d (Ω)	n_s (10^{18} cm^{-3})	D_1 ($10^{-6}\text{ cm}^2\text{s}^{-1}$)	V_{OC} (V)	J_{sc} (mA/cm^2)	FF (%)	EFF (%)
2.4	2.10	31.6	46.2	0.368	19	1.41	42.0	0.932	4.851	72.1	3.26
4.6	0.56	14.2	6.79	0.122	11.7	4.36	7.2	0.919	7.252	73.9	4.93
6.2	0.64	10	4.04	0.084	8.1	5.94	4.5	0.910	8.029	76.8	5.61
10.4	2.79	20	2.76	0.048	7.1	10.5	3.2	0.802	11.61	73.0	6.80
12.4	2.58	10	2.38	0.055	8.3	9.39	0.09	0.808	12.54	72.2	7.32
15.0	3.29	10	2.14	0.093	6.9	6.06	0.56	0.762	12.46	68.6	6.51
17.1	9.05	10	3.13	0.133	3.6	4.36	0.21	0.764	11.19	65.7	5.62

Table 1.
*Parameters for the best fit of the impedance data for the different thickness. Measured in **Figure 6**.*

Figure 8.

(a) XRD pattern and SEM images of TiO₂ film with and without post-treatment with TiCl₄ (b) BET and BJH analysis of the pristine TiO₂, and hydrothermal treated TiO₂ film with and without post-treatment with TiCl₄ (note: HT-TiO₂ is a hydrothermal treated TiO₂ nanoparticles).

XRD intensity of the rutile peak increased [57]. However, under well-controlled condition, no obvious different in the rutile content (20–25%) can be seen between treated and untreated TiO₂ from XRD analysis., while an increased size of TiO₂ NPs and densely packed TiO₂ NPs film is observed. **Figure 8(b)** shows Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) pore-size distribution plots of the pristine TiO₂ NP (P25), 2-step hydrothermalized (HT)-TiO₂ NP and TiCl₄ treated HT-TiO₂ NP. Hydrothermal treated samples show similar type-IV isotherms, which are representative of mesoporous solids.

The 2-step HT-TiO₂ NP show about 18.5% increased surface areas and 43.6% widened cumulative pore volume compared with the pristine TiO₂ NP (P25). However, TiCl₄ treated samples show ~16.7% decreased surface area compared with pristine TiO₂ film. However, the loss in actual electrode surface area after TiCl₄ treatment is small because of the increase in mass of approximately 10.3% TiO₂ volume on the electrode. From these observations it follows that, despite the substantial decrease in BET surface area, the film thickness is not affected. Therefore, the porosity must have decreased, as is shown in **Table 2**. In spite of the decreased surface area, the TiCl₄ treated TiO₂ film morphology is observed by about a 40% higher dye absorption at the 480 nm. (see **Figure 9(a)**) For more accurate experiment, the quantity of TiO₂ NPs surface-bound sensitizers was measured by desorption process [35]. UV–vis absorption spectra is used for calculating the number of desorbed sensitizer molecules (set as the extinction coefficient (ϵ) of the N719 sensitizer is about $3.748 \times 10^{-3} \text{ cm}^{-1} \text{ M}^{-1}$ at 535 nm). It is estimated that roughly 8.8% and 34.6% more dye molecules are attached to the surface of TiCl₄ treated TiO₂ ($\approx 3.97 \times 10^{-8} \text{ molmg}^{-1}$) compared to HT-TiO₂ NP ($\approx 3.65 \times 10^{-8} \text{ molmg}^{-1}$) and commercial TiO₂ NP ($\approx 2.95 \times 10^{-8} \text{ molmg}^{-1}$), respectively. The TiO₂ surface after the TiCl₄ treatment provides more specific binding sites, leading to reduce the fraction of the TiO₂ surface area that is inaccessible for the dye due to sterical constraints [56]. The enhanced dye loading results in an improvement in photocurrent and indeed, the TiCl₄ treatment is a 28.5% increase in the photocurrent along with a decreased in the fill factor (7.4%) and open circuit voltage (2.3%). (see in **Figure 9(b)** and more discussed in cell properties part (iii)).

		BET & BJH		Absorption Properties			Electrical Properties				Solar Properties			
		Surface area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	TiO ₂ mass (mg/cm ²)	λ_{max} (at 498 nm)	# of mole. ($\times 10^{-8}$ mol /mg)	D_{eff} ($\times 10^{-5}$ cm ² s ⁻¹)	R_k/R_w	n_s ($\times 10^{18}$ cm ⁻³)	R_{total} (Ω)	V_{OC} (V)	J_{sc} (mA/cm ²)	FF (%)	EFF (%)
(a)	TiO ₂	53.29	0.348	2.3	0.267	2.95	0.84	1.72	4.81	41.6	0.796	9.725	70.6	5.46
(b)	HT- TiO ₂	65.33	0.607	2.6	0.410	3.65	2.58	2.38	9.39	31.5	0.815	12.38	72.2	7.28
(c)	w TiCl ₄	55.98	0.445	2.9	0.504	3.97	3.24	2.14	11.2	23.7	0.796	15.92	66.8	8.47
(d)	w CF ₄ (10 min)	—	—	2.3	0.390	3.48	3.45	3.13	5.15	29.3	0.852	10.29	76.0	6.67
*	w CF ₄ (30 min)	—	—	1.4	0.211	2.45	2.11	2.84	3.24	58.9	0.838	6.52	75.1	4.10
(e)	w TiCl ₄ /CF ₄	—	—	2.6	0.432	3.72	2.59	2.52	8.14	19.8	0.835	13.68	74.5	8.50
(f)	w CF ₄ /TiCl ₄	—	—	2.6	0.503	3.94	4.12	2.48	10.4	13.1	0.813	15.75	71.8	9.20

Table 2.
*Parameters for the best fit of the impedance data for the different interfacial modified DSSC film. Measured in **Figures 9** and **12**.*

Figure 9. (a) Absorbance curve of aqueous dye solutions after desorption (b) JV characteristics and (c) EIS analysis from the pristine TiO_2 , and hydrothermal treated TiO_2 film with and without post-treatment with TiCl_4 (inserted in simple illustration of TiCl_4 treatments).

3.4.2 Fluorine plasma etching

As mentioned above, the best efficiency of cell can be found at about $11.5 \mu\text{m}$ thicked TiO_2 film. This resulting data shows mediately the importance of electrolyte's infiltration all of the way into the TiO_2 film. To minimize the effect on the penetration issues, plasma etching technique is introduced for widening the channels in TiO_2 films [51]. **Figure 10(a)** displays a schematic diagram of the plasma etching system. The detailed etching condition can be found in our earlier paper [51]. As etching gas, CF_4/O_2 of gas mixture (CF_4 and O_2) is used by generating the fluorine atoms in the plasma through complicated chemical reaction paths [58–62]. The plasma etching reaction is followed by:

TiO_2 surface is subsequently etched by free fluorine gas and several titanium fluoroxy compounds (ultimately TiF_4) are developed [61, 63]. Along with the etching process, it was expected that the surface of the NP would be populated with fluorine atoms and bonded to Ti sites as discussed below.

The evidence of etched TiO_2 surface can be found by X-ray photon spectroscopy (XPS) measurement. The peak is located at binding energies 458.5 eV ($\text{Ti } 2\text{p}^{3/2}$) and 464.2 eV ($\text{Ti } 2\text{p}^{1/2}$), respectively, which correspond to the signals characteristic for the Ti^{4+} state of titanium [64, 65]. This indicates that TiO_2 are formed. (see in **Figure 10(b)**). After plasma treatment the peak locations move to the somewhat higher binding-energies of 458.7 and 464.4 eV. The direct bonding with titanium and fluorine makes it possible to move higher binding-energy due to fluorine exhibit more electronegative than oxygen. From XPS analysis, the post-plasma F 1s peak shows is also indicative of the fluorine being bonded directly to the titanium. The majority of the F 1s peak (99%) is found at 684.8 eV which has been responsible for TiOF_2 . The minor (1%) energy shoulder at 686.8 eV is ascribed to the replacement of oxygen lattice site in TiO_2 by fluorine [66]. The fluorine shows at

Figure 10.
(a) Schematic diagram of the plasma etching system (b) pre- and post-etch Ti 2p, post-etch F 1 s XPS spectrum, and pre- and post-etch XPS O 1 s spectra. Reprinted from [51].

~14% the oxygen level. Two O 1 s peaks are observed prior to plasma treatment. The major peak with ~90% of the total oxygen is measured at a binding energy of 529.8 eV and 531.4 eV for Ti-O and Ti-OH bonding, respectively [67]. The plasma treatment make the TiO₂ peak move a little higher binding-energy of 529.9 eV.

Figure 11(a) shows SEM images of pre and post fluorine-treated films. It is clear from these images that fluorine effectively opens the channels among the NPs of the TiO₂ film. The variance of film thickness and weight as a function of plasma etching time can be seen in **Figure 11(b)**. With increased etching time, quantitative analysis (EDS) and morphology (SEM) of TiO₂ surface reveal the plasma expand the pores of the TiO₂ film surface. As the pore start to open up (~10 min), the surface etching process of removed TiO₂ and incorporated fluorine into the film is accelerated by active fluorine species. The detailed information can be found in our eailr paper [51].

As seen in **Figure 12(a)**, the plasma etched TiO₂ surface can rectify the interfacial property by decreased the electron-triiodine recombination rates taking place on the parts of the dye uncovered TiO₂ surface. According to CF₄ etching process, it function as diminishing the surface defects such as oxygen vacancies since fluorine atom comprised of stronger affinity for electrons compared with oxygen atom can

Figure 11.

(a) SEM images of top and side views of pre-etch film and CF_4 -etched TiO_2 film. (inserted in simple illustrations of etched film) (b) film thickness, weight and film morphologies images (top) and relative content of oxygen and fluorine in TiO_2 NPs (bottom) as a function of etching time. Reprinted from [51].

Figure 12.

(a) Schematic illustration for TiO_2 surface interfacial mechanism (b) JV curve and (c) AC impedance measurements of cells with different surface treatments.

enfeeble the bond in a titanium and oxygen [68]. Therefore, the TiO_2 surface comprised of less surface defects may play important role in a improvement of the open-circuit potential, V_{oc} , of the solar cell.

3.4.3 Cell properties for interfacial modification

The detailed solar cell research studied a series of five cells, each with a layer of $11.6 \mu\text{m}$ thick TiO_2 NP film. Each of the four samples were treated differently prior

to dye and electrolyte infiltration. As a first series of cells, TiO₂ film prepared for cell (a) commercial and cell (b) hydrothermal treatment is studied. Next, for understanding the influence on interfacial modified TiO₂ surface, post-treated cells with cell (c) with TiCl₄ treatment and Tare cell (c) with fluorine etching are investigated. **Figure 12(b)** and **(c)** give, respectively, the $J - V$ and the impedance measurements of each cells. Using the kinetic model discussed in section and extrapolating the parameters for the best fit to each of the measured impedance curves, summarized the results in **Table 2** for the electrical data for all cells. The model calculation and data fitting provide some physical insight into the differences in the transport properties and effects due to plasma etching of the TiO₂ NP films of the cells. Cell (b) can be considered as the control for the other three cells. There is no treatment to the TiO₂ NP film in this case. In general, J_{sc} can be approximated by the expression;

$$J_{sc} = q\eta_{lh}\eta_{inj}\eta_{cc}I_0 \quad (34)$$

where q is the elementary charge, η_{lh} is the light harvesting efficiency of a cell, η_{inj} is the charge-injection efficiency of the excited dye into the TiO₂, η_{cc} is charge collection efficiency, and I_0 is the incident photon flux [69]. From this equation, it is clearly that the short-circuit current density (J_{sc}) is directly proportional to the value of η_{lh} related to numerous specific anchoring sites on TiO₂ surface for dye absorption and light scattering events for optical absorption as an external property. As we mentioned earlier, the η_{cc} is related to the charge transfer kinetics and this value can be estimated by comparing the charge transport and recombination time constants when both values are measured by EIS measurements.

Cell (c) has a 25.5% increase in the D_{eff} , leading to about 19.3% increased electron density (n_s) compared with the cell (b). With increasing electron density, deeper traps become filled, and trapping/detrapping events occur more frequently in shallower traps, leading to faster transport. The increase in the photocurrent density is well explained by the higher electron density. However, the value of R_k/R_w related to the recombination related value is decreased by about 10%, leading to a decrease Voc. Cell (d) with the plasma etched device shows the resulting values for about 45.2% lower the charge density value (n_s), 31.5% higher the interfacial recombination rate (R_k/R_w) and 33.4% increased D_{eff} rather than that of the unetched sample (cell (b)). Although the fitted charge transfer properties on etched sample are substantial, the overall performance of cell is infinitesimal because the efficiency just increased by about 8% with etching.

These changes show that the etching has significant effect on the electron recombination and transport properties of the cell, but the overall effect is not pronounced because the cell efficiency only increased by 8% with etching. As suggested in **Figure 12(a)**, the fluorine etching can help to minimize the electron loss between TiO₂ surface and reduced iodide, leading to the highest V_{oc} and FF value (~ 0.852 V and 75.1%). The decreased electron transport properties are attributed to the less interconnection between NPs compared to the case of cell (b). However, when a film is treated in the much more time (~ 30 min), the morphology changed dramatically, and the pin-hole of TiO₂ film formed. This result can be confirmed by the dye desorption experiments and the weight loss of TiO₂ from etching process. While this situation should improve the dye molecule attachments to the NPs and allow further penetration of the molecules into the TiO₂ film, as indicated by a large increased in the values of D_{eff} in **Table 2**.

Finally, we believe that combination of TiCl₄ and fluorine etching post-treatment with the opposite physical properties make it possible to increase both the V_{oc} and J_{sc} , giving an efficiency higher than that of cell (b). Therefore, cell (e) is

treated with TiCl_4 coating with same treatment as cell (c), followed by fluorine etching with same treatment as cell (c), and cell (f) with the TiO_2 NP film etched by fluorine first and followed by TiCl_4 treatment and then high-temperature. As we expected, cell (f) has the lowest series resistance (i.e., $R_{\text{total}} = R_0 + R_1 + R_2 + R_3$) and therefore the highest efficiency. The contribution to this increase of cell efficiency comes primarily from the 27.7% increase in J_{sc} , no loss in the V_{oc} and FF value. It also notice from our model that the effective electron diffusion coefficient is a significant improved by as much as 59%, the interfacial recombination (k_{eff}) is decreased by 52.7%, which leads to large R_k compared with the cell (b). These changes are quite significant, and as a result, the cell efficiency was increased nearly 26%.

4. Photon management using three-dimensional photonic crystals

Besides the interfacial modification, cell performance can be improved by external source (such as anti-reflection film and photonic crystal etc.) as reflecting passed photons back into the absorbing film [26, 70]. For the photon trapping, two approaches for geometrical or wave optics are employed [71]. In this book, photon management concept using 3-dimensional photonic crystals (**PhC**) is introduced. Photonic crystals are highly ordered materials with a periodically modulated dielectric constant. The presence of photonic band gap can be confining and controlling the propagation of light propagation of light, a band of frequencies in which light propagation in the photonic crystal is forbidden [72]. Therefore, we can manage to reflect, transmit, and diffract light for specific wavelengths by appropriate designing the crystal structure. In fact, a diffuse scattering layer of large TiO_2 colloids [73] is typically introduced for this specific purpose [74]. There are successful demonstrations for enhancement in performance of silicon photovoltaic cells based on the realization of coherent scattering processes [75–81]. However, these concepts cannot be easily realized in DSSC. Herein, this book takes the most efficient cells and measure how much of the income light is actually being absorbed by the N719 dye as photons transit across the solar cell.

4.1 Photon management effect on DSSCs

For 3D PhC layer, the vertical deposition technique for polystyrene (PS) opal templates is employed [55] (see in **Figure 13(a)**). The experimental procedures are reported in earlier work [82, 83]. **Figure 13(b)** is a SEM micrograph of a ZnO PhC (or inverse opal) layer showing both the side view (cross sectional, top) and top view (bottom).

The optical property can be estimated by using UV- vis- NIR spectrophotometer in a wavelength range of 185 ~ 3300 nm. The quantum efficiency and transmission of the N719 cell with a thickness of about 11.5 μm as a function of the wavelength is shown in **Figure 13(c)** [76]. N719 dye displays a broad absorption spectral coverage in the region 400 ~ 700 nm, but a large proportion of infrared (IR) spectral range, which constitutes almost half the energy of the sun's radiation, cannot be utilized.

To make up for insufficient photon absorption, a reflector by either using a Ag mirror or a stack of the PhC was simply attached to the bottom cell or cathode electrode (**Figure 14(a)** and **(b)**). As seen in this illustration, there are two physical mechanisms by which wave optics approaches (based on reflector and photonic crystals) can improve light-trapping: reflection and diffraction. Firstly, Ag film can provide high reflection property like a mirror. Distributed Bragg reflectors exhibit high index contrast and they can reflect light over a extensive wavelengths region and incident light angles [84]. Likewise, a PhC can reflect incident light from broad

Figure 13.
(a) Fabrication procedure of the 3D PhC, (b) SEM micrograph of a typical ZnO PhC (or inverse opal) layer, showing both the side (cross sectional) view (top) and the top view (bottom) (c) quantum efficiency measurement of the N719 dye and the transmittance measurement of DSSCs using the same dye.

