Self assembled photonic crystals in solar cells

Yip, Chan Hoe

2011

Yip, C. H. (2011). Self assembled photonic crystals in solar cells. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/60523>

<https://doi.org/10.32657/10356/60523>

Self Assembled Photonic Crystals in Solar Cells

by

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SUBMITTED TO THE SMA OFFICE IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY
IN ADVANCED MATERIALS FOR MICRO- AND NANO- SYSTEMS
(AMM&NS)
AT THE
SINGAPORE-MIT ALLIANCE

2011

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ACKNOWLEDGMENT

Prof Wong Chee Cheong has been a great inspirer and guide for my research work. I am grateful to him for providing opportunities for my personal development and unrestrained space to experiment my brainwave. He has been a great salesman during my research topic selection, a motivator who encourages me to search for the light in the tunnel and a critic to raise the bar of my work. He is warm and his door is always open. Prof Yet-Ming Chiang has also offer me encouragement and advice, and the appreciation for value is one of which I had learned from him. He is my role model for finding value and to be enterprising. Thank you.

When I stepped into Prof Wong's research group, Yaw Koon and Lay Kuan could have felt intimidated because I was tasked to interview them and write a report on their strengths, skills and equipment handling and to present them in the subsequent group meeting. I was supposed to join them and learn about their colloidal self-assembly research and to carve out a tangential research direction for myself. On the contrary, Yaw Koon and Lay Kuan have been selfless and I learned quickly from them. Yaw Koon is a great mentor, and we grew in chemistry which led us to work on a paper together and later a business venture that unfortunately didn't work out. Lay Kuan is instrumental for introducing me the simulation packages which become the workhorse of my numerical analysis. Dr Yan Qingfeng joined our group later and I benefited tremendously from his flow-controlled vertical deposition setup, layer transfer technique and systematic scientific investigation. A big special thank you to my three mentors.

Over the years, there were many fellow researchers, students and interns in the group who had stimulated my thought process and contributed to my work. In the ascending order of seating position from me, I am grateful to Kwan Wee, Pierrick, Kwang Hong, Duen Yang, Yuhua, Xiaofang, Husen, Wang Xiu, Anantha, Eric, and my collaborators: Hongyu, Fedelia, Anabelle, Lin Hai, Xuchen, Lia, Zou Xin, Shimon, Yew Hown, and Wei Chiang. I thank Dr. Madhavi Srinivasan and Dr. Martin Schreyer for teaching me XRD post-analysis. I thank Prof Steven G. Johnson for teaching me the photonic crystal and simulation techniques during my second semester stay at MIT. I am grateful to Singapore-MIT Alliance for providing me a fellowship for graduate studies.

Life is ups and downs. I lost both grandmothers when I was away during the two separate semester stays at MIT. My illiterate grandmum once praised me on my good handwriting when I was 8 years old. Not particularly impressionable to a young child kid then, however the thought stays on these years for self-reflection. The handwritng has suffered over the years but she is still my guiding light to better myself in life. I like to express my deepest gratitude to my wife, Candy, and my family for their cheering and support. My father and mother have been role models to for me; on the values of humility and conscientiousness. Finally, I am indebted to the unsung heros of the MSE laboratory staff: Mastura, Yani, Sandy, Sharon, Irene, Poh Tin, Guo Jun, Lee Chin, Patrick, John, Yong Guang, Swee Kuan, Nelson and Wilson for making things running and their guidance. Thank you.

Chan Hoe

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ABSTRACT

Colloidal self-assembly (CSA) has been harnessed to fabricate nanoscale ordered structures with unique optical property for photovoltaic application. The self-assembly technique enables the fabrication of 3D photonic band gap (PBG) structures with (i) tunable periodicity; (ii) variable number of period; and (iii) the inclusion of a defect layer in a colloidal crystal thin film to enhance light-matter interaction in a dye-sensitized solar cell (DSSC). The increase in electric field near the dielectric band edge, where the group velocity of light is slow and the density of states is high, and the localization of permitted states in the gap have increased the photo-excitation of a photosensitive dye in a DSSC. This results in the increased light harvesting efficiency of the solar cell. This study provides an insight into the changes in optical absorption of an atom when the space surrounding that atom is modified. Finally, the PBG structure is most effective when it can be embedded as a back reflector in a photovoltaic cell and where its huge interfacial area can enhance the active area for photocurrent generation.

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1. Introduction

Bottom-up self-assembly process is the nature's most energy efficient tool to produce ordered nanostructures. Examples of naturally occurring ordered nanostructures are opal stones and feathers of peacock as illustrated in Figure 1-1. These crystalline solids contain periodic arrangement of dielectric materials and they reflect off brilliant hue of colours depending on which angle the person is looking at the crystals. A closer look on peacock's feather under the scanning electron microscope (SEM) reveals the ordering of dielectric spheres with air filling (see Figure 1-1(b), insert).

Figure 1-1. Naturally occurring ordered nanostructures. (a) opal stone and (b) feather of a peacock (insert: SEM image). Source: Images from the Internet.

From literature, the butterfly wing has been used as a template for fabricating 3D titanium dioxide (TiO_2) porous nanostructure. [1] Titanium precursor solution was filled into the butterfly wing template over a 40-cycles exposure. The sample was then calcined at high temperature to remove the template, and finally an

inverted porous nanostructure functionalized with TiO_2 was formed. This TiO_2 porous nanostructure is advantageous for use in biomedical, filtration, or optics applications where huge surface area and a photo-catalytic action are desired.[2] In another bio-inspired application, the fresh lotus leaf was used as a mold to create a super-hydrophobic surface for anti-fogging and self-cleaning application. Two cycles of PDMS casting were carried out to form the lotus leaf replica by molding against the fresh lotus leaf surfaces. The replicated PDMS film has a nanostructured surface of self-standing nanopillars which mimic the papillae of the lotus leaf. It was shown that the nanostructured surfaces exhibit superhydrophobic characteristics with the huge water contact angle. [3]

1.1 Colloidal Self-assembled Ordered Nanostructures

The diversity in nature has created a myriad of material structures and properties with immense complexity. Under the microscope, one can observe how one small building block can be replicated to form an interesting 3D structure of useful physical properties. Today, significant progress has been made to replicate synthetic nanostructures using top-down techniques such as electron beam lithography[4], nanoimprint lithography[5] and micro-fabrication methodologies.

Bottom-up self-assembly of colloidal particles offers a facile way to produce a 3D ordered structure. This assembled structure is known as a colloidal crystal or opal. The use of colloidal self-assembly has attracted wide interest because of numerous potential applications that can be derived from the porous template. For example, the 3D colloidal structures have found applications in the implementation

of optical filters, pH, temperature, glucose, chemical warfare agent sensors. [6-11]
Further, spin-coated monolayer of a colloidal particle film has been demonstrated in nanospheres lithography to enable seeding a template for nanowires growth. [12]

1.1.1 Colloidal and Surface Science

Colloid is a mixture of microscopic particles suspended in another matter.[13, 14]
Common examples of colloid are paints or slurries and these are known as sols (solid-in-liquid colloids). These colloidal particles have characteristic dimension in the range of 1 nm to 1 μm . The physical behavior of the small colloidal particles is strongly affected by their surface charges and Brownian motion in the liquid and less affected by gravitational force. A colloid acquired a static charged surface when dispersed in a liquid due to the dissociation of end groups at the surface. The charged surface attracts oppositely charged counterions from the surrounding liquid. Shown in Figure 1-2(a), an electrical double layer is created around the colloidal particle from the first layer of surrounding counterions and the second layer of the charged particle's surface. [15]

Figure 1-2. (a) Schematic drawing of an electric double-layer surrounding a charged colloidal particle. (b) DLVO interaction energy against distance from the center of the colloids.

The electric potential theory put forth by Derjaguin-Landau-Verwey-Overbeek (DLVO) has become the popular model governing the interaction among charged colloids, counter-ions and co-ions in the liquid. [16, 17] Particles tend to come together and aggregate by attractive London-van der Waals force at short separation distance. Figure 1-2(b) illustrated the DLVO interaction graph as a combined effect of electric repulsion and London-van der Waals attraction. Colloidal particles will be aggregated to one another when their separation distances are close to zero with respect to their radius. Thus the electrical double layer is an important parameter where the colloidal suspension can be made stable by adjusting the concentration of counter-ions (for example: salts) in the liquid with sufficient repulsion force to keep particles from coming together. [18]

The repeatability and large volume synthesis of monodisperse colloids have been instrumental for enabling the building blocks for assembling large area crystalline arrays.[19-22] Suspensions such as polystyrene[23, 24] or silica [25, 26] nanospheres or particles in water can be synthesized with programmable diameters, and with a very small spread in size. As a result, the monodisperse colloid can now be used to form ordered nanostructures through colloidal self-assembly. The most dominant order of a self-assembled colloidal crystal is the close packed face-centered cubic (FCC) structure.[27, 28] The methods for creating colloidal crystals include sedimentation [29, 30] , electrophoresis[31-33], vertical deposition [21, 22, 34] and template-directed growth [35, 36].

Vertical deposition technique is the most popular among the methods for creating high quality colloidal crystal thin film on a substrate. In a typical vertical

deposition colloidal self-assembly, a glass substrate is immersed vertically into a polystyrene colloidal particle suspension as illustrated in Figure 1-3. The suspension is heated inside an oven to provide convective heating in the liquid suspension. A meniscus is formed at the glass-suspension interface. The meniscus has a very low contact angle for a clean glass (hydrophilic) and this forms a vertical capillary channel. Under convective flow and capillary force, the colloidal particles are driven upwards from the suspension towards the meniscus. As the liquid evaporates, the meniscus recedes and the colloids are closely packed into a 2D monolayer (very low colloid concentration and high receding speed) or 3D multilayer (high colloid concentration and low receding speed) colloidal array on the glass substrate. Refer to Appendix A for images of vertical deposition.

Figure 1-3. Vertical deposition colloidal self-assembly. A hydrophilic substrate is inserted vertically in a heated colloidal suspension. The colloidal particles are driven up to the meniscus against the gravity due to convective and capillary forces.

1.2 Three-dimensional Photonic Crystal

Self-assembled colloidal crystal is a simple and inexpensive method to create a 3D ordered nanostructure employing natural forces. This colloidal crystal (also known

as artificial opal) is also known as a photonic crystal if the lattice periodicity is on the order of wavelength of light and consisting of dielectric materials only. [28, 37] In the example of assembled polystyrene (PS) colloidal crystal, the interstitial air volume accounts for a region of lower refractive index while particles fill the rest of the space with higher refractive index. It is the regular ordering of dielectric space that gives the colloidal crystal a unique optical reflection property at a certain wavelength, known as photonic band gap (PBG). [38-41] The spectral location of the PBG or the reflectance peak can be varied depending on the dimension of the periodicity (particle's size). This is an example of how the geometry of nanostructure can reflect off different colours of light while the constituent material - polystyrene in this case - is transparent.

Figure 1-4. SEM images of a polystyrene colloidal crystal (opal). (a) cross section view, (b) top view. The cross section view shows different crystallography planes of a FCC lattice. The top view shows the intrinsic defect of 'mud crack' effect. The scale bar represents 10 μm .

In a photonic crystal, photons move through a material with alternate regions of high and low refractive index. To a photon, this refractive index contrast looks just like the periodic potential wells that an electron experiences while traveling through a crystalline solid. Light entering the composite material will be scattered

off the myriad internal interfaces of high and low refractive index materials. Perfect cancellation in a certain direction for a particular wavelength gives rise to a photonic band gap where light is prohibited to propagate. It is being reflected back. The larger the contrast of refractive indices, the wider is the photonic band gap. The more the number of layers in the crystal, the stronger is the effect of reflection.

1.2.1 Properties of Photonic Crystal

Photonic crystals exhibit numerous optical properties such as the photonic band gap, negative index of refraction[42], increased density of modes and low group velocity at band edges[43, 44]. Engineering negative index in material can result in the reverse light bending property and has been shown in superprism and cloaking applications. [45, 46] In addition, the slow group velocity of light near the band edges were used to control the optical gain of stimulated emission.[47-49] and spontaneous emission[50, 51] in colloidal composite structures.

Figure 1-5. A reflectance spectrum for a typical photonic crystal (PC). The photonic band gap (PBG) presents as a reflectivity peak with peak wavelength (λ_p) at the mid-gap position. The greater the number of layers in a PC, the higher is the reflectivity. The greater the contrast in the PC materials' refractive indices, the wider is the PBG. At both sides of the PBG, these are the highly dispersive regions (band edges).

One of the interesting properties of photonic crystal capitalized in this thesis is the slow light phenomenon occurring near the gap's flat edges where the material dispersion is anomalously increased by the photonic crystal. The group velocity of light slows down when its wavelength is near to the flat band edges. When a packet of light transverses near the gap edges, each wavelength of light gets slows down by a different degree as specified by the material dispersion. This is quantified by the group velocity v_g , which defines the velocity for the light packet through a material.

In Ref. [52], a group velocity of light was measured to be about 6 times slower than speed of light in vacuum for a SiO_2/Si multilayers ($N=6$) 1D photonic crystal using a Mach-Zehnder interferometer. Ref. [52] also suggests that the group velocity reduces as the number of multilayer increases. As explained in the following sections, the phenomenon of slow light effect in photonic crystal is harnessed for applications to enhance the interaction between light and matter for the benefit in solar cell application.

1.2.2 Colloidal Crystal as a Photonic Crystal

Self-assembly of colloidal crystal (opal) is a simpler and inexpensive method to create a 3D photonic crystal compared to traditional micro-fabrication techniques. [53, 54] A colloidal crystal is also considered as a photonic crystal when its periodicity is in the order of visible light spectrum.

Figure 1-6. Intrinsic defects of a colloidal crystal. (a) Particle vacancy; (b) stacking fault; (c) cracks and (d) non-closely packed. All scale bars represent 1 μm length.

The size of a colloidal crystal film can scale up depending on the size of the deposition apparatus. However, the shortcomings of colloidal crystal include the presence of intrinsic defects such as particle vacancy, dislocations, non-closely packed structure and texture. The defects are illustrated in Figure 1-4 and Figure 1-6. Such defects are light scattering centers in photonic applications and they translate as signal propagation loss in telecommunication. However, studies have shown that the photonic bandgap is robust against such defects and the self-assembly technique can be capitalized as a low cost micro-fabrication model. [53, 55-57] Table 1 lists the advantages and disadvantages of colloidal self-assembly for photonic application.

Table 1-1. Advantages and disadvantages of colloidal self-assembly for photonic application.

Advantages	Disadvantage
1. Forms 3D ordered structure naturally.	1. Intrinsic defects are inherent during growth.
2. Tailors the lattice parameters and material properties.	2. Light scattering due to defects.
3. Fabricated using simple equipment and in parallel process.	3. FCC colloidal crystal restricts the choice of infiltration material for complete photonic bandgap compared to a diamond structure.
4. Can be functionalized to implement application specific devices	

In this thesis, 3D photonic crystal fabricated by colloidal self-assembly was introduced inside a photovoltaic cell. By tapping on the unique optical properties of a photonic crystal, the enhancement of the solar power conversion in a photonic crystal plus photovoltaic cell would be demonstrated in the subsequent chapters.

1.2.3 Electromagnetism in a Photonic Crystal

The theory of electromagnetism starts with an elementary understanding in ray optics. This is especially so in high school syllabus where geometric optics is used to understand light convergence using a lens. Here, the ratio of light wavelength (λ) to the radius of curvature (κ) of lens is almost zero ($\lambda/\kappa \rightarrow 0$), thus geometric optics serves its purpose very well.

Now, for the structures relevant to this thesis, the wavelength of interest is very close to the structure's natural dimension (a). Analysis of the electromagnetic wave in this structure becomes complex [58, 59], and most often numerical methods and simplification needs to be employed. The analysis can be simplified if the structure is ordered where Bragg law can be used to take advantage of symmetry and well-defined geometric rules. However, Bragg law is useful only for simple diffraction computation and is unable to compute dispersion relation and strength of diffraction (for example varying number of 1D multi layers). For such deeper analysis, the Transfer-Matrix Method for dielectric 1D multilayer structure can be used. [60]

For complete analysis on more complex ordered structure, numerical method such as planewave expansion [61] is the tool for casting the Maxwell equation into a linear Hermitian eigenvalue problem. As a result, the behavior of light propagating through a photonic crystal can now be formulated into a systematic calculation where several similarities can be drawn from the study of the established quantum-mechanics. [62] First, the symmetric structure allows the use of orthogonality of mode to explain the discrete wave localization together with boundary conditions and transversality constraint. The electromagnetic mode that couples into the symmetric structure mode is thus cast into Bloch form and solved as an eigenvalue problem. Second, in the assignment of orthogonal modes in a symmetric structure, the Variational Principle (VP) governs the smallest eigenvalue (lowest frequency mode) to correspond to the field pattern which minimizes the variational function. In other words, a field with high spatial oscillation is not

avored in VP. In the next higher orthogonal mode, variational function is computed again to give the next eigenvalue, and the cycle continues. Thus, the complete dispersion relation can be computed. Third, after the computation of the eigenvalue problem, small non-linearity and materials loss can be introduced by using perturbation theory. This is when material absorption and non-linearity can be included into the numerical study in order to mimic real practical situation.

Figure 1-7. Dispersion diagrams of three different structures. (a) Homogenous material plane with dielectric constant ϵ . The dispersion graph is a light line with the velocity of light in the plane reduced by a factor of square root of ϵ . (b) Similar homogenous block with an arbitrary

1D spatial division of a length. Symmetry allows the folding of the diagram into an irreducible Brillouin Zone. The band diagram repeats itself for every $k + 2\pi/a$. (c) Perturbations, $\Delta\epsilon$, are introduced to every alternate layer with regular thicknesses. Variational principle results in the formation of forbidden gaps.

1.2.4 Photonic Band Diagram of a Colloidal Crystal

The photonic band diagram shows the dispersion relation of an ordered structure. To understand the origin of photonic band gap (PBG), first consider a homogenous material with dielectric constant (ϵ) as shown in Figure 1-7(a). The dispersion graph is shown in the right panel of Figure 1-7(a) where the gradient of the line shows velocity of light in the material.

The homogenous material can be divided into 1D multilayer by a virtual lattice parameter (a) without any change to the physical behavior as depicted in Figure 1-7(b). Due to the symmetry, the band diagram now can be folded into Brillouin zones (BZ) in Figure 1-7(b) and the shaded section is the irreducible BZ. It can be observed that both the structure and the band diagram repeat itself for every $k + 2\pi/a$. Due to mirror symmetry, it is sufficient to study the irreducible BZ for the dispersion relation.

A small perturbation is added to the structure in Figure 1-7(c) where the dielectric constant (ϵ) of the alternative layers is added with a non-zero $\Delta\epsilon$. In the VP discussed earlier, low frequency energy modes concentrate in high ϵ region and high frequency energy modes concentrate in low ϵ region. When the dielectric index contrast is higher, the frequency difference between these 2 modes is

corresponding higher and a photonic band gap (PBG) is obtained. Figure 1-7(c) illustrates a band diagram where the forbidden gaps are shown in shade.

Moving on to 3D structure, the photonic band diagram of a polystyrene opal is shown in Figure 1-8 and it is simulated with a freely available software package MIT Photonic-Bands (MPB) by iterative eigenvalue solving techniques.[63] In the computational cell, the opal has a face cubic centered (FCC) lattice, and the dielectric spheres have a refractive index of 1.6 (polystyrene). The y-axis of Figure 1-8 is the angular frequency and it is normalized with $a/2\pi c$ unit. Therefore the scale invariant diagram applies to all sizes of polystyrene sphere in the order of visible light range (by normalizing to a). The x-axis is the wave vector and the letters symbolize the high-symmetry points across the irreducible BZ of the FCC opal. [61]

Figure 1-8. The photonic band diagram of polystyrene colloidal crystal. Band diagram is simulated in planewave basis, refractive indices of polystyrene and air are 1.6 and 1 respectively. A pseudo gap with a center frequency of 0.602 is formed between band 2 and 3 in Γ L direction.

In Figure 1-8, the wavevector ΓL is the $[111]$ direction of the FCC opal and this is the normal incidence angle looking on the top of an opal film. The shaded region between band 2 and band 3 in ΓL direction is the photonic band gap (PBG). This gap is commonly known as the pseudo gap where optical reflection occurs for that spectral location and direction. This is the forbidden spectral region where light of this wavelength range is forbidden in the photonic crystal or where light exists as a weak evanescent wave. In Figure 1-8, the mid gap location is about $0.602 \left(\frac{\omega a}{2\pi c} = \frac{a}{\lambda} \right)$. For FCC opal structure, the lattice parameter is related to the sphere's diameter (D) by $a = \sqrt{2} D$ and this relation will be explained in the next chapter. Combining these relationships, the wavelength of the first order reflectance peak (λ_p) can be estimated by this handy formula:

$$\lambda_p = 2.357 D , \quad (1-1)$$

by using the known polystyrene (PS) particle size (D). Therefore, the monodisperse polystyrene colloids' diameter can be estimated from reflectance spectroscopy, or vice versa, without the need for scanning electron microscopy (SEM). For example, a monodisperse PS suspension of 230 nm size purchased from a colloids vendor will have a $\lambda_p = 542$ nm approximately.

Further, in the direction LU as shown in Figure 1-8, there is a gap progressing to higher frequency as the direction moves closer to U direction. (These directions will be discussed in detail in next chapter) The direction U is the tilt angle from the normal incidence, that is why we will see a red-reflecting opal in the normal

incidence and it appears green→blue as we tilt the angle of view. This angle-gap property will be used for angle-resolved studies in Chapter 3.

1.3 Photonic Crystal in Solar Power Conversion

How much solar energy can be tapped for useful production of clean electricity? On a clear day, approximately 1000 W/m^2 of light power irradiates the earth's surface. As a yardstick, an average microwave oven consumes about 1000 W of power. The 1000 W/m^2 power represents the total available radiation ranging from ultraviolet through visible to infrared, all within 0.2 - 50 μm spectral range. Figure 1-9(a) illustrates the spectral spread of solar radiation in terrestrial and on the earth surface up to 3 μm wavelength. On the earth's surface, the irradiance is often shaped by the cloud cover, atmosphere absorption, latitude and elevation. The 0.2 - 3 μm spectral range contains about 99% of solar energy and the area under the irradiance curve is available for potential solar energy harvesting. Of this range of solar energy, the ultraviolet (UV) rays account for 5% of energy and visible light 46%.

Silicon, a semiconductor having electronic band gap energy of 1.1 eV, is well-suited to be the material of choice for p-n junction solar cells. This can be observed in Figure 1-9(b) where a large amount of solar energy above the Si band gap ($E=h\nu$; $\lambda=1.24/1.1=1.13 \mu\text{m}$) can be used for the photoexcitation of valence electrons into the conduction band of Si. For radiation with energy greater than band gap of Si, the excess energy is wasted as heat in Si. Near-infrared radiation above 1.13 μm and beyond does not get converted to useful energy and this loss

represents about 25% of all solar radiation energy at sea level. If the energy is greater than the band gap, the hot electrons relax to lower energy by phonon vibration. This limits the amount of solar energy in Figure 1-9(b) that can be converted to useful energy output. Nevertheless, the economic return is high for any scheme or system to absorb as much as the visible light spectrum because of the huge visible energy available as depicted in Figure 1-9(b).

Figure 1-9. Solar Reference Spectra (ASTM G173-03): (a) at the top of the atmosphere and sea level; (b) energy available for harvesting by the mainstream silicon photovoltaic technology.

Photons travel 149 million kilometers from the sun to the earth and losing much intensity along the way. Photons are important in illuminating the earth, regulating the weather and participating in photosynthesis. Only a very tiny part of the hemisphere facing the sun is gainfully used to convert the solar energy to indoor heating or converting into electricity. According to a renewable energy watchdog, the global fossil energy consumed in a year is less than the total solar energy falling on the earth's surface in one hour. There is still massive potential to deploy large scale solar energy harvesting to reduce the need of fossil fuel. Further, much of the solar energy can still be potentially tapped beyond powering 2 incandescent bulbs per square meter of PV system.

The use of well-designed photon management techniques in solar cells can enhance the optical absorption and power conversion efficiency.[64, 65] In optimizing the geometrical design of the solar cell to absorb more incident light, the external quantum efficiency of the solar cell can be improved through light trapping schemes.[66-68]

The benefit of having a back reflector scheme for a silicon based solar cell is limited. This is because silicon is inherently a weak light absorber. Hence, a thick silicon cell is needed to absorb light sufficiently, and incurs a relative increase in material cost. However, a thick silicon cell is non-transparent and any back reflecting mechanism inside the cell has diminishing benefit. The next few sections tackle this non-transparency issue and a photonic crystal is highlighted on the beneficial influence on a PV system.

1.3.1 Enhancing Light Intensity

Most often, a PV module is irradiated with an intensity that is below the designated power. For example, PV modules installed at temperate regions receive less sunlight annually compares to the installations near to the equator where there is an abundance of sunlight. Besides, cloud cover or rainy days will reduce the intensity of sun light reaching the PV modules on the ground level. As a result, the electricity generated is often below the rated wattage described in the datasheet. Hence, the above-mentioned PV modules have yet to realize their optimum performance and concentrating PV (CPV) technology have sprung up to squeeze more wattage from the PV system.

Under midday sunny condition when the irradiance from the sun is ideal for PV, there is still reflection loss at the air-solar cell interface (external quantum efficiency) due to Fresnel reflection. [69] Further, there is photon-electron conversion probability (internal quantum efficiency) and resistive loss in the solar cell contacts. A typical commercial silicon PV module has power conversion efficiency (PCE) rating of 12%. This translates to 120 W per 1m^2 of panel size (on sunny day) and represents roughly 2 regular incandescent bulbs' power consumption.

To counter the drawback of low irradiance situation, novel research is carried out in using quantum dots (QD) for multiplying charge generation process in a solar cell.[70] Multiple exciton generation (MEG) effect per photon has been reported in QD.[71] It claimed that MEG can challenge the thermodynamic limit of PV energy conversion by generating more electricity per photon of light. However,

the crucial step in separating the excitons and extracting charge carriers out to the external load remains to be realized for commercial success.

On another research front, the challenge of increasing PV efficiency has promoted the use of novel materials such as: CIGS (copper indium gallium selenide) thin film solar cell for its excellent light absorption property. However, the PV manufacturers of using rare earth materials will face the imminent shortage of indium available for extraction and commercial viability for large scale solar energy harvesting.

Most often, a solar cell can be made to function at its optimum point if sufficient sunlight is present. Therefore, a simple light reflector coupled to a solar cell could be a cost effective way to artificially increase the light intensity inside a photovoltaic cell. This is discussed in the next section.

1.3.2 Trapping Light with Nanostructured layer

The use of a nanostructured layer, to be discussed in the rest of the thesis, demonstrates the enhancement of photovoltaic application based on unique optical properties found in a photonic crystalline structure. As discussed in the preceding section, a photonic crystal has a tunable reflecting spectral range and a slow group velocity of light near to the flat band edges. By designing the position or configuration of photonic crystal in a solar cell, the reflectance and slow light properties can be harnessed for useful light trapping feature.

Collecting and retaining light inside a solar cell is the key for efficient solar cell design. In this aspect, all incident photons have a higher probability of getting

absorbed and converted to electricity if they are made to trap longer in the cell. The optical path length follows the thickness of a regular active absorbance layer of the photovoltaic cell. In optical terms, the light trapping phenomenon lengthens the effective optical path length inside the cell. In literature, this path is lengthened when schemes such as (i) shiny metal back reflector and (ii) textured surfaces are employed in a solar cell.

A shiny metal at the back of the active layer helps reflect un-harvested light to the active layer again, thus increasing the light absorption.[72] This light trapping mechanism is ideal for thin film solar cell where there is a lack of thick light absorber to realize its true potential in light absorption capability. An example is shown in Fig 1-10

Figure 1-10. Different components of a photovoltaic cell for aiding light entry and trapping in the active region.

Textured or roughened front surface on solar cell helps to reduce the escape angle of light out from the solar cell. Most of the incident rays are confined inside the solar cell by total internal reflection. As a result, the trapped light makes multiple passes inside the active medium with an increased chance of absorption. The following sections describe how a colloidal crystal can be coupled inside a

dye-sensitized solar cell to improve on light trapping by making use of slow light and back reflecting properties.

1.4 Trapping Light in a Dye-sensitized Solar Cell

A photovoltaic cell (or commonly known as a solar cell) is a device that is able to convert light energy into electricity. Dye-sensitized solar cell (DSSC) belongs to a family of photovoltaic (PV) cell which is different from the mainstream junction effect solar cell architecture.[73-75] DSSC is a photoelectrochemical PV cell and its distinct feature is the presence of a liquid electrolyte in the cell. DSSC is considered a 3rd generation solar cell technology after the development in silicon p-n junction cell and thin film solar cell such as cadmium telluride (CdTe) or copper indium gallium selenide (CIGS) compound materials.

DSSC is a promising clean energy generation device because of its low fabrication and materials cost requirement. DSSC can be scaled up for mass production and for large scale energy harvesting. The assembly of the cells does not required capital intensive facilities such as vacuum processing and their building parts are mainly obtained through solution processed route. Some of the reputable DSSC manufacturers include Dyesol (Australia), G24 Innovations Limited (UK) and Solaronix SA (Switzerland).

