EFFICIENCY ENHANCEMENT IN DYE-SENSITIZED SOLAR CELLS
THROUGH LIGHT MANIPULATION

A Thesis in
Chemistry
by
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ABSTRACT

Solar energy conversion is dominated by expensive solid-state photovoltaic cells. As low-cost cells continue to develop, the dye sensitized solar cell has generated considerable interest as an efficient alternative. Although already moderately efficient, this cell offers numerous areas for improvement, both electronically and optically. Solar conversion efficiencies have been studied by modifying optical pathways through these dye-sensitized solar cells, or Grätzel cells. Monochromatic incident-to-photon current efficiency (IPCE) data reveals that an inverse opal photonic crystal or other disordered layer coupled to a nanocrystalline TiO₂ layer enhances photocurrent efficiency by illumination from the counter electrode direction. Modifying the cell architecture to allow for illumination through the working electrode yields similar increased enhancements by proper selection of the photonic bandgap. Direct growth of TiO₂ inverse opals on a nanocrystalline slab was accomplished by polymer infiltration of the slab, followed by crystal growth and liquid phase deposition. Results demonstrate that the bilayer architecture contributes to the enhanced light harvesting rather than the inverse opal layer and is due, in part, to strong light localization, Bragg diffraction and enhanced scattering. These effects occur solely at the bilayer interface and largely contribute to the photocurrent enhancements in the 540 – 750 nm region where the sensitizer dye is a poor absorber. TiO₂ sculptured thin films were also studied and offer promise for the development of efficient solid-state dye cells.
Visible light undergoes effective solar energy conversion by the typical dye-sensitized solar cells, but is detrimental to silicon solar cells. In contrast, near-infrared light is not utilized by these dye cells, but results in high efficiencies for silicon. Spectrum-splitting tandem cell architectures consisting of a Grätzel cell and a silicon photovoltaic module have been designed and tested. Spectral ranges were separated by reflecting near-infrared light using a hot-mirror coating on the Grätzel cell. A cell module was fabricating using 12 individual Grätzel cells and a single silicon concentrator and tested under solar conditions, yielding proof-of-principle data for the development of future modules.

Colloidal crystals are large-scale analogs of inorganic crystals, and their synthesis has been developed into an educational lab for high school and undergraduate students. Colloidal crystals are self-assembled onto glass substrates, followed by polymer templating. This lab effectively introduces majors and non-majors alike to a unique area of materials synthesis with a modular approach towards synthesis, instrumentation, and characterization. The adaptability of this lab to various skill levels as well as opportunities for cooperative based learning makes this lab an excellent curricular addition.
TABLE OF CONTENTS

LIST OF FIGURES ..................................................................................................... vii
LIST OF TABLES ........................................................................................................ xiii
LIST OF ABBREVIATIONS ....................................................................................... xiv
ACKNOWLEDGEMENTS .......................................................................................... xvi

Chapter 1 Introduction ............................................................................................ 1
  1.1 Renewable and Solar Power ........................................................................... 1
    1.1.1 Solar Efficiency .................................................................................... 4
  1.2 The Dye Sensitized Solar Cell ........................................................................ 8
    1.2.1 Tandem Cells ..................................................................................... 10
  1.3 References ..................................................................................................... 15

Chapter 2 Photonic Crystals for use in Dye Sensitized Solar Cells ....................... 18
  2.1 Introduction ................................................................................................... 18
    2.1.1 Dye Sensitized Solar Cells ................................................................... 18
    2.1.2 Bilayer Structures ................................................................................. 24
    2.1.3 Theory of Photonic Structures .............................................................. 25
  2.2 Experimental .................................................................................................. 27
    2.2.1 General Synthesis of Photonic Crystals and their Replicas .................. 27
    2.2.2 Photonic Crystals for use in Grätzel Cells ............................................ 29
      2.2.2.1 TiO₂ Inverse Opals ..................................................................... 29
      2.2.2.2 Photonic Crystal Fabrication ...................................................... 30
      2.2.2.3 Disordered Structures ................................................................. 33
      2.2.2.4 Bilayer Structures ....................................................................... 34
    2.2.3 Grätzel Cell Assembly and Testing ...................................................... 36
    2.2.4 Characterization .................................................................................... 37
  2.3 Results ............................................................................................................. 37
  2.4 Discussion ....................................................................................................... 52
  2.5 Conclusions .................................................................................................... 58
  2.6 References ..................................................................................................... 59