Figure 14.
Schematic of a DSSC (a) with a typical geometric optic concept of reflection to trap light. And (b) with wave optics (3D PhC) to trap light with reflection and diffraction (c) reflection spectra of Ag film and 3D PC with different sphere diameters (198, 311, 375, and 410 nm).

range of angles for frequencies and polarizations within the photonic crystal in that it can reflect light within the bandgap incident from any angle or medium.

Secondly, wave optics-based devices were developed for diffracting incoming beams into indirect angles according to Bragg's law [85]. The diffraction originated from an interface improves light trapping with the distance increment that light

must go forward to the front surface of the cell as well as diffracted beam are internal reflected back into the solar cell when the angle of critical angle overcome the diffracted beam [86].

Figure 14(c) shows the reflection spectra of Ag film and 3D PC with 198, 311, 375, and 410 nm diameters. The reflectivity of the Ag film is more than 80% in wavelengths ranging from 400 to 800 nm; clearly, this Ag film has better reflectivity than the 3D PC. The red line represents the spectrum from the 198 nm inverse opal sphere; a reflection peak can be observed at 410 nm corresponding to the lowest photonic band gap (PBG). The orange line represents the spectrum from the 311 nm inverse opal sphere that shows the main reflection peak at 526 nm corresponding to the lowest PBG and additional reflection spectra peaks at 382 and 365 nm. The blue line shows the reflection spectrum of the 375 nm inverse opal sphere: it comprises a reflection peak at 661 nm corresponding to the fundamental PBG and additional reflection spectra peaks at 415 and 390 nm. The green line shows the reflection spectrum of the 410 nm inverse opal sphere that has a main reflection peak at 715 nm corresponding to the lowest PBG and additional reflection spectra peaks at 442 and 411 nm. The 3D PC show reflectivity peaks amplitudes of around 73% at the lowest PBG and around 25% at the high order PBG. This implies that we can recycle the photons back into the DSSC for further absorption and processing. The peak positions can be related to the sphere diameter and the effective refractive index of the medium using Bragg's law, $\lambda_{max} = 2n_{eff}d_{111}$, where d_{111} is the 111 lattice spacing and n_{eff} is the effective refractive index of the medium. Furthermore, the differences in the frequency of the reflection peaks are a result of the different sizes of the inverse opal spheres because the same effective refractive indices (ZnO) of the medium were used in all the experiments. Thus, the 3D PC can be devised to present a Bragg peak that matches the absorption band of the ruthenium dye but has a significant effect on longer wavelengths, thereby increasing the absorption efficiency.

4.2 Measurements and modeling of DSSCs with 3D PhC

The effects of selective light trapping, which was caused by the reflection and diffraction by 3D PhCs, on the solar-to-electric conversion efficiencies and AC impedance measurements of the cell, are analyzed by measuring the photocurrent-density-voltage ($J-V$) curves under simulated sunlight radiations of 1000 Wm^{-2} intensity. From a series of $J-V$ curves, samples coupling with Ag and PhC reflector display the increased photocurrent (seen in **Figure 15(a)**) The corresponding impedance measurements are plotted in **Figure 15(b)**, and the solid curves

Figure 15. (a) $J-V$ characteristics and (b) Nyquist plots of DSSC attached Ag metal and different sized PhC reflection (film thickness $\sim 11 \mu\text{m}$).

		$D_{\text{eff}} (10^{-5} \text{ cm}^2 \text{ s}^{-1})$	$k_{\text{eff}} (\text{Hz})$	$\tau_{\text{eff}} (\text{ms})$	R_k / R_w	$Con (\Omega \text{ cms}^{-1})$	$R_d (\Omega)$	$n_s (10^{18} \text{ cm}^{-3})$	$D_1 (10^{-6} \text{ cm}^2 \text{ s}^{-1})$	$V_{\text{OC}} (\text{V})$	$J_{\text{sc}} (\text{mA} / \text{cm}^2)$	$FF (\%)$	$EFF (\%)$
non		2.153	7.52	132	2.48	0.067	3.3	10.4	0.48	0.815	15.74	71.5	9.18
w Metal		2.273	7.52	132	2.54	0.069	3.0	10.6	0.06	0.818	16.58	71.2	9.64
w 3D PhC (nm)	198	2.175	7.52	132	2.60	0.064	3.0	10.5	0.06	0.815	16.00	71.7	9.36
	311	2.506	7.52	132	2.97	0.065	3.5	10.8	0.01	0.813	17.16	70.9	9.89
	375	2.725	7.94	125	3.06	0.068	3.0	10.9	0.12	0.818	17.51	70.9	10.1
	410	2.807	7.94	125	3.15	0.068	4.3	10.8	0.01	0.813	17.52	71.8	10.2
	Double (375/410)	2.647	7.94	125	2.97	0.068	3.7	11.1	0.12	0.812	18.10	71.4	10.5

Table 3.
Parameters for the best fit of the impedance data and Photovoltaic for the different sized 3D PhC attached DSSC film. Measured in Figure 15.

represent the best fits from our modeling calculations. The fitting parameters are tabulated in **Table 3**. (the photoanode comprised 11 μm thick TiO_2 film and approximately 0.332 cm^2 active area with mask). The DSSC with the Ag film and 3D PCs showed higher short-circuit current densities and solar-to-electric conversion efficiencies than the traditional DSSC. For the Ag film, the short-circuit current densities were increased by approximately 0.84 mA/cm^2 ; the open-circuit voltage and fill factor were almost identical; and the solar-to-electric conversion efficiency was enhanced by 5%.

In the case of the DSSCs with 3D PhCs, the solar-to-electric conversion efficiencies were enhanced by 1.94, 7.78, 10.7, 11.3 and 14.4% for the 198 nm, 311 nm, 375 nm, 410 nm, and double layer (375/410 nm), respectively, as compared to the traditional typed DSSC. The 3D PC with 198 nm sized PhC showed the lowest efficiency enhancements because the traditional DSSC absorbed most of the light, this corresponds to the reflection peak of this PhC, as shown in **Figures 13(c)** and **14(c)**. The 375 nm and 410 nm sized PhC showed high enhancements in the solar-to-electric conversion efficiencies because the traditional DSSC transmitted more than 50% of the light; this corresponds to the reflection peaks of these PhC. This enhancement in the solar-to-electric conversion efficiencies is higher than that in the Ag film even though the Ag film has a considerably higher reflection intensity; this can be explained by the diffraction effect of the PhC as shown in **Figure 14(b)**. The PhC with 375/410 nm double layers showed highest enhancements in the solar-to-electric conversion efficiencies because the double layer PhC has a significant overlap with the quantum efficiency spectra of the ruthenium dye; moreover, the diffraction effect of the PhC is also present. From **Table 3**, the multilayer whose PBG has a large overlap with the quantum efficiency spectra of the ruthenium dye leads to larger enhancements in the photocurrent. Furthermore, the PhC-based DSSC exhibits considerably higher short circuit photocurrents than the traditional DSSC and is much more effective than the conventional Ag film.

The generation of photocurrent is primarily influenced by the light absorption of the dye. Therefore, when coupling PhC with the back surface of the DSSC, light absorption is increased attributed to the reflection and diffraction of light. This directly reflect the enhancement of the short-circuit current densities and the overall efficiency, while the open-circuit voltage, fill factor is unaffected. The DSSC with the PhC of 375, 410 nm and double layer diameters showed higher conversion efficiency than that with the Ag film; this can be explained not only by the reflection but also the diffraction effect in the DSSCs. As a result, we demonstrated here that recycling of photons by PhC is an effective way to increase the cell efficiency.

5. Nanostructures TiO_2 electrode in DSSC from 0 to 3 dimensions

As the main core of DSSCs, the nanocrystalline morphology of the photoelectrode film is critical for the efficient operation. Large efforts have been paid to optimize the morphology of the nanostructured photoanodes with improved architectures for high dye loading and fast electron transport. Although 2-step HT-NPs films treated with the interfacial modification have been regarded as a paradigm of porous photoelectrode for use in DSSCs, there are still challenges to boost the photovoltaic performance or competitiveness. Therefore, the metal oxides in their nanoform can be synthesized under various morphologies with different shapes and sizes, thus offering the possibility for modulating their properties. In literature, a variety of preparation techniques, such as sol-gel, [87] hydrothermal/solvothermal, [88] electrochemical anodization, [89] electrospinning, [35] spray pyrolysis, [90] and atomic layer deposition [91], have been developed and applied

Figure 16.
 SEM images of different types of 0D 1D 2D 3D- TiO_2 . Produced in our lab.

to obtain different morphologies in photoanode materials. In this study, a variety of nanostructures from zero dimensional (0D) to three dimensional (3D) has been tested. Electro-spinning and spraying technique has been adopted to prepare the the different dimensional metal oxide semiconductor film by controlling the polymer host and solvents. The detailed results can be seen in followed section (**Figure 16**).

5.1 Titanium dioxide (TiO_2) nanomaterials as a photoelectrode

Various typed metal oxide semiconductors such as TiO_2 , ZrO_2 , SnO_2 , ZnO , Nb_2O_5 , Fe_2O_3 , Al_2O_3 , (binary compounds) and and ternary compounds such as SrTiO_3 and Zn_2SnO_4 can all act as photoelectrodes in DSSC due to their electronic structures which are characterized by a filled valence band and an empty conduction band [7, 92]. Among these heterogenous semiconductors, TiO_2 is the most widely used photoelectrode material because of the large amount of grain boundary and the large interface between the TiO_2 surface, dye and the electrolyte in the solar cell, further defects in the crystal structure are expected. In TiO_2 , the Ti ions are in a distorted octahedral environment and formally have a $\text{Ti}^{4+}(3d^0)$ electronic configuration. The different obital hybridized structure of valence band (VB) and conduction bands (CB) at Ti 3d states occur the decreased the transition probability of electrons to the VB when the electron–hole recombination probability is reduced [92]. Therefore, in view of the electronic configuration and recombination probability TiO_2 are the best choice as photoelectrodes among 3d transition metal oxides. TiO_2 exist naturally four commonly known crystalline polymorphs, i.e., anatase (tetragonal, $E_g = 3.23$ eV), rutile (tetragonal, $E_g = 3.05$ eV), brookite (orthorhombic, $E_g = 3.26$ eV) and metastable forms (monoclinic, orthrhombic, cotunnute) [93]. These structures can be described in terms of chains of TiO_6 octahedra. The crystal structures differ in the distortion of each octahedron and by the assembly pattern of the octahedra chains [94]. The crystalline struncture of TiO_2 can be seen in **Figure 17** [95]. Both rutile and anatase have tetragonal structure with $a = 0.46$ nm and $c = 0.29$ nm (rutile); $a = 0.3782$ nm and $c = 0.9502$ nm (anatase). Brookite has orthorhombic structure with $a = 0.5456$ nm, $b = 0.9182$ nm, and $c = 0.5143$ nm and it is very hard to synthesize in the laboratory, while the rutile and anatase can be easily prepared. For solar cell application, anatase structure is more prferred because of ~ 0.1 eV higher the Fermi level, lower recombination rate of electron–hole pairs and lower formation temperature [96].

Figure 17.

The schematic TiO_2 structure and the DOS calculated band structure for (a) anatase, (b) rutile and (c) brookite TiO_2 . The big green spheres represent Ti atoms and the small red spheres represent O atoms. Reprinted from [95].

Thermodynamic calculations based on calorimetric data predict that rutile is the stablest phase at all temperatures, exhibiting lower total free energy than metastable phases of anatase and brookite. The small differences in the Gibbs free energy (4 ~ 20 kJ/mole) between the three phases suggest that the metastable polymorphs are almost as stable as rutile at normal pressures and temperatures [97]. The physical and chemical properties of TiO_2 nanocrystals are affected not only by the intrinsic electronic structure, but also by their size, shape, organization, and surface properties. For example, if the particle sizes of the three crystalline phases are equal, anatase is most thermodynamically stable phase below 10 ~ 15 nm, brookite is most stable between 11 ~ 35 nm, and rutile is most stable at sizes greater than 35 nm [98]. Herein, interesting morphologies and properties have recently attracted considerable attention and many nanostructured TiO_2 materials, such as nanotubes, nanorods, nanofibers, nanosheets, and interconnected architectures, mesoporous material such as inverse opal and photonic crystal have been fabricated and applied in PV devices [35, 83, 99, 100]. In order to be effective photoelectrode, several parameters such as morphologies, pore volume, and the crystallinity of TiO_2 influence the charge transport and recombination processes.

5.2 0-dimensional (0D) titanium dioxide (TiO_2) Nanosphere

Particles which are more or less spherical in shape like fullerenes, quantum dots, nano-onions, nanoparticles, etc. are considered as 0D. These 0D nanomaterials are sized at nanoscale level in all three dimensions and must be amorphous or crystalline; single or polycrystalline; and composed of single- or multielement. Within 0D materials, all electrons are fully confined and their length equals the width. Due to confinement of both electrons and holes, the lowest energy optical transition from the valence to conduction band will increase in energy, effectively increasing the band gap. A 0D TiO_2 nanosphere (NS) film is noticed as an effective

photoelectrode because of its structural advantages such as high surface area, submicro- or meso-porous structure for light scattering function and better infiltration of electrolyte. There are several different efforts to produce spheres [101, 102]. Nevertheless, there are limitations for the quality control, large-scale production and flexibility. In this book, a simple electro-spraying technique is introduced [103, 104]. As a first step, well-dispersed TiO_2 suspensions is very important to make a continuous fluid jet. **Figure 18** show the three phase statues during E-spraying process: (i) TiO_2 suspension zone, which strong electric field extracts droplets from Taylor cone (the non-sphere formation), (ii) mixed zone of TiO_2 suspension and solid, which non-spheres and spheres are formed by solvent evaporates, leading to the droplet shrink, and (iii) solidified TiO_2 zone, depositing the TiO_2 NSs onto the conductive glass.

In this system, the formation of tight cluster sphere filled sphere is caused by the ultrafast evaporation of alcoholic solvent under an electric field. For the desirable sphere typed TiO_2 film, it is necessary to control several parameters such as electric field, feed rate, a size of tip and a distance between the nozzle and FTO substrate. It is noted that the sphere size is controlled by changing the TiO_2 concentration and the mixture of solvent in the dispersion solution. In order to find the optimized condition, TiO_2 SPs with the different concentration are tested at 6 μm thick film. **Figure 19(a)** show the SEM results for E-sprayed film prepared from the different concentration at 1 wt%, 3 wt%, 5 wt% and 10 wt%. With increasing the concentration, the diameters of sphere are almost linearly increased, while the number of molecules calculated from UV-vis absorption spectra of desorbed sensitizers reveal that a TiO_2 NSs with 5 wt% have about 11.6% and 13.9% higher value than that of 1 wt% and 10 wt% TiO_2 NSs film, respectively (see **Figure 19(b)**).

Experiemntally, E-spraying at the low weight percent of TiO_2 make it hard to achieve the competely formed sphere over 8 μm thick film. Therefore, in this reaserch, about 5 wt% TiO_2 suspension in EtOH is used as the best condition. The detailed phase diagram accroding to the electro spraying parameters can be seen in the literature [105]. **Figure 19(c)** displays the thickness profiler on the various

Figure 18.
The schematic diagram of the formation of hierarchically structured oD TiO_2 Nanosphere (NS).

Figure 19.

(a) SEM images and (b) absorbance curve of aqueous dye solutions after desorption and (c) the different thickness of E-sprayed TiO₂ spheres at the different concentration a. 1 wt%, b. 3 wt%, c. 5 wt% and d. 10 wt%.

thickness of TiO₂ NSs photoelectrode film. In an E-spraying process, the film can control the feeding volume. **Figure 19(c)** shows the cross-sectional image of an E-sprayed TiO₂ SPs film that demonstrates the uniform shape of the spheres from bottom to top. However, with increasing film thickness, TiO₂ NSs photoelectrode tends to increase the film roughness since intrinsic insulator properties of TiO₂ can influence on an electric field film during depositing process.