In the early studies, Gerischer et. al. studied the light harvesting performance of a ZnO electrode sensitized with organic dyes such as rose bengal, fluorescein, and rhodamine B in 1968. [76, 77] However, the power conversion efficiency was low because of two limiting factors as ascertained in later development. First, the

organic dyes that were used in their experiment have a narrow absorption range in visible light spectrum. Second, their ZnO electrodes did not have the necessary large surface areas so that more dye molecules can be adsorbed on the surface.

In 1991, Gratzel et. al. synthesized a new ruthenium (Ru) bipyridyl complex photosensitizers which have broad absorption range from the visible to near-infrared region and sensitized readily on a TiO₂ layer of huge porosity. [75, 78-81] Under transient photocurrent characterization for photocurrent lifetime, the dye injects photo-excited electrons rapidly into the conduction band of TiO₂ (in 10^{-15} ~ 10^{-12} second). The dyes are regenerated by a redox reaction with the electrolyte and this takes place at a slower pace at 10^{-12} second. The electron loss through charge recombination at interfacial sites happens at a very slow duration of 10^{-3} second range.[74, 82] Consequently, there is a net gain of electron generation and DSSC is viable as a PV device.

One key feature in fabricating a DSSC is the ease and stability of a monolayer of Ru complex dye molecules adsorbed on the TiO₂ nanoparticles' surfaces. What is the other desirable characteristic of TiO₂ as the material of choice for DSSC? First, TiO₂ is a wide band gap semiconductor and its absorption edge is towards the ultraviolet range. Consequently, TiO₂ does not absorb visible spectrum and visible rays can pass through the thin film without suffering much intensity loss. Secondly, the TiO₂ material can be developed with ease as a dense and mesoporous thin film structure, which is made up of 20 – 40 nm sized nanoparticles.[83] The TiO₂ mesoporous layer exhibits a large surface area and the specific surface area is about 70 – 96 m²/g.[84] Effectively, a DSSC offers a huge sensitized surface area to

capture more light. As a result, more surface area in the TiO_2 mesoporous film is a key parameter for efficient power conversion.[85, 86]

The TiO_2 mesoporous film has an optimum thickness at around 10 – 15 μm [84, 87]. For thinner film, light will not be absorbed by DSSC adequately. On the other hand, a thicker film will present more recombination sites [73] and the efficiency will suffer. As a result, due to the intrinsic optimal thickness of TiO_2 film in the moderate range (10 – 15 μm), a DSSC is largely transparent in visible light. This is the reason why a photonic crystal coupled into a DSSC could potentially enhance the light trapping property.[87-89]

1.4.1 Operating Principle of Dye-sensitized Solar Cell

A schematic drawing of the DSSC's operating principles is shown in Figure 1-11. The DSSC is sealed in between two transparent conductive oxide (TCO) glass substrates and they form the electrodes of the DSSC. The main harvesting layer is the mesoporous TiO_2 film of optimum thickness 10–15 μm . [84, 87] The mesoporous film is made up of TiO_2 nanoparticles of sized 20–40 nm which are sintered together to form a conductive path matrix. Other wide band gap oxides such as ZnO [90], and Nb_2O_5 [91] have also been studied as alternatives to TiO_2 . The pores of the TiO_2 mesoporous film are important as they help the liquid electrolyte to reach out to the dye molecules. Typically, the porosity is about 50–65%. [92] The pores are formerly composed of polymer binders which are turned into air separation after heat treatment.

A monolayer of dye sensitizer is attached onto the surface of TiO_2 through a process of dye soaking over 12–24 hours. An organic solvent, such as the iodide/triiodide couple fills the whole cell. The counter electrode consists of platinum (Pt) layer coated on the TCO. Pt helps to reduce the over-voltage [93] of the DSSC and helps to improve the conversion efficiency.

Upon light absorption, the excited dye injects an electron into the conduction band (CB) of the TiO_2 . Figure 1-12 shows the electronic band diagram of the DSSC where the LUMO level of the dye is higher than CB of TiO_2 . The injected electron (photo-generated current) diffuses through the TiO_2 network and TCO film, and finally to the external load. The potential difference that develops across the external load is the difference between the Fermi level of the TiO_2 and the redox potential of the electrolyte.

Figure 1-11. Schematic structure of the dye-sensitized solar cell (DSSC) from macro view (top) to micro view (bottom). Reference from G. Smestad, *Sol. Energy Mater. Sol. Cells*, 55, 157–178, (2002).

Figure 1-12. The electronic band diagram of a DSSC and the mechanism of electron transport.

The excited dye is regenerated back to the ground state by an electron donation from the electrolyte. In particular, the oxidized dye cations are reduced by iodide ions (I^-) and the latter is turned into triiodide (I_3^-). Finally, the redox system is restored by the reduction of triiodide at the Pt electrode by an electron after completing a loop around the external load.

Under an accelerated life testing, the redox reaction in a DSSC could sustain 10^8 number of cycles without suffering any permanent damaged. Consequently, 20 years lifespan of energy harvesting under the sun is projected for DSSC. [92] The current research activities are centered on (i) the improvement of dye extinction coefficient[94, 95] ; electron transport across TiO_2 film[96, 97]; and solid state DSSC [98, 99]. The state-of-the-art DSSC has reached power conversion efficiency of 10%. [68, 75]

1.5 Motivation

Dye-sensitized solar cell (DSSC) has attracted widespread research to realize a high efficiency and low cost photovoltaic cell. Today, much research efforts are focused on improving the light absorption performance of the dye sensitizer and electron transport. On the other end of design spectrum, the motivation of this thesis is to focus on the light confinement performance through the use of ordered nanostructures in the DSSC.

1.5.1 Nanostructure layer in Dye-sensitized Solar Cell

In several past reports [100-102] of photonic crystal DSSCs, Titanium dioxide (TiO_2) inverse opal photonic crystal were embedded into the nanocrystalline TiO_2 electrode layer of a DSSC. In Ref. [100], a 26 % increase of photocurrent was reported over the spectral range of 400–750 nm due to both slow photon propagation and multiple light scattering effects. This dye absorbance enhancement was reported to be occurring in the longer wavelength side of the photonic band gap (PBG). It was suggested that the enhanced absorption is due to the slow group velocity of light near to the band edge and the localization of light in the dye-sensitized TiO_2 . In Ref. [100], the sample consists of a 3 μm TiO_2 inverse opal deposited on top of a 7 μm TiO_2 mesoporous film. And their reference sample is a 10 μm TiO_2 mesoporous film. Here, the different amount of TiO_2 materials used in their test sample and reference sample do not give a proper direct comparison. A different amount of TiO_2 material results in different photo-generated current due

to different volume of dye loading. This non-ideality in sample comparison will be addressed in Chapter 3.

In later development [101, 102], reports suggested that the enhancement of light harvesting is largely contributed by backscattering effects from the disordered regions in the back reflector and less by the effect of slow photon localization. Further, their test sample and reference sample did not have the same amount of TiO_2 materials, and thus a better direct comparison is desired for conclusive claim.

To date, the effect of slow photons on the DSSC's power conversion has not been proven convincingly, even though the band edge effect of slow photon localization[103-105] has been shown in studies on photonic band edge lasers[47] and amplified photochemistry[106].

In this thesis, the phenomenon of slow light effect on DSSC will be elucidated with direct sample comparison and backed up with theoretical model. The goal is to investigate the photonic flat band edge effect on the light-to-electrical energy conversion efficiency (IPCE) of an inverse opal DSSC. The merit of band edge effect can be unambiguously highlighted in this thesis as the IPCE comparison was done using samples with and without periodic structures using almost similar inverse opal TiO_2 material volume and dye loading. The approach of achieving same material volume for both periodic and non-periodic structure was done by collapsing a section of TiO_2 inverse opal into a disordered structure. As a result, a true IPCE enhancement due to flat band edge effect can be quantified. However, a disordered structure has a more efficient carrier transport network which will be discussed in section 5.8. A disorder structure can also be obtained by mixing PS

particles of different sizes. However, this approach is not carried out in this work. In this work, to have a fair comparison, ordered and disordered structures were fabricated on the same solar cell so they both equally went through the same heating cycle, dye sensitization and electrolyte filling procedure. Disordered structures were then made from ordered film by collapsed the ordered structures in this work. On the other hand, to deposit a mixed PS disordered structure with the same thickness as the ordered film on the same substrate is technically challenging. Further, a mixed PS disordered structure will bring up another uncertainty of whether TiO_2 volume and dye loading is similar as the ordered structure's case. Thus, all disordered structures obtained through collapsing the order structures were consistently used as reference sample in all design of experiment (DOE) samples of this thesis.

1.6 Outline of Thesis

This thesis consists of 7 chapters starting with an introductory description of this work followed by a detailed account of nano-fabrication techniques in chapter 2. In chapter 3, the slow light phenomenon near the dielectric band edge is first described and measured in a dye-sensitized solar cell using angle-resolved irradiance. Next, a non-zero density of states in the forbidden photonic gap is created and harnessed for light harvesting as described in chapter 4. In chapter 5, the thickness dependence of the photonic crystal is investigated for the influence on the light harvesting performance. Further, the electron transport and dye extinction

in the nanostructures are explained. Finally, a primer chapter on the design consideration for putting a photonic crystal and solar cell together is presented.

2. Nanoscale Fabrication and Experimental Techniques

This chapter describes the experimental techniques employed in fabricating ordered nanostructures. Further, the subsequent chapters will briefly outline the combination of the said experimental techniques into a particular form of nanostructure. This chapter serves to explain the mechanism behind each fabrication methodology. Figure 2-1 shows a flowchart of synthesizing the basic building blocks and assembling them to form an inverse opal dye-sensitized solar cell. Each box in Figure 2-1 will be explained in detail in the following sections.

Figure 2-1. Flow chart of fabricating TiO₂ inverse colloidal crystal (opal) dye-sensitized solar cell (DSSC). * denotes the procedures to fabricate a TiO₂ inverse opal only.

2.1 Synthesis of Polystyrene Colloidal Suspension

Polymer colloids (latex) that is of uniform particle size (monodisperse) is the basic block for fabricating ordered nanostructures in this work. The synthesis of

polystyrene (PS) particles or nanospheres using emulsion polymerisation is a well known procedure since 1930s. [107, 108] The PS colloids suspension synthesized here follows the standard emulsion polymerization procedure where the use of surfactant allows a uniform control of the colloidal particle's resultant diameter in the range of 200-300 nm while maintaining a high concentration of PS particles in the suspension. On the other hand, emulsifier free polymerisation provides another route to achieve PS colloids [23, 24]. However, emulsifier free polymerisation without the use of surface-active agents produces larger bead sizes typically. To achieve smaller size of 200-300 nm in non-emulsion polymerization, the monomer precursor concentration has to be lower and the resultant PS colloids concentration is low (typically 0.1 wt-% of solid). In a typical vertical self-assembly procedure, the colloids concentration needed is about 2 wt-% of solid in suspension. Therefore, emulsion polymerization route was chosen.

The purpose of synthesizing a relatively smaller polystyrene bead size of 200-300 nm for this work is to achieve an assembled structure where its optical property is in the visible light regime. In essence, the self-assembled colloidal crystal will also be known as a photonic crystal if it is reflecting in the visible light spectrum. A handy formula to find out which wavelength the colloidal crystal is reflecting at normal incidence, multiply the diameter of the polystyrene bead by a factor of 2.357 as explained in section 1.2.4.

Figure 2-2. The apparatus setup of emulsion polymerization in the synthesis of monodisperse polystyrene colloidal suspension in water.

The synthesis of polystyrene colloids is described briefly as follows. De-ionised water is added into a three neck reaction flask fitted with a nitrogen gas inlet, a mechanical stirrer and a condenser as shown in the Figure 2-2. The flask is heated and the water is stirred. Nitrogen gas is passed continuously through the reaction flask in order to maintain an inert environment. The purpose of an inert atmosphere is to purge oxygen out of the reaction as oxygen will inhibit the formation of free radicals during the polymerization. Styrene monomer (Fluka, 99%, 10-30 mL) is then added into the water and follow by a small amount of surfactant (0-100 mg). Under stirring at 350 RPM, the water-insoluble monomer is well dispersed and is emulsified by the surfactant molecules. A solution of cationic or anionic initiator (20-200 mg) is added into the mixture. Under heat, the initiator forms radicals and these radicals initiate the chain reaction of polymerisation of monomers. Polystyrene chains grow and chains are crosslinked to form particle.

The reaction is carried for at least 8 hours to ensure all the monomers are polymerised.

Table 2-1 list all the reagents needed in the emulsion polymerization to form negative charged particles or positive charged particles. Typically, a solid concentration of about 5-8 wt-% in suspension is obtained corresponding to the amount of styrene monomer used.

Table 2-1. List of initiator and surfactant in polystyrene emulsion polymerization

	Positive charged surface	Negative charged surface
Initiator	Azobis(2-methylpropionamidine) dihydrochloride	Potassium persulphate (Unilab, 97%)
Surfactant	Dodecyltrimethyl ammonium bromide	Sodium dodecyl sulfate (SDS) (Aldrich, 98%)

The final polystyrene particle sizes are proportional to the amount of monomer and inversely proportional to the amount of surfactant and initiator. The typical size following the above procedures is between 150 - 550 nm and any larger size can be carried out in a 2-step polymerization method. [24, 109]

2.1.1 Polystyrene particle characterization

A high yield of monodisperse polystyrene colloids can be obtained through well dispersing the mixture, uniform heating, and maintaining an inert environment. The monodispersity can be quantified by statistical measurement of a sizable number of polystyrene particles under the scanning electron microscope (JEOL, FESEM 6340F), as shown in Figure 2-3(c). Typically in this work, a standard deviation of

diameter that falls under 15 nm was considered monodisperse and the suspension would be used in the subsequent experiments.

Figure 2-3. SEM images of polystyrene colloids. (a) monodisperse particles. (b) & (d) polydisperse particles. (c) physical measurement of particles and taking statistical data.

The polystyrene colloids can also be quantified by its surface charge using a zeta potential measurement. In this work, potassium persulphate (KPS) anionic initiator was used in the polystyrene synthesis, the resultant particles had sulfonate terminate group on their surface and this surface charge provides electrostatic stability against aggregation among the particles. Counter ions from the water or the sodium counter ions dissociated from the sulfonate group form an electric double layer with the negative charged particle's surface. Zeta potential is the potential difference across this electric double layer and can be measured by a zeta-

potential analyzer (Melvern). A zeta potential of $>|40|$ mV is a good figure for maintaining a good stable colloidal suspension (for positive and negative charged particles). A lower potential of about $|20|$ mV indicates that the repulsion force is weaker and aggregation is likely to occur in a shorter time. In this work, negatively charged polystyrene colloids are measured in the region of -49 mV and it remains stable for weeks in room temperature and as long as a year in cold storage (5°C).

2.2 Synthesis of Titanium Dioxide Nanoparticles

As described in the previous chapter, titanium dioxide (TiO_2 , titania) nanoparticle is the material of choice for fabricating inverse opal structure. In literature, fabrication of TiO_2 inverse opal has been carried out using atomic layer deposition[110], precipitation from liquid-phase precursors[111] and liquid-phase deposition[101]. Unlike the preceding references, TiO_2 nanoparticles in this work are synthesized first in a hydrolysis procedure before being introduced into the voids of the polystyrene opal. The advantages include the use of less chemical precursors, the non-use of costly vacuum equipment and the convenience of checking the crystalline phase of the TiO_2 nanoparticles. The challenges include making the TiO_2 nanoparticles filling up the each void of the opal voluntarily and obtaining a less TiO_2 filling volume compared to the liquid-phase deposition. These challenges will be discussed in detail in the following section.

TiO_2 nanoparticle suspended in water is formed by hydrolysis precipitation of titanium alkoxide modified with acid [112-114]. Carried out in a glove box with inert environment, the precursor consists of 25 mL of titanium isopropoxide (97 %

Aldrich, $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$) is added with 5 mL of acetic acid (97 % Flurka). The addition of acetic acid increases [113] surface area of TiO_2 which is desirable for DSSC performance.

Another acidic solution is prepared as follows: 4 mL of nitric acid (69 % Flurka) is added into 250 mL of de-ionised water in a reaction flask. This acidic solution is stirred in 600 RPM using a magnetic bead stirrer and it is heated to 80°C . Next, the titanium isopropoxide acid-modified solution is added rapidly into the acidic solution under stirring. Immediately, white precipitates can be observed and the mixture can be described as white milky appearance. The reaction flask is capped and the reaction is allowed to proceed on its own. After about 30 minutes, the mixture turned faint turbid in appearance. The mixture is left stirring for at least 8 hours to complete the synthesis process and the resulting suspension looks clear. Finally, the TiO_2 nanoparticle suspension is topped up to 500 mL mark with de-ionized water and the final TiO_2 solid concentration in water is about 1.5 wt-%. The resulting suspension is stable for several months of shelving under room temperature.

In the above hydrolysis reaction, titanium isopropoxide hydrolyzes into Ti-OH species upon contact with water according to the reaction $\text{Ti-OR} + \text{H}_2\text{O} \rightarrow \text{Ti-OH} + \text{R-OH}$ where R is the alkyl group. Titanium isopropoxide has the fastest rate of hydrolysis among the family of titanium alkoxide which include titanium butoxide and titanium ethoxide. In the experiment, the alkoxide:water ratio is 1:10 and a high proportion of water is required to promote nucleation of nanocrystals. [114]

The ensuing process in the hydrolysis is the polycondensation where metal oxide coalescence from Ti-OH species according to $\text{Ti-OH} + \text{Ti-OR} \rightarrow \text{Ti-O-Ti} + \text{R-OH}$ and $\text{Ti-OH} + \text{Ti-OH} \rightarrow \text{Ti-O-Ti} + \text{H}_2\text{O}$. Further, the use of nitric acid catalyzes hydrolysis reaction over the polycondensation reaction, thus resulting in more nucleation sites than coalescence formation. [114]

As a summary, the factors affecting the microstructure and crystalline phase of the TiO_2 nanoparticle consist of alkoxide:water ratio, pH level of the solution, reaction temperature, stirring condition, and hygroscopic nature of the precursor. For example, an alkoxide:water ratio of 1:50 can result in particle size of the region 6~10 nm. [114] A high acid concentration will promote the formation of smaller particle size and the formation of stable rutile phase in the TiO_2 phase diagram.

2.2.1 Titanium Dioxide Nanoparticle Characterization

The ideal TiO_2 nanoparticle for DSSC's mesoporous film is about 20 nm and in anatase phase. [113] A size of 20 nm is a compromise between maximizing the surface area while minimizing interfacial boundary. Anatase TiO_2 is a metastable phase and it has been found to have the most activated surface for DSSC and photocatalysis applications. In this work, a smaller size nanoparticle will aid in the infiltration into the interstices of the polystyrene opal. Figure 2-4 depicts a close packed polystyrene particle array and the calculation of the largest planar dimension (a_i) of the interstice found among three particles. For a typical range of particles' size 150 – 550 nm polystyrene particle used in this work, a_i is calculated

to be between 30 – 376 nm. The key design consideration is synthesizing nanoparticles smaller than a_i .

Figure 2-4. Schematic of the lateral dimension of FCC interstitial void in a polystyrene opal. (a) Hard sphere model of a close packed nanospheres, (b) geometry of the interstices. r is the radius of nanosphere. a_i is the largest lateral size of the interstices.

The powder x-ray diffraction was performed with TiO_2 nanoparticles synthesized at different acidic conditions and heated at 450°C for 2 hours. In the low acid experiment (1 mL acetic acid and 1 mL nitric acid), XRD result shows a very high percentage of TiO_2 anatase phase and negligible percentage of rutile phase. However, the lower acid concentration results in a highly turbid TiO_2 nanoparticles suspension. As a quick verification method, the turbidity of the suspension signals the formation of larger size nanoparticles. In the subsequent polystyrene opal infiltration procedures, it was verified that this high turbid suspension is not suitable for infiltration into the polystyrene opals as the large nanoparticles cannot fill into the interstices uniformly.

The acid concentration was added progressively and the optimum acid concentration was found (5 mL acetic acid and 4 mL nitric acid) as described previously. The drawback of using this amount of acid is the formation of non-

negligible rutile phase after the 450°C annealing step. Figure 2-5(a) shows the XRD of the TiO₂ nanoparticle (heat treatment 450 °C, 2 hours). Rietveld analysis reports a TiO₂ phase distribution of 75.7%, 19.6% and 4.7% for anatase, rutile and brookite phase respectively. [115] Figure 2-5(b) depicts the TEM image of TiO₂ nanoparticles and the average size of the nanoparticle is about 15 nm. This suspension is used for the rest of the experiment as it is found suitable for infiltrating into the interstices uniformly. As a yardstick, Degussa's TiO₂ nanopowder (P25) is a popular component in DSSC's fabrication, it has phase composition ratio of 70:30 (anatase:rutile).

Figure 2-5. (a) Powder XRD reported a predominantly anatase TiO₂ phase by Rietveld analysis; (b) TEM image of the synthesized TiO₂ nanoparticle. The mean size is about 15 nm.

2.3 Colloidal Self-assembly of Polystyrene Opal

Monodisperse polystyrene colloidal particles with a size ranging from 100 nm to several microns are assembled in a parallel process to form a thin film of a 2D periodic particle array (monolayer) or a 3D crystal (multilayer) structure.[54] Self-assembly is a fundamental mechanism by which monodisperse colloidal particles

arrange themselves spontaneously to generate ordered nanostructures. Flow-controlled vertical deposition (FCVD) is the technique used to obtain consistently high-quality large-area colloidal crystal. The FCVD technique is described as follows.

2.3.1 Preparation of Polystyrene Colloidal Suspension

The as-synthesized polystyrene colloidal suspension is adjusted to achieve a PS solid concentration in the region of 2 wt-% using de-ionised water dilution. This is the reason why high concentration of polystyrene is preferred during the emulsion polymerization for the convenience of dilution.

2.3.2 Preparation of Substrates

The substrates are thoroughly cleaned with glassware detergent to remove finger prints, oil stains and organic substances. A clean surface helps to lower the contact angle suitably for colloidal self-assembly process. Glass substrate or fluorine-doped tin oxide (FTO) coated glass substrates (TEC 7, Pilkington) are scrubbed clean using glassware detergent and rinsed with water. They are then cleaned with ethanol in an ultrasonic bath for 10 min, rinsed with copious de-ionized water and are blown dry.

2.3.3 Flow-controlled Vertical Deposition (FCVD)

Figure 2-6 shows the schematic and photograph of the flow-controlled vertical deposition (FCVD) apparatus. The polystyrene (PS) colloidal suspension is poured

into the main vessel of the FCVD. The main vessel is a double-walled glass container and it is heated by a circulating water bath at 35°C. The back plane of FTO substrate is pasted with a double-sided tape and placed vertically on the inner side-wall of the vessel, as shown in Figure 2-7. The front conducting plane of FTO substrates face the meniscus of the PS suspension. The FTO substrates can be adjusted partially or completely submerged in the PS suspension.

Figure 2-6. (a) Schematic diagram of the FCVD technique. Substrates are stuck onto the interior wall of the double-walled vessel, which is heated by circulating water. The water pump draws out the PS suspension slowly. The receding meniscus coat a layer of PS opal film on the substrate. (b) The picture of the FCVD setup in the laboratory.

Under bottom-up colloidal self-assembly process[21], the PS colloidal particles are assembled into opals (face cubic centered colloidal crystals) by both capillary force and convective flow. In the FCVD technique, the meniscus of the colloidal suspension is lowered slowly as suspension is drained away at a slow controlled rate by a mini-pump. The convective flow of the suspension causes the PS particles to move towards to the liquid contact line. At the meniscus, capillary action forces the particles to go against the gravity and move towards the contact

line as depicted in Figure 1-3. The receding meniscus, due to the slow draining of suspension, packs the particles closely to form FCC structures.[27, 28, 116] Typically, the self-assembling process is carried out for a duration of between 4–24 hours depending on growth length. The slower the receding speed, the more layers of opal is formed. The specific growth parameters are described in detail in the following chapters.

Figure 2-7. (a) Top view into the double-walled vessel with four substrates. The number (1-4) indicates the four substrates stuck onto the interior wall. (b) The retrieval of substrate from the vessel when FCVD is completed.

2.4 Fabrication of TiO₂ Inverse Opal

2.4.1 Preparation of PS Opal for Infiltrating TiO₂ Nanoparticle

PS opal film deposited on a FTO substrate will be subjected to subsequent dip coating procedure with the TiO₂ nanoparticles suspension. The water surface tension of the TiO₂ nanoparticle suspension can weaken the opal structure and may peel off the opal film from the FTO substrate. To enhance the mechanical strength of the polystyrene opal film, heat treatment slightly below the glass transition temperature (t_g) can improve the adhesive bonding among the polystyrene particles

and FTO substrate. The t_g of polystyrene ranges from 100-105°C depending on its polymer chain density. The PS opal film is annealed either at 100°C for 5 minutes (short cycle, Ref. [51]) or at 90°C for 2 hr (long cycle) to achieve a stronger mechanical structure.

2.4.2 Preparation of TiO₂ Nanoparticle Suspension for Dip Coating

The 500 mL TiO₂ nanoparticle suspension (1.5 wt-% solid) as described earlier is added with ethanol. The addition of ethanol serves two purposes: (a) lowering the surface tension of TiO₂ nanoparticle suspension; (b) aiding the infiltration into the voids of PS opal. The first reason is to circumvent the peeling of PS opal film due to surface tension of water, even if the PS opal film may have been annealed $< t_g$ before. The miscibility of ethanol and water helps to maintain a uniform suspension while lowering its surface tension. [117] The second reason is PS is hydrophobic and the addition of ethanol into the water suspension helps the infiltration of nanoparticles into the interstices of opal film. The modified TiO₂ nanoparticle suspension (pH=1) has a water:ethanol volume ratio of 70:30.

2.4.3 Infiltration of TiO₂ Nanoparticles into PS opal

TiO₂ nanoparticles are infiltrated into the interstices of the opal template by multiple dip coating cycles. Figure 2-8 illustrates the infiltration process. First, TiO₂ nanoparticle suspension is dropped and spread carefully onto the PS opal, which is positioned horizontally. The coated PS opal is kept in an air-tight container for about 6 hours and the TiO₂ nanoparticles are left to fill into the

interstices uniformly. Then, the PS opal is positioned vertically on paper towel for the excess TiO_2 suspension to drain off, during which the receding meniscus aids in the packing of TiO_2 nanoparticles into the opal template. The PS/ TiO_2 composite opal is then heated at 90°C to complete the drying of the water and also to obtain a strong adhesion between TiO_2 and PS. The preceding steps are repeated several times until the amount of TiO_2 infiltration saturates (see section 2.4.5 for more details).

2.4.4 Mechanism of TiO_2 Nanoparticles Infiltration Into PS Opal

The electrostatic charges and interaction of TiO_2 nanoparticles and PS opal film are important for the understanding of how TiO_2 nanoparticles are filling the voids of the PS opal. First, the zeta-potential of TiO_2 nanoparticle suspension ($\text{pH}\approx 1$) was measured (Malvern Nano-ZS) and it is positive at 25.4 mV. From literature, TiO_2 iso-electric point (IEP) is at $\text{pH}=5.8$. TiO_2 's surface charge goes positive toward $\text{pH}=1$ and goes negative towards $\text{pH}=14$.

The PS colloidal particles synthesized for this opal film have a negative electric charge (-49 mV) as explained previously. Under different medium and pH level, a surface may undergo charge reversal. To find out how the PS opal's surface charge behave in a TiO_2 suspension, the PS opal is re-dispersed in a solution (acidic) similar to TiO_2 suspension without the TiO_2 nanoparticles.

In brief, mimicking the acidic solution similar to the TiO_2 nanoparticle suspension, a 70 mL of acidic solution (adjusted to $\text{pH}=1$ by nitric acid) is mixed with 30 mL of ethanol. A PS opal is immersed into the acidic solution and it is

ultrasonicated to re-dispersed PS particles into the acidic solution. Large aggregated clumps of PS were filtered away using a filter paper. The final PS suspension in acidic solution is observed to be very faint turbid which is suitable for zeta-potential measurement (Malvern Nano-ZS).

The zeta-potential of the dispersed PS suspension is a positive 34.6 mV. The original PS particles are synthesized as negative surface charged and it goes charge reversal in an acidic solution. During TiO_2 infiltration into PS opal, the TiO_2 suspension fills all the PS opal's interstices due to capillary action. Both TiO_2 and PS are having like positive charge and they repel each other as depicted in Figure 2-8(f). This repulsion is important since the TiO_2 nanoparticles will not be attracted on the PS surface and will clog up the PS interstices easily. As a comparison, the zeta-potential of positively-charged synthesized PS colloids is measured to be 56.8 mV. When it disperses in an acidic solution as described above, the surface charge drops to 6.5 mV and there is no charge reversal.