Chapter 3 Improved Solar Efficiencies for Photonic Crystal Enhanced Dye Cells .... 65
  3.1 Introduction ................................................................................................... 65
  3.2 Experimental .................................................................................................. 69
    3.2.1 Photonic crystals on nanocrystalline TiO₂ .......................................... 70
    3.2.2 Indoor Cell Testing ............................................................................... 71
  3.3 Results ............................................................................................................. 72
LIST OF FIGURES

Figure 1.1: Comparison irradiance spectra of (● —) xenon, (— —) quartz tungsten halogen (QTH), and (←) solar light. .................................................................4

Figure 1.2: Efficiency-cost trade-off for the three generations of solar cell technology; wafers, thin films, and advanced thin films (2003 dollars). ..........7

Figure 1.3: Spectrum splitting tandem cell by spectrally filtering with dielectric mirrors and directing onto differing energy bandgap materials. ..................12

Figure 1.4: Tandem cell module designed by G. Barber to separate and reflect NIR light onto a silicon receiver and transmit the visible light onto a series of Grätzel cells. .........................................................................................................13

Figure 2.1: Energy diagram of a DSSC. ........................................................................................................21

Figure 2.2: Absorption spectrum of (■-) N719 dye versus (←) AM1.5 global irradiance. ........................................................................................................23

Figure 2.3: General synthesis of 200 – 1000 nm monodisperse silica spheres...............27

Figure 2.4: Vertical growth technique for colloidal crystal assembly. ..................29

Figure 2.5: A) Optical microscopy and b) SEM images of a photonic crystal from 243 nm polystyrene spheres..................................................................................31

Figure 2.6: Inverse TiO2 structure obtained from a) an ordered opal film from 243 nm spheres and b) a disordered film from a ½ mixture of 150/243 nm spheres. .................................................................................................................32

Figure 2.7: Powder diffraction pattern of synthesized titania with 17.1 nm crystallites as calculated by the Scherrer equation. Inset displays the polycrystalline structure taken obtained by HRTEM. ........................................33

Figure 2.8: Doctor-blade method for applying nanocrystalline TiO2 paste. ...............35

Figure 2.9: SEM image of a bilayer TiO2 photonic crystal/nanocrystalline TiO2 structure ................................................................................................................35

Figure 2.10: UV-visible absorption spectra of the dye solution (i) in ethanol, (ii) adsorbed on a nanocrystalline TiO2 film, and (iii) adsorbed on a titania inverse opal with stop-band centered at 490 nm in ethanol. Spectra are normalized to the absorbance at 400 nm. The spectra in (ii) and (iii) were collected after filling the void volume with ethanol (n = 1.36). Absorption spectra of the films before dye adsorption were subtracted from ii and iii. .......39
Figure 2.11: Photoaction spectra in a) backwall illumination and b) frontwall illumination of a dye-sensitized (i) TiO₂ disordered inverse opal film/nanocrystalline TiO₂ bilayer, (ii) a nanocrystalline TiO₂ film, and (iii) the disordered TiO₂ inverse opal film. The TiO₂ nanocrystalline film and the bilayer structure are 10-11 µm thick. Panel c) shows the IPCE (frontwall) normalized at 540 nm. .................................................................41

Figure 2.12: Photoaction spectra in (a) backwall illumination and (b) frontwall illumination of a dye-sensitized (i) TiO₂ inverse opal (stop band at 580 nm)/nanocrystalline TiO₂ bilayer, (ii) a nanocrystalline TiO₂ film, and (iii) the TiO₂ inverse opal. The inverse-opal film is 6 µm thick, and the TiO₂ nanocrystalline film and bilayer structure are 10-11 µm thick. The absorbance spectrum of this photonic crystal with ethanol filling the void is presented (right axis, panel a), showing the stop-band centered at 580 nm. Panel (c) shows normalized IPCE (frontwall), with spectra (iv) and (v) corresponding respectively to the sensitized PC of stop band at 488 nm, and the same PC coupled to a nanocrystalline TiO₂ film, presented for comparison............................................................................................................44