Figure 20(a) and **(b)** show SEM images of a distribution of mesoporous TiO₂ NSs in the anode electrode of E-sprayed TiO₂ NSs film. This film exhibits a range of diameters between 100 ~ 800 nm, formed from nucleation and crystallization of 10 nm TiO₂ particles. Also, the existence of such mesopores improved the electrolyte penetration. With the TiCl₄ treatment, a filled sphere with a relatively rough surface is generated. (seen in **Figure 20(b)**) This is beneficial for improving the interconnection between primary particles inside the TiO₂ NSs. **Figure 20(c)** shows a TEM image of the spheres with the crystalline nano particles. The surface area and porosity of both TiO₂ SPs and NPs film can be estimated by N₂ adsorption-desorption isotherm at 77 K (see in **Figure 20(d)**). The SPs films show a type-IV isotherm as well as an increase in the adsorbed amount at high relative pressure, indicating the existence of mesopores in the sample [106]. The measured specific surface area of TiO₂ SPs is ~ 188.47 m²g⁻¹, ~ 2.9 higher than that of similar amount of TiO₂ NPs electrode (65.33 m²g⁻¹). Furthermore, the cumulative BJH mesopore volume and maximum pore radius is 1.194 cm³g⁻¹ and 10.05 nm, respectively, while hydro-thermal nanoparticle film shows the pore volume of 0.607 cm³g⁻¹ and maximum pore radius of 7.50 nm. In the case of TiCl₄ treated SP, the surface area and the cumulative pore volume is decreased by as much as 65.3% and 65.2%, respectively compared with the non-treated SPs film. The amounts of dye adsorbed onto each of the pristine- and TiCl₄ treated TiO₂ SP layers at 11 μ m were 5.80×10^{-6} and 8.19×10^{-5} , respectively.

It shows about 2.1 times increased dye absorption properties compared with the NP. This high density of dye molecules onto TiO₂ NS can be explained by the high

Figure 20. SEM images of E-sprayed (a) TiO₂ NSs and (b) TiCl₄ treated TiO₂ NSs (c) TEM images of the TiO₂ NSs, which themselves are formed from crystallized ~10 nm particle. (d) N₂ adsorption-desorption isotherms of TiO₂ NPs and NSs.

intrinsic surface area of each TiO₂ NSs surface as well as the crack free surface morphology. In general, casting TiO₂ NPs from a polymer supporter for the thick TiO₂ layer onto substrates is by far the preferred method of depositing electrodes for DSSCs. Therefore, heating process at temperature ranging from 450–500°C is necessary to burn out the residual organic binder and to enhance the inter-particle connection between NPs. In this process, cracks are formed at the interface with TiO₂ NPs, leading to deteriorate dye absorption. (see **Figure 21(a)**). In the case of E-sprayed TiO₂ SPs from binder-free, the surface of the e-sprayed TiO₂ layer is uniform and without cracks, unlike the surfaces produced using paste methods as shown in **Figure 21(b)**.

The *J*–*V* curves, EIS analysis and IPCE data and detailed information of dye-sensitized NPs and SPs film of the same thickness with mask (0.220 cm²) at 1 sun light intensity are shown in **Figure 21(c)** and **(d)** and **Table 4**, respectively. Their photocurrent density is almost the same (10.6 mA/cm²), and *V*_{oc} of the SP-based solar cell (0.831 V) is only about 2% higher than that of the anatase-based cell (0.815 V). The respective overall energy conversion efficiencies of the NPs and SPs-based cells are a 7.28% and 7.46%. The predominant increase of cell efficiency at the TiO₂ SPs film can be obtained by TiCl₄ treatment because of the enhancement of the interconnection between TiO₂ SPs, which illustrated in **Figure 20(b)**. The TiCl₄ treated sample represents a 21.0% increase in the energy conversion over the non-treated SPs. This increment of SPs films is about twice higher than that of NPs because the presence of intrinsic microporous SPs structure, which make its more open structure increase amount of I₃[–] a in the pores. From the suggested impedance models, I confirm the electron diffusion coefficient rate of triiodide *D*₁ for TiCl₄ treated SP film is 4.3 × 10^{–7} cm²S^{–1}, 53% higher than that obtained from TiCl₄ treated SP film, at 2.1 × 10^{–7} cm²S^{–1}. This increase is in good agreement with the increase of *V*_{oc} and *FF* observed in **Figure 21(c)**. Hence the SPs based cell plays a key role in attaining the higher cell efficiency with solid state electrolyte.

Figure 21.

SEM images of TiO_2 film (a) doctor bladed and (b) E-sprayed TiO_2 film. (c) and (d) JV and IPCE data for TiO_2 NSs films.

Interestingly, despite of the decreased charge density of SPs film, the photocurrent density is nearly the same. This reason can be explained by scattering effect on the SPs film. **Figure 20(d)** shows the IPCE curves for each sample range from 350 to 800 nm. The films with SPs layer the entire IPCE curve is slightly shifted upward in the region between 550 and 800 nm. With TiCl_4 treatment, the increase is more pronounced, which is good agreement with those reported by Sommeling [56]. The effect of scattering clearly results in a much larger improvement of the red response than originates from the higher dye loading.

5.3 1-dimensional (1D) titanium dioxide (TiO_2) nanorod

One-dimensional (1D) nanostructures (e.g., nanowires, nanorods, nanotubes, nanobelts, cauliflower-shaped structures) have been widely considered to have superior electron transport characteristics compared to conventional nanorod (NP)-based systems. Earlier reported research have demonstrated that highly efficient TiO_2 nanorod-based NR DSSCs and compare charge transport properties to those of typical TiO_2 nanoparticle-based (NP, commercially available P-25) NP-DSSCs [35]. The electrospun TiO_2 NR based photoelectrodes exhibited about 2 times larger the pore volume and ~ 2.5 times more dye coverages at the same weight than those of TiO_2 NP. Therefore, NR based cell indicated about 40% higher efficiencies than NP-DSSCs attributed to ~ 8 times slower electron-hole recombination in NR-DSSCs. With the TiCl_4 post-treatment, further enhancement of electron diffusion coefficient, a charge collection efficiency and the efficiency can be demonstrated [35].

5.4 2-dimensional (2D) titanium dioxide (TiO_2) nanosheets

Two-dimensional (2D) anisotropic nanostructures of metal oxides and semiconductor possess pronounced quantum surface effects and dramatic changes in electronic structures and thus in the physical and chemical properties, which are

		BET & BJH		Absorption Properties		Electrical Properties				Solar Properties				
		Surface area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	λ_{max} (at 498 nm)	# of mole. ($\times 10^{-8}$ mol /mg)	D_{eff} ($\times 10^{-5}$ cm ² s ⁻¹)	R_k/R_w	n_s ($\times 10^{18}$ cm ⁻³)	D_1 ($\times 10^{-6}$ cm ² s ⁻¹)	R_{total} (Ω)	V_{OC} (V)	J_{sc} (mA/cm ²)	FF (%)	EFF (%)
NP	—	65.33	0.607	0.410	3.65	2.58	2.38	9.39	0.32	31.5	0.815	12.38	72.2	7.28
	w TiCl ₄	55.98	0.445	0.504	3.97	3.24	2.14	11.2	0.21	23.7	0.796	15.92	66.8	8.47
SP	—	188.47	1.365	0.514	5.80	1.83	6.79	6.07	0.78	33.0	0.831	12.28	73.1	7.46
	w TiCl ₄	114.0	0.915	0.772	8.06	3.29	3.39	9.40	0.45	19.2	0.829	15.96	71.4	9.45
	w TiCl ₄ / 3D	—	—	—	—	3.49	3.13	10.0	0.43	18.2	0.827	17.24	71.3	10.1

Table 4.
*Parameters for the best fit of the impedance and Photovoltaic data for doctor bladed and E-sprayed TiO₂ film. Measured in **Figure 21**.*

anticipated to inspire new fundamental and technological research [107]. In my earlier research, TiO_2 or ZnO nanofiber mat is used for employing DSSC. [108, 109] For empolying 2D TiO_2 film for DSSCs, two different technique are used for TiO_2 photoelectrode: (1) Nanofiber (NF) mats produced by electrospinning: (2) Nanotubes (NT) film from 2-step hydrothermal method. As see in **Figure 22(a)**, TiO_2 /poly(vinly acetate, PVAc) composite fiber mats are directly electrospun onto a FTO glass and then polymer binders are removed by two step process: (i) a THF solvent tratement for melting PVAc polmyer, (ii) calcination this mat at 500°C for 30 min. With the post treatment, the adhesion issues between TiO_2 NFs or NFs and FTO glass can be overcome. The TiO_2 NTs film is prepared from adjusting pH values [110]. Following this method, the well-grown NT poweders are deposited by mixing a mixture of PEO/PEG polymer binder as described in a section of “DSSC Fabrication for Conventional typed Cell.”

The detailed surface and cross sectional images can be confirmed by the SEM images (1.22(b)). as can bmodified 2-step hydrothermal process. **Figure 22(c)** show the nitrogen adsorption–desorption isotherm and Barret–Joyner–Halenda (BJH) pore size distribution plot of the NF mats and NT film, respectively. The specific surface area and pore volume of both samples is very small and it is difficult to obtain a sufficient photocurrent density. In agreement with the BET analysis, the JV curve of all cells display an obviously low photocurrent density, leading to the poor cell efficiency.

5.5 3-dimensional (3D) titanium dioxide (TiO_2)

In the section of “Photon Management using Three-Dimensional Photonic Crystals”, the effective use of three-dimensional photonic crystals (3D PhC) for photon management in our cells was demonstrated. Here, 3D PhC is used as a photoelectrode for DSSCs. An important approach to enhance DSSC efficiency is to increase the path length of light by enhancing light scattering in TiO_2 films by

Figure 22. 2D TiO_2 film (a) TiO_2 nanofiber (NF) film prepared by E-spraying technique (b) TiO_2 nanotube (NT) film by hydrothermal treatment. (c) JV and BET analysis of each cells.

coating the large particles onto the small sized of TiO₂ NPs [111]. To understand the effect on the PhC coupled DSSCs that feature enhanced photocurrent over a large spectral region, a double layered photoanode integrates a high surface mesoporous underlayer TiO₂ with an optically active TiO₂ PhC overlayer is fabricated as illustrated in **Figure 23(a)**. For the FTO/3D TiO₂ PhCs structure, the polystyrene (PS) opal template of sphere size 370 nm was prepared using a vertical deposition technique onto the nc-TiO₂ film and then TiO₂ is coated by ALD. The inverse opal structure can be made by ion etching (CF₄ 5 min).

Figure 23(b) shows the J-V curves for the different sized 3D PhC at liquid electrolyte. (as seen above) When the size of hole is increased from 198 nm to 410 nm, the V_{oc} values increased from 0.787 V to 0.849 V. The 311 nm 3D PhC bilayer exhibits the best PCE, which is a 46.1% increase in J_{sc} (8.657 mA/cm²) and 36.2% increase in PCE (5.102%) compared to the NPs layers (7.064 mA/cm² of J_{sc} , 3.258% of PCE) The significant improved PCE of 3D PhC indicates that the 3D PhC top layer is electrically connected and contributes to light harvesting over the entire spectrum.

Moreover, large porosity structures of the inverted 3D TiO₂ PhCs have enabled good infiltration for high-viscosity electrolytes. For solid state cell fabrication, we have chosen (P_{1,4}I)-doped succinonitrile plastic crystal electrolyte [112, 113]. This electrolyte has the best performance for solid state DSSC as reported in the literature [114]. At a room temperature, this compound electrolyte has a high conductivity of 3.3 mS/cm and fast ion transport of iodine and triiodine in its plastic phase of 3.7×10^{-6} and 2.2×10^{-6} cm²/Vs, respectively. The observed fast ion transport in this solid material can be seen as a decoupling of diffusion and shear relaxation times, which probably originates from local defect rotations in the succinonitrile plastic crystal [115–117]. Thus, this plastic electrolyte showed best high cell efficiency among other competing electrolyte materials. **Figure 23(c)** top shows the molecular structure of the compound. For better cell performance, we firstly injected the liquid state electrolyte into TiO₂ NP film and evaporated this electrolyte by putting it in the dry oven at 80°C for 12 hour. Next, the plastic electrolyte was heated until it became a liquid (>70°C) and injected into the warmed sandwiched cells. After the cells included the plastic electrolyte was cooled down to room

Figure 23. 3D TiO₂ film (a) schematic design (b) JV characteristics of 3D PhC TiO₂ at the different size (c) solid state results.

temperature, a waxy solid was obtained. **Figure 23(c)** shows the JV curve for solid state of 311 nm 3D PhC bilayer. Interestingly, no obvious efficiency change could be seen in all typed solid state electrolyte. The PCE of the solid state system is found to be 2% of that of the liquid electrolyte system. In conclusion, the design of 3D PhC bilayer film enables effective dye sensitization, electrolyte infiltration and charge collection because the layers are in direct physical and electronic contact, light harvesting in specific spectral regions was significantly increased by the 3D PhC effect and PC-induced resonances. This approach should be useful in solid-state devices where pore infiltration is a limiting factor as well as in weakly absorbing photovoltaic devices.

6. Photosensitizer for DSSC: state of the art.

6.1 Ruthenium (Ru) complex based photosensitizer

Since the advent of DSSCs, ruthenium-series dyes are considered as the most powerful photosensitizer because of the following reason: their strong metal to ligand charge transfer transition (MLCT) process, a broad absorption spectrum, suitable excited and ground state energy levels, relatively long excited-state life-time, and good (electro) chemical stability and power conversion efficiency (PCE) >11% [7]. In order to improve the efficiency of DSSCs, the sensitizer should be panchromatic, that is, absorb photons from the visible to near-infrared (NIR) region of the solar spectrum while maintaining sufficient thermodynamic driving force for the electron injection and dye regeneration process. Many efforts have been made to change the change the ligands of Ru complexes: [118, 119] As seen in **Figure 24**, ruthenium(II) – polypyridyl complexes such as the thiocyanato derivative, *cis*-(SCN)₂ bis (2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(II), (coded as N3), the doubly protonated form, (Bu₄N)₂(Ru(dcbpyH)₂(NCS)₂), (named N719)

Figure 24.

Incident photon to current conversion efficiency as a function of the wavelength for the standard ruthenium sensitizers N3 (red line), N719 (brown) the black dye N749 (black curve), and the blank nanocrystalline TiO₂ film (blue curve). Reprinted with permission from [7, 120, 121].

and the Ru center has three thiocyanato ligands and one terpyridine ligand substituted with three carboxyl groups, (also called the “**black dye**”) are widely used as reference and high efficiency sensitizers for DSSCs. The amphiphilic heteroleptic ruthenium sensitizer, known as **Z907**, reported noticeable thermal stability with stable 7% energy conversion efficiency [114]. For optimized DSSC with N3 or N719, the certified IPCE values are ~80% for wavelengths ~650 nm.

However, the IPCE increases only gradually from the absorption onset to shorter wavelengths due to relatively low extinction coefficients ($1.40 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) [7, 47]. In addition, this class of compounds contains expensive ruthenium metal and requires careful synthesis and tricky purification steps. Therefore, efforts in the synthesis of sensitizers for DSSCs step forward to the metal-free organic donor–acceptor (D–A) dyes system.

6.2 Porphyrins based sensitizer

The idea for mimicking the light harvesting processes based on chlorophyll occurring photosynthetic reaction centres inspire the research for porphyrins based sensitizer. The porphyrin-based dyes exhibit large absorption coefficients in the visible and infrared region as well as their rigid molecular structures consisted of four meso and eight β reaction sites, which can control their properties [122–124]. The designed porphyrin dyes with a π -conjugated link at the β -position of the porphyrin ring enhance the electronic coupling of the dye with the surface of TiO_2 , reaching $\eta = 7.1\%$ of a PCE [125]. Numerous series of porphyrins are reported for the DSSC application as an effective sensitizer. of DSSC synthesized. Among them, a class of sensitizer consisting of a push–pull porphyrins with an electron-donating diarylamino group and an electron-withdrawing carboxyphenylethynyl anchoring group shows the outstanding solar properties. For example, advances in optimization of the device performance for a zinc porphyrin sensitizer (YD2-oC8) co-sensitized with an organic dye (Y123) using a cobalt-based electrolyte to enhance photovoltage of the device attained an unprecedented power conversion efficiency of $\eta = 12.3\%$ [126]. (see **Figure 25(a)**) Further improvement can be found at

Figure 25.
(a) Typical structure of a porphyrin showing the four meso- and the eight β -positions to be functionalized for porphyrin-sensitized solar cells. Reprinted from [122, 123] (b) solar performance for the different series of porphyrin based DSSC at liquid electrolyte and TiO_2 NSs.

incorporation of the proquinoidal benzothiadiazole (BTD) unit into the functionalization of the porphyrin core with the bulky bis(2',4'-bis(hexyloxy)-(1,1'-biphenyl)-4-yl)amine donor and a 4-ethynylbenzoic acid yielded the green dye, which exhibited a slightly improved PCE of 13% [127]. The detailed physical and structural studies responsible for recent advances of the porphyrin-based DSSCs have been reviewed in several reports [122–124]. Thanks to Yeh group's support, various porphyrin with the different structure based sensitizers can be tested in my optimized condition and the detailed performance listed in **Figure 25(b)**. Interestingly, the cell performance is gradually improved upon light exposure and heat treatment. Specially, after 90 min light exposure, cell performance increased from 6.12% to 7.71% attributed to the increase of J_{sc} value (see **Figure 26(a)-(c)**). The improvement can be explained by the different charge recombination process. According to Mori et al., Li^+ ions are removed from the TiO_2 surface and replaced with $DMPIm^+$ ions under light exposure [128, 129]. This process is found to enhance the electron lifetime by decreasing charge recombination with the redox mediator (**Figure 26(d)**). This can be explained by initial limited injection and fast charge recombination processes. As a result, this process enhances the cell performance by decreasing recombination with the redox mediator. However, about 20.1% improved cell efficiency by light exposure indicate YD2-oC8 sensitizer exhibit the extra open space at the TiO_2 SP surface. Therefore, the best device performance in our system show about 7.7% of energy efficiency at the I^-/I_3^- liquid electrolyte and TiO_2 NSs samples.