When the substrate is held vertically as depicted in Figure 2-8(c), the excess TiO_2 suspension forms a meniscus and helps to pack TiO_2 nanoparticles into the interstices. Due to capillary force, the TiO_2 suspension will still be held at the interstices when the excess suspension is drained away. Finally, as the liquid evaporates, the TiO_2 nanoparticles are adhered on the PS surfaces as shown in Figure 2-8(g). Next, the sample were anneal at 90°C for an hour to strengthen the adhesion between TiO_2 and PS opal. The infiltration cycle is repeated until the PS opal's interstices are filled. The following section discusses the method to monitor the infiltration cycles.

Figure 2-8. Schematic of TiO_2 nanoparticles infiltration into PS opal. (a) Spread TiO_2 nanoparticles solution on the opal. (b) Equilibrate for 6 hours. (c) & (f) placed vertically to drain excess solution. (d) & (g) Receding solution helps to pack TiO_2 nanoparticles into the interstices. Anneal at 90°C for 30 minutes to remove moisture and to obtain a strong polystyrene- TiO_2 adhesion. Repeat (a) to (d) cycles to complete the infiltration process (e).

2.4.5 Characterization of TiO₂ Infiltration Process

To monitor the amount of TiO₂ infiltration, optical spectrometer is used to measure the shift in the Bragg's peak of the composite opal film. The Bragg's law states that

$$\lambda_p = d_{111} \sqrt{n_{eff}^2 - \sin^2 \theta} \quad , \quad (2-1)$$

where d_{111} is the inter-planar (111) spacing of the FCC structure, defined as $d_{111} = \sqrt{2/3}D$ and D is the PS colloidal particle diameter. θ is the incident angle of irradiance (0° for normal incidence) and the effective refractive index is defined as

$$n_{eff}^2 = 0.74n_{PS}^2 + (0.26 - ff)n_{air}^2 + ffn_{TiO_2}^2 \quad . \quad (2-2)$$

The filling factor ff is defined as the amount of air volume being replaced by TiO₂. The maximum value of ff is 0.26, which corresponds to the volume fraction occupied by the interstitials of a close-packed FCC. The refractive index of TiO₂ is 2.25. [118] The refractive index of PS (n_{PS}) can be found firstly by measuring the PS opal without TiO₂ infiltration and making $ff = 0$.

In Figure 2-9(a), the λ_p of a non-infiltrated opal is ~695nm and n_{PS} is calculated to be 1.57-1.6. In the first infiltration, the reflectance peak red-shifts towards the longer wavelength (711nm) as air is replaced by TiO₂ nanoparticles. For subsequent 3rd, 5th and 7th infiltration cycles, the Bragg's peaks are 736nm, 745nm and 749nm respectively in Figure 2-9(a). The corresponding filling factor ff is shown in Figure 2-9(b). It is observed that the ff saturates to approximately 0.08 volume fraction of a close-packed FCC structure after the 7th infiltration cycle.

Figure 2-10 shows the SEM images of infiltrated PS opal before removing the PS by heat treatment. In Figure 2-10, the necking rings on the PS particles' surfaces are the fracture markings during the SEM sample cross section preparation. The necking rings indicate the TiO_2 nanoparticles are sufficiently infiltrated into the interstices of the PS opal.

Figure 2-9. (a) Reflection spectra of PS opal and the red-shift of the reflectance peak with infiltration. From top to bottom, 0 infiltration, 1, 3, 5 & 7. Spectra are offset vertically for clarity. (b) The calculated filling factor ff of TiO_2 in PS opal. Maximum theoretical value is 0.26.

The PS template is removed by heat treatment procedures as described in section 2.4.6. Figure 2-11(a) and Figure 2-11(b) show the TiO_2 inverse opal for 5-cycle and 7-cycle infiltration procedure respectively. In the 5-cycle procedure, the top layer is partially covered by TiO_2 nanoparticles. The porosity of the TiO_2 inverse opal is therefore partially capped at the top layer as shown in Figure 2-11(a).

Figure 2-10. SEM images of infiltrated PS opal with TiO₂ nanoparticles before calcination. (a) Cross-section view (1 μm bar), (b) under high magnification (100 nm bar). The necking rings on the PS's surfaces indicate sufficient TiO₂ infiltration to achieve an inverted structure upon calcination.

On the other hand, the top layer is completely covered by TiO₂ nanoparticles as shown in Figure 2-11(b) for the 7-cycle procedure. This complete coverage on the top layer of TiO₂ inverse opal will prevent the liquid electrolyte (in the DSSC application) from reaching out to the whole thickness of the TiO₂ inverse opal.

Consequently, the excited dye molecule adsorbed at the bottom of the TiO_2 inverse opal may not be regenerated if the electrolyte is blocked out by the complete coverage at the top layer.

Figure 2-11. SEM top view images of TiO_2 inverse opal after calcination. (a) 5 infiltration cycles (1 μm scale bar). (b) 7 infiltration cycles (insert is cross section view, 100 nm scale bar).

The solution is to choose a 4-cycle TiO_2 infiltration procedure to prevent any partial or complete TiO_2 coverage at the top layer. This is chosen despite the fact that 4 cycles of infiltration is not the optimum ff as shown in Figure 2-9(b). Nevertheless, as carried out in the subsequent experiment (Chapter 3-5), 4 cycles are adequate to fill the PS opal and a TiO_2 inverse opal can be achieved without a TiO_2 top coverage film.

2.4.6 Calcination of TiO_2 -PS Filled Opal Film

The PS- TiO_2 composite thin film is calcinated in a normal air ambient furnace following the heat treatment profile in Figure 2-12. From room temperature, the furnace is programmed to ramp up to 450°C at a ramp rate of about $2\text{-}3^\circ\text{C}/\text{min}$. The glass transition temperature of PS is at about $100\text{-}105^\circ\text{C}$. A slow ramp up in temperature is necessary for PS to decompose slowly away while maintaining the TiO_2 ordered structure. The furnace is then set at 450°C for 2 hours to completely decompose PS while the TiO_2 nanoparticles are fused together to give a stronger mechanical bonding. After that, the furnace is let cool to room temperature for another 6 hours approximately.

During the heat treatment of 450°C , the amorphous TiO_2 nanoparticles undergo phase transformation to anatase. Anatase phase is a metastable phase not found in the TiO_2 phase diagram. Anatase is the preferred phase for application in dye-sensitized solar cell and photocatalysis. [2] It is important not to heat the TiO_2 nanoparticle above 600°C because they will phase transform to rutile, which is a stable phase and it has a poorer performance in DSSC application. [119]

Figure 2-12. Calcination ramp cycle programmed into the furnace timer system. The heat treatment results in both the phase transformation of TiO_2 and the polystyrene decomposition.

Figure 2-13 shows the reflection spectra of a PS opal (particle size of 285 nm) and the TiO_2 inverse opal after calcination. The PS opal has a peak reflectance at about 660nm. Figure 2-13(a) shows the image of the PS opal and it is reflecting orange-red tint. After TiO_2 infiltration and calcination, the peak reflectance blue-shifts to 440 nm and suffers a drop in absolute reflectivity. Figure 2-13(c) shows the image of the TiO_2 inverse opal and it is reflecting with a blue tint.

The reasons for the spectral shift include:

- 1) Change of material ($\text{PS} \rightarrow \text{TiO}_2$) and reflective index;
- 2) Change of volume (PS sphere $\rightarrow$ air sphere. Air void $\rightarrow$ TiO_2 filling);
- 3) Change in lattice parameters (TiO_2 inverse opal shrinkage).

TiO_2 inverse opal undergoes shrinkage during the PS calcination process. [120] This shrinkage reduces the lattice parameter of the colloidal crystal and ultimately the reflectance peak spectral position. Knowing the shrinkage is useful in the designing of the position of reflectance peak at the outset of synthesizing the size of the PS particles.

Figure 2-13. Illustrations of (a) PS opal, (b) reflectance spectra and (c) TiO_2 inverse opal. From top to bottom in (a) & (c): top SEM view, macro image of thin film deposited on glass substrate. All scale bars represent $1\ \mu\text{m}$.

Figure 2-14(a) shows the cross section view of a PS opal of size $285\ \text{nm}$ ($2r$). The lattice parameter is thus $a = 2\sqrt{2}r$ by following Figure 2-14(c). For the (111) inter-planar distance, d_{111} is simply equal to $\sqrt{8/3}r$. Therefore, the inter-planar distance of PS opal is calculated as $232\ \text{nm}$ ($d_{111,\text{PS}}$) and this can be verified in Figure 2-14(a). In Figure 2-14(b), the inter-planar distance of the TiO_2 inverse opal is about $195\ \text{nm}$ (d_{111,TiO_2}) and this represents a 16 % reduction from the $d_{111,\text{PS}}$ due to calcination shrinkage. On top of the effect of inverted structure explained with the aid of Figure 2-13, the shrinkage also causes an additional blue-shift in the reflectance peak position.

Figure 2-14. Verifying the inter-planar d_{111} distance from SEM images. (a) Cross section image, top plane is (111) texture. (Scale bar is 1 μm) (b) The lattice parameter calculated from FCC hard sphere model is $a = 2\sqrt{2}r$. (c) Cross section image of inverted structure. (Scale bar is 100 nm) (d) The relationship between inter-planar distance and lattice parameter of cubic structure.

2.5 Opal Deposition on an Unsuitable Substrate by Layer Transfer

For the successful deposition of a colloidal crystal film on a substrate using colloidal self-assembly technique, several requirements have to be satisfied:

- a) Clean and hydrophilic surface (This is to lower the contact angle of the meniscus and enhance packing);

b) Same electrostatic charges between PS particle and substrate's surfaces (Unlike charges cause the PS particles to be attracted to the substrate and there is less surface migration to form an ordered structure. This is the reason why positively charged PS colloids is not used for colloidal self-assembly. Glass substrate has an intrinsic negative surface charge in water);

c) Strong and sturdy surface (Substrate containing pre-existing thin film must be able to withstand the surface tension of water).

Layer transfer technique was pioneered by Yan et. al. to fabricate heterogeneous colloidal crystal. [121] Here, layer transfer method is used to deposit a PS opal film on top of the titania nanoparticulate film, which is hydrophobic because it contains polymeric binders. The titania nanoparticulate (mesoporous) film is the main harvesting layer for DSSC application while the PS opal enables the fabrication of backscattering layer.

In the experiment, multilayer PS opal film is grown on a glass substrate using the FCVD method. This glass substrate is then placed in an empty trough and is inclined at about 30~45° with reference to the base of the trough as shown in Figure 2-15(a). The setup is carried in a minimum shock disturbance environment. Next, water is slowly added into the trough using a flow-controlled pump. The rising rate of the water level is typically set at 10 mm/hour. As the water reaches the interface between the glass vessel and the PS opal film, the water preferentially seeps through the interface because glass is hydrophilic and PS is hydrophobic as shown in Figure 2-15(b) and Figure 2-16. With the rise of the water surface, the PS opal film peels off from the glass and floats on the surface of the water (Figure

2-15(b)). It is observed that the floating PS opal film remains as one sturdy piece and does not disintegrate in water.

Figure 2-15. The layer-transfer deposition technique. (a) PS opal film and substrate incline at 60° inside an empty dish; (b) Water is drawn into the dish very slow and peels off PS opal from the substrate; (c) another substrate is inserted into the water and positioned below the floating PS opal film; (d) the PS opal film is deposited onto substrate.

Figure 2-16. Effect of PS opal film peeling off from the glass substrate under slow rising water level. Water preferentially seeps between the interface of the hydrophobic PS and hydrophilic glass substrate.

Once the PS opal film is completely detached from the glass substrate, the pumping of water is terminated. The FTO coated substrate with titania

nanoparticulate film is then directly inserted into the water trough and positioned just below the floating PS opal film (Figure 2-15(c) and Figure 2-17(c)). It was observed that the titania nanoparticulate film remains strongly coated onto the FTO. To deposit the PS opal film onto the titania nanoparticulate film, the FTO is raised slowly out of the water horizontally, forming a two-layered heterostructure (Figure 2-15(d) and Figure 2-17(f)). Finally, the FTO is held vertically to drain off excess water on a paper towel. The sample is annealed at 90 °C for 2 hours to achieve a strong mechanical structure. TiO₂ nanoparticles infiltration is then carried out to fabricate a TiO₂ inverse opal as described earlier.

Figure 2-17. The images of the layer-transfer procedure. (a) PS opal film is grown on the inner wall of the FCVD vessel. (b) The vessel is inclined at about 30° in a water trough. (c) PS opal film is peeled off from the vessel under slow rising water level. It is floating on the surface of water. (d) A substrate is inserted into the water and positioned below the floating PS opal film; (e) the substrate is removed gently from the water; (f) the resulting PS opal film deposition on the substrate.

2.6 Dye-sensitized Solar Cell Assembly

The fabrication of the dye-sensitized solar cell involves many steps and the following flowchart illustrates a standard procedure.

Figure 2-18. Flow chart of assembling a dye-sensitized solar cell (DSSC). * denotes additional step for embedding a TiO_2 inverse opal in a DSSC.

In a quick cycle, a regular DSSC without a coupling TiO_2 inverse opal will take about 4 days (addition 3 more days to include TiO_2 inverse opal layer) to assemble. Typically, additional time is required for characterization such as film thickness and treatment such as TiCl_4 wash on TiO_2 film.[122] The TiCl_4 treatment is carried out before dye sensitization to plug fine TiO_2 nano-crystallites on the pores on TiO_2 mesoporous film (see section 2.6.4). As a result of TiCl_4 treatment, the mechanical structure and electron transport property in TiO_2 mesoporous film are improved.

2.6.1 TiO_2 Layer Deposition

The FTO substrates are cleaned following the procedures in 2.3.2. A combination of adhesive tapes (Kapton® Dupont, 60 μm or Scotch® Crystal Clear 3M, 40 μm)

is used to define a deposition window and the film thickness deposition. For example, the stacking of one layer of Kapton® and one layer of Scotch® will give about a total thickness of 100 μm . The exact thickness of the tapes combination is described below. Using a simple doctor-blading method, a layer of titania nanoparticulate paste (DSL 90-T, Dyesol) is coated on the FTO substrate (Figure 2-19) and left to cure in air for 12 hours. The TiO_2 nanoparticulate paste consists of polymeric binder for creating pores between TiO_2 nanoparticles after calcination. Besides, the paste is viscous and is formulated for doctor blading or spin coating. After curing for 12 hours, the paste layer spreads out in a smooth film on its own and it is hardened for subsequent coating procedure.

Figure 2-19. Doctor blade method to deposit a layer of viscous paste onto the substrate. The masking window is a commercial adhesion tape and this defines the thickness of the resulting thin film.

2.6.2 Colloidal Self-assembly and Infiltration

A polystyrene opal template will be deposited on top on the hardened titania nanoparticulate paste or on the bare FTO substrate using layer transfer (LT) or

flow-controlled vertical deposition (FCVD). This procedure is described in detail in section 2.3.3 and 2.4.3.

2.6.3 Calcination of TiO₂ Nanoparticulate Paste

A heat treatment of 450°C in a normal air ambient furnace is carried out to decompose the polymeric binder in the titania nanoparticulate paste (DSL 90-T, Dyesol). The heat treatment cycle follows the similar ramp up characteristic in Figure 2-12. In DSL 90-T material safety data sheet (MSDS), the binders consist of ethyl cellulose, terpineol and organic plasticizer to control the viscosity of the paste and to create spaces among the TiO₂ nanoparticles. At 450°C, all polymer spacers will be decomposed and the resultant TiO₂ layer is mesoporous as shown in Figure 2-20.

Figure 2-20. SEM top view images (a) low magnification (10 µm scale bar) and (b) high magnification (100 nm scale bar) of a TiO₂ mesoporous film after calcination at 450°C.

After calcination, a final mesoporous TiO₂ film thickness of 8~10 µm and 10~12 µm will be obtained due to shrinkage with adhesive tape thickness of 100

μm and $120\ \mu\text{m}$ respectively as discussed in section 2.6.1. A $10\sim 15\ \mu\text{m}$ thick TiO_2 mesoporous film is desired for the optimal performance of DSSC. [84, 87]

2.6.4 Treatment of TiO_2 Mesoporous Film Using TiCl_4

Titanium tetrachloride (TiCl_4) treatment on the mesoporous TiO_2 film improves the short circuit current of DSSC. [122] TiCl_4 is a highly hygroscopic compound and it forms dense fume of titanium dioxide (TiO_2) and hydrogen chloride (HCl) upon contact with moist air. TiCl_4 forms very fine particle of TiO_2 and help in plugging very small pore in the mesoporous structure and help to improve the conductivity of the TiO_2 structure. As a result, mesoporous structure maintains its high porosity while improving in the electron transport property in the structure.

TiCl_4 treatment is carried out after the TiO_2 film calcination step. A $0.05\ \text{M}$ TiCl_4 solution is prepared as follows: $2\ \text{mL}$ of water was frozen into ice. Another bottle of $38\ \text{mL}$ of water is cooled to about 5°C . $0.5\ \text{mL}$ of TiCl_4 (Sigma-Aldrich) is added directly into the ice. It can be observed that the reaction causes slight fuming and the ice is turned into a whitish turbid liquid. Then the solution is further diluted with the cold $38\ \text{mL}$ of water. The whole solution is homogenized in an ultrasonic bath for $5\ \text{minutes}$. Finally the solution was kept in a freezer where the solution was stored in solidified form.

TiCl_4 treatment is carried out by thawing the solution and spreading across the TiO_2 mesoporous film. The TiO_2 mesoporous film was placed horizontally on a hotplate at 80°C . The samples are covered with a Petri dish to prevent the TiCl_4 solution from evaporating. The treatment is completed after heating for $5\ \text{minutes}$

and the excess TiCl_4 solution is drained away using paper towel. Finally, another additional sintering at 400°C is carried for 30 minutes.

There is no observable change to the TiO_2 mesoporous film. TiCl_4 treatment helps to plug and deposit very fine TiO_2 particles onto the fine pores and surfaces on the TiO_2 film respectively. This results in higher electron transport path and higher surface area for dye attachment. The TiCl_4 treatment improves the short circuit current of DSSC.

2.6.5 Dye Sensitization

Dye sensitization of TiO_2 is carried out by soaking the samples into a 0.5 mM solution of Ru-complex dye such as N719 ($[\text{RuL}_2(\text{NCS})_2]:2\text{TBA}$; $\text{L}=2,2'$ -bipyridyl-4,4'-dicarboxylic acid ; $\text{TBA}=\text{tetra-n-butylammonium}$, Dyesol) or 535-bisTBA (Ruthenium dye 535-bisTBA, Solaronix SA). The soaking time is typically 24 hours and it is determined in this work that 48 hours soaking gives a better power conversion performance.

First the calcined TiO_2 samples are rinsed with ethanol to remove any carbon residue. Next, they are blown dry and baked in an oven at 100°C . The dye solution is prepared by dissolving 5 mg Ru-complex dye powder per 20 mL of absolute ethanol (99.99%, Sigma-Aldrich). The solution was stirred well in a dark container and was poured into a flat Petri dish. The baked samples were taken straight from the oven and gently drop into the dye solution in the Petri dish. The need for 100°C baking and immediate soaking of the samples is to prevent water from getting into the samples and dye solution. This is because water is extremely detrimental to the

Ru-complex dye. The soaking is carried out for 24-48 hours in a covered dark environment.

After dye soaking, the TiO_2 samples (denoted as photoanode for brevity) are rinsed with absolute ethanol to remove excess dye. The photoanode was blown dry gently and baked in 100°C oven to prevent moisture contamination.

2.6.6 Assemble with Platinum Counter Electrode

A counter electrode for DSSC consists of a FTO substrate coated with platinum paste (Dyesol) via doctor-balding. The counter electrode is calcined at 400°C for 30 minutes to remove the organic substance in the Pt paste. The counter electrode is rinsed with ethanol; blown dry and baked in 100°C oven to prevent moisture contamination.

A thermoplastic sealant sheet (Surlyn[®], 50/60 μm , Dupont) is cut according to the size of the TiO_2 mesoporous film as shown in Figure 2-21. Straight from the oven, the Surlyn sealant is placed around the perimeter of the between photoanode and the counter electrode. The TiO_2 film and Pt film face each other. The assembled device was placed horizontally on the 100°C oven and a 2 kg weight was used to press them together. Curing of Surlyn[®] occurs after 10 minutes of 100°C annealing.

Figure 2-21. Schematic procedures in sealing the DSSC with Surlyn® sealant film. The two drilled holes are for filling the liquid electrolyte in the subsequent procedure.

2.6.7 Electrolyte Infiltration

The two drilled holes on the counter electrode FTO facilitate the infiltration of electrolyte into the DSSC as shown in Figure 2-21. In particular, the electrolyte is injected into one hole and the electrolyte filled the rest of the enclosed space due to capillary force. The other hole facilitates the air escaping and ensures complete filling of the enclosed space.

2.6.8 Final Assembling of DSSC

In the final step, the two drilled holes are sealed with thin micro glass slides (microscope slide) and Surlyn® film. The exterior of drilled holes are wiped dry. A small piece of Surlyn® film covers the drilled hole, followed by the micro glass slide. Using a soldering iron, the micro glass slide is carefully heated around the hole and the Surlyn® film seals the glass slide to DSSC firmly.

2.7 Solar Cell Characterization

To assess the photovoltaic performance of a solar cell, two common tests are carried out and they are (i) current versus voltage (I –V) characterization and (ii) spectral responsivity versus wavelength characterization.

2.7.1 I-V Characterization

I-V characterization is the most common performance indicator for finding out the photovoltaic (PV) efficiency at peak power output under standard operation conditions (such temperature, spectral irradiance, total irradiance). Available in library, are copies of the international test standards and calibration data ASTM E 948 – 05a, ASTM G-173-03, ISO 9845-1 and IEC 61683.

To ensure irradiance of light sources are common in every test laboratories, air mass 1.5 (AM1.5) spectrum is the internationally recognized standard light spectral (at 100 mW/cm² intensity) for I-V characterization. AM1.5 mimics the irradiance at sea level where the receiver surface is tilted towards the equator at 37° and its

surface is facing the sun. In this work, an AM1.5 equivalent solar simulator is assembled by using a Xenon lamp (300W, Ozone Free, Newport) and an AM1.5 filter (Newport). The AM1.5 filter shapes the spectral profile of the Xenon light output close to the sun's spectrum as required by AM1.5 standard. Further, the intensity of the light is measured by a broadband radiometer (Newport) and is adjusted to 100 mW/cm^2 by putting metallic neutral density filters (Newport) together with the AM1.5 filter. The area of uniform illumination is a circle of 22 mm in diameter and all test cells have to be smaller than this area. The measurement is carried out in room temperature of 25°C .

As shown in Figure 2-22, the photoanode of DSSC is connected to a negative terminal of a sourcemeter (Keithley 2400). The counter electrode is connected to the positive terminal of the sourcemeter. The sourcemeter was programmed to measure current and voltage across the DSSC. As a result, the sourcemeter acts as a variable load and the I-V response of the DSSC can be measured as shown in Figure 2-22(b). The algorithm of V-I characterization is as follow: the sourcing voltage is set at zero and the short-circuited current (I_{SC}) is measured. The sourcing voltage increases in step of 10 mV and waits for 40 millisecond interval before measuring current.[123] At each step, the current is measured (negative value as solar cell is feeding current into the sourcemeter) until positive current is measured where the whole characterization procedure stops. An interpolation was carried out to find zero current point between the positive current point and the last negative current point. From the interpolation analysis on the current and voltage graphs, the zero current point indicates the open circuit- voltage (V_{OC}).

Figure 2-22. AM1.5 Solar simulated light source and IV characterization. (a) Setup using a Xenon lamp and AM1.5 filter to approximate solar spectra. Metallic neutral density filters used to lower the overall intensity to 100 mW/cm². (b) The I-V curve (solid line) and the VI-V curve (dotted line). The power graph is plotted by the product of VI against V. The peak output power (P_{max}) is the largest power point denoted by I_m and V_m points.

The PV conversion efficiency (η) is calculated from the P_{max} , device active area (A , in unit of cm²), and irradiance (P_s) as

$$\eta(\%) = \frac{P_{max}}{P_s A} \times 100 = \frac{V_m I_m}{P_s A} \times 100 = \frac{FF V_{OC} I_{SC}}{P_s A} \times 100$$

where P_s is 100 mW/cm², FF stands for filling factor and FF is equal to $(V_m I_m)/(V_{OC} I_{SC})$. FF is an indicator of the 'squareness' of the I-V profile and a value of $FF=1$ indicates that a perfect cell without any resistive loss.

2.7.2 Spectral Responsivity Measurement

The spectral responsivity describes the ability of a solar cell to convert incident light of varying wavelength to electric current. Responsivity is the ratio of output

current divided by incident light intensity (A/W). Incident Photon-to-current Conversion Efficiency (IPCE) is the spectral responsivity characterization by measuring the short-circuit current at various wavelength of incident light of known intensity. Available in library, is the international test standard ASTM E 1021 – 06. Frequently, the spectral responsivity is also known as the quantum efficiency (QE). QE is the ratio of the number of charge carriers generated to the incident photon flux (relates to the number of photons of a given energy).

Figure 2-23. The block diagram of the incident photon-to-electron conversion efficiency characterization.

Figure 2-23 shows the schematic setup of IPCE characterization. The main parts consist of a broadband light source (Xenon lamp, 300W, Newport), a variable wavelength selector (Monochromator, MS257, Oriel) and an intensity meter (silicon detector, Merlin, Oriel). The monochromator has a two port outputs where one port is attached to a silicon detector and another port is attached to a test sample. The output current of the test sample is measured by a sourcemeter configured as an ammeter. The silicon detector consists of a light chopper at the

front stage and it measures the light intensity from port 1. The light chopper cuts the light beam at a periodic interval and this effectively converts the light into an AC signal. AC signal processing in the silicon detector does not suffer from temperature drift and this is the advantage of using chopped light compared to direct light.

At a switch of an internal mirror inside the monochromator, the light can be directed from port 1 to port 2, where it illuminates the solar cell. Hence, with a two port system, there is a convenience of calibrating the light intensity and measuring the solar cell without dismantling any of the parts. The slight discrepancy of light intensity difference between port 1 and port 2 can be corrected by calibrated data easily. The wavelength selection, light and solar cell measurement are automated by the computer's control script. (Appendix)

The IPCE characterization algorithm follows the DC method.[124] Due to the slow electron diffusion in a DSSC, the DSSC's current output slowly ramps up to a steady value upon illumination of light. As a comparison, a silicon p-n junction solar cell has a much faster response time. Due to the slow response time of the DSSC, a very low chopping frequency is required (1 Hz). However, a low chopping frequency will cause the silicon detector to output a less stable reading. To circumvent the slow response of DSSC while maintaining a higher chopping frequency (70 Hz), a DC method was followed.

In the DC method, the monochromatic light at port 1 is measured by the silicon detector under chopped light (70 Hz). The full-width half-maximum (FWHM) bandwidth of the monochromatic light is optimized to 2 nm by adjusting

the slit width of monochromator. There is a UV filter (low wavelength cut off at 400 nm) in front of the monochromator to remove <400 nm wavelength irradiance and to prevent second-order light at the monochromator's output. In essence the 400 nm UV filter enables the IPCE characterization of up to 800 nm wavelength. The second-order light is an artifact of monochromator's grating diffraction mechanism. Next, the internal mirror directs the monochromatic light to the solar cell at port 2 and the chopper is disabled (direct beam). A short interval (3 sec) is allowed for the current to reach steady state and the current is then measured by the ammeter. The whole cycle continues with another wavelength of light. Finally, a series of monochromatic light intensity and output current can be computed into IPCE as a function of wavelength of light.

The DC method differs from the international standard ASTM E 1021 – 06 in the non-chopping of light on the solar cell illumination. The ASTM E 1021 – 06 mainly targets the fast response solar cell such as silicon p-n junction, hence DC method was adopted for slower response cell (e.g. DSSC). Further, in this work, IPCE is needed for relative comparison between a reference cell and a specimen cell; hence the absolute IPCE result is less critical. Besides, the DC method did not have an external bias light (as stipulated in ASTM E 1021 – 06) for setting DSSC in operation mode before impinging it with monochromatic light. In this work, the DSSC was verified to be operating under the monochromatic light illumination by integrating the IPCE result and close-matching with the overall PV conversion efficiency.

3. Photonic Crystal Dye-Sensitized Solar Cell

The fabrication of a nanostructured reflector described in preceding chapters can now be used to demonstrate the enhancement of photovoltaic application based on its unique optical property. Collecting and retaining light inside a solar cell is the key for efficient solar cell design. A DSSC is inherently a good transparent PV device; hence a back reflector is most suitable to couple onto a DSSC. In this aspect, all incident photons have a higher probability of getting absorbed and converted to electricity if they are made to be trapped longer in the cell. In optical terms, light trapping lengthens the equivalent optical path length inside the cell.

Figure 3-1. (a) DSSC with external PS opal reflector. (b) DSSC coupled with a TiO_2 inverse opal. The green spheres refer to PS opal, the red dots are the dye monolayer on all the TiO_2 surfaces (drawn not to scale), and the yellow region is the electrolyte filling.

The optical path length follows the thickness of a regular active absorbance layer of the photovoltaic cell. This path can be lengthened when schemes such as (i) shiny metal back reflector and (ii) textured surfaces are employed in a solar cell.