Figure 2.13: Photoaction spectra in (a) backwall illumination and (b) frontwall illumination of a dye-sensitized (i) TiO₂ disordered inverse opal film/nanocrystalline TiO₂ bilayer, (ii) a nanocrystalline TiO₂ film, and (iii) the disordered TiO₂ inverse opal. The TiO₂ nanocrystalline film and the bilayer structure are 10-11 µm thick. Panel (c) shows the IPCE (frontwall) normalized at 540 nm. ..........................................................................................46

Figure 2.14: UV-visible transmission spectra of (i) the disordered TiO₂ inverse opal film, and (ii) a nanocrystalline TiO₂ film. ............................................................................47

Figure 2.15: Photoaction spectra in (a) backwall illumination and (b) frontwall illumination of a dye-sensitized (i) TiO₂ disordered inverse opal film (LPD 2)/nanocrystalline TiO₂ bilayer, (ii) a nanocrystalline TiO₂ film, and (iii) the disordered TiO₂ inverse opal film. Panel (c) shows the IPCE (frontwall) normalized at 540 nm. ..........................................................................................49

Figure 2.16: Normalized frontwall photoaction spectrum of a dye-sensitized (i) TiO₂ inverse opal bilayer (580 nm stopband), (ii) nanocrystalline TiO₂, and (iii) disordered inverse opal TiO₂_2. Absorbance curves for (iv) the inverse opal photonic crystal and (v) the disordered inverse TiO₂_2 structure are present on the right hand axis. ............................................................................50

Figure 3.1: IPCE spectrum of (—) a bilayer with anode side irradiation and (□-□) corresponding photonic bandgap of the 2nd TiO2 LPD from 243 nm spheres....67
Figure 3.2: Image and diagram of a horizontally stacked Grätzel cell scattering structure. The SEM image (a) shows 243 nm spheres crystallized inside 20 µm lithographically defined channels (photoresist borders) and inset shows the extended structure. After this step, diagram (b) illustrates the infiltration with nanocrystalline TiO₂ paste. Anode side illumination results in light scattering and Bragg reflecting horizontally throughout the structure. .................. 68

Figure 3.3: Scheme depicting the fabrication and assembly of a TiO₂ inverse opal onto nanocrystalline TiO₂. Only a single LPD step is possible for this cell........ 71

Figure 3.4: Polymer film spin cast on a 10 µm thick nanocrystalline TiO₂ film........... 75

Figure 3.5: Grätzel cell assembly for a photonic crystal placed on the counter electrode................................................................. 76

Figure 3.6: IPCE data for Grätzel cells with (─■─) a 2nd LPD 243 nm photonic crystal on platinized FTO counterelectrode, (─●─) a platinized counterelectrode, and (─▲─) a photonic crystal counterelectrode. Inset shows the normalized spectra above and (─) a bilayer film for comparison. ....... 77

Figure 3.7: Transmittance spectrum of a polystryrene colloidal crystal from 291 nm spheres in air (─) and the crystal after a first (- - -) and second (— — — ) infiltration and calcination (in EtOH).................................................................. 78

Figure 3.8: Optical image of a) a photonic crystal/nano bilayer (114 nmol/cm² dye) and b) standard nanocrystalline film (104 nmol/cm² dye) illuminated through a light box with equivalent dye coverage. The light path is through the nano layer, then the PC. ................................................................. 79

Figure 3.9: Single deposition inverse opal structure from 291 nm PS spheres measuring 13.5 µm thick. ................................................................. 80

Figure 3.10: Normalized IPCE spectra of nanocrystalline TiO₂ (▲), and 1st LPD 291 nm (—) and 243 nm (■) spheres, anode side irradiation. Inset shows the non-normalized spectrum. ................................................................. 81