6.3 Tetrathienoacenes (TTAs) based sensitizers

Metal-free organic dyes have attracted much attention to researchers due to chemical or optical versatility, environmental compatibility and potential cost reductions [7]. In spite of these attractions and efforts, a little lower cell performance and difficulty in synthesis cannot meet the requirement for commercialization.

A donor- π -acceptor (D- π -A) structure is a promising strategy for metal-free organic sensitizers because of the effective photoinduced intramolecular charge

Figure 26. Solar cell performance (a) V_{oc} , (b) J_{sc} and (c) eff versus light exposure time (d) schematic representation of light-induced cation exchange. Reprinted with permission from [129].

transfer property [7, 130]. Thanks to support from Chen's group, a new series of organic dye based on tetrathienoacene are applied for DSSC [105, 131]. In this design, triphenylamine electron-donor (D) unit and cyanoacrylic acid electron-acceptor (A) unit is connected to an electron rich a lipophilic dihexyloxy-substituted thiophene-based fused tetrathienoacene. (TPA-TTAR-TA); (1) the triphenylamine unit composed of a large conjugated tertiary amine system is known as a strong electron donor in its initial state as well as act as stabilize the charge-transferred state [132]. (2) The cyanoacrylic acid, which is an anchoring group to bind to a TiO_2 surface functions as an effective electron acceptor. (3) As the π -system, we used fused tetrathienoacene cores produced by the newly designed one-pot synthetic routes [133]. Fused-thiophenes offer the attraction of good charge transport properties with extensive molecular conjugation and strong intermolecular $\text{S} \cdots \text{S}$ interactions, [134, 135] which might enhance the efficiency of DSSC. (see in **Figure 27(a)**).

Several fused thiophene derivatives have already been demonstrated to have excellent charge transport performance. For example, dithienothiophene (DTT) and tetrathienoacene (TTA) based OTFTs exhibited mobilities up 0.42 (p-channel) and 0.30 (n-channel) $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively [136]. Relative to organic semiconductors, the potential of fused thiophene-based DSSCs has not been well explored until recently, and only for a limited range of TT and DTT materials. To the best of our knowledge, the first example of a TT-based small molecule DSSC with a PCE of 7.8% was reported by P. Wang and M. Gratzel et al. in 2008 [137]. For DTT, was reported by the same team in the same year with a PCE of 8.0% [138]. Presumably, due to high coplanarity of poly fused thiophenes may lead to aggregation of dye molecules on nanocrystals, caused a dissipative intermolecular charge transfer, and then rendered an unfavorable effect on the cell efficiency. As a result, the more conjugated TTA-based small molecules have never been explored for DSSCs yet. Nevertheless, in terms of tuning the energy-level of chromophores to attain a better capability of panchromatic light-harvesting, conjugated TTAs elevate the HOMO and lower a suitable LUMO compared to TT and DTT based DSSCs. Red shifted absorption with high molar coefficient and better charge transport (*vide infra*)

Figure 27.
(a) Schematic representation of the donor- π -bridge-acceptor molecular dye design concept and (b) the chemical structures with solar performance and (c) UV-vis absorption spectra of dyes 1-5 and their corresponding molar absorption coefficients measured in o-DCB in concentration of 10^{-5} M of TTAR series dyes.

might enhance the efficiency of DSSC thus offering TTA a potential good conjugation unit for a new organic dye. The detailed synthetic route and procedures aren't described in my thesis.

The effects of thiophene introduction between the bridge and the donor and/or acceptor moieties can be systematically understood. Starting from the simplest **TTAR** structure, **TTAR-1**, a thiophene spacer is either inserted on the acceptor side between TTAR and cyanoacrylic acid to yield **TTAR-2**, and finally on both acceptor and donor sides to yield **TTAR-3**. These π -extended systems should enhance panchromatic light-harvesting, as the result of the uplifted TTA HOMO and lower LUMO compared to TT and DTT based molecules. In addition, to maintain adequate dye processability, a long alkyl substituent ($R = n\text{-C}_{15}\text{H}_{31}$) on the TTA core in all sensitizers are introduced, which also suppresses dye aggregation and charge recombination on the TiO_2 surface. (**Figure 27(b)**). The linear C15-alkyl chain substituent not only prevents dye aggregation but also curtails charge recombination. However, it does not efficiently suppress intermolecular π - π interactions when the molecules assemble on the TiO_2 surface. Therefore, the TTA unit effectiveness can be compared with two different branched alkyl group (b- C_8H_{17}), **TTAR-4** and (n- C_9H_{19}) **TTAR-5**.

The optical absorption spectra of the five organic dyes are displayed in **Figure 27(c)**, indicating the presence of two strong absorptions from a charge-transfer band (~ 482 nm (**TTAR-1**), ~ 498 nm (**TTAR-2**), ~ 513 nm (**TTAR-3**), ~ 485 nm (**TTAR-4**), ~ 519 nm (**TTAR-5**)) and a higher energy π - π^* transition (~ 340 nm (**TTAR-1**), ~ 369 nm (**TTAR-2**), ~ 402 nm (**TTAR-3**), ~ 373 nm (**TTAR-4**), ~ 375 nm (**TTAR-5**)). Significantly, **TTAR-2** ~ **5** with one or two thiophenes show red-shifted the absorption onset compared to **TTAR-1** due to their extended conjugation lengths. Presumably the reduced molecular co-planarity of **TTAR-4** due to the branched alkyl substituents may perturb the conjugation efficiency of the chromophore, and hence hypsochromically shift the absorption maximum wavelength. Electronic structure and solar performance of each dye from cyclic voltammograms (CV) and the B3LYP/6-31G** level of density functional theory (DFT) is shown in **Table 5**. Among 5 dyes, **TTAR-4** show the best cell efficiency (η) as high as 10.21%, attributable to the relatively lower aggregation of the dye due to the bulky 3-methyl-5,5-dimethylhexyl substituents. Generally, dye aggregation on the surface of TiO_2 reduces the electron lifetime and facilitates charge recombination in DSSCs fabricated using metal-organic or organic dyes [139].

To understand the exciton dynamics in dyes, femtosecond time-resolved photoluminescence (FTR-PL) was used [140, 141]. The electron injection efficiency can be calculated by the followed equation, $\eta = (1/\tau_1)/(1/\tau_2 + 1/\tau_3)$, where τ_1 is the electron injection time from the dye to TiO_2 , τ_2 is the exaction-exciton annihilation time, and τ_3 is the lifetime of an exciton in the dye [141]. The calculated time constants and electron injection efficiency for the dye coated TiO_2 film are summarized in **Table 5**. The electron injection efficiency of 5 dyes shows almost 97% at $\lambda = 420$ nm, which is well matched results for IPCEs data ($>93\%$) at the same wavelength.

6.4 Multi-sensitized DSSC

Designed sensitizers with higher molar extinction coefficient have allowed significant improvement of cell performance. Nevertheless, possible efficiency boosts can be obtained by extending the dye absorption range while simultaneously avoiding a negative impact on other parameters, such as ground- and excited-state redox potential, intensity of absorption, or stability. Many series of dyes have been developed to find an efficient absorber with high extinction coefficients particularly

Dye	λ_{max} (nm)	E_g (eV)	Energy level (eV)		Energy level (eV)		Photoexcited Electron Dynamics			Electron injection efficiency (%)	Solar Performance			
			E_{HOMO}^a	E_{LUMO}^a	E_{HOMO}^b	E_{LUMO}^b	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)		V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	EFF(%)
TTAR-1	482	2.08	-5.16	-3.08	-5.01	-2.69	0.68	4.35	23.56	97.2	0.893	10.1	68.1	6.15
TTAR-2	490	2.08	-5.22	-3.14	-5.06	-2.78	0.74	3.08	19.30	96.3	0.833	16.5	73.7	10.1
TTAR-3	513	2.04	-5.09	-3.05	-4.95	-2.80	0.84	2.77	15.07	94.7	0.832	11.8	70.3	6.91
TTAR-4	485	1.92	-5.19	-3.27	-5.02	-2.71	0.71	3.37	24.74	97.2	0.811	17.5	72.0	10.2
TTAR-5	519	1.91	-5.20	-3.29	-4.99	-2.71	0.77	4.59	29.86	97.5	0.781	15.5	62.0	7.67

^aMeasured in o-DCB at a concentration of 10^{-5} M^{-1} .

^b $E_{\text{HOMO}} - \text{CV} = -(4.8 + E_{\text{ox}})$ where E_{ox} = Onset potential of the first oxidation peak when the Fc/Fc + internal standard is referenced to 0.0 V.

Table 5.
Summary of optical, electrical properties, solar properties of dyes. Reprinted from [141].

in the solar spectrum from 350 ~ 1,000 nm that is also environmentally benign and inexpensive to use. However, it's a big challenge. Therefore, scientists are tried to mix two or more dyes with different absorption range [142–144]. Although this concept is very sensible, the multi-sensitizers system should meet some essential conditions: (i) strong molar extinction coefficients to minimize the thickness of the mesoscopic TiO₂ film; (ii) a suitable structure to avoid unfavorable dye aggregation; (iii) to reduce the recombination of electrons in the TiO₂ film with I₃[−] and other acceptors materials through the formation of a compact molecule monolayer covering the bare TiO₂ surface. With the continuous efforts, the co-sensitized DSSC has achieved an 11.5% efficiency record with the liquid state electrolyte, [145] but the energy conversion efficiency of mixed sensitizer still lags behind a champion cell made from the single dye. The reason is that the formation of molecular aggregates onto the TiO₂ surface having a finite number of anchoring sites as well as the deactivation of dye excited states due to energy or electron transfer processes between the different sensitizers [146].

In this book, three sensitizers with the different main absorption position and D- π -A framework (a Zn based porphyrin dye (YD2-oC8) [126] and the more conjugated TTA-based small molecules (TTAR) [141], which hold records of solar performance as a single dye) are applied by modified stepwise approach. For the efficient cosensitization, a good understanding of the intermolecular interactions such as matchable size, shape, and orientations as well as compensating light-harvest between or among the coadsorbed dyes must take precedence. In addition dye aggregation on the surface of TiO₂ significantly must be avoided because the formation of dye aggregates significantly decrease the efficiency of electron injection. Attached long alkoxy chains at phenyl group is plausible strategies to suppress effectively the dye aggregation. The key structural feature of YD2-oC8 involves long alkoxy chains in the *ortho*-positions of the *meso*-phenyls so as to envelope effectively the porphyrin ring to decrease the degree of dye aggregation and also protect the porphyrin core for retarded charge recombination [126].

For supporting the lack of light-harvesting ability beyond 700 nm, near-IR dyes, named as YDD6, is employed [147]. The *ortho*-substituted alkoxy chains in YDD6 can be contributed as not only a light-harvesting ability extending beyond 800 nm but also failed to prevent dye aggregation for this porphyrin. A weakly absorption around $\lambda = 520$ nm at the YD2-oC8 can be improved by TTAR dye molecules. In addition, several papers reported the co-sensitization of different molecular sizes allowed a better surface coverage, yielding a high short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) and resulting in a high PCE [147–149]. Similarly, the covering empty space on TiO₂ NS surface demonstrated from the light soaking test lead to enhance the efficiency. Therefore, inserting small sized TTAR dye molecules (estimated molecular length = 24.9 Å) into the gaps within the YD2-oC8 (about 167 Å) saturated TiO₂ surface can help to boost cell performance.

The possibility of dye aggregation of TTAR are test with various amounts of chenodeoxycholic acid (CDCA) co-adsorbed on the photoanodes. The effect of CDCA concentration on the photovoltaic properties of the DSSCs fabricated with **TTAR-4** was first investigated, and the results are shown in **Figure 28(a, left)**. Although dye aggregation should be suppressed by CDCA incorporation among the dye molecules, this would also decrease the dye coverage on the TiO₂, leading to decrease J_{sc} and cell performance. The **TTAR-4** may be sufficient to suppress aggregation, and adsorption of the added CDCA may compete with dye adsorption on the TiO₂. The electron-transport resistance (R_{ct}) and electron lifetimes (τ_e) as a function of the concentration of CDCA can be obtained by EIS analysis (see **Figure 28(a, right)**).

Figure 28.
(a) The normalized efficiency (η) and normalized photocurrent density (J_{sc}) from the photocurrent density–voltage (J–V) characteristics (left) and the electron-transport resistant (R_{CT}) and electron lifetime (τ_e) fitted from EIS analysis of the DSSCs using **TTAR-4** dye with various CDCA concentrations, measured under 1 sun illumination (b) molar absorption coefficients measured in *o*-C₆H₄Cl₂ in a concentration of 10^{-5} M (insert: Schematic process for cosensitized system).

For the effective co-sensitization deposition, there are two well known approaches: (i) the cocktail approach uses a mixture of dye solutions with certain molar ratios of the two dyes [147, 150] and (ii) the stepwise approach accomplishes sequential adsorptions of the two sensitizers [151, 152]. In our experiment, the fabrication of a co-sensitized onto the TiO₂ sphere film is performed by the modified stepwise deposition method. (see **Figure 28(b)**) Considering the energetic band position, the TiO₂ electrode is firstly immersed into a 1 M **TTAR** solution in a mixture of 1,2-dichlorobenzene (DCB) and ethanol (volume ratio: 1:10) and kept at room temperature for 1 h. After spin-coating at 3000 rpm for 45 sec, a small quantity of the dye solutions (YD2-oC8) prepared from the same ratio of the mixture solvent (DCB: EtOH) is then dropped onto TTAT/TiO₂ sphere at room temperature and left for 5 min before spin coating at 3000 rpm for 60 sec. The well covered sensitizer layer could be obtained by repeating the coating procedure until the optimized condition. After YD2-oC8 sensitizer coating, as-synthesized YDD6 solution dissolved in the mixture solvent (DCB:EtOH) is deposited onto YD2-oC8/TTAR/ TiO₂ sphere in the same procedure. **Figure 28(b)** shows the molar extinction coefficient of individual and multiple sensitized system. The absorption spectra of YD2-oC8 is well matched in the literature [122, 152]. The YD2-oC8 observed along with the Soret band (400–520 nm, $\log \epsilon/M^{-1} cm^{-1} = 5.33$ at 448 nm) and Q-band absorption (550 ~ 600 nm, $\log \epsilon/M^{-1} cm^{-1} = 4.49$ at 644), while the absorption spectrum of TTAR is found in the range of 350 ~ 560 nm with the molar extinction coefficients at 449.5 nm ($\log \epsilon/M^{-1} cm^{-1} = 5.01$). As a near IR dye, the absorption spectrum of YDD6 shows a broad split feature for the Soret band (380–550 nm, $\log \epsilon/M^{-1} cm^{-1} = 5.51$ at 491 nm) and Q-band absorption (550–800 nm, $\log \epsilon/M^{-1} cm^{-1} = 4.94$ at 741 nm) Therefore, this dye can help to cover the lack of light-

harvesting ability beyond 700 nm. As a result, the combination of complementary porphyrin and organic dyes produces a panchromatic spectral feature to promote the performance of DSSC.

Figure 29(a) and **(b)** show the current–voltage characteristics and the corresponding IPCE action for the TTAR, YD2-oC8, YDD6 and Multiple (TTAR/YD2-oC8/YDD6) sensitized DSSC, respectively. The photovoltaic parameters are listed in **Table 6**. An impressive cell performance of ca 11.2% ($J_{sc} = 18.6 \text{ mAcm}^{-2}$, $V_{oc} = 0.818 \text{ V}$, $FF = 72.8\%$, 998 mW cm^{-3}) is attainable by increasing J_{sc} value of the TTAR and YD2-oC8 (each 14.3 mAcm^{-2}) to ca. 18.6 mAcm^{-2} when the multiple sensitization is used. For the multisensitized DSSCs, the IPCE spectra showed two major differences compared to the individual dye DSSCs: no dip is observed in the visible region as the efficiency remained above 80% from 400 to 650 nm compared with YD2-oC8 dye, As compared with the corresponding IPCE maxima of the single dye systems, the IPCE value of the multisensitized cells remain between 75–85% from 410 nm to 670 nm and current respond is respond above 710 nm. This effect is consistent with the absorption spectral feature shown in **Figure 34(b)**. To understand the charge transport kinetics of cell, electrochemical impedance spectroscopy (EIS) is next performed from my fitting model (see in **Figure 29(c)**). The estimated total resistance (R_{IR}) of multi-sensitized DSSC at $1 \sim 0.3 \text{ MHz}$ frequency region was about 18.51Ω , which is about 1.58, 2.23 and 3.41 times lower values than that of TTAR, YD2-OC8 and YDD6, respectively. From simulated data, the multi-sensitized DSSC displays about 40.2%, 74.9% and 84.9% lower interfacial recombination rate in TiO_2 , k_{eff} and 0.8%, 129% and 294% higher R_k/R_w value rather than those of TTAR, YD2-oC8 and YDD6 based DSSC. The higher interfacial recombination rate of porphyrin series sensitizer compared with TTAR sensitizer reveals recombination between iodide and oxidized electron at the TiO_2 open space surface between dyes. For similar reasons, a multisensitized DSSC give rise to a denser packing and coverage and lead to the highest k_{eff} . The schematic illustrating melucular

Figure 29.