A shiny metal at the back of the active layer helps reflect un-harvested light back to the active layer again, thus increasing the light absorption. As a result, more light can be confined and sufficiently absorbed after making two passes inside the solar cell.

In this chapter, two different types of light reflectors are configured in the DSSC as depicted in Figure 3-1. The first is a polystyrene opal placed outside a DSSC. The second is a TiO_2 inverse opal placed inside a DSSC.

3.1 Back Reflector External Coupling

In literature, the use of a PC concentrator has been demonstrated to increase the harvesting efficiency of DSSC.[125] The concentrator consists of a polystyrene (PS) colloidal crystal assembled on a curved glass dish and it is much larger than the DSSC. The position of the concentrating dish was adjusted behind the DSSC so that the collected light converged to the DSSC. As the PC concentrator is made up of colloidal crystal, its reflectivity spectrum is tuned to the visible light. This optical property has an added advantage over metallic concentrator because of its selective wavelength reflectivity. The reflected rays do not contain any ultraviolet (UV) and near-infrared (NIR) components. It has been well documented that additional UV and IR spectra can degrade the DSSC's dye stability and cause heating. [126-129]

Figure 3-2. Transmission and reflection spectroscopy of (a, c) PS opal, and (b, d) DSSC coupled with PS opal. The reflection peak and transmission dip in (d) indicate that the opal causes a narrow spectral (in the vicinity of 638 nm) optical effect on the DSSC.

3.1.1 Effect of Polystyrene Opal Back Reflector

Here, a PC back reflector is demonstrated to increase the harvesting efficiency of DSSC while eliminating high form factor of using a concentrating dish. The back reflector consists of polystyrene (PS) colloidal crystal assembled on a micro glass slide, as depicted in Figure 3-2(a). The reflectance peak or the photonic band gap (PBG) is at 638 nm as shown in Figure 3-2(c). In Figure 3-2(b), the opal film is placed just behind and in contact with the DSSC, such that the transmitted light through the DSSC reflects back into the cell as verified by the spectrometer measurement in Figure 3-2(d). Consequently, the increased light intensity inside

the cell increases the probability of photon-to-current conversion at the spectral region around 638 nm. The spectral response in the efficiency of the cell with and without opal film can then be traced to the backreflector's spectral position of peak reflectivity.

3.1.1.1 Fabrication of Opal backreflector

3.1.1.1.1 Materials

Monodisperse polystyrene (PS) (diameter ~270 nm) colloidal suspension is used to assemble an opal film. The opal is grown on a micro glass slide (Deckglaser, 22×22 mm, Menzel-Glaser). In the assembly of DSSCs, titania nanoparticulate paste (Dyesol, DSL 90-T); N719 dye (Dyesol [RuL₂(NCS)₂]:2TBA ; L=2,2'-bipyridyl-4,4'-dicarboxylic acid ; TBA=tetra-n-butylammonium); platinum (Pt) paste (Dyesol, PT1) and iodide/triiodide electrolyte (Dyesol, EL-HPE) are used. The transparent conductive oxide (TCO) substrate are fluorine-doped tin oxide coated glass substrates (F:SnO₂ or FTO, Pilkington, TEC7). All solvents used are de-ionized (DI) water (Millipore, 18.0 MΩ/cm) and absolute ethanol (Aldrich, 99.99%). Other chemical used is sulfuric acid (Aldrich, 69%, H₂SO₄) and hydrogen peroxide (Aldrich, 30%, H₂O₂).

3.1.1.1.2 Flow controlled vertical deposition (FCVD)

Micro glass slides are cleaned in DIW and then treated with Piranha solution (3:1 volume mixture of H₂SO₄ and H₂O₂) to improve on the wetting angle. Finally, the

glass slides are rinsed with copious of DIW and blown dry. A layer of PS opal is grown on the micro glass slide using the FCVD technique. The PS opal film has an average thickness of 6.5 μm as measured by a surface profiler (KLA-Tencor AlphaStep).

3.1.1.1.3 Assembly of DSSC with opal back Reflector

The assembly of the DSSC is carried out as the procedure described in section 2.6. The mesoporous TiO_2 layer is measured to be 9.2 μm thick. The opal film is placed on the DSSC's counter electrode side as depicted in Figure 3-2(b). Adhesive tape is carefully adhered the micro glass slide's edges onto the DSSC's counter electrode side for support. For reference cell comparison, the opal layer (on glass slide) is removed from the DSSC in the IPCE characterization, thus there will be no opal back reflection at 638 nm wavelength.

3.1.1.2 Optical Characterization of DSSC with Opal Back Reflector

The PS opal film is characterized by using optical reflectance and transmittance spectroscopy setup. The reflectance/transmission spectrum of the PS opal film has a spectral peak/dip at approximately 638 nm shown in Figure 3-2(c). It is the centre wavelength of photonic band gap (PBG) of the PS opal. Further, the DSSC coupled with the PS opal back-reflector is also measured using reflectance and transmittance spectroscopy as shown in Figure 3-2(d). This experiment is carried out to prove that light through the assembled device have the similar spectral peak/dip as the bare PS opal film. Thus, the coupled PS opal film would exert an

influence on the DSSC and allow reflected light to pass through the DSSC. This leads to the enhancement of quantum efficiency as discussed in the next section.

Figure 3-3. The IPCE graph for DSSC device coupled with/without a PS opal (solid line) and the enhancement factor F_{IPCE} (dashed line).

3.1.1.3 Quantum Efficiency Characterization

Incident photon-to-current conversion efficiency (IPCE) measurement is carried out with the monochromatic light directed towards the photoanode side. The light leaves the DSSC and the spectrum of light matching the PBG of the PS opal gets reflected back to the DSSC again. The IPCE and enhancement factor (F_{IPCE}) are shown in Figure 3-3. The enhancement factor F_{IPCE} is defined as $(IPCE^{PC} - IPCE^{no-PC}) / IPCE^{no-PC}$ where PC denotes photonic crystal and $no-PC$ denotes without photonic crystal. The F_{IPCE} graphs have distinct peak at approximately 640 nm which corresponds closely to the PBG in Figure 3-2(d). The peak F_{IPCE} at around 640 nm is about 12% while the rest of the spectral region is

close to zero. This illustrates the use of tunable PBG in PS opal to enhance the power conversion efficiency in a particular spectral region of a DSSC.

3.1.2 Effect of Gold Film Back Reflector

Following the motivation of placing a back reflector behind a DSSC, a highly reflecting gold thin film on glass substrate (obtained by sputtering with thickness of 50 nm) was used for the study. The gold back reflector is expected to cause a broadened spectral reflection compared to the narrower PBG of an opal film.

The IPCE and enhancement factor (F_{IPCE}) of gold back reflector are shown in Figure 3-4. The gold back reflector causes a broader F_{IPCE} increment across the spectral range 500~700 nm as shown in Figure 3-4. In the UV range (<500 nm), there is a marginal increase in F_{IPCE} , and this suggests that DSSC has limited room for electron generation improvement in the UV range. For NIR spectral (> 650 nm), there is a greater F_{IPCE} improvement (> 50%) due to higher light intensity because of gold back reflection. However, a high F_{IPCE} improvement may not yield maximum benefit. As shown in Figure 3-4, a 100% F_{IPCE} is measured at wavelength 700 nm. Here, twice the amount of electrons is generated for every incident photon due to high reflecting gold film. However, the IPCE of a DSSC without gold back reflector at 700 nm is inherently low at about 1%. Thus a 100% F_{IPCE} may not be exciting for a already low quantum efficiency.

The important question of why an ordered nanostructure is used in back reflection compared to using a simple shiny metallic film needs to be answered. As

discussed earlier, the used of tunable opal reflector helps to reflect light in the visible ray spectral range. The opal's reflected rays do not contain any UV and NIR components; and DSSC's dye UV stability and thermal heating are circumvented. [126-129] Further, metallic reflector can tarnish and fade over time.

Figure 3-4. The IPCE graph for DSSC device coupled with/without a gold film (solid line) and the enhancement factor F_{IPCE} (dashed line).

3.1.3 Effect of Back Reflector on Power Conversion Efficiency

In the previous section, a PS opal is placed outside a DSSC to enhance the quantum efficiency at a selected spectral region. The peak F_{IPCE} measures about 12% and the benefit of using a tunable PBG (over a gold film) is to avoid reflecting UV or NIR rays back to DSSC as these rays may degrade the performance of a DSSC. On the other hand, a broader spectral gold film reflector measures a peak F_{IPCE} as high as 100% at 700 nm wavelength. How does the preceding quantum efficiency measurements translate to the overall power conversion efficiency? Figure 3-5

illustrates the IV characterization under the simulated AM1.5 solar irradiance (100 mW/cm²).

Figure 3-5. IV characterization (AM1.5 100 mW/cm²) of a DSSC with polystyrene opal and gold film back reflector.

The overall power conversion efficiency, η , is tabulated in Table 3-1. The η of a DSSC coupled with a gold back reflector is 1.73% and this represents a 10.6% improvement over the reference DSSC (1.56%). On the other hand, the narrower spectral reflection property of an opal back reflector has a relatively smaller η of 1.61% (3.2% improvement).

Table 3-1. The overall efficiency η of a DSSC with opal or metallic reflector.

	η	Increment over DSSC
DSSC	1.56%	-
DSSC+Opal	1.61%	3.2%
DSSC+Gold	1.73%	10.6%

In a η cell efficiency measurement, the short-circuited current density and open-circuited voltage of the cell are measurement. In an IPCE measurement, short

-circuited current densities at each wavelength are measured. Therefore, to examine the relationship of IPCE and η cell efficiency, their current density component is compared. To reconcile the measured η with the earlier IPCE measurements in Figure 3-3 and Figure 3-4, the $J_{sc}^{QE}(\lambda)$ of the IPCE measurements can be integrated to show the consistency with $J_{sc}(V_{oc} = 0)$ in Figure 3-5 [Ref: A. Luque, S. Hegedus, *Handbook of Photovoltaic Science and Engineering*, John Wiley & Sons 2003]. Table 3-2 shows the integrated current density of the IPCE measurements for wavelength $450\text{nm} \leq \lambda \leq 700\text{nm}$. The integration technique is finding the area under the curve by summing all the trapezoids in a spreadsheet program.

Table 3-2. The integrated $J_{sc}^{QE}(\lambda)$ from IPCE measurement and from $J_{sc}(V_{oc} = 0)$ measurement.

	Integrated $J_{sc}^{QE}(\lambda)$, $450\text{nm} \leq \lambda \leq 700\text{nm}$	$J_{sc}(V_{oc} = 0)$, Figure 3-5
DSSC	1.97 mA	3.12 mA
DSSC+Opal	2.02 mA	3.37 mA
DSSC+Gold	2.15 mA	3.42 mA

From Table 3-2, all the integrated current densities are about 1 mA lower than measured $J_{sc}(V_{oc} = 0)$ in Figure 3-5. The η and $J_{sc}(V_{oc} = 0)$ values are broadband measurement. On the other hand, the integrated $J_{sc}^{QE}(\lambda)$ does not take into account the current densities for $\lambda < 450\text{ nm}$ and $\lambda > 700\text{ nm}$. This explains why the integrated current densities are consistently lower than $J_{sc}(V_{oc} = 0)$ by

approximately 1 mA. In summary, both the IPCE and η cell efficiency measurement are consistent with each other.

The next section discusses the use of a TiO_2 inverse opal layer inside a DSSC. Potentially, it has a higher light reflecting capability compared to back reflector coupled on the exterior of a DSSC. This is because there is no FTO glass and liquid in between a TiO_2 inverse opal coupled to a TiO_2 mesoporous layer, as shown in Figure 3-1(b). Hence, there is no reduction in back reflected light intensity in a TiO_2 inverse opal case compared to polystyrene opal and gold film cases.

3.2 TiO_2 Inverse Opal Internal Coupling

In this section, a TiO_2 inverse opal coupled inside a DSSC is studied as depicted in Figure 3-1(b). The solar cell is irradiated monochromatically at different angles and the corresponding quantum efficiency is characterized. The photonic band gap (PBG) of a photonic crystal varies at different angles, and hence, under angle-resolved monochromatic irradiance, the effect of slow light at the band edges can be pinpointed.

The focus of this study is on the use of experiment and numerical models to demonstrate slow light effect at the PBG's band edges on the enhancement in IPCE of an inverse opal DSSC over a reference cell. The merit of band edge effect can be unambiguously highlighted here as the IPCE comparison is done using samples with and without periodic structures using almost similar inverse opal TiO_2 material volume and dye loading. In previous studies[100-102], the IPCE comparisons were done using different TiO_2 material volume and thus a different

amount of photo-generated current due to different volume of dye. Our approach of achieving same material volume for both periodic and non-periodic structure is obtained by collapsing[106] a section of TiO_2 inverse opal. As a result, a true IPCE enhancement due to band edge effect can be quantified.

3.2.1 Experiment

3.2.1.1 Materials

Monodisperse polystyrene (PS) colloids of diameter 285 nm (section 2.1) are used for the self- assembly. TiO_2 nanoparticles suspension (15 nm, 1.5 wt-%, section 2.2). Methyl Cellulose (molecular weight 14000, Aldrich) powder in the making of TiO_2 thin film paste. Transparent conductive oxide (TCO) substrates are fluorine-doped tin oxide coated glass substrates (F:SnO_2 or FTO, TEC7, Pilkington). DSSC's materials are Ruthenium 535-bisTBA dye (cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato, Solaronix SA) and Iodolyte electrolyte (TG50, Solaronix SA). All solvents used are de-ionized water (DIW, 18.0 M Ω /cm, Millipore), absolute ethanol (99.99%, Aldrich) and toluene (purum, $\geq 99.0\%$, Fluka).

3.2.1.2 Formulation of TiO_2 Thin Film Paste

The main harvesting mesoporous TiO_2 layer is a coating of TiO_2 thin film paste. Another layer of PS opal would be grown on top of this TiO_2 thin film. The TiO_2 paste which can be purchased from vendors does not have suitably hydrophilic

surface for colloidal self-assembly. This is because the commercial TiO_2 pastes contain ethyl cellulose based binders, which give a high water contact angle upon curing. Therefore there is no meniscus for successful colloidal self-assembly.

The solution is to prepare a TiO_2 thin film paste with a high wetting property using methyl cellulose (MC) based binder. First, the 1.5 wt-% TiO_2 suspension is concentrated to 14 wt-% with a rotary evaporator. A binder solution is prepared by dissolving 4 g of MC in 20 mL of DIW. Finally, a sol-gel of final mixture of 20 ml of concentrated TiO_2 suspension and 20 mL of MC binder solution is stirred overnight. A TiO_2 thin film is then doctor-bladed onto the FTO glass aided with adhesive tapes as masking window. The film is annealed at 350°C for 2 hours to achieve a mechanically robust platform for the subsequent colloidal self-assembly process.

3.2.1.3 Fabrication of TiO_2 Inverse Opal Layer and Collapsed Layer on TiO_2 Thin Film

Polystyrene (PS) opal film (colloids' diameter 285 nm) is deposited on top of the TiO_2 thin film by flow-controlled vertical deposition (section 2.3.3). The interstitial of the PS opal is infiltrated with TiO_2 nanoparticles (1.5 wt-% suspension) by repeated dip coating (section 2.4).

To ensure a similar volume of TiO_2 nanoparticles for comparison across samples, a section of a composite PS opal/ TiO_2 infiltrated structure is collapsed using toluene and 10-minute ultrasonic treatment. The sample is placed horizontally in an empty Petri dish with the PS opal/ TiO_2 infiltrated structure facing up. A few drops of toluene are carefully spread across a selected section of

the polystyrene opal/ TiO_2 infiltrated structure. Then, the petri dish is placed in an ultrasonic bath in order to collapse the TiO_2 matrix. Toluene dissolves the polystyrene opal and evaporates within 10 minutes. The TiO_2 matrix collapses and disperses on ultra-sonication. The dispersed TiO_2 nanoparticles are confined to the same area where toluene is applied. The toluene drop does not spread out even under ultra-sonication. The sample is carefully handled in the horizontal orientation and is placed in a furnace for calcination. Thus, the energy conversion efficiency can be compared between a PC bilayer electrode and a collapsed photonic crystal (C-PC) bilayer electrode at almost same amount of TiO_2 in one cell.

Figure 3-6. Cross-section SEM images of (a) TiO_2 inverse opal (layer 1) on a mesoporous TiO_2 film (layer 2); (b) TiO_2 inverse opal (PC); (c, d) collapsed TiO_2 inverse opal (C-PC). Scale bar is 1 μm for (a, c) and 100 nm for (b, d).

The thicknesses of an ordered and disordered structure are different. Thus, their optical path lengths are different. The ordered structure is thicker and offered more matter-light interaction opportunity. On the other hand, the disordered structure of this thesis is thinner and less matter-light interaction opportunity. However, the analysis of the disordered structure is further convoluted by being a denser structure with higher efficiency in carrier transportation which is one of key factors of a solar cell. Thus, the issue of ordered and disordered direct comparison is addressed in section 5.8 with the aim of addressing the optical path difference with quantum efficiency measurement

3.2.1.4 Calcination of TiO₂ Film and DSSC Device Assembly

The PS opal template and MC binder in the TiO₂ thin film are removed by calcination at 450°C for 2 hours (section 2.4.6). The film-PC bilayer and film-C-PC bilayer measured approximately 6.4 μm and 4.7 μm thick respectively (alpha-step profilometer, KLA-Tencor Instrument). Figure 3-6(a)-(b) depict the cross-section scanning electron micrographs of the film-PC bilayer and Figure 3-6(c)-(d) show the C-PC layer. The SEM cross-section samples are prepared as follows. A small crack is made at the edge of the non-sensitized sample using a diamond scribing pen. Then the crack is carefully propagated through the sample. Scanning electron microscopy is performed on the cross-section of the fracture surface.

3.2.2 Effect of Angular Irradiance on IPCE Enhancement

The final bilayer electrode structure is shown in Figure 3-7(a) and the angular optical setup is configured as shown in Figure 3-7(b) to measure the transmission spectrum. A broadband light source is directed onto the DSSC's photoanode side. The transmission spectrum can be measured directly by a spectrometer placed behind the counter electrode side. Denoting the following light setup as front illumination, irradiance is performance on the DSSC's TiO₂ bilayer (photoanode) side so that the Ru-dye would be exposed to the light before attenuation in the electrolyte. The electrolyte solution attenuates the strength of the irradiance so rear illumination is not considered. The incidence angle θ_i is varied along the Γ LU direction[130]; defined from the normal of the (111) inverse face centered cubic structure. Optical transmission spectra measurements are carried out to simulate the passage of light through DSSC and to probe the PC's effect on the energy conversion efficiency spectrum.

Figure 3-7(c) suggests the expected distribution of generated electron concentration with respect to distance traveled as light propagates through the PC. The x-axis corresponds to the PC thickness as illustrated in Figure 3-7(b). The electron generation is expected to be greater closer to the light source, and decreasing with PC thickness due to light attenuation and scattering. The distribution of the electron generation will be discussed further in following section.

Figure 3-7. (a) Schematic of a PC and C-PC bilayer electrode on the same FTO substrate. (b) Angular transmission setup for the film-PC bilayer electrode. d_{PC} is the thickness of the PC layer. θ is the incidence angle to the DSSC. θ_i is the refracted angle in the glass substrate and the incident angle to the PC. (c) The expected distribution of the electron injection concentration as the light intensity reduces in the PC.

In Figure 3-7(b), the incidence angle θ is the angle light makes on the air-glass interface of the DSSC. Inside the glass, the refracted angle changes according to the law of refraction, $n_i \sin \theta_i = n_{i+1} \sin \theta_{i+1}$, at air-glass interface. The refractive index of glass is 1.5 and air has an index of 1. The light path passes through the inhomogeneous layers of fluorine-doped thin oxide (FTO) and mesoporous TiO₂. And it reaches the TiO₂ inverse opal layer with an incidence angle θ_i . As a summary, the angular irradiance experiment for $\theta = 0^\circ$, 15° and 30° results in the incidence angle $\theta_i = 0^\circ$, 9.93° and 19.47° respectively at the TiO₂ inverse opal. Angular transmission spectra are shown in Figure 3-8(a) for θ of 0° (transmission dip at wavelength 641nm), 15° (630nm) and 30° (612nm).

As the incidence angle increases, there is a blue shift in the transmission dips, which correspond to the central wavelength of the PBG[41, 131] of the inverse

opal. The transmittance plots presented in Figure 3-8(a) do not have sharp dips. This is because some amount of light is absorbed by the mesoporous film layer before reaching the inverse opal layer. Nevertheless, the variation in PBG with incidence angle can be observed from the transmittance plot and this is confirmed by matching the dips with numerical simulation result in the following section.

Under angle-resolved non-collimated monochromatic irradiance for the same incidence angles, the incident photon-to-current conversion efficiency (IPCE) measurement is carried out. The IPCE and enhancement factor (F_{IPCE}) for $\theta_i = 0^\circ$, 9.93° and 19.47° are shown in Figure 3-8(b)-(d). The enhancement factor F_{IPCE} is defined as $(IPCE^{PC} - IPCE^{C-PC}) / IPCE^{C-PC}$. The F_{IPCE} graphs have distinct peaks in the red-edge of the PBG (dielectric band edge). Unlike previous reports [100, 101], the F_{IPCE} peaks appearing at the spectral location of the dielectric band are unambiguous because the samples are compared based on the same volume of TiO_2 material with and without a photonic crystal. In the past, the general increase in F_{IPCE} as observed in Figure 3-8(b)-(d) over the spectral range 500 nm to 760 nm

Figure 3-8. Angled-resolved transmission measurement of the bilayer electrode DSSC for angular irradiance (θ) experiments 0° ($\theta_i=0^\circ$), 15° ($\theta_i=9.93^\circ$) and 30° ($\theta_i=19.47^\circ$). (b)-(d). The IPCE graph for DSSC devices: PC bilayer electrode (solid circles) and C-PC bilayer electrode (solid triangles). The arrows indicate the gap centers for the three different incidence angles. The dashed lines are the enhancement factor F_{IPCE} plots.

range has been attributed to the scattering effect[101, 102] of the photonic crystal as a back reflector. In the curves of Figure 3-8(b)-(d) depicting as F_{IPCE} plateau over the 500 nm to 760 nm range, the scattering effect account for nearly 60% increment over C-PC samples.

For PBG reflection back to the DSSC, their effects are pointed by vertical dashed lines in Figure 3-8(b)-(d). At these PBG spectra locations, the F_{IPCE} levels are about 60-65%, almost same value as the scattering effect (the plateau curves).

To separate the PBG effect from the scattering effect, angular monochromatic irradiance measurements are necessary for the distinction. As the angle of irradiation on the PC varies, the PBG (together with its two band edges) spectral position shifts in accordance to the photonic band diagram. However, the spectral shift in scattering effect due to angular change is not well defined. In Figure 3-8(b)-(d), there are additional 10% peak F_{IPCE} increments (ridge-like) approximately on top of the F_{IPCE} plateau. The ridge-like F_{IPCE} increments are next to the vertical dashed line in Figure 3-8(b)-(d). Further, the ridge-like F_{IPCE} blue-shifts with the increase in the angle of incidence. The ridge-like F_{IPCE} spectral positions correspond to the higher wavelength of the PBG band edge which is known as dielectric band edge.

The following section discusses dielectric band edge effect on the F_{IPCE} enhancement by considering the electric field of light inside the PC due to a change in incidence angle θ_i .

3.2.3 Effect of Angular Irradiance on Electric Field Computation

The angular irradiance of a TiO_2 inverse opal can be represented with the aid of a photonic band diagram. First, the angles of incidence are explained before moving on to the band diagram. Figure 3-9 illustrates the varying angle of incidence (θ_i) on an opal film (also applicable for inverse opal film). The symbolic labels Γ U refers to normal incidence on the (111) textured FCC opal film. [130] For angles normal to the opal plane and perpendicular to the opal growth direction, it is Γ U direction.

Figure 3-9. Illustration of incident ray on the opal film (applicable to inverse opal too). (a) Normal incidence on the opal (111) plane and this is Γ L direction. (b) Variable angle incidence perpendicular to the opal growth direction (Γ U direction).

For computing the photonic band diagram, the lattice parameter, a , is first obtained from the cross section SEM image of the inverse opal film in Figure 3-6(b). Inverse opal undergoes shrinkage under calcination[120] and the FCC (111) inter-planar distance of 195 nm ($d_{111} = \sqrt{8/3} r$) is obtained. Therefore, a of the inverse opal is computed to be 337 nm ($a = 2\sqrt{2} r$).

Figure 3-10. Left panel: Photonic band diagram of a TiO_2 PC in the LU direction. The y-axis is the angular frequency, ω , normalized with the lattice constant, a , and the speed of light in vacuum, c , and a factor of 2π . The x-axis is the magnitude of the parallel wave vector in the LU direction. L_1 - L_6 denotes the modes at the respective locations in the photonic band diagram. The black dots indicate the transmission dips (0° , 9.93° , and 19.47°) in the angle-resolved transmission measurement (from Figure 3-8a). Right panel: The intensity plot $|E|^2$ of modes L_1 and L_2 (0°), L_3 and L_4 (9.93°), and L_5 and L_6 (19.47°). White indicates high intensity.

The photonic band diagram is calculated using the plane-wave expansion method[63], using the following values[102]: $n_{\text{TiO}_2}=2.25$, $n_{\text{TG-50}}=1.43$, and a filling factor[131] of 45 % for TiO_2 in air interstices. The transmission dips from Figure 3-8(a), are denoted as black dots in the photonic band diagram in Figure 3-10(left panel). $\bar{k}$ is the wavevector and θ_1 is the angle between ΓL - ΓU directions and the parallel wavevector is defined $k_{||}(2\pi/a) = \bar{k} \sin \theta_1$ from ΓL towards ΓU .

To estimate the effect of electric field localization, the eigenfunction $|E|^2$ in the inverse opal is computed by exciting eigenmodes L_1 , L_2 , L_3 , L_4 , L_5 and L_6 as

shown in Figure 3-10(right panel). The interior of a sphere represents the region of TG-50 electrolyte while the exterior is the TiO_2 region. Figure 3-10(right panel) shows plots of electric intensity $|E|^2$ of modes L_1 & L_2 (0° incidence), L_3 & L_4 (9.93°) and L_5 & L_6 (19.47°). White color represents high intensity. Localizations of $|E|^2$ in the TiO_2 region are found in modes L_1 , L_3 and L_5 , where they are in the dielectric band collectively. Therefore, dielectric band localization helps in the Ru-dye absorption and electron injection in the TiO_2 region.

Conversely, localization of $|E|^2$ in the TG-50 electrolyte region is found in the air band: L_2 , L_4 and L_6 modes. Because there is no Ru-dye and electron injection in the TG-50 electrolyte region, there is no effect from air band localization. Therefore, the F_{IPCE} peak at the dielectric band (640~740 nm for 0° incidence) is deduced from enhanced photocurrent generation due to light localization at the TiO_2 PC while the general improvement (~60 %) of F_{IPCE} over the 460~760nm spectral range is the result of increased photocurrent generation of the TiO_2 film from the scattering effect of the PC layer.

Photons propagate slowly near the PBG edge due to the flatter photonic band and could enhance the interaction between light and matter. In this section, a quantitative analysis is performed on the field enhancement phenomenon due to the band edge effect.[103-105, 132] The intensification of electric field strength inside the PC layer ($|E_{ePC}|^2$) against C-PC layer ($|E_{eC-PC}|^2$) is simulated using a finite-difference time-domain (FDTD) simulator [133-135] for $\theta_I = 0^\circ$, 9.93° and 19.47° in Figure 3-11. The frequency-dependent material dispersion of TiO_2 is

represented as the sum of harmonic resonances[136] and the parameters used in the simulator are $\omega_n=3.1$ rad, $\gamma_n=0.008$, and $\Delta\epsilon_n=0.1$ [135-135]. For TG-50 electrolyte, the measured absorbance spectrum is relatively flat between spectral range of interest (500~800 nm) and is assumed to be non-dispersive. The geometry of the structures is based on the film thicknesses stated earlier. The rest of the simulation parameters are similar to those used in the plane-wave expansion method earlier.

Figure 3-11. Angled-resolved FDTD simulation of the transmission spectra and time-averaged $|E_{ePC}|^2 - |E_{eC-PC}|^2$ electric field strength plots. The incidence angle (θ_i) at the PC is (a) 0° , (b) 9.93° and (c) 19.47° for the angular placement of DSSC at 0° , 15° and 30° respectively. The PC enhances electric field strength near the PBG red-edge which shifts in accordance with the PBG.

First, the film-PC bilayer's transmission spectrum is simulated to study the light propagation behavior through the bilayer. In Figure 3-11, the computed transmission dip center locations match well with experimental transmission result

shown in Figure 3-8(a). The experimental dip width is larger than the numerical solution due to the inhomogeneous broadening effect [56] and computation non-ideality. No dip is computed for a film-C-PC bilayer. In addition, the overall transmittance obtained from the simulation is relatively higher than the experimental result in Figure 3-8. This is because the model has uniform long range order, on the other hand, the experimental sample has intrinsic defects which scatters light away. This causes a lower transmittance level for experimental result. Secondly, the FTO substrate does not have anti-reflective coating, and some incident light is reflected away. These two reasons caused a lower transmittance level for the experimental result.