Figure 3.11: Current-voltage curves for 291nm bilayer cells without the presence of a Pt counter electrode. Cathode side irradiation (♦) and anode side (●) shows similar curves compared to the diode-like behavior of the platinized electrode (─). ................................................................. 82
Figure 3.12: Through-dye photoaction spectrum normalized at 480 nm (preceeding the stopband) of a) (—) 1st LPD PC on nanoTiO$_2$ from 291 spheres and b) (-■-) 2nd LPD nanoTiO$_2$ on PC from 243 nm spheres. The backscattering in (b) contributes to a large decrease in IPCE in the region of the stopband (580 nm).

Figure 3.13: Anode side irradiation with Pt counter electrode of nano-on-PC 2nd LPD bilayers from 291 nm (—)and 243 nm (-■-) and a nanocrystalline TiO$_2$ layer (-▲-) demonstrating the increased red side enhancement of the bilayers, but in the case of the 243 nm replicas, also a sharp a decrease in the efficiency corresponding to the photonic stopband.

Figure 3.14: Cathode-side irradiation of nano-on-PC (-♦-) 2nd LPD 243 nm, (—)1st LPD 291 nm, and (-▲-) nanoTiO$_2$ films. The extended red-side enhancement can be seen extending past 605 nm for the 2nd LPD structure.

Figure 3.15: Normalized back-side photoaction spectrum for 291 nm TiO$_2$ inverse opal bilayers of (—) a 1st LPD PC-on-nano structure with 580 nm stopband and (—) a 2nd LPD nano-on-PC structure with 660 nm stopband. A spectrum of typical nanoTiO$_2$ is shown as a reference (—▲—).

Figure 4.1: UV-vis-NIR reflectance and transmittance spectrum of FTO glass with and without hot mirror coating. It is evident that the hot mirror coating reflects NIR light but FTO has a weak absorption that begins at 800 nm and continues beyond 2300 nm.

Figure 4.2: Diagram of a hot mirror coating fabricated by alternating layers of high index (n$_H$) and low index (n$_L$) materials where the number of layers is proportional to the % reflectance and the ratio of n$_H$/n$_L$ indicates the width of the reflectance zone.

Figure 4.3: Visible light transmission and NIR reflection on a hot mirror coated FTO anode.

Figure 4.4: Two sets of data reporting concentration efficiency for a Grätzel cell with hot-mirror coated anode. The cell efficiency has a maximal increase of 3.5 once the hot mirror is placed in the beam path.

Figure 4.5: Open circuit voltage vs. time for (top) a Si PV concentrator cell operating at 100 mW/cm$^2$ for each respective incidence range and (bottom) 1.2 W incident light split into the corresponding white, visible, and NIR ranges.
Figure 4.6: Tandem cell module consisting of (a) 12 individual Grätzel cells connected in parallel and focused on (b) a 1.44 cm² Si concentrator cell. The Grätzel cells were masked with black electrical tape prior to alignment and testing.

Figure 4.7: Powder XRD pattern of a TiO₂ STF before and after calcination at 425°C for 12 hours. Crystallite size is calculated to be 27 nm by the Scherrer equation.

Figure 4.8: SEM image of a TiO₂ STF on Si with a 95 nm helical periodicity. Inset shows the stopband in EtOH corresponding to a complex set of interference phenomenon from the circular Bragg stack. The peak at 540 nm corresponds to dye absorbance on the film.

Figure 4.9: Current vs. voltage curve for a nanorod network and corresponding IPCE spectrum. The measured dye loading is 13.2 nmol/cm².

Figure 4.10: Transient photocurrent time trace for a TiO₂ STF network. The measured time constant is 23.6 ms with a calculated electron diffusion coefficient of 1.28 x 10⁻⁶ cm²/s.