(a) photocurrent density–voltage (J–V) characteristics (b) IPCE analysis and (c) EIS analysis for the individual and multiple sensitized DSSC (d) Schematic illustrating molecular structure and adsorption sites of YDD6, YD2-oC8 and TTAR dyes on TiO_2 .

	$D_{\text{eff}} (10^{-5} \text{ cm}^2 \text{ s}^{-1})$	$k_{\text{eff}} (\text{Hz})$	$\tau_{\text{eff}} (\text{ms})$	R_k	R_w	R_k/R_w	$Con (\Omega \text{ cms}^{-1})$	$R_d (\Omega)$	$n_s (10^{18} \text{ cm}^{-3})$	$R_{\text{IR}} (\Omega)$	$V_{\text{OC}} (\text{V})$	$J_{\text{sc}} (\text{mA/cm}^2)$	$FF (\%)$	$\text{EFF} (\%)$
TTAR	1.918	19.9	314.7	8.3	3.3	2.5	0.102	3.5	5.378	29.40	0.842	14.3	72.7	8.73
YD2-oC8	2.014	47.5	132.1	10.3	9.3	1.10	0.302	4.3	1.822	41.21	0.769	14.3	67.5	7.45
YDD6	1.142	79.1	79.42	7.9	12.3	0.64	0.387	5.7	1.121	63.21	0.687	6.42	68.7	3.03
Triple	1.952	11.9	527.1	6.1	2.4	2.52	0.044	2.9	12.07	18.52	0.818	18.6	72.8	11.2

Table 6.
*Parameters for the best fit of the impedance and Photovoltaic data for a single dye (TTAR, YD2-oC8 and YDD6) and multi sensitized DSSC. Measured in **Figure 29**.*

structure for single and multi sensitized film can be seen in **Figure 29(d)**. Therefore, the charge density in TiO_2 conduction band (n_s) with multisensitized system was increased by about 124%, 562% for TTAR and YD2-oC8 single dye. The relative competition between electron-hole recombination and electron diffusion is conveniently described by the electron diffusion length, L_n , the relation $L_n = (D_{\text{eff}} \times \tau_{\text{eff}})^{1/2}$. The effective diffusion length L_n of the conduction band electrons for single- (TTAR, YD2-oC8, YDD6) and multi-sensitized DSSC can be calculated from this equation. The L_n for all samples is estimated to be $\sim 24.6 \mu\text{m}$ of TTAR, $16.3 \mu\text{m}$ of YD2-oC8, $9.52 \mu\text{m}$ of YDD6 and $\sim 32.1 \mu\text{m}$ of TTAR/ YD2-oC8/YDD6, respectively. This calculated data suggests that multisensitized sensitizer leads to enhance the collection of being photogenerated electrons in comparison to those in single sensitizer. The detailed parameters can be seen in **Table 6**.

7. Electrolyte and solid state hole transport material

The liquid electrolytes possess some important features such as easy preparation, high conductivity, low viscosity, and good interfacial wetting between electrolytes and electrodes and thus high conversion efficiency for the DSSCs [153, 154]. Today, the best working redox-couple known so far is the iodide/triiodide system. The unique performance of I^-/I_3^- based liquid electrolytes is mainly attributed to the favorable penetration into the nanoporous semiconductor film, very fast dye regeneration, and relatively slow recombination losses through reaction with injected photoelectrons. Cobalt based redox mediators bring the concomitant improvements in the V_{oc} , which produced the highest efficiency of 13% for traditional DSSCs [127]. However, there are several negative features limiting industrial application following reason: (1) iodine is extremely corrosive toward metals such as copper or silver, which are used as current collectors in some DSSCs; (2) acetonitrile as a main solvent has a relatively high vapor pressure, which makes proper encapsulation of the cells challenging; (3) the I_3^- ion absorbs a significant part of visible light, stealing photons from the sensitizing dye. These drawbacks can be potentially remedied via the use of solid-state hole transport materials (HTM). The premise of the effective solid state DSSC is that viscous HTM materials would penetrate into the all the deep lying empty spaces in the porous TiO_2 network, and form a continuous film that connects these filled pores all the way up to the back electrode. Hence, our sphere typed TiO_2 electrode give many advantages for solid state electrolyte system and used by default.

In our research, three different classes of solid state electrolyte are investigated (i) iodide based plastic crystal electrolyte prepared by mixing synthesized N-methyl-N-butylpyrrolidinium iodide ($\text{P}_{1,4}\text{I}$), I_2 , and succinonitrile [51]; (ii) a novel cross-linkable organosiloxane cross-linkable molecule, 4,4'-bis((*p*-trichlorosilylpropylphenyl)phenylamino) biphenyl (TPDSi₂) [155]; (iii) perovskite typed inorganic materials, CsSnI_3 and Cs_2SnI_6 . (this part did not deal with this book) [104, 156]. $\text{P}_{1,4}\text{I}$ based electrolyte exhibit the highest value, reaching about 9% using a masked frame measurement technique [51]. The detailed information is explained in earlier section.

As an organic molecule system, several different systems have been proposed including melt processing, [157] in-situ polymerization, [158] use of low T_g materials, and even use of small molecule/polymeric blends [159]. Among them, silane chemistry based cross linkable hole transport material 4,4'-bis((*p*-trichlorosilylpropylphenyl)phenylamino) biphenyl (TPDSi₂) is applied for organic HTM. Silane chemistry has not been previously employed in DSSC, but our group and others have exploited their property of forming a robust cross-linked network of

charge carriers for use its various optoelectronic devices. Both the performance and the stability of the devices improved dramatically when TPDSi₂ was used the interfacial layer in OLED (organic light emitting diode) and OPV (organic photovoltaic) devices. The TPDSi₂ molecule has two key components-widely used hole transport moiety triphenyldiamine (TPD) and a trichlorosilyl (SiCl₃) pendant. The SiCl₃ subgroups can be easily introduced into a charge conducting moiety like TPD via the highly efficient catalytic hydrosilylation reaction. The Si-Cl bonds are very stable during storage under inert atmosphere, but they are readily hydrolyzed by hydroxyl (OH-) groups. Moisture content of ambient atmosphere and surface OH groups that are present on oxides surfaces of ITO (indium tin oxide), SiO₂ (silicon dioxide) and TiO₂ [160, 161] substrates, along with water molecules that are physisorbed on the surface, are the relevant sources of such OH groups. Once the SiCl₃ groups come in contact with the OH groups, they get hydrolyzed at a rapid pace and inadvertently, Si-Cl groups from two different molecules get hydrolyzed by the two OH groups of the same water molecule. The very strong Si-O-Si bond hence formed, covalently linking two TPDSi₂ molecules. Alternatively, Si-O-Si bonds are formed when two neighboring silanol groups undergo condensation reaction. The Si-O-Si bonds will extend over the length and breadth of the film in all directions and hence form a tightly held network of TPD units. While TPDSi₂ is a very soluble organic solid, when it is cast onto a film allowed to hydrolyze, it will form a heavily cross-linked network that is rigid, insoluble and rugged. Our strategy in this study was to fill up the TiO₂ pores with the soluble small molecule TPDSi₂ and then to allow the molecules to cross link and form an extensive network that is in contact with both the deep lying dye molecules and the back electrode and hence shuttle holes from the former to the latter with great efficiency. **Figure 30(a)** shows the schematic image and the chemical structure of DSSCs utilizing P3HT and TPDSi₂ organic semiconductor as HTM. A mesoporous TiO₂ nanocrystalline film is

Figure 30. (a) Device architecture (top) of ss-DSSC and chemical structures with transmission electron microscope image (bottom) of P3HT and TPDSi₂ (b) illustration of p-doping effect on TPDSi₂ by additive treatment (top) and complete energy diagram of FTO/TiO₂/Z907/HTM/Au ssDSSC (bottom) (c) photovoltaic performance of Z907 dye based ssDSSCs employing P3HT and TPDSi₂ as HTMs with and without additive treatment.

deposited on top of FTO-coated glass substrate. Z907 dye molecules are attached to the surface of TiO_2 to form a bicontinuous nanocomposite active layer, which is then subsequently infiltrated by the organic HTM. Finally, a Au counter electrode is deposited to form contact with HTM and encapsulates the device. In this system, the HTM extracts hole from photo-oxidized sensitizer molecules and transfers the holes to the Au counter-electrode, allowing complete dye regeneration. TEM specimens are prepared by transferring spin-coated thin films from poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)-coated Si substrates onto lacey carbon TEM grids. P3HT exhibits typical semicrystalline polymer features. Such relatively large, continuous domains as a result of polymer aggregation are indicative of poor HTM infiltration into pores of TiO_2 /sensitizer. On the contrary, TPDSi₂ molecular HTM shows significantly smaller features, while forming homogenous and organized networks. Such features are could be advantageous for large-scale processability of TPDSi₂ as an efficient HTM.

Figure 30(b) shows a scheme on the possible change of electronic structure by additive treatment by the UPS spectra of P3HT before and after additive treatment. The detailed information can be seen in **Table 7**. In HOMO emission regions, the HOMO band onsets also show no significant difference, corresponding to IPs of 4.94 and 4.98 eV for P3HT before and after additive treatment, respectively. This result is in perfect agreement with CV data (**Table 7**). However, for TPDSi₂ films, the additive treatment result in a clear shift both in high binding energy cutoff (HBEC) and HOMO emission regions. In particular, the HBEC position shifts to lower binding energy after additive treatment, whereas the HOMO cutoff shifts close to 0 eV. This effect could indicate a strong p-doping effect of additives on TPDSi₂. Scholin et al. [162] observed a similar effect of Fermi level shift to move closer to the HOMO level on Spiro-OMeTAD by Li-TFSI doping. Here, by using the same substrates and a common vacuum level, the shift of Fermi energy to the move closer to the HOMO position is confirmed. In addition, IPs also shift from 5.36 to 5.12 eV after additive treatment, which is in excellent agreement with CV-derived HOMO energies.

The overall energy alignment including all DSSC device components, specifically, FTO/ TiO_2 /Z907/HTMs (P3HT + additives or TPDSi₂ + additives)/Au is presented as **Figure 30(b)**.

The exact energetic alignment of HTMs are carefully derived from optical absorption, cyclic voltammetry and ultraviolet photoemission spectroscopy and is discussed below. To carefully investigate the charge transport properties of HTMs, both TFT and space charge limited current (SCLC) measurements are performed. For TFT mobility measurements, bottom-gate/top-contact configurations were employed for all devices fabricated by spin-coating of a 5 mg/mL chlorobenzene solution onto Si/ SiO_2 substrates using Au source and drain contacts. All TFT and SCLC mobilities are summarized in **Table 7**. For P3HT, typical p-type TFT behavior was observed both in pristine films and films treated with additives. A noticeable increase in p-type mobility from 4.3×10^{-3} to 1.1×10^{-2} is observed. However, TPDSi₂ exhibit relatively low TFT performance, as a result of disconnected domains in the lateral direction. In real DSSC condition, hole transport through the HTMs to the counter electrode can significantly influence charge recombination and device performance. Therefore, SCLC method which directly measures the charge transport in the direction perpendicular to substrate can be employed as a good indicator mimicking real device conditions [163]. For the cross-linked TPDSi₂ HTM, it show about 2.8 time higher p-type hole mobility than that of pristine, which is indicative of favorable charge transport properties in DSSCs. Therefore, power conversion efficiency (PCE) of DSSCs of >2% is achieved when using standard amphiphilic dye and TPDSi₂ as HTM (see **Figure 30(c)**).

Sample	E _{HOMO} ^a (eV)	IP ^b (eV)	E _{opt,gap} ^c (eV)	E _{LUMO} ^d (eV)	μ _{TFT} (cm ² /Vs)	μ _{SCLC} (cm ² /Vs)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
P3HT	?	−4.94	1.91	−3.03	4.3 × 10 ^{−3}	1.0 × 10 ^{−3}	0.166	0.38	32.1	0.02
P3HT + additives	?	−4.98	1.90	−3.08	1.1 × 10 ^{−2}	2.3 × 10 ^{−3}	0.497	1.69	39.4	0.33
TPDSi ₂	−5.31	−5.37	2.90	−2.47	NA	4.6 × 10 ^{−4}	0.485	2.81	46.7	0.64
TPDSi ₂ + additives	−5.09	−5.11	2.90	−2.22	NA	2.8 × 10 ^{−3}	0.683	4.97	60.3	2.05

^aDetermined by CV.
^bDetermined by UPS.
^cDetermined at the UV absorption onset.
^dELUMO = IP + E_{opt,gap}.

Table 7.
 Summary of electrochemical, optical, charge transport and photovoltaic data for the HTMs used in this study.

8. Carbonaceous cathode for DSSC

In this part, we show our effort on developing the counter electrode (CE). Generally, CE mainly functions as reducing the redox species from I_3^- to I_2 . A suitable redox charge mediator should effectively perform the function of shuttling the generated positive charge away from the light absorbing sensitizer residing on the semiconductor surface to the CE, thus completing the electrical circuit. For being an effective CE, it exhibit high electrical conductivity and electrocatalytic activity toward I_3^- reduction and corrosion resistant to iodide/triiodide electrolyte [164]. To date, a platinum (Pt) is the most common catalyst material for DSSC [165]. However, its cost remains a concern for the large-scale commercialization of the DSSC. Therefore, numerous researchers are trying to find new CE materials. Carbonaceous materials such as graphite [166, 167] carbon black [168, 169], activated carbon [170], hard carbon sphere [171], carbon nanotube [172], fullerene and graphene [173], conductive polymers [174], metal compounds [175] and composites have been developed and tested as promising counter electrodes. So far, carbonaceous materials are regarded as the most attractive option.

In this book, we introduce large-effective-surface-area polyaromatic hydrocarbon (LPAH) for DSSC. A detailed description for generating LPAH species has been reported in an earlier publication [176]. The catalytic properties of LPAH can be calculated by EIS method. Device symmetric structure and the Randles-typed equivalent circuit model consisting of charge transfer resistance (R_{ct}), a constant phase element (CPE) and a series resistance (R_s) can be seen in **Figure 31**. Here, the R_{ct} is a barrier for the charge transfer process at the LPAH/electrolyte interface [177]. The CPE is the interfacial capacitance, considering the roughness of the electrodes. In more detail, the impedance of CPE is described as $Z_{CPE} = B(i\omega)^{-\beta}$ ($0 \leq \beta \leq 1$) where, ω is the angular frequency, B and β are frequency-independent parameters of the

Figure 31.

(a) *a.* Equivalent circuit of a symmetrical cell used to fit the impedance spectra; *b.* Nyquist plots of different counter electrode catalytic materials (Platinum, carbon black and LPAH) prepared with identical electrodes; *c.* CVs of carbon black and LPAH films. (b) *a.* Nyquist plot of different counter electrodes. Equivalent circuit of the complete DSSC is given in the inset and *b.* $J-V$ Characteristics of different counter electrode catalytic materials.

CPE. β indicated the capacitance of CPE and the deviation from the semicircle probably due to the porosity of electrode surface, respectively [41, 44, 178]. R_s indicate the ohmic resistance of the electrolyte, the conductive glass and the carbon layer. In order to confirm the catalytic mechanism operating in an electrochemical system with I^-/I_3^- redox, cyclic voltammetry (CV) measurement was carried out. A carbon electrode was used as the working electrode, a Pt coil as the counter electrode, and an Ag/Ag⁺ electrode as the reference electrode. **Figure 31(a).c** shows the CV curves obtained using CB and LPAH (versus Ag/AgCl). The negative current was assigned to the reduction of I_3^- to I^- and positive current was the oxidation of I^- at the carbon surface, respectively [179]. The LAPH sample showed a negative peak potential (-0.82 V) and a much higher current density (-0.02 mA/cm²), indicating a better reduction rate comparable to that CB (-1.4 V, -0.017 mA/cm²). In cyclic voltammetry, the anode peak and the cathodic peak are related to the redox couple (I^-/I_3^-) reactions and they can be used to estimate the diffusion coefficient (D) using the Randles-Sevcik equation. The Randles-Sevcik equation: $i_p = (2.687 \times 10^5) n^{3/2} \nu^{1/2} D^{1/2} AC$ where, i_p is the peak current (A), n is number of electrons transferred in the redox event (usually 1), ν is scan rate in V/s, A is the area of working electrode, C is the bulk concentration of analyte in mol/cm³. In the anodic and cathodic reaction, the calculated D values of 1.05×10^{-4} cm²/s and 1.76×10^{-4} cm²/s for LPAH were larger than 6.70×10^{-5} cm²/s and 6.3×10^{-5} cm²/s for CB. This result indicates that the LPAH would speed up the I^-/I_3^- redox reaction ascribed to a higher catalytic activity, leading to a more efficient DSSC.