The time-averaged difference in electric field intensity $|E_{ePC}|^2 - |E_{eC-PC}|^2$ are shown in Figure 3-11 at dielectric bands at different incidence angles. The electric field strength enhancement is greatest at the edge of dielectric band, i.e. approx. 679 nm, 677 nm and 669 nm for incidence angles (θ_i) 0° , 9.93° and 19.47° respectively. The difference in the electric field intensity blue-shifts with the increase in incidence angle and this is the evidence of dielectric band edge enhancement.

3.2.4 Dielectric Band Edge Enhancement Model

The intensification of electric field strength inside the PC influences the interaction between light and the Ru-dye. The Maxwell-Bloch equation[137] is commonly used to study the dynamics of electron excitation in a simplified two-level atom model. Here we consider the Ru-dye to be a two-level atom with an electron

excitation frequency ω_{EG} corresponding to its peak absorption frequency.

Absorption of a photon of energy $\hbar\omega$ takes place when an electron is excited from the ground to the excited energy level. The Maxwell-Bloch equation is described by the dynamic relationships for a singly polarized, unidirectional traveling wave,

$$\partial P_e / \partial t + [\gamma_{EG} + i(\omega_{EG} - \omega)] P_e = ip^2 E_e N / \hbar , \quad (3-1)$$

$$\partial N / \partial t - i2(E_e^* P_e - E_e P_e^*) / \hbar = -\gamma_{EE} N , \quad (3-2)$$

where N , γ_{EG} and γ_{EE} denote the two-level inversion density, polarization and population damping constant respectively. Under influence of electric field, the distorted electron cloud leads to the induction of dipoles in the dye atom. The matrix p indicates the strength of dipole transition induced by an incident wave.

The envelope amplitude of the electric field and dipole polarization are denoted as E_e and P_e respectively. Population inversion is lost through electron-hole recombination and electron injection to the TiO_2 conduction band. To model the replenishment in the loss of inversion, an excitation rate of $\gamma_{EE} G(\omega)$ is added to the RHS of (3-2). The excitation density $G(\omega)$ is dependent on the excitation frequency and has units of reciprocal volume. The population damping constant has units of reciprocal time. Under steady state condition, the time derivatives of P_e and N go to zero ($\partial P_e / \partial t \rightarrow 0$ & $\partial N / \partial t \rightarrow 0$) and the excitation density of

Eqn. (3-1) is simplified to

$$P_e = \left[\frac{(\omega_{EG} - \omega) + i\gamma_{EG}}{\gamma_{EG}^2 + (\omega_{EG} - \omega)^2} \right] \frac{p^2}{\hbar} E_e N . \quad (3-3)$$

Substituting (3-3) into (3-2)

$$\begin{aligned}
 \gamma_{EG}(N - G) &= \frac{i2}{\hbar} \left[E_e^* \left(\frac{(\omega_{EG} - \omega) + i\gamma_{EG}}{\gamma_{EG}^2 + (\omega_{EG} - \omega)^2} \frac{p^2}{\hbar} E_e N \right) - E_e \left(\frac{(\omega_{EG} - \omega) + i\gamma_{EG}}{\gamma_{EG}^2 + (\omega_{EG} - \omega)^2} \frac{p^2}{\hbar} E_e^* N \right) \right] \\
 \gamma_{EG}(N - G) &= \frac{-4}{\hbar^2} |E_e|^2 \frac{\omega_{EG} N p^2}{\gamma_{EG}^2 + (\omega_{EG} - \omega)^2} \\
 G &= \left[1 + \frac{4\gamma_{EG} p^2 N}{\gamma_{EE} \hbar^2 [\gamma_{EG}^2 + (\omega_{EG} - \omega)^2]} \right] |E_e|^2 .
 \end{aligned} \tag{3-4}$$

From (3-4), $G(\omega)$ is proportional to $|E_e|^2$, resulting in a higher excitation density or dye absorption for increased light field.[137] For simplicity, Eqn (3-4) is denoted $G(\omega) = [\bullet] |E_e|^2$ henceforth for all analysis that follows. For simplicity, $G(\omega)$ is assumed to be the effective excitation density at all dye-TiO₂ locations, independent of spatial position.

3.2.4.1 Photo-generated Electron Distribution in the Inverse Opal Layer

The overall electron action in the dye-TiO₂ can be examined and modeled using a continuity equation, which equates the overall change in electron concentration with time by considering the net flow in and out of that region. Only the injected electrons $\Delta n(x, \omega)$ from the Ru-dye is considered while assuming that the bulk concentration n_0 of n-type[138] TiO₂ remains unchanged. Unless specified otherwise, $\Delta n(x, \omega)$ is denoted simply as Δn . The continuity equation takes the following form:

$$\partial \Delta n / \partial t = \partial \Delta n / \partial t \Big|_{\text{GEN}} - \partial \Delta n / \partial t \Big|_{\text{REC}} - \nabla \cdot J_n / q . \tag{3-5}$$

The time derivative of the Δn due to electron generation is the product of the dye concentration per unit volume N_{dye} and the excitation density rate $\gamma_{EE} G(\omega)$.

The difference in N_{dye} between the C-PC and PC is expectedly small since the volume of TiO_2 remains unchanged. For ease of analysis, N_{dye} is assumed to be constant throughout the PC and C-PC.

The time derivative of the Δn due to electron recombination is the product of Δn and charge recombination rate k_{rec} described as electron trapping/detrapping processes and electron hole recombination in the electrolyte by tunneling through the dye.[139] The electron current density, J_n , can be represented in a compact form[140] $J_n = \mu_n \Delta n \nabla F_n$, where μ_n and ∇F_n are the electron mobility and spatial derivative of the quasi Fermi level respectively.

Irradiance is directed on the bilayer electrode side of the DSSC as depicted in Figure 3-7(b). Hence, more electrons are excited nearer to electrode side where the irradiance is the strongest. This results in a concentration gradient of Δn , where $\Delta n(d, \omega) > \Delta n(0, \omega)$ as illustrated in Figure 3-7(c). The concentration gradient creates an anti-flow of electrons away from the electrode. In practice, the DSSC supplies electrons out from the electrode and holes out from the counter-electrode. Thus, a negative term $-(1/q)\nabla \cdot J_n$ accounts for the loss of electrons due to the concentration gradient. Re-writing the continuity equation,

$$\partial \Delta n / \partial t = N_{dye} \gamma_{EE} G(\omega) - \Delta n k_{rec} - (\mu_n \nabla F_n / q) \partial \Delta n / \partial x . \quad (3-6)$$

It is assumed that ∇F_n is independent of position and constant across the entire film.[140] At the boundary $x=0$, the surface exposure of the dye atom and TiO_2 nanoparticles to the electrolyte is higher. Larger number of electron loss is expected at the surface due to tunneling effect.[141] Simplifying the boundary

condition to be $\Delta n(0, \omega) \rightarrow 0$ and at steady state condition, the distribution of Δn is

$$\Delta n = (N_{dye} \gamma_{EE} G(\omega) / k_{rec}) [1 - \exp(-Ax)] , \quad (3-7)$$

where A represents the factor $qk_{rec} / \mu_n \nabla F_n$. The exponential relationship in (3-7) matches well with predicted electron distribution described earlier Figure 3-7(c) and in Ref. [142] and it is re-plotted in Figure 3-12. Excitation rate $\gamma_{EE} G(\omega)$ is directly in competition with the recombination rate k_{rec} . In the case of PC, Δn is higher for larger excitation density rate $\gamma_{EE} G(\omega)$, which corresponds to higher $|E_e|^2$.

Figure 3-12. Electron distribution in a TiO₂ inverse opal in accordance to Eqn. (3-7). B represents the factor $N_{dye} \gamma_{EE} G(\omega) / k_{rec}$. Refer to Figure 3-7(c) for direction of light.

3.2.4.2 Unifying Electric Field Enhancement with Photo-generated Current

To study the F_{IPCE} peaks in Figure 3-8(b)-(d) and the effect of large $|E_e|^2$, the analysis is restricted to a comparison between electron action in PC region and that of the C-PC regions. The increase of photocurrent density in PC structure

compared to that of C-PC can be calculated as $\Delta J(\omega) = (q\nabla F_n \mu_n)$

$\left[\int_0^{d_{PC}} dx \Delta n_{PC} / d_{PC} - \int_0^{d_{C-PC}} dx \Delta n_{C-PC} / d_{C-PC} \right]$ and simplified to

$$\nabla J(\omega) = q\nabla F_n \mu_n N_{dye} \gamma_{EE}[\bullet] \left\{ |E_{ePC}|^2 - |E_{eC-PC}|^2 \right\} / k_{rec} , \quad (3-8)$$

by approximating $|\exp(-Ad_{PC}) - 1/Ad_{PC}| \ll 1$ and $|\exp(-Ad_{C-PC}) - 1/Ad_{C-PC}| \ll 1$.

From (3-8) the enhancement of photocurrent density is proportional to the difference between $|E_{ePC}|^2$ and $|E_{eC-PC}|^2$. In Figure 3-11, the relationship of Eqn. (3-8) is illustrated by comparing the experimental F_{IPCE} peaks with the numerically computed $\Delta J(\omega)$ term, thus linking the photonic crystal's increased light field and photo-current density.

The peak positions of F_{IPCE} in Figure 3-8(b)-(c) and the computed $\Delta J(\omega)$ in Figure 3-11 match well. Both relation plots blue-shift synchronously with the incidence angle. This dielectric band edge enhancement is most effective at the edge and decreases in prominence at wavelengths far from the edge. This can be seen in Figure 3-11 where the wavelengths to the left side and right side of $\Delta J(\omega)$ peak show reduced $\Delta J(\omega)$ even though F_{IPCE} is still generally maintained constant at about 60%. This constant F_{IPCE} region can be ascribed to the back-scattering effect of PC as described earlier. Thus we show that the intensification of $|E_{ePC}|^2$ in the dielectric band causes the enhancement in photo-excitation and photocurrent density, and hence a higher IPCE for a film-PC bilayer electrode.

3.3 Conclusion of Chapter 3

In this chapter, two types of nanostructured and one metallic back reflectors were demonstrated to improve the incident photon-to-current conversion efficiency (IPCE) of a DSSC. The peak enhancement factor in IPCE of a TiO_2 inverse opal bilayer DSSC is 75% at the dielectric band edge compared to 12% in a polystyrene opal back reflector DSSC and 100% in a gold film reflector. To pinpoint the slow light phenomenon effect near to the dielectric band edge, the angle of incidence on the TiO_2 inverse opal bilayer DSSC is varied, and the IPCE enhancement peaks match well with the blue-shift in dielectric band edge. Numerical simulation shows that the intensification of electric field strength at the photonic band edges' where group velocity of light is low. Using a Maxwell-Bloch model of the Ru-dye atom as a simplified two-level atom, the excitation density or the absorption of the Ru-complex dye is found to increase with the electric field strength in the photonic crystal. The increased excitation density rate causes a greater electron injection into the conduction band of TiO_2 , which consequently increases the photocurrent and improves the IPCE.

4. Planar Defect in the Photonic Crystal Dye-Sensitized Solar Cell

Similar to impurity doping in semiconductors, the introduction of linear or planar defect [116, 143-145] into photonic crystal can add permitted states in the photonic band gap (PBG). This optical doping effect has been used to create waveguide or microcavity in optics applications. Linear defects can be fabricated by multiphoton polymerization[146, 147] and lithography patterning[148, 149].

Figure 4-1. A multi layers structure with defect. n_1 and n_2 are the different refractive indices. The curve is the electric field inside the structure.

Figure 4-1 illustrates a simple 1D planar periodic structure with a thicker layer at the centre. This thicker layer is the defect which destroys the periodicity of the structure. By considering the multiple layers far away from the defect layer at both ends, they resemble periodic structures and they exhibit PBG property at both ends. Now, consider there is no defect layer, i.e. the 'defect layer' has the similar

thickness as rest of the layers. The whole structure is a perfect periodic lattice and the PBG is void of any forbidden state. As the 'defect layer' starts to increase in thickness, the translational symmetry is now perturbed. Localized mode is now permitted to exist and this defect state lies inside the PBG depending on the thickness to periodicity ratio.[61]. In essence, the defect layer creates a non-zero density of states inside the forbidden gap and a localized mode can be supported in this defect. Another example of creating a defect layer is to change the refractive index differing from the n_1 and n_2 materials of Figure 4-1.

Figure 4-2. The schematics and terminologies used in the architecture description of DSSC + TiO₂ inverse opal + TiO₂ planar defect layer (a) with TiO₂ mesoporous layer and (b) without TiO₂ mesoporous layer. (drawn not to scale).

In this chapter, a defect state[143] is introduced inside the prohibited photonic band gap (PBG) by sandwiching a planar defect layer in between two opal layers through layer-by-layer deposition.[150-153]. Earlier in section 2.5, the layer-transfer technique allows layer-by-layer assembly to enable the planar sandwich

structure[121] and this procedure is used for the successful fabrication of the sandwich structure.

In the layer-transfer method, polystyrene opal film assembled on a hydrophilic glass substrate can be peeled off one surface and deposited onto another substrate. The layer transfer enables the deposition of an opal film onto a hydrophobic substrate, which is not possible in the normal vertical self-assembly technique.

The feasibility of the above layer-transfer technique to engineer a planar defect in opal enables the fabrication of a photonic crystal dye-sensitized solar cell[78] with a planar defect layer. In previous reports[100-102, 154], TiO_2 inverse opal photonic crystal has been used to improve the power conversion efficiency of a dye-sensitized solar cell (DSSC) by coupling the photonic gap edge's slow light phenomenon for solar energy harvesting.

In this work, two following types of structures were fabricated and studied:

- 1) TiO_2 inverse opal (with defect layer) on TiO_2 mesoporous film DSSC (denoted as IO+DL+Me, Figure 4-2(a)),
- 2) TiO_2 inverse opal (with defect layer) DSSC (denoted as IO+DL, Figure 4-2(b)).

The first structure is a regular DSSC with a TiO_2 mesoporous layer coupled with the additional TiO_2 inverse opal (sandwiching a TiO_2 defect layer) as depicted in Figure 4-2(a). The objective is to create a permitted propagation mode in the PBG by introducing a planar defect layer in the TiO_2 inverse opal. This achieves a cavity where the defect mode can promote a stronger light-matter interaction which

enhances the photo-excitation or light absorption of ruthenium-complex dye in the DSSC. **Figure 4-3** shows the cross section view of the IO+DL+Me specimen.

Figure 4-3. (a) SEM image of the cross-section view of DSSC with TiO_2 inverse opal and TiO_2 planar defect layer, simply denoted as IO+DL+Me specimen (starting from bottom: FTO substrate, mesoporous film, inverse opal, defect layer, inverse opal). Scale bar is 10 μm . (b) higher resolution SEM cross section view of the TiO_2 defect layer. The average thickness of the defect layer is 127 nm. Scale bar is 1 μm .

The second structure involves the construction of a DSSC (without a TiO_2 mesoporous layer) with TiO_2 inverse opal sandwiching a TiO_2 planar layer as

shown in Figure 4-2(a). Figure 4-4 shows the cross section view of the IO+DL specimen.

Figure 4-4. SEM image of the cross-section view of DSSC with TiO_2 inverse opal and TiO_2 planar defect layer, simply denoted as IO+DL specimen (top region reveals that domains are separated by cracks). Scale bar is $10\mu\text{m}$. (b) Higher magnification SEM cross-section view of the TiO_2 defect layer. The average thickness of the defect layer is 150 nm. Scale bar is $1\mu\text{m}$.

4.1 Experimental Methods

In this section, fabrication techniques of both structures (Figure 4-2) are described with the help of following procedure as illustrated in Figure 4-5.

Figure 4-5. Procedures of the fabrication of DSSC with TiO_2 inverse opal and TiO_2 planar defect layer. (a) deposition of titania nanoparticulate film on FTO substrate (this is not done for IO+DL cell); (b) deposition of PS opal film by layer-transfer method; (c) TiO_2 nanoparticles infiltration; (d) deposition of planar defect film by doctor-blading; (e) deposition of PS opal film by layer-transfer method; (f) TiO_2 nanoparticles infiltration; (g) calcination and the formation of TiO_2 mesoporous layer.

For ease of reading the terminologies use in the subsequent section, a list is tabulated below to describe the function of each layer in Figure 4-2.

Table 4-1. Terminologies and definitions of each layers in Figure 4-2.

Before calcination		After calcination	
1) Titania nanoparticulate film	A commercial (Dyesol) paste to be deposited on substrate by doctor blading.	TiO ₂ mesoporous layer	The main harvesting layer of DSSC.
2) TiO ₂ defect film	A viscous paste formulated with Degussa P25 TiO ₂ powder.	TiO ₂ defect layer	The layer which is sandwiched in the TiO ₂ inverse opal.
3) Polystyrene opal film	An opal template to be filled with TiO ₂ nanoparticles.	TiO ₂ inverse opal	The photonic crystal structure.

4.1.1 Materials

Monodisperse polystyrene (PS) colloids of diameter 230 nm and 216 nm (section 2.1) are used for the ordered nanostructure assembly. TiO₂ nanoparticles suspension is synthesized as explained in section 2.2. In the preparation of TiO₂ defect film, commercial TiO₂ nanopowder (Degussa, P25, 20nm) and ethyl cellulose (Aldrich, 46 cP, 5 % in toluene/ethanol 80:20) are used. In the assembly of DSSCs, titania nanoparticulate paste (Dyesol, DSL 90-T); N719 dye (Dyesol [RuL₂(NCS)₂]:2TBA ; L=2,2'-bipyridyl-4,4'-dicarboxylic acid ; TBA=tetra-n-butylammonium); platinum (Pt) paste (Dyesol, PT1) and iodide/triiodide electrolyte (Dyesol, EL-HPE) were used. The transparent conductive oxide (TCO)

substrate are fluorine-doped tin oxide coated glass substrates (F:SnO₂ or FTO, Pilkington, TEC7). All solvents used are deionized (DI) water (Millipore, 18.0 MΩ/cm) and absolute ethanol (Aldrich, 99.99%). Acetic acid (Aldrich, 69%) is used without further purification

4.1.2 Deposition of Titania Nanoparticulate Film

This procedure is carried out only for IO+DL+Me cells. FTO substrates are cleaned with glassware detergent and ultrasonically cleaned in ethanol for 10 minutes. They are rinsed with copious of DI water and then blow dried in an air stream. A 100 μm thick adhesive tape is used to define a deposition window on the conductive side of the FTO. Using a simple doctor-blading method, a layer of titania nanoparticulate paste is coated on the FTO substrate (Figure 4-5(a)) and left to cure in air for 12 hours.

4.1.3 Preparation of PS Colloidal Crystal Template

The PS colloidal suspension is diluted with DI water to a concentration of 2 wt-% of solid. Using flow-controlled vertical deposition (FCVD) technique[155], the PS colloids are assembled into on a glass (OL+DL+Me cells or for TiO₂ defect layer) or directly onto FTO substrate (OL+DL cells). 230 nm and 216 nm sized colloidal suspensions are used for OL+DL+Me and OL+DL cells respectively.

4.1.4 Layer-transfer of PS Opal Film onto TiO₂ Nanoparticulate Film

One requirement of colloidal self-assembly is that the surface on which the opal film is to be deposited has to be hydrophilic. Hence, layer-transfer method is used to deposit a PS opal film on top of the titania nanoparticulate film and TiO₂ defect film, which are hydrophobic because it contains polymeric binders. The PS template is peeled off (section 2.5) from the glass substrate and ready for transfer to other substrates.

Once the PS opal film is completely detached from the glass substrate, the FTO with titania nanoparticulate film or with TiO₂ defect film is then directly inserted into the water trough and positioned just below the floating PS opal film (Figure 2-15(c)). Even under water, it is observed that the existing deposited film on FTO adhered sturdily on the FTO. To deposit the PS opal film onto the titania nanoparticulate film, the FTO is raised slowly out of the water horizontally, forming a layer-by-layer heterostructure (Fig Figure 4-5b and Figure 2-15d). Finally, the FTO is held vertically to drain off excess water and is annealed at 90°C for 2 hours to achieve a strong mechanical structure.

4.1.5 Infiltration of TiO₂ Nanoparticles into PS opal Interstices

TiO₂ nanoparticles are infiltrated into the interstices of the opal template by multiple dip coating cycles (section 2.4.3). The preceding steps are repeated 3 more times to completely fill the interstices of opal (Figure 4-5c).

4.1.6 Deposition of TiO₂ Defect Layer

A sol-gel was prepared for the coating of the defect layer on top of the PS/TiO₂ composite layer. A 0.6 g of P25 TiO₂ nano-powder is grind in a mortar with the addition of 0.1 mL of acetic acid, 0.5 mL of DI water and 10 mL of ethanol following the procedures outlined by Ito et. al.[156] To increase the viscosity of the TiO₂ suspension, a binder solution of 0.3 g of ethyl cellulose was prepared in 2 mL of ethanol. While stirring the TiO₂ suspension, the binder solution was added into the TiO₂ suspension and finally top up with another 100 mL of ethanol to complete the defect layer TiO₂ sol-gel preparation.

A 120 μ m thick adhesive tape is pasted on the FTO beside the thin film. The sol-gel prepared above is coated on top of the infiltrated composite opal layer by doctor-blading. It is observed that the sol-gel dries quickly and forms a smooth TiO₂ defect layer film over the infiltrated composite opal layer. Finally, the sample is annealed in 90°C for 15 min to form a stronger mechanical structure (Figure 4-5d).

4.1.7 Layer-transfer of PS Opal Film into TiO₂ Defect Layer Film.

Following the method described in the previous section, a PS opal film is deposited on top of the TiO₂ defect film via the layer-transfer technique. This PS opal film forms the top layer of the sandwich structure. Again, the sample is held vertically to drain off excess water and is annealed at 90°C for 2 hours to achieve a stronger mechanical structure (Figure 4-5e).

4.1.8 Infiltration of TiO₂ Nanoparticles into PS Opal Interstices

The interstices of PS opal are filled with TiO₂ nanoparticles by multiple dip coating cycles as described previously. It is stressed that in each dip coating cycle, the PS opal is anneal at 90°C for 15 minutes to complete the drying of the water and also to obtain a strong adhesion between TiO₂ and PS (Figure 4-5f).

4.1.9 Calcination of Sample

The sample is calcined at a high temperature furnace with ambient air environment to remove PS template through heat decomposition (section 2.4.6). The final TiO₂ electrode structure is a mesoporous TiO₂ film (from titania nanoparticulate film) and an inverse TiO₂ opal with a TiO₂ defect layer as depicted in Figure 4-5(g).

4.1.10 Assembly of Dye-sensitized Solar Cell

The assembly of DSSC was similar as described in section 2.6. Noted that TiO₂ of both inverse opal and defect layer are sensitized with Ru-dye.

4.2 DSSC TiO₂ inverse opal + Defect Layer with Mesoporous Layer (IO+DL+Me)

The effect of the defect mode on the quantum efficiency of the DSSC can be studied with the incident photon-to-electricity conversion efficiency (IPCE) spectral measurement. The IO+DL+Me DSSC coupled with a TiO₂ inverse opal, TiO₂ planar defect layer on mesoporous layer (denoted as PC DSSC) is compared to a reference cell (denoted as CPC DSSC). This reference CPC DSSC is obtained

by collapsing a PC DSSC, thus achieving a disordered TiO_2 . Thus, the quantum efficiency can be compared directly between a PC and CPC DSSCs, and the net difference in result can be attributed to photonic crystal effect.

4.2.1 Effect of Defect Mode on Optical Property

The reflectance and transmittance spectra of the PC DSSC sample at normal incidence are shown in Figure 4-6(b). The reflectance spectrum shows a PBG or Bragg diffraction centered at 534 nm approximately and the PBG is between 480 – 560 nm. The λ_{D1} arrow in Figure 4-6(b) indicates a dip in the maximum reflectance Bragg diffraction which is the result of the localized defect mode induced by the planar defects in the TiO_2 inverse opal. The observation of the defect mode due to the defect state in the photonic crystal with defect layer is in agreement with other reports in the literature.[151-153] Here, the defect mode is used to study the effect of the quantum efficiency on the DSSC

Figure 4-6. The reflection and transmission spectra of the DSSC coupled with a TiO_2 inverse opal and TiO_2 defect layer on TiO_2 mesoporous layer. Measured at normal incidence. The defect state (λ_{D1}) is approximately at 534 nm.

In Figure 4-6(b), the wavelength within 480 – 560 nm is the PBG of the TiO₂ inverse opal. A defect mode is created due to the planar defect in the inverse opal. Consequently, this defect mode is observed at $\lambda_{DI}=534$ nm and registered as a dip in the PBG. The spectral position of the defect mode can be adjusted by changing the defect layer thickness and this is discussed in detail in Ref. [151]. From **Figure 4-3(b)**, the interplanar distance (d_{111}), lattice parameter (a) and defect layer thickness (d_{def}) are 150 nm, 242 nm and 150 nm respectively. The ratio a/d_{def} is approximately 0.61 and this leads to a defect mode near to the mid gap as illustrated in Figure 4-6(b).

4.2.2 Effect of Defect Mode on Quantum Efficiency

Monochromatic light is directed towards platinum-coated counter electrode at normal incidence as depicted in Figure 4-7(a). Most light is reflected away by the inverse opal due to PBG. This resulted in less light reaching the TiO₂ mesoporous layer. Therefore the IPCE^{PC} is lower than IPCE^{C-PC} in the PBG spectral range (500 - 560 nm) as shown in Figure 4-7(b). On the other hand, the inverse opal does not reflect the defect mode and the finer IPCE measurement in Figure 4-7(c) is used to analyze the defect mode.

In Figure 4-7(c), the F_{IPCE} peak is -21.9% and is observed at wavelength 538 nm which is close to the defect state ($\lambda_{DI}=534$ nm) measured in reflectance/transmittance spectroscopy (Figure 4-6(b)). The baseline reference is estimated to be -24.4% around the F_{IPCE} peak, thus an approximate increment of 2.5% F_{IPCE} peak is obtained at the defect state.

Hence, the study above shows that defect mode propagates through the PC DSSC and participates in light-to-electricity conversion. The defect mode in the TiO_2 defect layer photo-excites the Ru-complex dye in the defect layer. Consequently, this defect mode enhances the light-to-electricity conversion and increases the F_{IPCE} at 538 nm (which is closed to 534 nm).

Figure 4-7. (a) IPCE characterization. The PBG (480 – 560 nm) of the inverse opal reflects light away from the DSSC. The defect mode (534 nm) is passed through the nanostructure. The IPCE and the enhancement factor F_{IPCE} spectra. PC stands for DSSC coupled with a TiO_2 inverse opal and TiO_2 defect layer. CPC stands for DSSC coupled with a disordered structure through collapsing the TiO_2 inverse opal and TiO_2 defect layer. IPCE characterization: (b) coarse and (c) fine wavelength step.

4.3 DSSC with TiO_2 Inverse Opal + Defect Layer (IO+DL)

Here, the IO+DL structure is fabricated as an electrode in the DSSC to investigate the defect mode enhancement effect only. In the previous section, the IO+DL coupled to a 'Me' layer to act as both a back reflector to the mesoporous layer and

demonstrating the defect mode enhancement effect. Here, the IO+DL DSSC consists of a TiO_2 planar defect layer sandwiched inside a TiO_2 inverse opal (denoted as PC DSSC) only and this is compared to a reference cell (C-PC DSSC), which is prepared by collapsing a PC DSSC.

4.3.1 Effect of Defect Mode on Optical Property

The reflectance spectrum shows a PBG centered at 502 nm approximately and the PBG range between 460 – 550 nm in Figure 4-8(b). The arrow in Figure 4-8(b) indicates a dip (at 502 nm) in the maximum reflectance peak which is the result of the localized defect state induced by the planar defects in the TiO_2 inverse opal. From Figure 4-4, d_{111} , a and d_{def} are 180 nm, 311 nm and 160 nm respectively. The ratio a/d_{def} is approximately 0.51 and this leads to a defect mode near to the mid gap as shown in Figure 4-8.

Figure 4-8. The reflectance spectra of the IO+DL DSSCs coupled with a TiO_2 inverse opal and TiO_2 defect layer. The defect state (λ_D) is approximately at $\lambda_{D2} = 502$ nm.

Figure 4-9. (a) The PBG at 502 nm reflecting light away while passing the monochromatic 502 nm wavelength through the nanostructure. The IPCE and the enhancement factor F_{IPCE} spectra. PC stands for DSSC coupled with a TiO_2 inverse opal and TiO_2 defect layer. CPC stands for DSSC coupled with a disordered structure through collapsing the TiO_2 inverse opal and TiO_2 defect layer. IPCE characterization: (b) coarse and (c) fine wavelength step.