Figure 4.11: Series-paralleling module utilizing 3 parallel strings, 2 series blocks, and 2 cells per substring (reproduced from Green).²

Figure 4.12: Solar tandem cell concentrator designed by Goetzberger for collecting direct and diffuse irradiation.²⁷

Figure 5.1: Outline of the modular laboratory approach, showing the primary experimental sections (left) and the available options (right).

Figure 5.2: Scanning electron microscope images of (a) 301 nm SiO₂ spheres synthesized by the controlled base-catalyzed hydrolysis of tetraethylorthosilicate, (b) an edge-on view of a close-packed colloidal crystal of 420 nm SiO₂ spheres, and (c) a top-down view of a colloidal crystal of 236 nm SiO₂ spheres. An optical microscope image (200 × magnification) of a colloidal crystal of 3.6 μm polystyrene spheres synthesized by emulsion polymerization is shown in (d). Note the comparison between the close-packed lattice and the fcc unit cell shown in (c) and the defects highlighted in (d).

Figure 5.3: Two views of the unit cell of an fcc crystal. Using geometrical relations, the distance between planes, \( d \), is related to sphere diameter, \( D \), by \( d = D \sqrt{(2/3)} \). The (111) plane is designated by the bisecting triangle.
Figure 5.4: (a) Photograph of self-assembled colloidal crystal film of 236 nm SiO$_2$ spheres on glass, and (b) its UV-visible transmission spectrum. .................................. 145

Figure 5.5: Experimental setup for lattice spacing calculation. As incident light (from a laser pointer) passes through the photonic crystal, it is diffracted according to the Fraunhoffer law. The distance from the photonic crystal and the incident spot can be measured, as well as the spacing between the incident spot and the 1st order diffraction. Trigonometric calculations lead to the lattice spacing, $d$. .......................................................... 146
LIST OF TABLES

Table 1.1: Maximum theoretical efficiencies under direct and global irradiation and potential technologies. ................................................................. 8

Table 2.1: IPCE ratio at a nanocrystalline TiO₂ film and photonic crystal (PC) or disordered titania inverse opal, compared to the ratio of respective surface areas, and the corresponding enhancement factor in the conversion efficiency in the red. a,b ................................................................................................................ 51

Table 3.1: Anode side photocurrent enhancement for bilayer structures compared to a typical single layer TiO₂ film. Non-normalized increases are minimal over the entire spectral region, but demonstrate increased red-side conversion except for 1st LPD 243 structure. ................................................................................................. 85

Table 4.1: Grätzel cell characterization and efficiency under 1 sun illumination. ...... 103

Table 4.2: Efficiency data for the Sunpower silicon concentrator cell. Rows list efficiencies for the cell at 100 mW for the specified spectral ranges. ............... 108

Table 4.3: Characteristics for 12 parallel connected DSSCs and reflected NIR light on a single Si concentrator cell......................................................... 112

Table 4.4: Characterization results of an STF before and after calcination......... 114

Table 4.5: Characterization data for various TiO₂ sculptured films. ................. 117

Table 4.6: Reflectance, transmittance, and attenuation powermeter data of white light through a hot mirror coated FTO (hot mirror first surface) and FTO. ........ 120