In general, the equivalent circuit of the complete solar cell may be represented as indicated in **Figure 31(b)** [37, 176]. From right to left, it demonstrates impedance for charge transfer at electrolyte/catalytic materials-FTO interface, diffusion of I_3^- species in the electrolyte, electron transport and electron capture by the I_3^- at the TiO₂/electrolyte interface and the electron transport at the FTO/TiO₂ interface, respectively. These components can be simplified from proposed in DSSC model: R_{FTO/TiO_2} is the resistance of the FTO/TiO₂ contact and CPE_1 is the capacitance of this interface. TiO₂ network consists of a diffusion element Z_{W1} that is in series connected with the charge-transfer element R_{TiO_2} , the two being in parallel with a capacitive (constant phase angle) element CPE_3 . Z_{W2} is the Warburg impedance describing the diffusion of I_3^- in the electrolyte. R_{CE} is the charge-transfer impedance at the counter electrode, and CPE_2 is the double layer capacitance at the electrolyte/catalytic materials-FTO interface [180].

The catalytic activity described the exchange current density (J_0) using followed equation,

$$J_0 = RT/\eta FR_{ct}.$$

Here, J_0 is a kinetic parameter that depends on the reaction and on the electrode surface upon which the electrochemical reaction occurs, R is the gas constant, T is temperature (here $T = 300$ K), n is the gas constant and F is Faraday constant [44]. From the value of J_0 , we can know how easily the electrochemical reaction can occur on the electrode surface. The R_{ct} of LPAH based CE shows approximately 35 times lower value at ~ 3 μ m thick film than that of a symmetric CB electrode at ~ 8 μ m thick film, leading a better energy efficiency at the DSSC (see **Figure 31(b)**). Furthermore, the relatively thin film of LPAH can be expected by reducing the internal series resistance of devices. The shifting the peaks of Bode phase at the high frequency region of the cells supported this expectation [181]. Consequently, LPAH would speed up the I^-/I_3^- redox reaction, leading to improve the fill factor and cell efficiency.

Figure 31(c).b described fitted Nyquist plot and J - V curves of the different CE (Pt, CB and LPAH) on DSSCs. The detailed parameters for internal resistance (R_{IR})

sample	d^* (μm)	BET & BJH analysis			Symmetric Cell				Complete DSSC (w/o mask)				
		Surface area (m ² /g)	Pore Volume (cm ³ /g)	Pore diameter (nm)	CPE:B (S.s ^β)	CPE: β	R _{CT} (Ωcm ²)	J _o (mA/cm ²)	V _{OC} (V)	J _{sc} (mA/cm ²)	FF (%)	EFF (%)	R _{IR} [*] (Ohm)
(a) pt		—	—	—	2.9×10^{-5}	0.87	0.61	22.0	0.824	13.4	73.8	8.12	17.1
(b) CB	7.5 ± 0.8	69.6	0.094	5.93	2.3×10^{-5}	0.76	70.3	0.190	0.804	11.5	68.9	6.35	111
(c) LPAH	3.2 ± 0.6	216.8	0.474	13.3	2.3×10^{-3}	0.85	2.12	6.31	0.820	13.1	73.2	7.89	21.9

Table 8.
Characteristic of different counter electrode materials (platinum, carbon black and LPAH). Reprinted from [176].

and photovoltaic properties are summarized in **Table 8**. The internal resistance (R_{IR}) can be calculated by the sum obtained from each resistance, $R_{IR} = R_0 + R_1 + R_2 + R_3$. Although LPAH counter electrode has somewhat lower catalytic property compared with the Pt counter electrode, V_{oc} , fill factor is close to Pt based DSSC electrode due to relatively similar R_{IR} values. Finally, LPAH based DSSC show an overall energy conversion efficiency of 9.3% without mask, which is higher than the 7.5% achieved for CB counter electrode devices reported recently [169]. Therefore, we believe LPAH is a good candidate as a next catalytic material.

9. Optimization of the DSSC performance for having maximum performance

Based on these fundamental achievements, our efforts are headed for achieving an energy efficiency of over 12.3% by combining new materials and concept. For a photoanode, the ITO NR array with over 3 μm spacing and 10 μm thickness is used as the 3D cell [52]. In this design, it is very important how well the TiO_2 nanoparticles have infiltrated among the ITO nanowire. In our earlier research, TiO_2 solution including polymer binder is air-sprayed into ITO NWs. Although this method is easy and efficient enough to fill TiO_2 NPs into ITO NW, it formed surface defect (such as crack) on the surface of TiO_2 film during sintering process (see **Figure 32**). Through Electro-spraying process, crack free TiO_2 film is deposited into

Figure 32.
(a) SEM images of TiO_2 /ITO NRs on the different deposition technique; doctor-blade, air-sprayed from TiO_2 solution including polymer binder and E-sprayed technique from EtOH and EtOH/terphineol (b) E-sprayed TiO_2 /ITO NRs film inserted in the JV characteristic.

ITO NW. For an electro-spraying, aqueous solvent in the hydrothermal treated TiO₂ nanoparticle solution is replaced by ethanol and then alpha-terpineol is added into the ethanol solution of TiO₂ particles. The replaced solution was loaded into a syringe equipped with a 27-gauge stainless steel needle. The spraying rate (25 µL/min) was controlled using a syringe pump. The electric field (12–15 kV) was applied between a metal orifice and the aluminum foil at a distance of 10 cm using a power supply and was electro-sprayed onto ITO NWs substrate. The TiO₂ coated electrode was gradually calcined under an air flow at 150°C for 15 min, at 320°C for 10 min, at 500°C for 30 min. As seen in **Figure 32(a)**, TiO₂ sphere solution prepared from pure EtOH formed the film on the top of ITO NWs, which make it difficult to penetrate into the ITO NWs. Therefore, adding alpha-terpineol solvent with viscous and low evaporation rate into TiO₂ solution, TiO₂ solution is directly dropped into highly charged ITO NWs in between and spreading through x-y-z moving robot system. As a result, completely filled and crack free TiO₂ film in ITO NWs can be obtainable (see **Figure 32(b)**). A J_{sc} of 17.2 mAcm⁻², a V_{oc} of 0.846 V, and a FF of 0.75.2% are derived from the JV curve with purified N719 dye and liquid electrolyte, thus giving an overall power conversion efficiency (η) of 10.9% under illumination with standard AM 1.5G simulated sunlight (1000 mWcm⁻²). While attached with a 3D PhC, the efficiency is further improved to 12.45% (J_{sc} = 19.75 mAcm⁻², V_{oc} = 0.838 V, FF = 75.2%). The dramatically improved PCE can be achieved by using cosensitization system with a TTAR/ YD2-oC8/YDD6 and 3D PhC designed structure.

Figure 33(a) presents the solar performance for the best cell. Form an effective approach to enhance the light-harvesting ability and to retard the charge recombination, the maximum PCE is about 13.26%, with short-circuit current density (J_{sc}) = 22.3 mAcm⁻², open circuit voltage (V_{oc}) = 0.811 V, fill factor (FF) = 73.3% and maximum power (P_{max}) = 1.99 mW. In conclusion, our concept and designed material and concept lead to significant promotion of the overall performance of a DSSC.

Figure 33. I-V and P-V curve for the best performance DSSC with the cosensitization and 3D PhC.

10. Future prospects of ESC

Compared with traditional silicon solar cells, the DSSC device promises to be less expensive (the ease of fabrication and cost effectiveness of materials, which do not need to be highly purified process), thinner, more flexible, and amenable to a wide range of lighting conditions, all of which makes it viable and efficient solar cells for the future. Therefore, they said that ESC along with its good performance will definitely replace c-Si dominated photovoltaic markets very sooner. However, although each material is extremely inexpensive, the cost of silicon continues to fall as well. Silicon photovoltaics module are a mature technology and their costs have continued to reduce from US \$1.52 W⁻¹ in 2010 to just US\$ 0.39 W⁻¹ in 2018, with module efficiencies ranging from 15–20% and lifetime guaranteed to 25 years [182]. Unfortunately, the ESC technology is not so trivial that the highest module efficiency, the fastest production methods, or the lowest materials cost necessarily provides the best module solution. In addition, long term stability is the big challenge. Therefore, for surviving the future photovoltaic market, we believe ESCs have to develop the system of transparency with esthetics ability.

Building integrated photovoltaic (BIPV) technology has become an emerging research hotspot of solar PV technology because it intends to achieve “zero energy building (ZEB)” consumption through transformations of buildings from energy consumers to sustainable energy producers [183]. A sustainable building can minimize energy consumption, while at the same time supplying its own energy demand through self-generation. PV was generally installed on building's roofs, but it's very harsh to meet strict requirements of ZEB regulation. The potential power of rooftop in the United States is approximately estimated as 1400 TWh/yr. (0.16TW) at about 16% of module efficiency cell, nearly 40% of the total electricity generation of the US [184]. In buildings rooftop system with conventional PV application, the available area for PV installation is limited and it cannot fulfill the building's energy needs. On the other hands, transparent or semi-transparent PV windows have a tremendous potential to increase harvesting area as well as reduce the annual electricity consumption for cooling and heating. Therefore, we believe transparent PV is the most promising future energy system and research efforts for minimizing the tradeoff relation between the average visible transparency (AVT) and power conversion efficiency (PCE) can decide ESC's fate [185].

11. Summary

The main aim of this book is to put a comprehensive review how to improve and what kind of factors are influence on cell performance. Fundamental and professional understanding of the DSSC has been gained by means of experimental, electrical and optical modeling and advanced characterization techniques. In this book, TiO₂ photoanode under the category of 0D and 3D structures, organic photosensitizer, solid state transporting materials and catalytic carbon as a material field was studied by using various optical and electrical tools. The combined research efforts have led to the important technical achievements: by controlling the nanocrystal structure, size, shape, organization and interface of titanium dioxide, we have made great progress in controlling the light harvesting, charge transfer and transport properties in the devices and have greatly boosted the performance of the devices.. By using specially designed photonic crystals to confine the photons in the cells, the overall cell efficiency can reach to about 13.26%.

Acknowledgements

The Northwestern University authors acknowledge the support of the Argonne-Northwestern Solar Energy Research (ANSER) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES) under Award Number DE-SC0001059. This work made use of the EPIC, Keck-II, and SPID facilities of Northwestern University's NUANCE Center, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS), the MRSEC program (NSF DMR-1121262 and 1542205) at the Materials Research Center, the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois,

Author details

Byunghong Lee^{1,2*} and Robert Bob Chang²

¹ Future Energy Research Team, Hyundai Motor Group, Uiwang-si, Gyeonggi-do, South Korea

² Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois, USA

*Address all correspondence to: redboho@gmail.com

IntechOpen

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

References

- [1] Gregg, B.A., *Excitonic Solar Cells*. The Journal of Physical Chemistry B, 2003. **107**(20): p. 4688–4698.
- [2] Snaith, H.J., *Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells*. The Journal of Physical Chemistry Letters, 2013. **4** (21): p. 3623–3630.
- [3] Becquerel, A.E., *Mémoire sur les effets électriques produits sous l'influence des rayons solaires*. Comptes Rendus des Séances Hebdomadaires, 1839. **9**: p. 561–567.
- [4] Moser, J., *Notiz über Verstärkung photoelektrischer Ströme durch optische Sensibilisierung*. Monatshefte für Chemie und verwandte Teile anderer Wissenschaften, 1887. **8**(1): p. 373–373.
- [5] O'Regan, B. and M. Gratzel, *A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films*. Nature, 1991. **353**(6346): p. 737–740.
- [6] Best Research-Cell Efficiency Chart <https://www.nrel.gov/pv/cell-efficiency.html>
- [7] Hagfeldt, A., et al., *Dye-Sensitized Solar Cells*. Chemical Reviews, 2010. **110** (11): p. 6595–6663.
- [8] Listorti, A., B. O'Regan, and J.R. Durrant, *Electron Transfer Dynamics in Dye-Sensitized Solar Cells*. Chemistry of Materials, 2011. **23**(15): p. 3381–3399.
- [9] Martinson, A.B.F., et al., *New Architectures for Dye-Sensitized Solar Cells*. Chemistry – A European Journal, 2008. **14**(15): p. 4458–4467.
- [10] Fabregat-Santiago, F., et al., *Characterization of nanostructured hybrid and organic solar cells by impedance spectroscopy*. Physical Chemistry Chemical Physics, 2011. **13**(20): p. 9083–9118.
- [11] Bae, E., et al., *Effects of Surface Anchoring Groups (Carboxylate vs Phosphonate) in Ruthenium-Complex-Sensitized TiO₂ on Visible Light Reactivity in Aqueous Suspensions*. The Journal of Physical Chemistry B, 2004. **108**(37): p. 14093–14101.
- [12] Thavasi, V., et al., *Controlled electron injection and transport at materials interfaces in dye sensitized solar cells*. Materials Science and Engineering: R: Reports, 2009. **63**(3): p. 81–99.
- [13] Wang, X. and D.M. Stanbury, *Oxidation of Iodide by a Series of Fe(III) Complexes in Acetonitrile*. Inorganic Chemistry, 2006. **45**(8): p. 3415–3423.
- [14] Wang, P., et al., *Charge Separation and Efficient Light Energy Conversion in Sensitized Mesoscopic Solar Cells Based on Binary Ionic Liquids*. Journal of the American Chemical Society, 2005. **127** (18): p. 6850–6856.
- [15] Pelet, S., J.-E. Moser, and M. Grätzel, *Cooperative Effect of Adsorbed Cations and Iodide on the Interception of Back Electron Transfer in the Dye Sensitization of Nanocrystalline TiO₂*. The Journal of Physical Chemistry B, 2000. **104**(8): p. 1791–1795.
- [16] Tiwana, P., et al., *Electron Mobility and Injection Dynamics in Mesoporous ZnO, SnO₂, and TiO₂ Films Used in Dye-Sensitized Solar Cells*. ACS Nano, 2011. **5** (6): p. 5158–5166.
- [17] J. Frank, A., N. Kopidakis, and J.v.d. Lagemaat, *Electrons in nanostructured TiO₂ solar cells: transport, recombination and photovoltaic properties*. Coordination Chemistry Reviews, 2004. **248**(13–14): p. 1165–1179.
- [18] Bisquert, J., et al., *Determination of Rate Constants for Charge Transfer and the Distribution of Semiconductor and Electrolyte Electronic Energy Levels in Dye-Sensitized Solar Cells by Open-Circuit Photovoltage Decay Method*.

- Journal of the American Chemical Society, 2004. **126**(41): p. 13550–13559.
- [19] Nelson, J. and R.E. Chandler, *Random walk models of charge transfer and transport in dye sensitized systems*. Coordination Chemistry Reviews, 2004. **248**(13–14): p. 1181–1194.
- [20] Ansari-Rad, M., Y. Abdi, and E. Arzi, *Monte Carlo Random Walk Simulation of Electron Transport in Dye-Sensitized Nanocrystalline Solar Cells: Influence of Morphology and Trap Distribution*. The Journal of Physical Chemistry C, 2012. **116**(5): p. 3212–3218.
- [21] Bisquert, J., *Interpretation of electron diffusion coefficient in organic and inorganic semiconductors with broad distributions of states*. Physical Chemistry Chemical Physics, 2008. **10**(22): p. 3175–3194.
- [22] Bisquert, J., E. Palomares, and C.A. Quiñones, *Effect of Energy Disorder in Interfacial Kinetics of Dye-Sensitized Solar Cells with Organic Hole Transport Material*. The Journal of Physical Chemistry B, 2006. **110**(39): p. 19406–19411.
- [23] Jennings, J.R., et al., *Dependence of Dye-Sensitized Solar Cell Impedance on Photoelectrode Thickness*. The Journal of Physical Chemistry C, 2012. **116**(1): p. 1556–1562.
- [24] Mao, X., et al., *High Efficiency Dye-sensitized Solar Cells Constructed with Composites of TiO₂ and the Hot-bubbling Synthesized Ultra-Small SnO₂ Nanocrystals*. Scientific Reports, 2016. **6** (1): p. 19390.
- [25] Wu, J., et al., *Counter electrodes in dye-sensitized solar cells*. Chemical Society Reviews, 2017. **46**(19): p. 5975–6023.
- [26] Lee, B., et al., *Materials, Interfaces, and Photon Confinement in Dye-Sensitized Solar Cells*. The Journal of Physical Chemistry B, 2010. **114**(45): p. 14582–14591.
- [27] Grätzel, M., *Dye-sensitized solar cells*. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 2003. **4**(2): p. 145–153.
- [28] Thavasi, V., et al., *Controlled electron injection and transport at materials interfaces in dye sensitized solar cells*. Materials Science & Engineering R-Reports, 2009. **63**(3): p. 81–99.
- [29] Gratzel, M., *Photoelectrochemical cells*. Nature, 2001. **414**(6861): p. 338–344.
- [30] Frank, A.J., N. Kopidakis, and J. van de Lagemaat, *Electrons in nanostructured TiO₂ solar cells: transport, recombination and photovoltaic properties*. Coordination Chemistry Reviews, 2004. **248**(13–14): p. 1165–1179.
- [31] Goncalves, L.M., et al., *Dye-sensitized solar cells: A safe bet for the future*. Energy & Environmental Science, 2008. **1**(6): p. 655–667.
- [32] Chen, C.Y., et al., *Highly Efficient Light-Harvesting Ruthenium Sensitizer for Thin-Film Dye-Sensitized Solar Cells*. Acs Nano, 2009. **3**(10): p. 3103–3109.
- [33] Toivola, M., et al., *Nanostructured dye solar cells on flexible substrates - Review*. International Journal of Energy Research, 2009. **33**(13): p. 1145–1160.
- [34] Sastrawan, R., et al., *New interdigital design for large area dye solar modules using a lead-free glass frit sealing*. Progress in Photovoltaics: Research and Applications, 2006. **14**(8): p. 697–709.
- [35] Lee, B.H., et al., *Charge Transport Characteristics of High Efficiency Dye-Sensitized Solar Cells Based on Electrospun TiO₂ Nanorod Photoelectrodes*. The Journal of Physical Chemistry C, 2009. **113**(51): p. 21453–21457.