4.3.2 Effect of Defect Mode on Quantum Efficiency

Monochromatic light is directed towards the Pt electrode side as shown in Figure 4-9(a) for the IPCE characterization. Similar to the previous section, light within PBG is reflected and the defect mode is allowed to propagate. In Figure 4-9(b), the coarse IPCE measurement shows that the broader dip is at around 480 - 520 nm. The PBG of the inverse opal is approximately 502 nm as illustrated in Figure 4

8(b). This represents the reflectivity effect of PBG preventing light from participating in the energy conversion in an inverse opal DSSC compared to a collapsed inverse opal DSSC. Thus $IPCE^{C-PC}$ is greater than $IPCE^{PC}$ at wavelength 500 nm. One more point to note, the peak (6.8%) at 550 nm wavelength (dielectric band edge) represents the permitted defect mode in the gap as discussed in section 4.2.

To study the effect of the defect mode, the finer-step IPCE plots are shown in Figure 4-9(c). From the reflectivity plot in Figure 4-8(b), the defect mode is at 502 nm. The defect mode contributes to photo-generation and improves on F_{IPCE} . This 502 nm defect mode corresponds well with the slight F_{IPCE} peak at 502 nm in Figure 4-9(c). This F_{IPCE} peak is about -1.0% and an average baseline of -6.5% can be estimated from wavelength 490-510 nm. The F_{IPCE} peak represents a slight 5.5% increment over the baseline resulting from the defect mode effect.

4.4 Summary of the Defect Mode Enhancement

As a summary of the defect mode enhancement, the following table summarizes the result findings from the quantum efficiency characterization from the IO+DL and IO+DL+Me structures. The objective is to study any increment in photo-generation of electron carriers due the existence of defect mode in the center of the prohibited PBG region. The defect mode in the gap is also a result of occurrence of the non-zero density of states (DOS) effect, and this is studied in detail in next chapter. From Table 4-2 below, the improvement in light-to-electricity conversion ranges from 2.5% to 5.5% due to defect mode effect.

Table 4-2. Quantum efficiency of defect layer inverse opal DSSC at defect mode wavelength.

Cell structure	Peak F_{IPCE} improvement at defect mode over its adjacent modes.
IO+DL	5.5%
IO+DL+Me	2.5%

4.4.1 Power Conversion Efficiency Characterization

The power conversion efficiency (η) of the PC and C-PC DSSCs of the IO+DL+Me cell structure are characterized in IV measurement under a simulated AM 1.5G solar spectra at 100 mW/cm². The experiment setup was different from the proceeding section. Here, the light is directed to the photoanode side instead of the counter electrode side. In this setup, the PC can act as a backreflector of light and give a higher enhancement in overall power conversion efficiency over the CPC sample. In Figure 4-10, the η of the PC and C-PC DSSCs are measured to be 4.78% and 3.58% respectively. The PC DSSC has an improved η of 33.5% over C-PC DSSC.

Table 4-3. The overall efficiency η of DSSC with IO+DL+Me structure and a reference cell.

IO+DL+Me DSSC	η	Increment over reference cell
C-PC (reference)	3.58%	-
PC	4.78%	33.5%

The improved η of 33.5% using an inverse opal layer is much greater than using a gold film back reflector, as discussed in section 3.1.3, which is 10.6% improvement. This is due to the proximity of the 'IO' layer to the 'Me' layer and the effect of the back reflection is stronger. On the other hand, the gold film is separated by the electrolyte and Pt-coated FTO substrate, and the back reflection is weaker. As a result of using inverse opal as a coupling layer, the merit of using a TiO_2 inverse opal in DSSC is validated in terms of maximizing power conversion efficiency using light trapping management.

Figure 4-10. IV characterization ($\text{AM1.5 } 100 \text{ mW/cm}^2$) of an IO+DL+Me DSSC. PC stands for DSSC coupled with a TiO_2 inverse opal and TiO_2 defect layer. C-PC stands for DSSC coupled with a disordered structure by collapsing.

4.5 Conclusion of Chapter 4

In this chapter, the fabrication techniques employed in the assembly of a dye-sensitized solar cell with TiO_2 inverse opal and TiO_2 defect layer are described. Under transmission and reflection spectroscopy, a defect state can be observed in the center of the PBG and this is an indication of the opening up of a state in the

prohibiting photonic band gap. In the incident photon-to-current conversion efficiency characterization, a small 1.2% - 5.5% increment is measured in the defect mode. This enhancement in light-to-electricity conversion is due to defect mode propagating through the TiO_2 inverse opal and participates in photo-generation of electron carriers. Finally, an overall power conversion efficiency of the photonic crystal DSSC is measured to be 4.78% under the AM1.5G solar simulator, and this represents a 33.5% improvement over the reference cell.

5. Thickness-dependent Optical Absorption in Photonic Crystal Dye-Sensitized Solar Cell.

In the preceding chapters, the focus is to enhance light capturing performance in a dye-sensitized solar cell (DSSC) by coupling to (i) a photonic crystal (PC) configured in a back reflecting layer and (ii) a planar defect layer in PC configured as a cavity structure. In this chapter, a study is carried out on the influence of the TiO_2 inverse opal's thickness on the localization of increased electric field at the flat dielectric band edge. The motivation is to study the optical absorption of the photosensitive dye coupled to a finite ordered structure with varying spatial dimension. The goal is to provide an insight into the changes in optical absorption of an atom when the space surrounding that atom is modified.

Figure 5-1. Schematic diagram of multilayer reflectors of different number of layers. The corresponding sinusoidal waves are the electric field strength at the flat dielectric band edge.

External light couples to the Bloch modes inside the photonic crystal. At the edges of the photonic band gap (PBG), the flat photon dispersive curve results in

an increased density of states[27, 157] (DOS) and slow photon group velocity of the Bloch modes inside the photonic crystal.[158-160] According to Galli et. al.[52], the greater the number of periods of the photonic crystal, the slower is the group velocity at the band edges. The PBG edge's Bloch modes, likened to stronger localized electromagnetic fields as shown in Figure 5-1, can give rise to stimulated gain enhancement of a photonic band edge laser. [47]

In this chapter, the PBG's band edge effect on improving light absorption of a dye is demonstrated with different inverse opal thickness and identical lattice parameter, as shown in Figure 5-2. They are assembled into DSSC and solar cell characterization is done to quantify the light absorption performance.

Figure 5-2. Schematic of TiO₂ inverse opal electrode with increasing thickness and number of layer (from left to right).

The photonic crystal DSSC consists of photosensitive ruthenium (Ru) complex dye molecules anchoring on the surfaces of the TiO₂ nanoparticles. In Figure 5-2, the air voids of the TiO₂ inverse opal film are filled with an iodide electrolyte ($n=1.43$) and this correspond to the lower dielectric or air band of the photonic band diagram. On the other hand, the interstices are made up of TiO₂ nanoparticles

and sensitized with dye. These interstitial regions correspond to the higher dielectric or dielectric band of the photonic band diagram.

As explained in previous chapters, the dielectric bands consist of Bloch modes concentrated in the dielectric regions of the photonic crystal, whereas the air bands consist of Bloch modes concentrated in the air regions. Due to the PBG's edge effect, Bloch modes localized in the dielectric band edge are intensified as explained in Chapter 3.[154, 161] This leads to a strong light-matter interaction which enhances the photoexcitation or light absorption of Ru-complex dye in the TiO_2 inverse opal structure. As a result, there is a higher possibility of charge injection from dye into the TiO_2 electrode[162], leading to higher photo-generated current.

On the other hand, no similar enhancement is expected for mode excitation at the air band edge. This is because this is the lower dielectric region where the liquid electrolyte is. Hence, there is no enhancement of dye photo-excitation due to band edge effect.

In this chapter, the influence of the TiO_2 inverse opal's thickness on the enhancement of incident photon-to-electricity conversion efficiency (IPCE) and the localization of light field in a photonic crystal DSSC are studied. The IPCE of a DSSC is used as a metric of light absorption in 3D photonic crystals with varying thicknesses. The charge generating Ru-complex dyes are embedded everywhere in the photonic crystal matrix, hence the light absorption of the dyes can be studied as a function of photonic crystal's number of periods. In the experiment, the lattice parameter of the inverse opal, refractive index of TiO_2 and electrolyte are

considered so that the dielectric band edge spectral location is optimized to coincide near to the optimum Ru-complex dye's optical absorption peak. The dye molecules are attached onto the TiO_2 inverse opal structure, which is made up of TiO_2 nanoparticles. The TiO_2 inverse opal DSSC is compared to a collapsed TiO_2 inverse opal DSSC so that the material's intrinsic absorption can be cancelled out and the resulting difference can be attributed solely to the photonic crystal effect.

Following previous chapters, the IPCE comparison reveals the change in the photocurrent generation due to a change in optical absorption of Ru-complex dye in an ordered and disordered structure with almost similar TiO_2 material volume and dye loading. Optical absorption of Ru-complex dye measured via extinction spectroscopy is a challenge due to the different light scattering characteristics in different nanostructures. Hence, the IPCE was used to provide a proxy for direct comparison. In addition, this chapter discusses the computation of DOS for finite-sized TiO_2 inverse opal photonic crystal using a finite-difference time-domain (FDTD) technique[163] and analyzes the relationship between PBG's edge effect and the electron transition in Ru-complex dye located in a changing environment.

5.1 Experimental Methods

5.1.1 Materials

Monodisperse polystyrene (PS) colloid of diameter 230 nm (section 2.1) is used for the ordered nanostructure assembly. TiO_2 nanoparticles suspension (15 nm, 1.5 wt-%, section 2.2) is used for the infiltration in a opal template. In the assembly of

DSSCs, titania nanoparticulate paste (Dyesol, DSL 90-T); N719 dye (Dyesol [RuL₂(NCS)₂]:2TBA ; L=2,2'-bipyridyl-4,4'-dicarboxylic acid ; TBA=tetra-n-butylammonium); platinum (Pt) paste (Dyesol, PT1) and io-dide/triiodide electrolyte (Dyesol, EL-HPE) are used. The transparent conductive oxide (TCO) substrate are fluorine-doped tin oxide coated glass substrates (F:SnO₂ or FTO, Pilkington, TEC7). All solvents used are de-ionized (DI) water (Millipore, 18.0 MΩ/cm) and absolute ethanol (Aldrich, 99.99%).

5.1.2 Flow Controlled Vertical Deposition (FCVD)

FTO substrates are scrubbed cleaned using glassware detergent and rinsed with water. The substrates are then ultra-sonicated in an ethanol cycle and acetone cycle (10 minutes cycle each). The solvent ultra-sonication processes help to remove organic contamination and improve on wetability. Finally, the substrates are rinsed with copious amount of DIW and blown dry. A layer of PS opal with varying thicknesses is grown on the FTO substrates using the FCVD technique (see section 2.3.3). The drawing speed of the meniscus is varied to produce opals of three different thicknesses on the same substrate, see Figure 5-3(a). The meniscus dropping speed is 15 mm/hr, 10 mm/hr and 5 mm/hr where the fastest speed produced the thinnest layer.

5.1.3 Infiltration of TiO₂ Nanoparticles into PS Opal Interstices

TiO₂ nanoparticles are infiltrated into the interstices of the opal template by multiple dip coating cycles (section 2.4). A segment of a PS opal/TiO₂ infiltrated

(for three different grown films) structure was collapsed in toluene ultra-sonication so that an IPCE comparison can be made between photonic crystal (PC) and collapsed PC (C-PC) structured DSSC.

5.1.4 Calcination of Sample

The samples are calcined at a high temperature furnace with ambient air environment to remove PS template through heat decomposition (see section 2.4.6). The final TiO_2 electrode structure was inverse TiO_2 opal with varying thickness. Figure 5-4 shows a picture of the inverse opal film. The three sections of the opal film are measured with surface profiler and the average thicknesses are $2.92\ \mu\text{m}$, $5.53\ \mu\text{m}$ and $7.76\ \mu\text{m}$.

Figure 5-3. Picture of (a) PS opal film and (b) as-assembled DSSC with TiO_2 inverse opal electrode. In (a), the PS opal consists of three different thicknesses, starting from top to bottom: thicker, thinner and follows by normal thickness.

Figure 5-4. Cross-sectional scanning electron microscopy (SEM) images of (a) TiO_2 inverse opal (PC). The cross section view was obtained by fracturing through the sample. Inserted picture reveals an ordered inverse opal structure. (b) collapsed TiO_2 inverse opal (C-PC). Inserted picture reveals a disordered structure. The scale bars represent 1 μm in length.

5.1.5 Assembly of DSSC

The assembly of the DSSC is carried out as the procedure described in section 2.6. Figure 5-3(b) shows the image of 3 different sections of inverse opal in a same DSSC. There is an advantage of eliminating experimental uncertainty by having all different inverse opals on the same cell. This is because the samples can be compared among themselves directly since they have undergone same heat

treatment, dye sensitization, electrolyte condition and resistive path of the FTO substrate.

5.2 Effect of Inverse Opal Thickness on Optical Property

Reflectance spectroscopy is performed to measure the PBG or Bragg peak of the TiO_2 inverse opal DSSC at normal incidence. Broadband light source is directed toward the TiO_2 inverse opal electrode. The spectrometer is along side with the light source. Prior to the reflectance measurement, the spectrometer is calibrated with two FTO substrates without the active materials and a highly reflective mirror as reference.

Figure 5-5. (a) Reflectance measurement of TiO_2 inverse opal DSSC with different opal films thicknesses: 2.92 μm (S), 5.53 μm (M) and 7.76 μm (L). λ_1 and λ_2 indicate the location of air band edge and dielectric band edge respectively on L specimen. (b) FDTD simulated peak

reflectance of TiO₂ inverse opals with varying number of layers (black line) and overlapping dots of measured reflectance peaks from (a).

Figure 5-5(a) shows the reflectance spectra for the thinnest to the thickest inverse opal film. The peak reflectivity of the PBGs are at 534 nm (denotes the thickest 'L' specimen), 519 nm ('M') and 486 nm ('S') respectively for the three different specimens. The absolute reflectivity increases for thicker inverse opal film due to stronger wave diffraction of thicker photonic crystal. In Figure 5-5(b), the reflectance peaks for inverse opals red shift to the longer wavelength with increasing thickness due to PC finite size and substrate effects.[130] Hence, even for the same lattice periodicity, the spectral locations of the PBG differ for TiO₂ inverse opals with different film thicknesses.

Reflectance spectroscopy is also carried out on the collapsed TiO₂ inverse opal electrode and it is observed that there is no reflectance peak and therefore no PBG. This is the optical confirmation that a disordered porous structure of TiO₂ does not have any photonic crystal property. The cross section SEM image shown in Figure 5-4(b) consists of largely porous and disordered structure. The disordered TiO₂ electrode obtained from collapsing a similar thickness TiO₂ inverse opal film helps to ensure a similar volume of TiO₂ nanoparticles across samples, thus allowing a clearly discriminated assessment of the photonic crystal effect.

5.3 Electric Field Distribution from FDTD Computation

Reflectance computation on TiO₂ inverse opal immersed in an iodide electrolyte is simulated with the three dimensional FDTD method, using a freely available

software package MEEP.[135] The inverse opal electrode is modeled to be assembled in a DSSC and immersed in an iodide electrolyte. In Figure 5-4(a), the (111) inter-planar distance of the cross-sectional inverse opal in the SEM image was measured to be 166 nm. It was noted that the inverse opal structure underwent shrinkage during the calcination from the PS opal template. Based on this inter-planar distance and the average surface profiler measurements stated in the previous section, the number of layers of the inverse opal was modeled to be 18 (to match 'S' sample), 33 ('M') and 48 ('L') layers (N). The 3D computation cell was a close-packed FCC structure with repeating ABC sequence planes in the x-axis. In the transverse directions (yz-axes), the planes were N=4 layers thick, afforded by the existing computation power and processing time, and terminated with Bloch-periodic boundaries.

A broad-band continuous electric field plane source is positioned away from the inverse opal along the $[111]$ propagating x-axis. The parameters used in the simulation are: refractive index of nanoparticle TiO_2 (2.25 [118]) and iodide electrolyte (1.43 [102]). As confirmed in reflectance spectroscopy measurements, there is no change to the PBG spectral position with or without Ru-complex dye sensitization on the TiO_2 surfaces. The dye molecular monolayer was not modeled both in the inverse opal and reference cells. The numerical studies are carried out to analyze any optical property arising from an ordered structure compared to a disordered structure. By removing Ru-complex dye totally from these two structures, changes in light absorption factor can be unambiguously attributed to the periodicity of the ordered structure. The simulator was set with a resolution of

20 pixel/ λ in the highest dielectric material of the computation cell. The radius (r) of the hard sphere model was optimized to 96nm, which gave the (111) inter-planar distance of 157 nm ($d_{111} = \sqrt{8/3} r$), in close agreement with the SEM micrograph in Figure 5-4(a). The radius of the hard sphere model is smaller than the experimental PS nanosphere due to nanostructure shrinkage under calcination.[120] Both ends of the propagating axis $[111]$ are terminated with air pad ($10r$ thick) and perfectly matched layer (PML, $5r$ thick).

In Figure 5-5(b), the simulated reflectance peak versus varying number of layer of inverse opal is shown together with the measured reflectance peaks taken from Figure 5-5(a). In the simulated plot, depicted as solid line in Figure 5-5(b), there is a gradual reduction in the peak reflectance spectral position with decreasing number of inverse opal layer between 20 – 50 range. For 20 layers and less, there is a relatively sharper reduction in the spectral position. The measured reflectance peak position of ‘L’ and ‘M’ specimens follows fairly closely with the simulated result. However for ‘S’ specimen, there is an unexpected larger drop in the measured reflectance compared to the trend of the simulated result. This discrepancy is attributed to experimental uncertainty where the film thicknesses of ‘L’, ‘M’ and ‘S’ specimens are averaged from different film areas obtained from the surface profiler (KLA-Tencor AlphaStep).

To illustrate the electric field localization when the inverse opal is illuminated with a monochromatic radiation in $[111]$ direction, Figure 5-6(a)-(b) shows the intensity $|E|^2$ distribution map of inverse opal, overlooking ABC stacking sequence

planes of the FCC structure in the $[1\bar{1}0]$ direction. Incident sinusoidal plane wave with frequency in the air band, denoted by λ_1 in Figure 5-5(a) as an indication on blue side of the reflectance peak, is observed to be concentrated in the lower dielectric region (sphere interior) in Figure 5-6(a).

Figure 5-6. Intensity field distribution of TiO₂ inverse opal with monochromatic irradiance (a) air band, λ_1 ; (b) dielectric band, λ_2 . The distribution map is the top view of a FCC structure in $[1\bar{1}0]$ direction, showing the repeating ABC plane sequence. Area inside the spheres contains lower dielectric material (electrolyte) and the outside contains higher dielectric material (TiO₂).

Incident sinusoidal planewave with frequency in the dielectric band, denoted by λ_2 in Figure 5-5(a) on red side of the reflectance peak, is observed to be concentrated in the higher dielectric region (sphere exterior) in Figure 5-6(b). The TiO₂ inverse opal consists of air spheres (iodide electrolyte) and the dielectric matrix (TiO₂ nanoparticles and Ru-complex dye). Consequently, irradiation using dielectric band wave λ_2 results in increased $|E|^2$ localization in the same space

where Ru-complex dye is located. In the subsequent section, the effect on the strength of the $|E|^2$ localization on the photo-excitation of the Ru-complex dye will be carried out using varying thickness of TiO₂ inverse opal films.

Figure 5-7. The IPCE comparison graphs for three DSSC devices with different electrode thicknesses (a) S, (b) M and (c) L. The enhancement factor F_{IPCE} is defined as $(IPCE^{PC} - IPCE^{C-PC}) / IPCE^{C-PC}$ (%) and denoted as green triangular points. The IPCE graphs are PC layer electrode (blue diamonds) and C-PC layer electrode (pink squares).

5.4 Solar Cell Characterization on Thickness-dependence Inverse opal DSSCs

IPCE measurement is carried out with the PC and C-PC DSSC with an active area of 0.8 cm^2 . The IPCE and enhancement factor (F_{IPCE}) are shown in Figure 5-7(a)-(c). The enhancement factor F_{IPCE} is defined as $(IPCE^{PC} - IPCE^{C-PC}) / IPCE^{C-PC}$ (%). In Region I, the IPCE of PC DSSC is lower than that of C-PC DSSC and F_{IPCE} are -3.8% and -5.3% for ‘M’ and ‘L’ specimens. These negative F_{IPCE} spectral regions correspond to the measured PBG peaks in Figure 5-5(a). At frequencies within these PBGs, light is reflected away and less light is absorbed by the DSSC, hence resulting in a negative F_{IPCE} . For specimen ‘S’ shown in Figure 5-7(a), the effect of reflectivity is weaker and there is no measurable drop in F_{IPCE} between PC and C-PC DSSCs.

In Region II, the F_{IPCE} peaks are 1.5%, 3.2% and 8.3%, located at approximately 515 nm (‘S’), 570 nm (‘M’) and 585 nm (‘L’) respectively. These peaks correspond to the photonic crystal dielectric band edges. It is observed that the peak level of F_{IPCE} increases with increasing inverse opal thickness. Above wavelength 650 nm, the effect of the dielectric band edge weakens because of its spectral distance from the PBG. Here, due to the higher density of TiO_2 interconnection in C-PC structure compared to PC structure, the IPCE of C-PC DSSC is generally higher than that of PC DSSC as the electron transport is more effective in the denser C-PC matrix. This effect is more prominent for ‘S’ sample as shown in Figure 5-7(a) where F_{IPCE} dips to the negative range beyond 520 nm.

This electron transport effect will be discussed in section 5.8. In summary, the PBG reduces F_{IPCE} by reflecting light away and F_{IPCE} is increased at the dielectric band edge. Away from these two spectral regions and due to the more effective electron transport of denser C-PC structure, the IPCE of C-PC is generally higher than PC's case.

5.5 Effect of Inverse Opal Thickness on Photoexcitation

An insight into the photoexcitation taking place in a photonic crystal can be obtained numerically from the spectral analysis of electric field traversing across the photonic crystal. Monochromatic radiation field impinges on the photonic crystal and the resulting electric field is recorded inside the structure. Essentially, the excitation of electrons from ground state to excited state is proportional to the intensity of the electric field. This excitation can then be used as a proxy to link the relation of electron injection and IPCE in DSSC.

The electric field intensity around the dielectric band edge is simulated to demonstrate the coupling of the radiation field to Ru-complex molecules in a space modified by a photonic crystal. Using the same FDTD parameters described earlier, the PC and C-PC DSSC are excited by a continuous narrow-band electric field source. The C-PC layer is simply modeled as a uniform layer with TiO_2 filling factor of 55%. After waiting for the initial transient to decay, values of $|E(\omega, \bar{r})|^2$ are taken at several points $\bar{r}$ within the dielectric regions through the

thickness of the PC and C-PC layers. $|E(\omega)|^2$ spectrum can be plotted by repeating the simulation for several wavelengths.

Figure 5-8. Numerical computation of the enhancement in electric field intensity spectrum PC over C-PC layer, F_E , for films (a) 'S' (N=18), (b) 'M' (N=33) and (c) 'L' (N=48). (Dotted solid line) The enhancement factor F_{IPCE} from the IPCE measurement as plotted in Fig 5-7(a)-(c). Δ denotes the peak offset between the numerical F_E and the measured F_{IPCE} .

The intensification of electric field due to band edge effect can be computed as the average enhancement in electric field intensity of PC as a percentage over C-PC layer,

$$F_E = \frac{1}{n} \sum \frac{|E_{PC}(\omega, \bar{r})|^2 - |E_{C-PC}(\omega, \bar{r})|^2}{|E_{C-PC}(\omega, \bar{r})|^2} (\%) \quad (5-1)$$

where n is the total number of points computed. Figure 5-8 shows the F_E spectra computed for all $N=18, 33$ and 48 layers PC in the vicinity of dielectric band edge, $550 - 650$ nm. The F_E provides a representation of the collective electric field enhancement effect through the thickness of PC, over the C-PC layer. The F_{IPCE} profiles are re-plotted again in Figure 5-8 from Figure 5-7(a)-(c). In Figure 5-8(a)-(c), the profiles of F_E offers a direct comparison with F_{IPCE} . The peak F_E for $N=18, 33$ and 48 layers PC are approximately 1.8% , 4.6% and 5.5% respectively.

In Figure 5-8(c), the computed F_E graph of $N=48$ has the closest match to the experimental F_{IPCE} graph of specimens 'L'. The peak offset Δ is about 10 nm in Figure 5-8(c). The peak offset between F_E and F_{IPCE} for $N=18$ and $N=33$ computational cell is 25 nm and 75 nm respectively as depicted on Figure 5-8(a)-(b). The reason of this offset is due to the mismatch in reflectance peaks of the numerical and experimental results as shown in Figure 5-5(b). The F_E graph of $N=33$ has a profile suggestive of F_{IPCE} graph in Figure 5-8(b) except for the spectral offset. The F_E graph of $N=18$ does not look close to the specimen 'S' F_{IPCE} graph in Figure 5-8(a) and this suggests that for weaker electric field enhancement, IPCE measurements could be dominated by electron transport property in a thinner

film. The electron transport in an inverse opal structure of varying thickness is a good research subject in the future. Looking at the absolute percentage, both F_E and F_{IPCE} graphs have close peak enhancement percentage level in Figure 5-8(a)-(c). To conclude this section, the numerical analysis has shown that at the dispersive dielectric band edge, there is an increased electromagnetic wave field which promotes a higher photoexcitation and IPCE in a DSSC.

5.6 Effect of Inverse Opal Thickness on Density of States

The flat photonic bands near to the photonic crystal band edges give rise to high dispersion effect. This effect leads to the slow group velocity of light near to the band edges which promote the interaction between the dye molecules and the slow light. In addition, a photonic crystal exhibits a suppressed photon density of states (DOS) in the gap and an increased DOS at the gap edges. DOS is a measure of the number of electromagnetic modes that are permitted to exist per unit frequency in a volume of space. DOS has been useful for studying the radiative emission of an atom in a photonic crystal where rate of the spontaneous emission can be increased[47] or inhibited[50]. In addition, a phenomenological relationship on the rate of absorption transitions has been described by Einstein, $W = B_{12}\rho$, where B_{12} is the Einstein B coefficient for the transition and ρ is the optical DOS. It is evident that a higher ρ causes a higher absorption transition rate.

A recent work by John et. al. had shown that periodic micro-structuring in a thin film photonic crystal results in a continuum of optical resonances associated with an increased DOS in the structure.[67] Incident light coupled with the

resonances in the structure can give rise to an enhancement of light absorption. Here the DOS of a finite size photonic crystal is studied and the different DOS characteristics can be computed with varying TiO₂ inverse opal film thickness. In literature, DOS has been computed using plane wave expansion method and first principles for an infinite 3D opal structure.[27, 164]. Here, FDTD technique permits the calculation of DOS in a finite size TiO₂ inverse opal immersed in electrolyte in a DSSC configuration.[165] Thus the effect of the TiO₂ inverse opal film thickness can be modeled. The local density of states (LDOS) of a 3D photonic crystal is obtained by the trace of the imaginary part of the Green's tensor, $G(\omega, \bar{r} - \bar{r}_0)$, at a point $\bar{r}$ due to an oscillating dipole source at location $\bar{r}_0$: $\rho(\omega, \bar{r}) = (-2k_0/c) \text{Im}[G(\omega, \bar{r} - \bar{r}_0)]$. The DOS, $\rho_\omega(\omega)$, is the weighted average of LDOS over the volume of the finite 3D PC structure: $\rho(\omega) = \frac{1}{V} \int_V \epsilon(\bar{r}) \rho(\omega, \bar{r}) d\bar{r}$, where $\epsilon(\bar{r})$ is real part of the dielectric function.

The DOS computation cell follows the previous FDTD setup except that all the boundaries and air pad are replaced by perfectly matched layers (PML) with sufficient thickness to absorb any stray reflection at the cell boundaries. A broadband gaussian point source (electric current in y direction) is placed slight off the center of the inverse opal structure in order to excite all eigen modes. The initial transient is allowed to decay and then the eigen modes at several $\bar{r}$ points in the photonic crystal are recorded at every Δt time steps. The points $\bar{r}$ are located at least a distance away from the PML. The recording times for N=18, 33 and 48 cells were between: 21-81, 28-88 and 33-93 time units respectively. For 3D

photonic crystal, the Green tensors are the trace of the electric eigen modes along x, y and z directions and their imaginary parts are summed. The Green tensor $G_{PC}(\omega, \bar{r} - \bar{r}_0)$ spectrum is obtained efficiently[166] by taking a 512-point Fourier transform of the time response. For normalizing the $G_{PC}(\omega, \bar{r} - \bar{r}_0)$, the Green tensor $G_0(\omega, \bar{r} - \bar{r}_0)$ of a void computation cell (no photonic crystal) is carried out by a similar method. Finally, the DOS is calculated by averaging the $(-2k_0\epsilon(\bar{r})/c)\text{Im}[G_{PC}(\omega, \bar{r} - \bar{r}_0)/G_0(\omega, \bar{r} - \bar{r}_0)]$ spectra at each $\bar{r}$ point throughout the finite photonic crystal.[157, 167]

Figure 5-9. The density of states, $\rho(\omega)$, of a TiO_2 inverse opal for $N =$ (a) 18, (b) 33 and (c) 48.