- [36] Fabregat-Santiago, F., et al., *Decoupling of Transport, Charge Storage, and Interfacial Charge Transfer in the Nanocrystalline TiO₂/Electrolyte System by Impedance Methods*. The Journal of Physical Chemistry B, 2001. **106**(2): p. 334–339.
- [37] Wang, Q., J.-E. Moser, and M. Gratzel, *Electrochemical Impedance Spectroscopic Analysis of Dye-Sensitized Solar Cells*. The Journal of Physical Chemistry B, 2005. **109**(31): p. 14945–14953.
- [38] Fabregat-Santiago, F., et al., *Correlation between Photovoltaic Performance and Impedance Spectroscopy of Dye-Sensitized Solar Cells Based on Ionic Liquids*. The Journal of Physical Chemistry C, 2007. **111**(17): p. 6550–6560.
- [39] Adachi, M., et al., *Determination of Parameters of Electron Transport in Dye-Sensitized Solar Cells Using Electrochemical Impedance Spectroscopy*. The Journal of Physical Chemistry B, 2006. **110**(28): p. 13872–13880.
- [40] Kern, R., et al., *Modeling and interpretation of electrical impedance spectra of dye solar cells operated under open-circuit conditions*. Electrochimica Acta, 2002. **47**(26): p. 4213–4225.
- [41] Bisquert, J., et al., *Theoretical models for ac impedance of finite diffusion layers exhibiting low frequency dispersion*. Journal of Electroanalytical Chemistry, 1999. **475**(2): p. 152–163.
- [42] Bisquert, J., *Theory of the Impedance of Electron Diffusion and Recombination in a Thin Layer*. J. Phys. Chem. B, 2002. **106**(2): p. 325–333.
- [43] Han, L.Y., et al., *Improvement of efficiency of dye-sensitized solar cells by reduction of internal resistance*. Applied Physics Letters, 2005. **86**(21).
- [44] Hauch, A. and A. Georg, *Diffusion in the electrolyte and charge-transfer reaction at the platinum electrode in dye-sensitized solar cells*. Electrochimica Acta, 2001. **46**(22): p. 3457–3466.
- [45] Tsai, C.-C. and H. Teng, *Structural Features of Nanotubes Synthesized from NaOH Treatment on TiO₂ with Different Post-Treatments*. Chemistry of Materials, 2005. **18**(2): p. 367–373.
- [46] Park, N.-G. and K. Kim, *Transparent solar cells based on dye-sensitized nanocrystalline semiconductors*. physica status solidi (a), 2008. **205**(8): p. 1895–1904.
- [47] Nazeeruddin, M.K., et al., *Conversion of light to electricity by cis-X₂bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(II) charge-transfer sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on nanocrystalline titanium dioxide electrodes*. Journal of the American Chemical Society, 1993. **115**(14): p. 6382–6390.
- [48] Schlichthörl, G., et al., *Band Edge Movement and Recombination Kinetics in Dye-Sensitized Nanocrystalline TiO₂ Solar Cells: A Study by Intensity Modulated Photovoltage Spectroscopy*. The Journal of Physical Chemistry B, 1997. **101**(41): p. 8141–8155.
- [49] Boschloo, G., L. Häggman, and A. Hagfeldt, *Quantification of the Effect of 4-tert-Butylpyridine Addition to I-/I³⁺-Redox Electrolytes in Dye-Sensitized Nanostructured TiO₂ Solar Cells*. The Journal of Physical Chemistry B, 2006. **110**(26): p. 13144–13150.
- [50] Kopidakis, N., N.R. Neale, and A.J. Frank, *Effect of an Adsorbent on Recombination and Band-Edge Movement in Dye-Sensitized TiO₂ Solar Cells: Evidence for Surface Passivation*. The Journal of Physical Chemistry B, 2006. **110**(25): p. 12485–12489.
- [51] Lee, B., et al., *Optimizing the Performance of a Plastic Dye-Sensitized Solar Cell*. The Journal of Physical

- Chemistry C, 2011. **115**(19): p. 9787–9796.
- [52] Lee, B., et al., *Three Dimensional Indium–Tin-Oxide Nanorod Array for Charge Collection in Dye-Sensitized Solar Cells*. ACS Applied Materials & Interfaces, 2014. **6**(20): p. 17713–17722.
- [53] *Front Matter A2 - Nishinaga, Tatau*, in *Handbook of Crystal Growth (Second Edition)*. 2015, Elsevier: Boston. p. iii.
- [54] *Tapping Solar Power With Perovskites*. Chemical & Engineering News Archive, 2014. **92**(8): p. 10–15.
- [55] *Index A2 - Nishinaga, Tatau*, in *Handbook of Crystal Growth (Second Edition)*. 2015, Elsevier: Boston. p. 1157–1182.
- [56] O'Regan, B.C., et al., *Influence of the TiCl₄ Treatment on Nanocrystalline TiO₂ Films in Dye-Sensitized Solar Cells. 2. Charge Density, Band Edge Shifts, and Quantification of Recombination Losses at Short Circuit*. The Journal of Physical Chemistry C, 2007. **111**(37): p. 14001–14010.
- [57] Lee, S.-W., et al., *Effects of TiCl₄ Treatment of Nanoporous TiO₂ Films on Morphology, Light Harvesting, and Charge-Carrier Dynamics in Dye-Sensitized Solar Cells*. The Journal of Physical Chemistry C, 2012. **116**(40): p. 21285–21290.
- [58] Pearton, S.J. and D.P. Norton, *Dry Etching of Electronic Oxides, Polymers, and Semiconductors*. Plasma Processes and Polymers, 2005. **2**(1): p. 16–37.
- [59] Rauf, S., *Model for photoresist trim etch in inductively coupled CF₄/O₂ plasma*. Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures, 2004. **22**(1): p. 202–211.
- [60] Mogab, C.J., A.C. Adams, and D.L. Flamm, *Plasma etching of Si and SiO₂*—The effect of oxygen additions to CF₄ plasmas. Journal of Applied Physics, 1978. **49**(7): p. 3796–3803.
- [61] Fracassi, F. and R. Dagostino, *CHEMISTRY OF TITANIUM DRY ETCHING IN FLUORINATED AND CHLORINATED GASES*. Pure and Applied Chemistry, 1992. **64**(5): p. 703–707.
- [62] Norasetthekul, S., et al., *Dry etch chemistries for TiO₂ thin films*. Applied Surface Science, 2001. **185**(1–2): p. 27–33.
- [63] d'Agostino, R., et al., *Plasma etching of Ti in fluorine-containing feeds*. Journal of Applied Physics, 1992. **71**(1): p. 462.
- [64] Biesinger, M.C., et al., *Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn*. Applied Surface Science, 2010. **257**(3): p. 887–898.
- [65] C.D. Wagner, W.M.R., L.E. Davis, J. F. Moulder and G.E. Muilenburg, ed. *Handbook of X-Ray Photoelectron Spectroscopy*. ed. 2nd. 1979, Perkin-Elmer Corp: Eden Prairie, MN.
- [66] Li, D., et al., *Fluorine-doped TiO₂ powders prepared by spray pyrolysis and their improved photocatalytic activity for decomposition of gas-phase acetaldehyde*. Journal of Fluorine Chemistry, 2005. **126**(1): p. 69–77.
- [67] Yang, H. and X. Zhang, *Synthesis, characterization and computational simulation of visible-light irradiated fluorine-doped titanium oxide thin films*. Journal of Materials Chemistry, 2009. **19**(37): p. 6907–6914.
- [68] Tang, J., H. Quan, and J. Ye, *Photocatalytic Properties and Photoinduced Hydrophilicity of Surface-Fluorinated TiO₂*. Chemistry of Materials, 2006. **19**(1): p. 116–122.
- [69] Zhu, K., et al., *Enhanced Charge-Collection Efficiencies and Light Scattering*

in Dye-Sensitized Solar Cells Using Oriented TiO₂ Nanotubes Arrays. Nano Letters, 2006. 7(1): p. 69–74.

[70] Kumar, K.R.T., M. Ramakrishna, and G.D. Sukumar, *A review on PV cells and nanocomposite-coated PV systems*. International Journal of Energy Research, 2018. 42(7): p. 2305–2319.

[71] Bermel, P., et al., *Improving thin-film crystalline silicon solar cell efficiencies with photonic crystals*. Optics Express, 2007. 15(25): p. 16986–17000.

[72] Shao, J., G. Liu, and L. Zhou, *12 - Biomimetic nanocoatings for structural coloration of textiles*, in *Active Coatings for Smart Textiles*, J. Hu, Editor. 2016, Woodhead Publishing. p. 269–299.

[73] Kay, A. and M. Gratzel, *Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder*. Solar Energy Materials and Solar Cells, 1996. 44(1): p. 99–117.

[74] Ito, S., et al., *High-efficiency organic-dye-sensitized solar cells controlled by nanocrystalline-TiO₂ electrode thickness*. Advanced Materials, 2006. 18(9): p. 1202–+.

[75] Johnson, D.C., et al. *Advances in Bragg stack quantum well solar cells*. in *International Conference on Physics, Chemistry and Engineering of Solar Cells*. 2004. Badajoz, SPAIN: Elsevier Science Bv.

[76] Nishimura, S., et al., *Standing Wave Enhancement of Red Absorbance and Photocurrent in Dye-Sensitized Titanium Dioxide Photoelectrodes Coupled to Photonic Crystals*. Journal of the American Chemical Society, 2003. 125(20): p. 6306–6310.

[77] Rogers, J.A., M. Meier, and A. Dodabalapur, *Using printing and molding techniques to produce distributed feedback and Bragg reflector resonators for plastic lasers*. Applied Physics Letters, 1998. 73(13): p. 1766–1768.

[78] Takahashi, S., et al., *Direct creation of three-dimensional photonic crystals by a top-down approach*. Nat Mater, 2009. 8(9): p. 721–725.

[79] Noda, S., et al., *Full Three-Dimensional Photonic Bandgap Crystals at Near-Infrared Wavelengths*. Science, 2000. 289(5479): p. 604–606.

[80] Bielawny, A., et al., *Intermediate reflectors for enhanced topcell performance in photovoltaic thin-film tandem cells*. Opt. Express, 2009. 17(10): p. 8439–8446.

[81] Wijnhoven, J.E., et al., *Preparation of Photonic Crystals Made of Air Spheres in Titania*. Science, 1998. 281(5378): p. 802–804.

[82] Dae-Kue, H., et al., *Efficiency Enhancement in Dye-Sensitized Solar Cells by Three-Dimensional Photonic Crystals*. Applied Physics Express, 2012. 5(12): p. 122301.

[83] Hwang, D.-K., B. Lee, and D.-H. Kim, *Efficiency enhancement in solid dye-sensitized solar cell by three-dimensional photonic crystal*. RSC Advances, 2013. 3(9): p. 3017–3023.

[84] Schubert, M., et al., *Distributed Bragg reflector consisting of high-and low-refractive-index thin film layers made of the same material*. Applied Physics Letters - APPL PHYS LETT, 2007. 90.

[85] Vos, W.L., et al., *Strong effects of photonic band structures on the diffraction of colloidal crystals*. Physical Review B, 1996. 53(Copyright (C) 2010 The American Physical Society): p. 16231.

[86] Bielawny, A., et al., *3D photonic crystal intermediate reflector for micromorph thin-film tandem solar cell*. physica status solidi (a), 2008. 205(12): p. 2796–2810.

[87] Bahramian, A., *High Conversion Efficiency of Dye-Sensitized Solar Cells Based on Coral-like TiO₂ Nanostructured*

Films: Synthesis and Physical Characterization. Industrial & Engineering Chemistry Research, 2013. **52**(42): p. 14837–14846.

[88] Wu, H.-P., et al., *Hybrid Titania Photoanodes with a Nanostructured Multi-Layer Configuration for Highly Efficient Dye-Sensitized Solar Cells*. The Journal of Physical Chemistry Letters, 2013. **4**(9): p. 1570–1577.

[89] Mir, N., et al., *Optimizing TiO₂ Nanotube Top Geometry for Use in Dye-Sensitized Solar Cells*. Chemistry – A European Journal, 2012. **18**(38): p. 11862–11866.

[90] Huo, J., et al., *Mixed Solvents Assisted Flame Spray Pyrolysis Synthesis of TiO₂ Hierarchically Porous Hollow Spheres for Dye-Sensitized Solar Cells*. Industrial & Engineering Chemistry Research, 2013. **52**(32): p. 11029–11035.

[91] Son, H.-J., et al., *Dye Stabilization and Enhanced Photoelectrode Wettability in Water-Based Dye-Sensitized Solar Cells through Post-assembly Atomic Layer Deposition of TiO₂*. Journal of the American Chemical Society, 2013. **135**(31): p. 11529–11532.

[92] Jose, R., V. Thavasi, and S. Ramakrishna, *Metal Oxides for Dye-Sensitized Solar Cells*. Journal of the American Ceramic Society, 2009. **92**(2): p. 289–301.

[93] Carp, O., C.L. Huisman, and A. Reller, *Photoinduced reactivity of titanium dioxide*. Progress in Solid State Chemistry, 2004. **32**(1–2): p. 33–177.

[94] Linsebigler, A.L., G. Lu, and J.T. Yates, *Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results*. Chemical Reviews, 1995. **95**(3): p. 735–758.

[95] Zhang, J., et al., *New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO₂*.

Physical Chemistry Chemical Physics, 2014. **16**(38): p. 20382–20386.

[96] Kavan, L., et al., *Electrochemical and Photoelectrochemical Investigation of Single-Crystal Anatase*. Journal of the American Chemical Society, 1996. **118**(28): p. 6716–6723.

[97] Zhang, H. and J. F. Banfield, *Thermodynamic analysis of phase stability of nanocrystalline titania*. Journal of Materials Chemistry, 1998. **8**(9): p. 2073–2076.

[98] Barnard, A.S. and H. Xu, *An Environmentally Sensitive Phase Map of Titania Nanocrystals*. ACS Nano, 2008. **2**(11): p. 2237–2242.

[99] Grimes, C.A. and G.K. Mor, *TiO₂ Nanotube Arrays: Synthesis, Properties, and Applications*. 2009: Springer US.

[100] Wen, P., et al., *Single Nanocrystals of Anatase-Type TiO₂ Prepared from Layered Titanate Nanosheets: Formation Mechanism and Characterization of Surface Properties*. Langmuir, 2007. **23**(23): p. 11782–11790.

[101] Liao, J.-Y., et al., *Effect of TiO₂ morphology on photovoltaic performance of dye-sensitized solar cells: nanoparticles, nanofibers, hierarchical spheres and ellipsoid spheres*. Journal of Materials Chemistry, 2012. **22**(16): p. 7910–7918.

[102] Wang, H.-E., et al., *Rapid Microwave Synthesis of Porous TiO₂ Spheres and Their Applications in Dye-Sensitized Solar Cells*. The Journal of Physical Chemistry C, 2011. **115**(21): p. 10419–10425.

[103] Lee, B., et al., *Air-Stable Molecular Semiconducting Iodosalts for Solar Cell Applications: Cs₂SnI₆ as a Hole Conductor*. Journal of the American Chemical Society, 2014. **136**(43): p. 15379–15385.

[104] Lee, B., et al., *Solution processing of air-stable molecular semiconducting*

iodosalts, Cs₂SnI_{6-x}Br_x, for potential solar cell applications. Sustainable Energy & Fuels, 2017.

[105] Hwang, D., et al., *Electrospray Preparation of Hierarchically-structured Mesoporous TiO₂ Spheres for Use in Highly Efficient Dye-Sensitized Solar Cells*. ACS Applied Materials & Interfaces, 2011. **3**(7): p. 2719–2725.

[106] Kruk, M. and M. Jaroniec, *Gas Adsorption Characterization of Ordered Organic–Inorganic Nanocomposite Materials*. Chemistry of Materials, 2001. **13**(10): p. 3169–3183.

[107] Ma, R. and T. Sasaki, *Nanosheets of Oxides and Hydroxides: Ultimate 2D Charge-Bearing Functional Crystallites*. Advanced Materials, 2010. **22**(45): p. 5082–5104.