The y-axes are normalized with speed of light in vacuum, c . (d) Photonic band diagram (k-

vector versus $\omega a / 2\pi c$) of a TiO_2 inverse opal immersed in an electrolyte. A pseudo gap exists at L-direction between band 2 and 3.

Figure 5-9(a)-(c) shows the DOS for the 3D inverse opals with 18, 33 and 48 layers respectively and their absolute values increasing with number of layers. In Figure 5-9(d), the photonic band diagram is computed using plane wave basis[27, 168] and the pseudo PBG forms approximately at frequency $\omega = 0.52(2\pi c/a)$ under normal incidence (symbol L k-vector) between band 2 and 3.[27] In Figure 5-9(a)-(c), dips are formed around $\omega = 0.55(2\pi c/a)$, which is slightly higher than plane wave's calculation because of the finite crystal size computation.[130] The plane wave calculation is an exact solution of an infinite structure, while FDTD is finite cell. Further, the DOS graphs are greater at the band edges where they are highly dispersive. The spectral region of interest in this dye photoexcitation analysis lies at the dielectric band edge, where the lower frequency band edge is.

In the experiment, the influence on IPCE due to the amount of photosensitive dye and TiO_2 materials are removed from the comparison studies using PC and C-PC structures. The difference in this comparison study is the use of varying finite size of ordered structure that allows a corresponding number of photons per bandwidth per volume. It can be observed that the DOS of N=48 is much greater than N=18 near to the dielectric band edge in Figure 5-9. In other words, a thicker ordered structure can support a higher number of electromagnetic modes than a thinner ordered structure. Alternatively, the higher number of electromagnetic modes in the structure can be seen as a promotion of optical resonance and intensification of electric field, which leads to a higher light absorption.

In this section, a high DOS improves light absorption at the dielectric band edge spectral position in an inverse opal DSSC. However, band edge spectral position is next to the PBG, which is reflecting light away from the solar cell. Thus the optimal design for solar energy harvesting can be as follows. The above analysis of using a single inverse opal layer can be applied to a bilayer DSSC to capitalize on both the dielectric band edge enhancement and the PBG's reflection effects [154, 169, 170]. In a bilayer DSSC, a TiO_2 inverse opal is deposited onto a TiO_2 mesoporous layer. Here, the TiO_2 inverse opal is configured as a light back reflector to the energy harvesting mesoporous layer where light is confined. Secondly, the dielectric band edge (beside the gap) can provide additional dielectric band edge enhancement. In summary, the use of well-designed photon management techniques in solar cells could enhance the optical absorption and power conversion efficiency.

5.7 Effect of Optical Extinction of Photosensitive Dye in Ordered and Disordered Nanostructures

The absorption of light by the Ru-complex dye molecules in a TiO_2 inverse opal is further studied on the effect of radiation field intensification near the dielectric band edge. In the preceding sections, the change of photocurrent generation from Ru-complex dye is studied due to the change in the surrounding space. In particular, the Ru-complex dye molecules are adsorbed on the surface of the TiO_2 inverse opal and this inverse opal is in turn assembled into a DSSC for an overall photocurrent generation characterization.

In practice, the optical extinction is obtained, instead of optical absorption, under spectroscopy characterization for the composite structure of Ru-complex dye combining with nanostructures. The measurement of optical extinction can be carried out using reflection (R) and transmission (T) spectroscopy methods where extinction (E) is defined as $E=1-R-T$ at normal incidence. Extinction is a combination of (i) optical absorption of the Ru-complex dye and TiO_2 ; and (ii) the scattering effect of the nanostructures.

Figure 5-10. Reflectance / Transmittance spectroscopy of a TiO_2 inverse opal with PBG at 611 nm before dye sensitization. The dielectric band edge is at 677 nm approximately. (a) inverse opal thin film (ordered); (b) collapsed inverse opal film (disordered).

In the experiment, a TiO_2 inverse opal (denoted as PC, 3.94 μm thick) and a collapsed TiO_2 inverse opal (disordered and denoted as C-PC) deposited on glass substrates are characterized using the reflectance and transmittance spectroscopy at normal incidence. Figure 5-10(a) and (b) show the reflectance/transmittance spectra of the PC and C-PC samples respectively. The PBG is at 611 nm as shown in Figure 5-10(a). Note that there is no dye loading on these samples and no liquid electrolyte is used. The avoidance of electrolyte for these samples is to remove the

uncertainty of the liquid volume and experimental error it may cause during the spectroscopic measurement and between PC/C-PC samples comparison.

The PC and C-PC samples are sensitized with Ru-complex dye and their spectroscopic spectra are measured again. Figure 5-11(a) and (b) show the reflectance / transmittance spectra of the PC and C-PC samples with dye loading respectively. Compared to Figure 5-10, the reflectance and transmittance graphs in Figure 5-11 are reduced due to the presence of optical absorption by the dye. The PBG remains unchanged at 611 nm as shown in Figure 5-11(a).

Figure 5-11. Reflectance / Transmittance spectroscopy of a TiO_2 inverse opal with PBG at 611 nm after dye sensitization. (a) inverse opal thin film (ordered); (b) collapsed inverse opal film (disordered).

Now, the extinction graphs can be defined as follows and are shown in Figure 5-12(a). For non-dye loading samples, the extinction graphs for PC and C-PC structures are $e_{PC}=1-r_{PC}-t_{PC}$ and $e_{CPC}=1-r_{CPC}-t_{CPC}$ respectively. The use of small letter e , r , and t is to distinguish these as non-dye loading extinction graphs. Similarly, for dye loading samples, the extinction graphs for PC and C-PC

structures are $E_{PC}=1-R_{PC}-T_{PC}$ and $E_{CPC}=1-R_{CPC}-T_{CPC}$ respectively (note the use of capital E , R , and T letters for dye loaded spectra).

Figure 5-12. (a) Extinction spectra of samples e_{PC} , e_{CPC} , E_{PC} and E_{CPC} . (b) 'Disordered' graph (pink line) is the difference between E_{C-PC} and e_{C-PC} ; 'Ordered' graph (blue line) is the difference between E_{PC} and e_{PC} ; the dashed line is the absorption spectrum of Ru-complex dye powder.

Taking reference at wavelength 500 nm in Figure 5-12(a), the extinction properties of different samples in ascending order is e_{PC} , e_{CPC} , E_{PC} and E_{CPC} . The highest extinction (E_{CPC}) occurs for a C-PC structure with dye loading. This corresponds to the combination of high optical absorption of dye and high scattering effect of a collapsed TiO_2 inverse opal structure. On the other hand, the

lowest extinction (e_{PC}) occurs for a PC structure without dye loading. This corresponds to the absence of dye absorption and scattering effects.

To point out the effect of dye's extinction in different structures, the following two relations can be plotted. First, the extinction difference between E_{PC} and e_{PC} gives the effective dye extinction due to the influence of ordered structures. This is plotted in Figure 5-12(b) and the graph is denoted as 'Ordered'. Secondly, the extinction difference between E_{CPC} and e_{CPC} gives the effective dye extinction due to the influence of disordered structure. This is plotted in Figure 5-12(b) and the graph is denoted as 'Disordered'. In Figure 5-12(b), the 'Disordered' graph is expected to have an absorption characteristic of the Ru-complex dye if the scattering effect of e_{CPC} and E_{CPC} are canceled out completely.

In addition, the Ru-complex dye absorption graph is plotted as dashed line in Figure 5-12(b). This graph is plotted by the relation $E_{dye}=1-R_{dye}-T_{dye}$ where the sample consists of Ru-complex dye fine powder deposited on smooth glass substrate. Scattering effect is expected to be minimal. This dye absorption graph is in close resemblance of dye optical absorption spectrum reported in literature. [171] Now, comparing this dye absorption graph with 'Disordered' graph in Figure 5-12(b), the two curves nearly have the same profile and 'Disordered' graph appears to flatten out relatively. This suggests that the scattering effect of e_{CPC} and E_{CPC} are not canceled out completely, and thus the 'Disordered' graph does not match Ru-complex dye absorption graph completely. All the measurements above were carried out using the same sample and exact spot on the sample.

Next, the change in the dye's extinction in an ordered structure is analyzed. The 'Ordered' graph shown in Figure 5-12(b) is the difference between E_{PC} and e_{PC} . At spectral wavelength 670 – 720 nm, there are improvements of extinction difference in 'Ordered' graph compared to the 'Disordered' graph in Figure 5-12(b). This is the spectral region of the dielectric band edge as evident in Figure 5-11(a) where PBG is at 611 nm and dielectric band edge is at 667 nm. This is in agreement with the dielectric band edge enhancement effect as discussed in earlier section.

In Figure 5-12(b) at wavelength 621 nm, there is a peak of 'Ordered' graph higher than the 'Disordered' graph. This is attributed to the artifact arising from difference between E_{PC} and e_{PC} . Here, the challenge of extracting clean optical absorption of Ru-complex dye from extinction is highlighted. Earlier, the profile of the 'Disordered' graph is flattened out relative to the Ru-dye absorption graph (dashed line in Figure 5-12(b)) and was attributed to scattering problem. Here again, the measurement of optical absorption of the dye in an ordered TiO_2 inverse opal is a non-trivial matter as the nanostructure will provide light scattering problem. The problem is made worse for comparison between an inverse opal to a collapsed inverse opal as light scattering will be different.

Nevertheless, the spectra in Figure 5-12 can still bring an insight to the dielectric band edge enhancement effect on dye absorption, though it cannot be qualitatively stated in this thesis. Appendix E illustrates the extinction characterization for another set of data where the PBG is at 535 nm (thicker sample, 6.82 μm). Again in appendix E, there is clear observation that there is

improvement of extinction difference in 'Ordered' graph compared to the 'Disordered' graph in dielectric band edge.

5.8 Effect of Electron Collection in an Ordered/Disordered Structure DSSC

In the preceding section, a disordered TiO_2 electrode was prepared in order to compare the effect of power conversion efficiency of an ordered TiO_2 electrode in a DSSC. The disordered TiO_2 electrode is obtained by collapsing from a TiO_2 infiltrated opal template with a drop of toluene solution in ultra-sonication. The objective is to achieve an ordered and a disordered TiO_2 electrode with almost identical TiO_2 material volume, dye loading and electrolyte encapsulation. This allows a direct comparison in the same device. In essence, any power conversion enhancement can be linked to the photonic crystal effect.

There is another issue of using collapsed TiO_2 electrode that needs to be addressed in order to present a complete comparison study. A disordered TiO_2 electrode obtained by collapsing a TiO_2 infiltrated opal template is denser than an ordered inverse opal structure. A denser TiO_2 electrode has better electron conduction path, shorter conduction path (due to thinner film thickness) and less recombination interfaces. This is depicted in Figure 5-13 where the interfaces joining TiO_2 nanoparticles together are the recombination centres for electrons. The resulting effect is the amount of electrons collected at the electrode.

The matter is further convoluted that the denser disordered TiO_2 electrode is less porous than an ordered structure. The Ru-complex dye is less efficient in being

regenerated by the electrolyte in a less porous structure. Here, by comparing the two structures via IPCE comparison, a holistic comparison can be made on the electron generation and collection without being aided by the photonic crystal effect.

Figure 5-13. Cross section schematic diagrams of (a) an inverse opal; (b) a disordered inverse opal resulting from collapsing in ultrasonic solvent treatment. (c) The high magnification view of (a) and the electron transport path is illustrated. (d) The high magnification view of (b) and the electron transport path has more degree of freedom in the denser structure.

5.8.1 Optical Property of Large and Small Lattice Parameter

In order to have an ordered structure without the photonic crystal effect inside the wavelength of interest (450 nm – 750 nm), opal template with larger or smaller periodicity can be chosen, as seen in Figure 5-14. Consequently, an ordered structure with poorer electrons conduction path, higher recombination interfaces and non-photonic crystal can now be compared to a collapsed disordered TiO_2 electrode.

In this work, a polystyrene colloids suspension of size 180 nm in diameter is used to assemble into an opal film. The PBG of this assembled opal will be around 420 nm. After TiO₂ infiltration and PS calcination, the resulting TiO₂ inverse opal will have PBG deep into the UV regime at approximately 350 nm. This sample will be studied for the changes in quantum efficiency in the blue-end of the visible light spectrum.

Figure 5-14. Inverse opal structures with photonic band gap in the regime of (a) ultraviolet, (b) visible light and (c) near infrared. The PS particles size, and thus the lattice constant, determine the spectral location of the gap.

On the red-end of the visible light spectrum, PS colloids suspension of 550 nm in diameter is used. The PBG of the assembled opal is estimated at the infrared regime of 1296 nm and its TiO₂ inverse opal will have PBG at about 900 nm by estimation. This sample will be studied for the changes in quantum efficiency in the red-end of the visible light spectrum.

With the PBG designed outside wavelength of interest (460 nm – 740 nm) for the study in quantum efficiency of DSSC, the electron transport of an ordered and disordered electrode can be compared. Further, both of these structures do not have photonic crystal effect in the visible light regime, and the result finding can help

provide an insight to quantum efficiency in a porous structure of different degree of porosity.

5.8.2 Experiment

The experimental procedures are similar as described in section 5.1. In this case, PS nanospheres of 180 nm (denotes SS specimen) and 550 nm (denotes LL specimen) colloid suspensions are used to assemble opal template. Similarly, corresponding disordered TiO₂ inverse opal was prepared by collapsing an adjacent area of opal template in a drop of toluene under sonication.

The thickness of the 'SS' sample is 3.02 μm and its collapsed layer is 0.97 μm . The thickness of the 'LL' sample is 5.97 μm and its collapsed layer is 1.52 μm .

The assembled DSSCs were measured with a reflectance/transmittance spectrometer. It is confirmed that no reflectance peak or transmittance dips was observed in either inverse opal or collapsed inverse opal regions in the DSSCs. IPCE characterization is carried out to compare the power conversion efficiency of inverse opal to the collapsed inverse opal electrodes separately.

5.8.3 Quantum Efficiency of Ordered and Disordered TiO₂ Inverse Opal DSSC

IPCE measurement is carried with the PC and C-PC DSSC samples for 'SS' and 'LL' specimens. As before, PC is a short form for photonic crystal and it is the TiO₂ inverse opal. And C-PC is the collapsed photonic crystal which is the disordered

TiO₂ structure. The IPCE and enhancement factor (F_{IPCE}) of 'SS' and 'LL' are shown in Figure 5-15(a)-(b).

Figure 5-15. The IPCE comparison graphs for inverse opal assembled from different PS particles size (a) 'SS' 180 nm diameter, (b) 'LL' 540 nm diameter. The enhancement factor F_{IPCE} is defined as $(IPCE^{PC} - IPCE^{C-PC}) / IPCE^{C-PC}$ (%) and denoted as green triangular points. The IPCE graphs are PC layer electrode (blue diamonds) and C-PC layer electrode (pink squares). The PBG of (a) & (b) are at the UV regime and NIR regime respectively.

From Figure 5-15, it can be observed that F_{IPCE} is negative for both 'SS' and 'LL' specimens. In essence, the C-PC DSSC is greater than PC DSSC throughout the spectral range of interest: 450-750nm. Photo-generation of electrons of both PC and CPC DSSCs can be considered to be almost the same since TiO₂ materials, dye loading and electrolyte encapsulation are kept similar as much as possible in the same cell. Thus, in conclusion, the electron transport is more efficient in a denser CPC DSSC since electrons percolate better through the denser connection TiO₂

network and meet fewer recombination interfaces. As a result, higher current density is measured for a CPC DSSC.

In the preceding section (5.4) the PBG is shown to give higher F_{IPCE} near the dielectric band even though the inverse opal structure has inferior electron transport path than a collapsed structure (Figure 5-14). This shows that the inverse opal DSSC with photonic crystal effect can enhance F_{IPCE} due to slow light effect and is able to compensate its poorer electron transport performance.

5.9 Conclusion of Chapter 5

In this chapter, TiO_2 inverse opals of varying film thickness are fabricated as an electrode in a DSSC without the TiO_2 mesoporous layer. The finite size effect of the photonic crystal is studied for the enhancement in the light-matter interaction near the dielectric band edge spectral position. Incident photon-to-electricity conversion efficiency (IPCE) peak enhancement factors of 1.5%, 3.2% and 8.3% were recorded in PC cells with inverse opal thicknesses of 2.92, 5.53 and 7.76 μm normalized with respective dye loading. A stronger photonic crystal effect is induced by the larger range order. This is evident in the simulated density of states (DOS) of finite size structure where a high DOS improves light absorption at the dielectric band edge spectral position. An optimal design is proposed to couple the inverse opal layer on a mesoporous layer for efficient solar energy harvesting.

Secondly, the comparison of extinction spectra between a TiO_2 inverse opal and a collapsed TiO_2 inverse opal shows that the extinction is enhanced at the dielectric band edge. Finally, the electron transport is found to be more efficient in

a disordered inverse opal DSSC, which is used as a reference sample for all experiment in this thesis. As a result, the IPCE enhancement factor in a TiO_2 inverse opal shown in all case studies is an improvement over and above the more efficient electron transport of the reference sample.

6. Design Rule on Embedded Photonic Crystal Photovoltaics

In the preceding chapters, dye-sensitized solar cell is the platform on which the beneficial effect of an embedded photonic crystal layer is showcased. Here, this chapter strives to present a general design consideration on the use of photonic crystal in some popular photovoltaic technologies.

At the press of this thesis, SunPower Corporation[172], a major silicon solar cell manufacturer, has announced the shipment of 22.5% efficiency single junction cell which is closed to the highest efficiency ever report from a laboratory research (24.7% on year 2000). [173] In comparison, a single junction silicon solar cell has a practical maximum efficiency of 31% (Shockley-Queisser limit). [174] A combination of thermal and material integrity problems will still be the barrier for the commercial or laboratory grade solar cell from closing in to the Shockley-Queisser limit. Why is pushing the frontier of efficiency important? The reason lies in the high cost in producing and installing a solar panel for solar energy harvesting. To convince homeowners or utility authorities to invest on this renewable energy, the period of return on investment (ROI) must be shortened. For that to happen, cell efficiency is important. There are two other technologies to improve on the ROI as follow.

Increase the amount of light in the cell. Using photon management features such as concentrator[175], textured surface[176], anti-reflection coating[177], back

plane reflector/grating[72, 178], plasmonic effect[179] or photonic crystal[178] can improve incident light concentration and retention for higher probability of absorption by the solar cell.

Reduce the amount of active material to improve cost. This is achieved by using thin film solar cell, such as good light absorber but costly CdTe and CIGS materials. Even thin film silicon, a poor light absorber, is a good candidate if coupled with photon management features.

From the above, photon management features are important for improving light absorption in a solar cell. The idea is to confine the light to the active region as long as possible until it is sufficiently absorbed. The following discusses the anatomy and design consideration to configure a photonic crystal for improving the solar energy harvesting efficiency in a solar cell.

1) A photonic crystal consists of periodic arrangement of materials with different refractive indices and the periodicity is in the order of wavelength of visible light.

2) A photonic crystal can be in 1D, 2D or 3D.

3) An ideal photonic crystal has infinite dimension.

4) A photonic crystal has a photonic band gap (PBG).

5) A PBG is an optical property which shares the same characteristic as a band stop filter; it prevents the propagation of light of a band of wavelength by reflection.

6) The center of the gap can be tuned according to the periodicity.

7) The width of the gap can be adjusted by the refractive index contrast of the materials; the higher is the contrast the wider is the gap.

8) A photonic crystal has a crystalline structure and consists of interfaces that separate regions of different material with different refractive index.

9) A practical photonic crystal has a finite dimension and thus it has a weaker reflection and less distinct gap width characteristics.

10) A photonic crystal is reflecting useful light away and the front configuration of photonic crystal on a solar cell is only suitable for the following reasons. (i) To protect solar cell from harmful rays such as ultraviolet or infrared.[126, 127] Photonic crystal can be tuned outside the ultraviolet or infrared regime. (ii) To allow a narrow bandwidth of light to enter the solar cell, 100% in theory, by making use of the principles of Q-matching resonant absorption.[65]

11) A photonic crystal configured as a back reflector of a solar cell is most useful for light retention in thin film solar cell. In most implementations[72, 178, 180, 181], Bragg reflector or 1D multilayer reflector is used, as shown in Figure 6-1, for reflecting light back to the active region with a typical broad spectral width of 450 – 900 nm.[178] One reliability advantage the photonic crystal reflector enjoys is that it will not suffer in reflectivity compared to aluminum back plane as aluminum oxidizes.

Figure 6-1. Common implementation of 1D Bragg reflector on the back plane of thin film solar cell.

12) The optimal light trapping design often couples the 1D Bragg back reflector with (i) front anti-reflection coating to allow more light into cell[178]; (ii) front textured surface to reduce front reflective loss[72]; (iii) textured grating at the back plane to send light back at an oblique angles, thus enhancing light trapping property [178, 180, 182]. These configurations are illustrated in Figure 6-2.

Figure 6-2. 1D Bragg reflector in a solar cell is further optimized with (a) front anti-reflection coating (ARC); (b) front textured surface by wet etching; (c) grating coupled with the Bragg reflector.

13) 2D photonic crystal configured in a back plane of a solar cell can enhance the cell efficiency. Rod-like structures have been patterned in organic photovoltaic (OPV) and efficiency enhancement are reported at narrow spectral region due to multiple excitation resonances[183] and slow light effect[160] as shown in Figure 6-3(a). Further special light absorber schemes are proposed for light absorption

enhancement by parallel interface refraction[67] and increase optical path length[184]. Figure 6-3(b) illustrates the 2D photonic crystal schemes for enhanced light absorption. However, the use of 2D array of long rod-like structure often suffered from poor conductive path and may affect the overall efficiency of the solar cell.

Figure 6-3. (a) Schematic of an organic solar cell with 2D photonic crystal. Image is taken from Ref. [183] (b) A light absorber scheme with 2D square rods in air; however this is a compromise between improved light absorption versus higher resistive path for electron conduction. Image is taken from Ref. [184]

14) 3D photonic crystal configured in a back plane of a solar cell can enhance the cell efficiency. This is proposed in this thesis through (i) excitation of electric field at the dielectric band edge and (ii) back reflection of the inverse opal. Further, light absorption enhancement by parallel interface refraction is also proposed for a 3D photonic crystal structure.[67]

15) For solar cell technologies that have charge collection back planes, the choice of materials for the photonic crystal back reflector is a constraint. These

technologies include junction effect solar cells such as silicon and OPV. The charge collection back plane needs to be conductive and oxide layer is not suitable. For instance, a Si-SiO₂ Bragg reflector has a high refractive indices contrast for a beneficial wider reflection spectral width and this configuration is not suitable as SiO₂ is insulating. Further, there is a need for "base doping" for practical solar cell; the back side of a silicon solar cell needs to be highly-doped for improving the collection of minority carriers[185]. Thus an optimal design scheme should include (i) a transparent conductive layer for separation, and (ii) a textured metal contact plate. Figure 6-4(a) illustrates an indium tin oxide (ITO) as a charge collection layer and separation layer in between a silicon solar cell (or OPV) and the photonic crystal. Figure 6-4(b) shows a scheme of using the metal back contact plate[186] as a charge collection layer and the inclusion of grating surface for trapping the light in the active layer.

Figure 6-4. Schematic of a silicon solar cell with (a) photonic crystal and (b) grating metal back plate in situations where the base doping and minority carrier collection are important parameters. The dotted line is region of base doping.

16) A photonic crystal consists of many interfaces. The presence of interfacial boundaries in the light absorption layer can be detrimental to charge transport due

to recombination centers. As a result, photonic crystal needs to be separated from the active light absorption layer. On the contrary, interfaces are beneficial for dye-sensitized solar cell (DSSC) as shown in this thesis. TiO_2 inverse opal is implemented in the active layer to harness both back reflection and excited electric field effects. The greater the number of interfaces in a TiO_2 inverse opal, the greater the dye coverage on the TiO_2 surfaces, as shown in Figure 6-5(a). Therefore there will be a greater enhancement of excited electric field for photocurrent generation. To effect a reflective and dielectric band edge enhancement in the visible ray spectrum, the choice of the PS particle should be in the range of 230 – 300 nm in diameter (refer to section 3.2 and 4.1). The mesoporous TiO_2 layer should face towards the sun, while the TiO_2 inverse opal layer provides reflective and electric field enhancement functions.

On the other hand, the interfacial characteristic of a photonic crystal can be advantageous in a 2D array of silicon nanowires with radial p–n junction solar cell, as shown in Figure 6-5(b). In this scheme, slow light property can be harnessed as well as superior light trapping property in between the nanowires.[187, 188] However, the challenges of the radial p–n junction silicon nanowires device include making metallization contact at all nanowires and maintaining reliability and integrity for a huge number of p–n junctions.

Figure 6-5. Examples of photonic crystal solar cell where its multitude interfacial characteristic is useful. (a) an inverse opal layer in a DSSC; (b) radial p–n junction silicon nanowires.

7. Conclusion and Outlook

This thesis discusses the increase in light harvesting efficiency of a self-assembled photonic crystal inside a dye-sensitized solar cell over a narrow spectral range (approximately 50 nm) near to the dielectric band edge. The key property of photonic crystal capitalized in this research is the slow light phenomenon occurring near the photonic band gap's flat edges where the material dispersion is anomalously increased by the photonic crystal. The group velocity of light slows down when its wavelength is near to the flat band edges. The slow light effect promotes the interaction between the photosensitive dye molecules and light. To quantify the effect of improved light harvesting efficiency due to slow light effect, electric field inside the photonic crystal is used as a proxy. Here, incident light couple to the Bloch modes inside the photonic crystal is examined. Along the edges of the photonic band gap, the flat band edges result in an increased density of states and the intensification of Bloch modes. The increase in electric field (Bloch modes) near the dielectric band edge (where slow light effect is) increases the photo-excitation of a photosensitive dye in a DSSC. This results in the increased light harvesting efficiency of the solar cell.

The achievement of this work is the introduction of an incremental processing step to improve the DSSC power conversion efficiency (η) by 33.5%. The improvement magnitude does not produce a disruptive improvement in

photovoltaic advancement; nevertheless, an insight of the photonic crystal's effect on a photovoltaic cell has been described.

In the methodology of this research work, colloidal self-assembly (CSA) has been harnessed to fabricate nanoscale ordered structure with unique optical property for photovoltaic application. Using flow-controlled vertical deposition (FCVD), layer transfer, nanoparticles infiltration and sintering technique, titanium dioxide (TiO_2) inverse opal thin film is fabricated from a polystyrene (PS) opal template. The TiO_2 inverse opal and PS opal are used a photon management scheme for a dye-sensitized solar cell (DSSC) and different configurations have been carried out and investigated. First, a TiO_2 inverse opal was coupled on a TiO_2 mesoporous film electrode in a DSSC to form the bilayer DSSC. The TiO_2 inverse opal is designed to be a light reflector to the TiO_2 mesoporous film as well as to capitalize its slow light phenomenon effect near to the dielectric band edge of a photonic crystal. Angle-resolved monochromatic irradiance is carried out on bilayer DSSC in order to pinpoint the effect of highly dispersive dielectric band edge blue-shifting with the increase in incidence angle. Numerical simulation shows that the intensification of electric field intensity at the photonic band edges, where group velocity of light is low. The Ru-complex dye is sensitized on the dielectric region of the TiO_2 inverse opal. Using a Maxwell-Bloch model, the Ru-complex dye molecule is simplified as a two-level atom for analysis, the photo-excitation density of the Ru-complex dye increases with the electric field intensity in the dielectric region of the TiO_2 inverse opal. The increased excitation density rate causes a greater electron injection into the conduction band of TiO_2 , which

consequently increases the photocurrent and improves the incident photon-to-current conversion efficiency (IPCE). The injected electron distribution by the dielectric band edge effect is modeled using a rate equation. On the performance indicators, the back reflection of the TiO_2 inverse opal enhance the IPCE by 65% at the visible ray regime and the dielectric band edge effect contribution another 10%. Therefore, a peak enhancement factor of 75% in IPCE is measured in the bilayer DSSC over a reference cell near to the dielectric band edge. As a comparison, a PS opal is coupled outside of the DSSC and a peak enhancement factor of 12% in IPCE is measured over a reference cell.

Secondly, a permitted propagation mode or defect mode was created in the photonic band gap by sandwiching a planar TiO_2 defect layer in between a TiO_2 inverse opal. This creates a non-zero density of states in the center of the photonic band gap (PBG). Under transmission and reflection spectroscopy, a defect state at 534 nm was confirmed. Under rear illumination in the incident-photon to electricity efficiency (IPCE) characterization, a small 2% increase in IPCE enhancement factor near 534 nm was measured. Finally, an overall power conversion efficiency of the bilayer DSSC was measured to be 4.78% under the AM1.5G solar simulator over a reference cell (3.58%) and this represents 33.5% improvement. On the other hand, the improvement is found to be 3.2% and 10.6% for an external polystyrene opal and gold film reflector respectively over the reference cell. Table 7-1 lists the advantage of using TiO_2 inverse opal in a DSSC over a metallic reflector.

Table 7-1. Advantage of TiO₂ inverse opal as a reflector in DSSC over an external metallic reflector.