[108] Kim, I.-D., et al., *Dye-sensitized solar cells using network structure of electrospun ZnO nanofiber mats*. Applied Physics Letters, 2007. **91**(16): p. 163109.

[109] Kim, I.-D., et al., *Ultrasensitive Chemiresistors Based on Electrospun TiO₂ Nanofibers*. Nano Letters, 2006. **6**(9): p. 2009–2013.

[110] Tsai, C.-C. and H. Teng, *Structural Features of Nanotubes Synthesized from NaOH Treatment on TiO₂ with Different Post-Treatments*. Chemistry of Materials, 2006. **18**(2): p. 367–373.

[111] Kroon, J., et al., *Nanocrystalline Dye-Sensitized Solar Cells having Maximum Performance*. Progress in Photovoltaics, 2007. **15**: p. 1–18.

[112] MacFarlane, D.R., et al., *Pyrrolidinium Imides: A New Family of Molten Salts and Conductive Plastic Crystal Phases*. The Journal of Physical Chemistry B, 1999. **103**(20): p. 4164–4170.

[113] Dai, Q., D.R. MacFarlane, and M. Forsyth, *High mobility I⁻ / I₃⁻ redox*

couple in a molecular plastic crystal: A potential new generation of electrolyte for solid-state photoelectrochemical cells. Solid State Ionics, 2006. **177**(3–4): p. 395–401.

[114] Wang, P., et al., *Ambient Temperature Plastic Crystal Electrolyte for Efficient, All-Solid-State Dye-Sensitized Solar Cell*. Journal of the American Chemical Society, 2004. **126**(42): p. 13590–13591.

[115] Dai, Q., et al., *Rapid I⁻/I₃⁻ Diffusion in a Molecular-Plastic-Crystal Electrolyte for Potential Application in Solid-State Photoelectrochemical Cells*. Angewandte Chemie, 2005. **117**(2): p. 317–320.

[116] Cardini, G., R. Righini, and S. Califano, *Computer simulation of the dynamics of the plastic phase of succinonitrile*. The Journal of Chemical Physics, 1991. **95**(1): p. 679–685.

[117] Hawthorne, H.M. and J.N. Sherwood, *Lattice defects in plastic organic solids. Part 2.-Anomalous self-diffusion in succinonitrile*. Transactions of the Faraday Society, 1970. **66**: p. 1792–1798.

[118] Nazeeruddin, M.K., et al., *A swift dye uptake procedure for dye sensitized solar cells*. Chemical Communications, 2003(12): p. 1456–1457.

[119] K. Nazeeruddin, M., P. Pechy, and M. Gratzel, *Efficient panchromatic sensitization of nanocrystalline TiO₂ films by a black dye based on a trithiocyanato-ruthenium complex*. Chemical Communications, 1997 (18): p. 1705–1706.

[120] Nazeeruddin, M.K., et al., *Combined Experimental and DFT-TDDFT Computational Study of Photoelectrochemical Cell Ruthenium Sensitizers*. Journal of the American Chemical Society, 2005. **127**(48): p. 16835–16847.

[121] Zedler, L., et al., *Ruthenium dye functionalized gold nanoparticles and their*

- spectral responses. RSC Advances, 2012. **2** (10): p. 4463–4471.
- [122] Li, L.-L. and E.W.-G. Diau, *Porphyrin-sensitized solar cells*. Chemical Society Reviews, 2013. **42**(1): p. 291–304.
- [123] Higashino, T. and H. Imahori, *Porphyrins as excellent dyes for dye-sensitized solar cells: recent developments and insights*. Dalton Transactions, 2015. **44**(2): p. 448–463.
- [124] Griffith, M.J., et al., *Porphyrins for dye-sensitized solar cells: new insights into efficiency-determining electron transfer steps*. Chemical Communications, 2012. **48**(35): p. 4145–4162.
- [125] Campbell, W.M., et al., *Highly Efficient Porphyrin Sensitizers for Dye-Sensitized Solar Cells*. The Journal of Physical Chemistry C, 2007. **111**(32): p. 11760–11762.
- [126] Yella, A., et al., *Porphyrin-Sensitized Solar Cells with Cobalt (II/III)–Based Redox Electrolyte Exceed 12 Percent Efficiency*. Science, 2011. **334**(6056): p. 629–634.
- [127] Mathew, S., et al., *Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers*. Nat Chem, 2014. **6** (3): p. 242–247.
- [128] Wagner, K., et al., *Significant Performance Improvement of Porphyrin-Sensitized TiO₂ Solar Cells under White Light Illumination*. The Journal of Physical Chemistry C, 2011. **115**(1): p. 317–326.
- [129] Griffith, M.J., et al., *Cation Exchange at Semiconducting Oxide Surfaces: Origin of Light-Induced Performance Increases in Porphyrin Dye-Sensitized Solar Cells*. The Journal of Physical Chemistry C, 2013. **117**(23): p. 11885–11898.
- [130] Mishra, A., M.K.R. Fischer, and P. Bäuerle, *Metal-Free Organic Dyes for Dye-Sensitized Solar Cells: From Structure: Property Relationships to Design Rules*. Angewandte Chemie International Edition, 2009. **48**(14): p. 2474–2499.
- [131] Byung-Hong LEE, S.-Y.J., Seong Mu Jo, Dong Young Kim, Hyun-Ju Kim, *Dye-sensitized solar cell comprising metal oxide nanoball layer and preparation method thereof*. 2010: USA.
- [132] Teng, C., et al., *Molecular Design of Anthracene-Bridged Metal-Free Organic Dyes for Efficient Dye-Sensitized Solar Cells*. The Journal of Physical Chemistry C, 2010. **114**(19): p. 9101–9110.
- [133] Youn, J., et al., *Versatile α,ω -Disubstituted Tetrathienoacene Semiconductors for High Performance Organic Thin-Film Transistors*. Advanced Functional Materials, 2012. **22**(1): p. 48–60.
- [134] Fong, H.H., et al., *Tetrathienoacene Copolymers As High Mobility, Soluble Organic Semiconductors*. Journal of the American Chemical Society, 2008. **130** (40): p. 13202–13203.
- [135] Huang, J., et al., *Dibenzoannelated Tetrathienoacene: Synthesis, Characterization, and Applications in Organic Field-Effect Transistors*. Organic Letters, 2012. **14**(13): p. 3300–3303.
- [136] Letizia, J.A., et al., *Variable Temperature Mobility Analysis of n-Channel, p-Channel, and Ambipolar Organic Field-Effect Transistors*. Advanced Functional Materials, 2010. **20**(1): p. 50–58.
- [137] Wang, M., et al., *High-Performance Liquid and Solid Dye-Sensitized Solar Cells Based on a Novel Metal-Free Organic Sensitizer*. Advanced Materials, 2008. **20** (23): p. 4460–4463.
- [138] Qin, H., et al., *An Organic Sensitizer with a Fused Dithienothiophene Unit for*

Efficient and Stable Dye-Sensitized Solar Cells. Journal of the American Chemical Society, 2008. **130**(29): p. 9202–9203.

[139] Lu, M., et al., *Organic Dyes Incorporating Bis-hexapropyltruxeneamino Moiety for Efficient Dye-Sensitized Solar Cells*. The Journal of Physical Chemistry C, 2011. **115**(1): p. 274–281.

[140] Chang, S.H., et al., *Broadband charge transfer dynamics in P3HT:PCBM blended film*. Optics Letters, 2013. **38** (24): p. 5342–5345.

[141] Zhou, N., et al., *Metal-Free Tetrathienoacene Sensitizers for High-Performance Dye-Sensitized Solar Cells*. Journal of the American Chemical Society, 2015. **137**(13): p. 4414–4423.

[142] Cid, J.-J., et al., *Molecular Cosensitization for Efficient Panchromatic Dye-Sensitized Solar Cells*. Angewandte Chemie, 2007. **119**(44): p. 8510–8514.

[143] Sayama, K., et al., *Efficient sensitization of nanocrystalline TiO₂ films with cyanine and merocyanine organic dyes*. Solar Energy Materials and Solar Cells, 2003. **80**(1): p. 47–71.

[144] Lee, B., et al., *Cs₂SnI₆-Encapsulated Multidye-Sensitized All-Solid-State Solar Cells*. ACS Applied Materials & Interfaces, 2019. **11**(24): p. 21424–21434.

[145] Xie, Y., et al., *Porphyrin Cosensitization for a Photovoltaic Efficiency of 11.5%: A Record for Non-Ruthenium Solar Cells Based on Iodine Electrolyte*. Journal of the American Chemical Society, 2015. **137**(44): p. 14055–14058.

[146] Clifford, J.N., et al., *Sensitizer molecular structure-device efficiency relationship in dye sensitized solar cells*. Chemical Society Reviews, 2011. **40**(3): p. 1635–1646.

[147] Wu, H.-P., et al., *Molecular engineering of cocktail co-sensitization for efficient panchromatic porphyrin-sensitized solar cells*. Energy & Environmental Science, 2012. **5**(12): p. 9843–9848.

[148] Nguyen, L.H., et al., *A selective co-sensitization approach to increase photon conversion efficiency and electron lifetime in dye-sensitized solar cells*. Physical Chemistry Chemical Physics, 2012. **14** (47): p. 16182–16186.

[149] Pei, K., et al., *Cosensitization of D-A- π -A Quinoxaline Organic Dye: Efficiently Filling the Absorption Valley with High Photovoltaic Efficiency*. ACS Applied Materials & Interfaces, 2015. **7** (9): p. 5296–5304.

[150] Yum, J.-H., et al., *Efficient co-sensitization of nanocrystalline TiO₂ films by organic sensitizers*. Chemical Communications, 2007(44): p. 4680–4682.

[151] Fan, S.-Q., et al., *Improved Efficiency of over 10% in Dye-Sensitized Solar Cells with a Ruthenium Complex and an Organic Dye Heterogeneously Positioning on a Single TiO₂ Electrode*. The Journal of Physical Chemistry C, 2011. **115**(15): p. 7747–7754.

[152] Lan, C.-M., et al., *Enhanced photovoltaic performance with co-sensitization of porphyrin and an organic dye in dye-sensitized solar cells*. Energy & Environmental Science, 2012. **5**(4): p. 6460–6464.

[153] Yu, Z., et al., *Liquid electrolytes for dye-sensitized solar cells*. Dalton Transactions, 2011. **40**(40): p. 10289–10303.

[154] Wu, J., et al., *Electrolytes in Dye-Sensitized Solar Cells*. Chemical Reviews, 2015. **115**(5): p. 2136–2173.

[155] Zhou, N., et al., *Cross-Linkable Molecular Hole-Transporting*

Semiconductor for Solid-State Dye-Sensitized Solar Cells. The Journal of Physical Chemistry C, 2014. **118**(30): p. 16967–16975.

[156] Chung, I., et al., *All-solid-state dye-sensitized solar cells with high efficiency*. Nature, 2012. **485**(7399): p. 486–489.

[157] Law, C., R. Spence, and B. C. O'Regan, *Brief air heating of TiO₂/dye films, to 120–250 [degree]C; the effect on resulting liquid junction dye sensitised solar cells (DSSCs) and melt-processed solid-state DSSCs*. Journal of Materials Chemistry A, 2013. **1**(45): p. 14154–14161.

[158] Liu, X., et al., *An Efficient Organic-Dye-Sensitized Solar Cell with in situ Polymerized Poly (3, 4-ethylenedioxythiophene) as a Hole-Transporting Material*. Advanced Materials, 2010. **22**(20): p. E150–E155.

[159] Johansson, E.M.J., et al., *Combining a Small Hole-Conductor Molecule for Efficient Dye Regeneration and a Hole-Conducting Polymer in a Solid-State Dye-Sensitized Solar Cell*. The Journal of Physical Chemistry C, 2012. **116**(34): p. 18070–18078.

[160] Ukaji, E., et al., *The effect of surface modification with silane coupling agent on suppressing the photo-catalytic activity of fine TiO₂ particles as inorganic UV filter*. Applied Surface Science, 2007. **254**(2): p. 563–569.

[161] Zhao, J., et al., *Surface modification of TiO₂ nanoparticles with silane coupling agents*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2012. **413**: p. 273–279.

[162] Scholin, R., et al., *Energy Level Shifts in Spiro-OMeTAD Molecular Thin Films When Adding Li-TFSI*. Journal of Physical Chemistry C, 2012. **116**(50): p. 26300–26305.

[163] Leijtens, T., et al., *Hole Transport Materials with Low Glass Transition Temperatures and High Solubility for Application in Solid-State Dye-Sensitized Solar Cells*. ACS Nano, 2012. **6**(2): p. 1455–1462.

[164] Papageorgiou, N., W.F. Maier, and M. Gratzel, *An Iodine/Triiodide Reduction Electrocatalyst for Aqueous and Organic Media*. Journal of The Electrochemical Society, 1997. **144**(3): p. 876–884.

[165] Papageorgiou, N., *Counter-electrode function in nanocrystalline photoelectrochemical cell configurations*. Coordination Chemistry Reviews, 2004. **248**(13–14): p. 1421–1446.

[166] Acharya, K.P., et al., *Pulsed laser deposition of graphite counter electrodes for dye-sensitized solar cells*. Applied Physics Letters, 2010. **97**(20): p. 201108–201103.

[167] Veerappan, G., K. Bojan, and S.-W. Rhee, *Sub-micrometer-sized Graphite As a Conducting and Catalytic Counter Electrode for Dye-sensitized Solar Cells*. ACS Applied Materials & Interfaces, 2011. **3**(3): p. 857–862.

[168] Murakami, T.N., et al., *Highly Efficient Dye-Sensitized Solar Cells Based on Carbon Black Counter Electrodes*. Journal of The Electrochemical Society, 2006. **153**(12): p. A2255–A2261.

[169] Murakami, T.N. and M. Grätzel, *Counter electrodes for DSC: Application of functional materials as catalysts*. Inorganica Chimica Acta, 2008. **361**(3): p. 572–580.

[170] Imoto, K., et al., *High-performance carbon counter electrode for dye-sensitized solar cells*. Solar Energy Materials and Solar Cells, 2003. **79**(4): p. 459–469.

[171] Huang, Z., et al., *Application of carbon materials as counter electrodes of dye-sensitized solar cells*.

Electrochemistry Communications, 2007. **9**(4): p. 596–598.

[172] Trancik, J.E., S.C. Barton, and J. Hone, *Transparent and Catalytic Carbon Nanotube Films*. Nano Letters, 2008. **8** (4): p. 982–987.

[173] Roy-Mayhew, J.D., et al., *Functionalized Graphene as a Catalytic Counter Electrode in Dye-Sensitized Solar Cells*. ACS Nano, 2010. **4**(10): p. 6203–6211.

[174] Saranya, K., M. Rameez, and A. Subramania, *Developments in conducting polymer based counter electrodes for dye-sensitized solar cells – An overview*. European Polymer Journal, 2015. **66**: p. 207–227.

[175] Gnanasekar, S., et al., *Pt-free, low-cost and efficient counter electrode with carbon wrapped VO₂(M) nanofiber for dye-sensitized solar cells*. Scientific Reports, 2019. **9**(1): p. 5177.

[176] Lee, B., D.B. Buchholz, and R.P.H. Chang, *An all carbon counter electrode for dye sensitized solar cells*. Energy & Environmental Science, 2012. **5**(5): p. 6941–6952.

[177] Yuan, X.-Z., et al., *Electrical Fundamentals*

[178] *Electrochemical Impedance Spectroscopy in PEM Fuel Cells*. 2010, Springer London. p. 39-93.

[179] Kavan, L., J.H. Yum, and M. Grätzel, *Optically Transparent Cathode for Dye-Sensitized Solar Cells Based on Graphene Nanoplatelets*. ACS Nano, 2010. **5**(1): p. 165–172.

[180] Macagno, V.A., M.C. Giordano, and A.J. Arví, *Kinetics and mechanisms of electrochemical reactions on platinum with solutions of iodine-sodium iodide in acetonitrile*. Electrochimica Acta, 1969. **14**(4): p. 335–357.

[181] Liberatore, M., et al., *Using EIS for diagnosis of dye-sensitized solar cells performance*. Journal of Applied Electrochemistry, 2009. **39**(11): p. 2291–2295.

[182] Zhu, G., et al., *Electrophoretic deposition of reduced graphene-carbon nanotubes composite films as counter electrodes of dye-sensitized solar cells*. Journal of Materials Chemistry, 2011. **21** (38): p. 14869–14875.

[183] Liu, Z., et al., *Revisiting thin silicon for photovoltaics: a technoeconomic perspective*. Energy & Environmental Science, 2020. **13**(1): p. 12–23.

[184] Kim, J.-H., H.-R. Kim, and J.-T. Kim, *Analysis of Photovoltaic Applications in Zero Energy Building Cases of IEA SHC/EBC Task 40/Annex 52*. Sustainability, 2015. **7**(7): p. 8782–8800.

[185] Traverse, C.J., et al., *Emergence of highly transparent photovoltaics for distributed applications*. Nature Energy, 2017. **2**(11): p. 849–860.