1	Tunability of the photonic band gap spectral position to match the optimal absorption peak of the dye.
2	Less reflectivity at UV and IR regimes to prolong reliability effect of dye.
3	Close proximity of inverse opal to the mesoporous layer for optimal back reflection compared to an external metallic reflector.
4	No issue of oxidation problem to reduce reflectivity over long operation term.

Thirdly, the thickness dependence of TiO₂ inverse opal film electrode DSSC is studied on the effect of light-matter interaction in the dielectric band edge. IPCE peak enhancement factors of 1.5%, 3.2% and 8.3% were recorded in PC cells with inverse opal thicknesses of 2.92, 5.53 and 7.76 μm respectively. By computing the photo-excitation of dye and the density of states (DOS) in a TiO₂ inverse opal photonic crystal using the finite-difference time-domain method, the increase in IPCE is attributed to the increased light intensity at the highly dispersive dielectric band edge. At the same time, the numerical simulation shows the increase in the DOS with the increase in thickness of the inverse opal which promotes the optical absorption of the Ru-complex dye. This study provides an insight into the changes in optical absorption of an atom when the space surrounding that atom is modified.

Fourthly, the comparison of extinction spectra of the Ru-complex dye in a TiO₂ inverse opal and in the collapsed TiO₂ inverse opal shows that the extinction

of the dye is enhanced at the dielectric band edge. This further strengthens the evidence of the highly dispersive dielectric band edge on optical absorption in an ordered structure.

Fifthly, the electron transport is found to be more efficient in a disordered (collapsed) inverse opal DSSC, which is used as a reference sample for all experiment in this thesis. As a result, the IPCE enhancement factor in a TiO_2 inverse opal shown in all prior case studies is an improvement over and above the more efficient electron transport of the reference sample.

Finally, the thesis is concluded with a general design rule consideration of coupling a photonic crystal to a solar cell. The photonic crystal is most effective when it can be harnessed as back reflector in a photovoltaic cell and where its huge interfacial area can enhance the active area for photocurrent generation.

For future work, this thesis can be enhanced by looking at the following suggestive points for improvement. A rapid fabrication technique of TiO_2 inverse opal can be adopted for commercial viability in the production of DSSC.[189] Slurry of PS/ TiO_2 core-shell can be synthesized and doctor-bladed on top of the mesoporous TiO_2 film. The PS core and other polymeric binder can be removed by heat decomposition. Long range order of TiO_2 inverse opal may not be achieved through this route, but it will present a good optical back reflection.[89]

Secondly, a disordered structure is prepared by collapsing an ordered structure as reference comparison. The purpose is to carry out a direct IPCE comparison on samples with and without periodic structures using almost similar TiO_2 material volume and dye loading. As the result of using a collapsed opal, the thickness of

the resulting structure is reduced. The collapsed layer (disordered) has a denser electron conductive path network (lower porosity) and a thinner thickness than a non-collapsed layer (ordered). Besides the work as described in the fourth point of the conclusion above, a more detailed study is needed on the electron percolation through the various structures using transient photocurrent study.[190]

In the percolation theory, electron transport dynamics is studied due to the influence of randomness in conductive network geometry. In a lower porosity network (disordered layer in this thesis), there is more degree of freedom in electron transport path and electron transport becomes faster in the transient photocurrent study. On the flip side, the electron transport is convoluted with more trapping and detrapping events in a denser network. This results in more recombination loss and more degradation in the conductive performance. Further, the use of electrochemical impedance spectroscopy (EIS) can help to quantify the various impedance indicators in said structures for improvement in electron transport.

8. List of Original Contribution

In summary, the author has made an engineering contribution in this thesis by explaining the fabrication and design of ordered nanostructures using colloidal self-assembly and solution-processed techniques for enhancing light trapping property in a dye-sensitized solar cell. Further, the author has made a scientific contribution by explaining the high dispersion band edge of a photonic crystal that causes a higher electric field for promoting photo-excitation in a dye for increasing light harvesting efficiency.

The original contributions carried out by the author are as follow:

1. Preparation of TiO_2 nanoparticles suspension suitably for filling PS colloidal crystal via dip coating process (section 2.2 and 2.4).
2. Preparation of a TiO_2 sol-gel suitably for depositing as a thin film with high-wetting characteristic (section 3.2.1).
3. Description of a systematic monitoring of TiO_2 infiltration procedure into PS colloidal crystal (section 2.4.5).
4. Preparation of a reference cell ('collapsed cell') from a design of experiment (DOE) cell for a direct solar efficiency comparison (section 3.2.1.3).
5. Description of the enhancement factor due to dielectric band with angle-resolved irradiance (section 3.2.2).
6. Description of the dielectric band edge enhancement model (section 3.2.4).
7. Preparation of a planar defect layer in a photonic crystal dye-sensitized solar cell (section 4.1).
8. Description of the enhancement factor due to increased in thickness of photonic crystal and in density of states (section 5.5 and 5.6).

9. Description of the electron transport efficiency in ordered and disordered structures (section 5.8).

The list of published works is as follow:

Journal:

Chan-Hoe Yip, Yet-Ming Chiang, and Chee-Cheong Wong, "*Optical absorption in a finite three-dimensional photonic crystal thin film solar cell*", J. Opt. Soc. Am. B (2010) 27, pp. 920–926

Lia Augustine Herman, Chan Hoe Yip, and Chee Cheong Wong, "*Opaline Backreflector Coating in Dye-Sensitized Solar Cell*", J. Nanosci. Nanotechnol. (2010) 10, pp. 4657-4662

Chan-Hoe Yip, Yet-Ming Chiang, and Chee-Cheong Wong, "*Dielectric Band Edge Enhancement of Energy Conversion Efficiency in Photonic Crystal Dye-Sensitized Solar*" Cell, J. Phys. Chem. C (2008) 112, pp. 8735-8740

Koh YK, Yip CH, Chiang YM, Wong CC, "*Kinetic stages of single-component colloidal crystallization*", Langmuir (2008) 24, pp. 5245-5248

Conference:

5th International Conference on Materials Processing for Properties and Performance (MP3)

Singapore, DECEMBER 11-15, 2006

"*Top-down versus bottom-up Photonic Crystal Devices.*"

C. H. YIP, C. C. WONG

5th International Symposium on Nanomanufacturing (ISNM-5)

Singapore, 23 - 25 January 2008.

"*Large-area Ordered Nanoporous TiO₂ Structure Through Colloidal Self-Assembly And Solgel Infiltration*"

C. H. Yip, Y. M. Chiang, and C. C. Wong

Materials Research Society (MRS) Spring Meeting 2008

San Francisco, March 24 – 28, 2008

"*Dielectric Band Edge Enhancement of Energy Conversion Efficiency in Photonic Crystal Dye-Sensitized Solar Cell*"

C. H. Yip, Y. M. Chiang, and C. C. Wong

Thinfilms 2008 / nanoMan 2008

Singapore, 13 Jul – 16 Jul 2008

“Opaline backreflector coating in dye-sensitized solar cell “

Lia Augustine Herman, Chan Hoe Yip and Chee Cheong Wong

Thinfilms 2008 / nanoMan 2008

Singapore, 13 Jul – 16 Jul 2008

“TiO₂ Mesoporous Thin Films for Dye-Sensitized Solar Cell Application “

Chen Xu, Chan Hoe Yip, Xin Zou and Chee Cheong Wang

Thinfilms 2008 / nanoMan 2008

Singapore, 13 Jul – 16 Jul 2008

“The effect of inverse opal film thickness on efficiency of a photonic crystal dye-sensitized solar cell.”

C. H. Yip, Y. M. Chiang, and C. C. Wong

Poster:

Singapore-MIT Alliance (SMA) 10th Anniversary Symposium

Singapore, 21 - 22 January 2009

“The fabrication of a photonic crystal dye sensitized solar cell with a planar defect”

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Appendix A : Exhibits

Exhibit 1:

Colloidal self-assembly using the traditional evaporative vertical deposition. As concentration of suspension gets higher, the film deposited gets thicker and finally peels off (see arrow) starting from the initial growth front.

Exhibit 2:

Colloidal self-assembly using the traditional evaporative vertical deposition. Effect of thickness (arrow indicates the growth direct and the progressive increase in thickness) and poor adhesion of opal on the substrate. Peeling of film occurs after taken out from the growth vessel.

Exhibit 3:

Colloidal self-assembly using the flow-controlled vertical deposition (FCVD). Uniform growth of opal film on substrate.

Appendix B : Error Bar Charts

Error bar diagrams from the IPCE characterization results.

B.1 as shown in Figure 3-8(b).

B.2 as shown in Figure 3-8Error! Reference source not found.(c).

B.3 as shown in Figure 3-8(d).

B.4 as shown in Figure 4-7(b).

B.5 as shown in Figure 4-7(c).

B.6 as shown in Figure 4-9(b)

B.7 as shown in Figure 4-9(c).

B.8 as shown in Figure 5-7(a).

B.9 as shown in Figure 5-7(b).

B.10 as shown in Figure 5-7(c).

Appendix C : MPB file listing

To simulate band diagrams of polystyrene (PS) opal in MPB (<http://Ab-initio-mit.edu/mpb>).

```
; FCC lattice
; Air/dielectric spheres in dielectric/air space.
; Source: "Data Analysis Tutorial" of the MPB manual. http://Ab-initio-mit.edu/mpb
; Author: C H Yip (saved in MMLAB/project/mpb/after/2009-11-03)
; TG-50 Iodite refractive index is 1.43, epsilon is 1.43^2
; TiO2 nano-crystal refractive index is 2.25, epsilon is 2.25^2

(define PS (* 1.6 1.6))
(define TG50 (* 1.43 1.43))
(define TiO2 (* 2.25 2.25))

(define-param eps PS) ; the dielectric constant of the spheres
(define-param r (/ (sqrt 0.5) 2)) ; the radius of the spheres = sqrt(0.5)/2 =
0.35355
(set! default-material (make dielectric (epsilon eps)))

(set! geometry-lattice (make lattice
  (basis-size (sqrt 0.5) (sqrt 0.5) (sqrt 0.5))
  (basis1 0 1 1)
  (basis2 1 0 1)
  (basis3 1 1 0)))

Corners of the irreducible Brillouin zone for the fcc lattice,
in a canonical order:
(set! k-points (interpolate 4 (list
  (vector3 0 0.5 0.5) ; X
  (vector3 0 0.625 0.375) ; U
  (vector3 0 0.5 0) ; L
  (vector3 0 0 0) ; Gamma
  (vector3 0 0.5 0.5) ; X
  (vector3 0.25 0.75 0.5) ; W
  (vector3 0.375 0.75 0.375))) ; K

(define diel (make dielectric (epsilon PS)))

; A diamond lattice has two "atoms" per unit cell:
(set! geometry (list (make sphere (center 0 0 0) (radius r)
  (material diel))
))

(set-param! resolution 16) ; use a 16x16x16 grid
(set-param! mesh-size 5)
(set-param! num-bands 6)

(run)
```

Appendix D : MEEP file listing

To simulate reflection/transmission/electric field of TiO₂ inverse opal in electrolyte. MEEP simulator (<http://Ab-initio-mit.edu/meep>)

```
; TiO2 inverse opal in electrolyte (variable-angle reflection/transmission)
; Source: MEEP manual. http://ab-initio-mit.edu/meep
; Author: C H Yip (saved in /meep/after/2009-10-12/)
; Parameter: fcen, df, ANGLE, COL, pad, dpml, r, PHC?, MODETRANS, MODEREFL?)

(define-param pad 4) ; x-dir, padding between last sphere and PML edge
(define-param dpml 2) ; PML thickness
(define-param PHC? false)
(define-param COL 6)
(define-param r 0.104)

(define sr3 (sqrt 3))
(define sr2 (sqrt 2))
(define r_ (- r 0.05))
(define TIO2TG50 3.8) ; 60% of 2.25^2 + 40% of 1.43^2 =3.1
(define TG50 (* 1.43 1.43))

(define xA 0 )
(define xB (* sr2 (* 2 r) (/ 1 sr3) ) )
(define xC (* sr2 (* 4 r) (/ 1 sr3) ) )
(define stepcell (+ xC xB))
(define unitcell (+ xC (* 2 r)))
(define sy (* 4 r) )
(define sx (* 2 (+ pad dpml (* (- COL 1) unitcell) ))) ;COL
(define sz (* 2 r sr3) )
(define sx6 (* 2 (+ pad dpml (* (- 6 1) unitcell) ))) ;COL
(define FIELDESCR (+ dpml (* -0.5 sx6) pad))

(set! eps-averaging? true)
(set! geometry-lattice (make lattice (size sx sy sz)))
(set-param! force-complex-fields? true)
(set-param! resolution 40);
(set! pml-layers (list (make pml (direction X) (thickness dpml))))

(if PHC?
  (begin
    (set! default-material
      (make dielectric (epsilon TIO2TG50) ;*****3
        (polarizations
          (make polarizability
            (omega 3.1) (gamma 0.008) (delta-epsilon 0.1))
          (make polarizability
            (omega 4.0) (gamma 4) (delta-epsilon 0.05))
          (make polarizability
            (omega 4.1) (gamma 4) (delta-epsilon 0.05))
        )
      ))

    (define FILM-material
      (make dielectric (epsilon 4.76) ;

    ))
```

```

(define COLLAPSE-material ;
(make dielectric (epsilon TIO2TG50) ;
)
)
)
(begin
(set! default-material (make dielectric (epsilon TG50)))

(define COLLAPSE-material
(make dielectric (epsilon TIO2TG50)
)
)
)
)
)
(if PHC?
(begin
(set! geometry
(append
(geometric-objects-duplicates (vector3 stepcell) 0 (- COL 1)
(list
;Plane A

( make sphere (center xA (* -2 r) (* -1 r) ) ; sphere 1
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xA (* -1 r) (- (* r sr3) r) ) ; sphere 2
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xA (* -2 r) (- (* 2 r sr3) r) ) ; sphere 3
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xA 0 (- (* 2 r sr3) r) ) ; sphere 4
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xA (* 2 r) (- (* 2 r sr3) r) ) ; sphere 5
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xA (* 1 r) (- (* r sr3) r) ) ; sphere 6
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xA (* 2 r) (* -1 r) ) ; sphere 7
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xA 0 (* -1 r) ) ; sphere 8
(radius r_)
(material (make dielectric (epsilon TG50))))

;Plane B

( make sphere (center xB (* -1 r) (* -1 r sr3) ) ; sphere 1
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xB (* -2 r) 0 ) ; sphere 2
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xB (* -1 r) (* 1 r sr3) ) ; sphere 3
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xB (* 1 r) (* 1 r sr3) ) ; sphere 4
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xB (* 2 r) 0 ) ; sphere 5
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xB (* 1 r) (* -1 r sr3) ) ; sphere 6
(radius r_)
(material (make dielectric (epsilon TG50))))
( make sphere (center xB 0 0) ; sphere 7
(radius r_)
(material (make dielectric (epsilon TG50))))

```

```

;Plane C
      ( make sphere (center xC (* -2 r) (+ (* 2 r sr3) r) ) ; sphere 1
        (radius r_)
        (material (make dielectric (epsilon TG50))))
      ( make sphere (center xC (* -1 r) (+ (* -1 r sr3) r) ) ; sphere 2
        (radius r_)
        (material (make dielectric (epsilon TG50))))
      ( make sphere (center xC (* -2 r) r ) ; sphere 3
        (radius r_)
        (material (make dielectric (epsilon TG50))))
      ( make sphere (center xC 0 r ) ; sphere 4
        (radius r_)
        (material (make dielectric (epsilon TG50))))
      ( make sphere (center xC (* 2 r) r ) ; sphere 5
        (radius r_)
        (material (make dielectric (epsilon TG50))))
      ( make sphere (center xC (* 1 r) (+ (* -1 r sr3) r) ) ; sphere 6
        (radius r_)
        (material (make dielectric (epsilon TG50))))
      ( make sphere (center xC (* 2 r) (+ (* 2 r sr3) r) ) ; sphere 7
        (radius r_)
        (material (make dielectric (epsilon TG50))))
      ( make sphere (center xC 0 (+ (* 2 r sr3) r) ) ; sphere 8
        (radius r_)
        (material (make dielectric (epsilon TG50))))
    ) ;end of list
  ) ;end of duplicate
  (list ; previously no air

      (make block (center (* -0.25 sx) 0 0) (size (* 0.5 sx)
        sy sz) (material (make dielectric (epsilon 1)))) ;
air
      (make block (center (- (* 0.5 sx) (* 0.5 (+ pad dpml) ) 0 0)
        (+ pad dpml) sy sz
        (material (make dielectric (epsilon 1))))

    ) ; end of list
  ) ; end of append
) ;end of set geometry
); end of PHC begin
(begin ; NO PHC
  (set! geometry
    (list
      ;;;;;;;;;AIR NS Reflectance and transmittance;;;;;;;;
      (make block (center 0 0 0) (size sx sy sz)
        (material (make dielectric (epsilon 1))))
      ;;;;;;;;;MARKER;;;;;;;;
      ; ( make sphere (center (- (* 0.5 sx) dpml 1) ) ; sphere MARKER
      ; (radius 0.2)
      ; (material (make dielectric (epsilon TG50))))
      ; ( make sphere (center FIELDSCR 0 0) ; sphere MARKER
      ; (radius 0.2)
      ; (material (make dielectric (epsilon 4))))
      ;;;;;;;;;MODE EFIELD (TG50);;;;;;;;
      ; (make block (center 0 0 0) (size sx sy sz)
      ; (material (make dielectric (epsilon TG50))))
      ; (make block (center (* -0.25 sx) 0 0) (size (* 0.5 sx)
      ; sy sz) (material (make dielectric (epsilon 1)))) ;
      ; (make block (center (- (* 0.5 sx) (* 0.5 (+ pad dpml) ) 0 0)
      ; (size (+ pad dpml) sy sz)
      ; (material (make dielectric (epsilon 1))))
      ;;;;;;;;;MODE EFIELD (TiO2);;;;;;;;
      ; (make block (center 0 0 0) (size sx sy sz)
      ; (material COLLAPSE-material)) ; previously TIO2TG50
      ; (make block (center (* -0.25 sx) 0 0) (size (* 0.5 sx)
      ; sy sz) (material (make dielectric (epsilon 1)))) ;
      ; (make block (center (- (* 0.5 sx) (* 0.5 (+ pad dpml) ) 0 0)
      ; (size (+ pad dpml) sy sz)
      ; (material (make dielectric (epsilon 1))))
      ;;;;;;;;;
    )
  )
)

```

```

    ) ; end of list
  ) ; end of set geometry
) ; end of No PHC begin
); end of if

;@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
;@@@@SOURCE DEFINITION@@@@@@@@@@@@
;@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
(define-param fcen 1.5) ; pulse center frequency          ;!!!CHANGE FROM 1.32 T
(define-param df 2.0) ; pulse width (in frequency)          ;!!!CHANGE FROM 0.4 T 1.2
DOS
(define-param ANGLE 0)
(define theta (/ (* ANGLE pi) 180))
(define kz (* fcen (sin theta)))
(set! k-point (vector3 0 0 kz))
(define (my-amp-func p) (exp (* 0+2i pi kz (vector3-z p))))

(define-param nfreq 200) ; number of frequencies at which to compute flux

(define-param MODEEFIELD? false) ; if not specify, do the TRANS/REFL analysis

(if MODEEFIELD? (begin
  (set! sources (list
    (make source
      (src (make continuous-src (frequency fcen) (fwidth df)
        (start-time (* (random:uniform) 3)) ))
      (component Ey)
      (center (+ FIELDSCR (/ (random:uniform) 3)) 0 0)
      (size 0 sy sz)
      (amp-func my-amp-func))

    (make source
      (src (make continuous-src (frequency fcen) (fwidth df)
        (start-time (* (random:uniform) 3)) ))
      (component Ez)
      (center (+ FIELDSCR (/ (random:uniform) 3)) 0 0)
      (size 0 sy sz)
      (amp-func my-amp-func))

    (make source
      (src (make continuous-src (frequency fcen) (fwidth df)
        (start-time (* (random:uniform) 3)) ))
      (component Ex)
      (center (+ FIELDSCR (/ (random:uniform) 3)) 0 0)
      (size 0 sy sz)
      (amp-func my-amp-func))
  ))
)
(begin
  (set! sources (list
    (make source
      (src (make gaussian-src (frequency fcen) (fwidth df)))
      (component Ey)
      (center (+ dpml (* -0.5 sx)) 0 0)
      (size 0 sy sz)
      (amp-func my-amp-func))
  ))
)
)
(define-param MODETRANS? false)
;TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT
;TTTT TRANSMISSION CALCULATION TTTTTT
(define transpt (- (* 0.5 sx) dpml))
(define ssy (/ sy 6))
(define ssz (/ sz 6))
(define do-get-transpt-field
  (lambda () (print
    "EY-T01: " (real-part (get-field-point Ey (vector3 transpt 0 0))) " "
    (imag-part (get-field-point Ey (vector3 transpt 0 0))) "\n"
  ))
)

```

```

" " "EY-T02: " (real-part (get-field-point Ey (vector3 transpt (* -2 ssy)
0))) " "
(imag-part (get-field-point Ey (vector3 transpt (* -2 ssy)
0))) "\n"

" " "EY-T03: " (real-part (get-field-point Ey (vector3 transpt (* -1 ssy)
0))) " "
(imag-part (get-field-point Ey (vector3 transpt (* -1 ssy)
0))) "\n"

" " "EY-T04: " (real-part (get-field-point Ey (vector3 transpt ssy 0))) " "
(imag-part (get-field-point Ey (vector3 transpt ssy 0))) "\n"

" " "EY-T05: " (real-part (get-field-point Ey (vector3 transpt (* 2 ssy) 0)))
" "
(imag-part (get-field-point Ey (vector3 transpt (* 2 ssy) 0)))
"\n"

" " "EY-T06: " (real-part (get-field-point Ey (vector3 transpt 0 (* -2
ssz)))) " "
(imag-part (get-field-point Ey (vector3 transpt 0 (* -2
ssz)))) "\n"

" " "EY-T07: " (real-part (get-field-point Ey (vector3 transpt 0 (* -1
ssz)))) " "
(imag-part (get-field-point Ey (vector3 transpt 0 (* -1
ssz)))) "\n"

" " "EY-T08: " (real-part (get-field-point Ey (vector3 transpt 0 ssz))) " "
(imag-part (get-field-point Ey (vector3 transpt 0 ssz))) "\n"

" " "EY-T09: " (real-part (get-field-point Ey (vector3 transpt 0 (* 2 ssz))))
" "
(imag-part (get-field-point Ey (vector3 transpt 0 (* 2 ssz))))
"\n"
))
)
;TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT
;RRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRR
;RRRRRR Reflectivity calculation RRRRRR
(define refl ; reflected flux
  (add-flux fcen df nfreq
    (make flux-region
      (center (+ (* -0.5 sx) dpml 1) ) (size 0 sy sz) )))
;RRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRR

(define-param MODEREFL? false)

;RRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRR
;RRR Routine for REFLECTIVITY RRRRRRRR
(if MODEREFL? (if PHC? (load-minus-flux "refl-flux" refl)))
;RRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRR

(define epspt (+ 0.00 xB))
(define E1 (* 1 stepcell))
(define E2 (* 2 stepcell))
(define E3 (* 3 stepcell))
(define E4 (* 4 stepcell))
(define E5 (* 5 stepcell))
(define E6 (* 6 stepcell))
(define E7 (* 7 stepcell))
(define E8 (* 8 stepcell))
(define E9 (* 9 stepcell))
(define E10 (* 10 stepcell))
(define E11 (* 11 stepcell))
(define E12 (* 12 stepcell))
(define E13 (* 13 stepcell))
(define E14 (* 14 stepcell))

```

```
(define E15 (* 15 stepcell))
; EEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE
; EEEEE Run Efield EEEEEEEEEEEEEEEEEEEEEEEEEEE
(define do-get-efield
  (lambda () (print

    "EY-E01: " (real-part (get-field-point Ey (vector3 (+ epspt E1) 0 (* -1 r)))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E1) 0 (* -1 r))))
    "\n"
    "EY-E02: " (real-part (get-field-point Ey (vector3 (+ epspt E2) 0 (* -1 r)))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E2) 0 (* -1
r)))) "\n"
    "EY-E03: " (real-part (get-field-point Ey (vector3 (+ epspt E3) 0 (* -1 r)))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E3) 0 (* -1
r)))) "\n"
    "EY-E04: " (real-part (get-field-point Ey (vector3 (+ epspt E4) 0 (* -1 r)))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E4) 0 (* -1
r)))) "\n"
    "EY-E05: " (real-part (get-field-point Ey (vector3 (+ epspt E5) 0 (* -1 r)))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E5) 0 (* -1
r)))) "\n"
    "EY-E06: " (real-part (get-field-point Ey (vector3 (+ epspt E1) 0 (* 1 r)))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E1) 0 (* 1
r)))) "\n"
    "EY-E07: " (real-part (get-field-point Ey (vector3 (+ epspt E2) 0 (* 1 r)))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E2) 0 (* 1 r))))
    "\n"
    "EY-E08: " (real-part (get-field-point Ey (vector3 (+ epspt E3) 0 (* 1 r)))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E3) 0 (* 1
r)))) "\n"
    "EY-E09: " (real-part (get-field-point Ey (vector3 (+ epspt E4) 0 (* 1 r)))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E4) 0 (* 1
r)))) "\n"
    "EY-E10: " (real-part (get-field-point Ey (vector3 (+ epspt E5) 0 (* 1 r)))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E5) 0 (* 1
r)))) "\n"
    "EY-E11: " (real-part (get-field-point Ey (vector3 (+ epspt E1) (* -1 r) 0))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E1) (* -1 r)
0))) "\n"
    "EY-E12: " (real-part (get-field-point Ey (vector3 (+ epspt E2) (* -1 r) 0))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E2) (* -1 r)
0))) "\n"
    "EY-E13: " (real-part (get-field-point Ey (vector3 (+ epspt E3) (* -1 r) 0))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E3) (* -1 r)
0))) "\n"
    "EY-E14: " (real-part (get-field-point Ey (vector3 (+ epspt E4) (* -1 r) 0))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E4) (* -1 r)
0))) "\n"
    "EY-E15: " (real-part (get-field-point Ey (vector3 (+ epspt E5) (* -1 r) 0))) "
    "          (imag-part (get-field-point Ey (vector3 (+ epspt E5) (* -1 r)
0))) "\n"
    "EY-E16: " (real-part (get-field-point Ey (vector3 (+ epspt E1) (* 1 r) 0))) "
```



```
(imag-part (get-field-point Ey (vector3 (+ epspt E1) (* 1 r)
0))) "\n"
      "EY-E17: " (real-part (get-field-point Ey (vector3 (+ epspt E2) (* 1 r) 0))) "
"
      (imag-part (get-field-point Ey (vector3 (+ epspt E2) (* 1 r)
0))) "\n"
      "EY-E18: " (real-part (get-field-point Ey (vector3 (+ epspt E3) (* 1 r) 0))) "
"
      (imag-part (get-field-point Ey (vector3 (+ epspt E3) (* 1 r)
0))) "\n"
      "EY-E19: " (real-part (get-field-point Ey (vector3 (+ epspt E4) (* 1 r) 0))) "
"
      (imag-part (get-field-point Ey (vector3 (+ epspt E4) (* 1 r)
0))) "\n"
      "EY-E20: " (real-part (get-field-point Ey (vector3 (+ epspt E5) (* 1 r) 0))) "
"
      (imag-part (get-field-point Ey (vector3 (+ epspt E5) (* 1 r)
0))) "\n"
    ))
  )
; EEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE

(define-param T 1) ; run time 1
(define-param AT 1) ; after this time , start recording

(run-until T ;(at-beginning output-epsilon)
;;;;;;;;;;TRANSMISSION;;;;;;;;;;;;;;;;;;;;;
      (at-every 0.2 do-get-transpt-field) ;MODETRANS
;;;;;;;;;;MODE EFIELD;;;;;;;;;;;;;;;;;;;;;;;;;
;      (after-time AT (at-every 0.1 do-get-efield)) ;MODEEFIELD
;;;;;;;;;;
)

;RRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRR
;RRR Routine for REFLECTIVITY RRRRRRRR
(if MODEREFL? (if (not PHC?) (save-flux "refl-flux" refl)))
(if MODEREFL?(display-fluxes refl))
;RRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRRR
```

Appendix E : Dye extinction effect in nanostructured layers

(refer section 5.7)

E1. Reflectance / Transmittance spectroscopy of a TiO_2 inverse opal with PBG at 535 nm before dye sensitization. The dielectric band edge is at 600 nm approximately. (a) inverse opal thin film (ordered); (b) collapsed inverse opal film (disordered).

E2. Reflectance / Transmittance spectroscopy of a TiO_2 inverse opal with PBG at 535 nm after dye sensitization. (a) inverse opal thin film (ordered); (b) collapsed inverse opal film (disordered).

E.3 (a) Extinction spectra of samples e_{PC} , e_{CPC} , E_{PC} and E_{CPC} . (b) 'Disordered' graph (pink line) is the difference between E_{C-PC} and e_{C-PC} ; 'Ordered' graph (blue line) is the difference between E_{PC} and e_{PC} ; the dashed line is the absorption spectrum of Ru-complex dye powder.

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