Table 5.1: Synthesis variables and results for various SiO₂ sphere preparations. .... 139
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIBN</td>
<td>2,2’-Azobisisobutyronitrile</td>
</tr>
<tr>
<td>APCE</td>
<td>absorbed photon to current efficiency</td>
</tr>
<tr>
<td>CIGS</td>
<td>copper indium gallium selenide</td>
</tr>
<tr>
<td>DSSC</td>
<td>dye sensitized solar cell</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>fcc</td>
<td>face-centered cubic</td>
</tr>
<tr>
<td>ff</td>
<td>fill factor</td>
</tr>
<tr>
<td>FTO</td>
<td>fluorine doped tin oxide</td>
</tr>
<tr>
<td>i-V</td>
<td>Current-voltage</td>
</tr>
<tr>
<td>IPD</td>
<td>incident photon density</td>
</tr>
<tr>
<td>IPCE</td>
<td>incident photon to current efficiency</td>
</tr>
<tr>
<td>Isc</td>
<td>short circuit photocurrent (mA)</td>
</tr>
<tr>
<td>ITO</td>
<td>indium doped tin oxide</td>
</tr>
<tr>
<td>Jsc</td>
<td>short circuit photocurrent density (mA/cm²)</td>
</tr>
<tr>
<td>LHE</td>
<td>light harvesting efficiency</td>
</tr>
<tr>
<td>LPD</td>
<td>liquid phase deposition</td>
</tr>
<tr>
<td>MA</td>
<td>methacrylic acid</td>
</tr>
<tr>
<td>N3</td>
<td>cis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato)-ruthenium(II) bis-aqua</td>
</tr>
<tr>
<td>N719</td>
<td>cis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>$\eta$</td>
<td>efficiency (%)</td>
</tr>
<tr>
<td>nanoTiO$_2$</td>
<td>nanocrystalline titania</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared</td>
</tr>
<tr>
<td>PC</td>
<td>photonic crystal</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>PV</td>
<td>photovoltaic</td>
</tr>
<tr>
<td>PXRD</td>
<td>powder X-Ray diffraction</td>
</tr>
<tr>
<td>QTH</td>
<td>quartz tungsten halogen</td>
</tr>
<tr>
<td>STF</td>
<td>sculptured thin film</td>
</tr>
<tr>
<td>TCO</td>
<td>transparent conductive oxide</td>
</tr>
<tr>
<td>$V_{mp}$</td>
<td>Voltage at the maximum power point</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>open circuit voltage</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
</tbody>
</table>
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Chapter 1

Introduction

1.1 Renewable and Solar Power

Global energy use is currently at the level of 13 TW, and ever growing with increasing population and devices that use energy. Unfortunately, a majority of this energy comes from non-renewable sources and, although there is not an immediate need for a change to renewable resources, the scarcity of such supplies could arrive as early as 2050.¹ For decades now, the perception of dwindling fossil fuels has motivated government, economists, and scientists to find an alternative that is not only perpetual in supply, but also inexpensive and comparable in terms of storage density and capacity to fossil fuels. Fuel cells are an exciting class of devices for converting energy, with many researchers focusing on the production, delivery, storage, and use of hydrogen. Ironically enough, the current alternative energy sources allude to the four ancient elements- earth, wind, water, and fire. Geothermal heating currently produces over 8,000 MW of power with the opportunity to harvest more heat from deep beneath the Earth’s crust. Power originating from steam plants results in water vapor as the primary byproduct, but also generates small amounts of NO₂, CO₂, and sulfur. There are also a variety of challenges associated with maintaining an efficient geothermal power plant including improved heat exchange and stability in corrosive environments.² Wind power results in zero emissions, but can only be effectively utilized in a limited number of locations. Startup costs are
large and require large areas of land to establish such a “wind farm”. Hydroelectric power is also limited in sources and its capacity has been essentially maximized. Solar energy is a constant renewable resource (within the geological timescale) available in many areas of the world and offers a continuous increase of achievable efficiencies.

“In this era of depleting fossil fuel resources, it would be highly desirable to have an efficient and economical way of directly converting and storing solar energy as a chemical fuel”.\(^3\) This statement, made by Bolton shortly after the gas crisis in the 1970’s seems truer than ever with the nation’s current dependence on foreign sources of fuel and increasing costs of that fuel. The solar constant, or power reaching the Earth from the sun, is 1.76 x 10\(^5\) TW and of this, 600 TW strikes the Earth in areas where solar energy collection is a feasible option.\(^4\) By the year 2050, it is estimated the global need for carbon-free energy will be between 10 – 30 TW, depending on CO\(_2\) levels at the time. The current global population consumes 13 TW of energy in all forms, meaning there will need to be 1-3 times increase in energy, but little of it available from fossil fuel sources.

The near blackbody radiation of the sun drives all solar devices, as well as supports terrestrial life. Air mass zero (AM0) radiation is defined as the intensity of light of the sun at a distance of the Earth to the sun (92 million miles), outside the Earth’s atmosphere. The accepted value of AM0 sunlight is 1.353 kW/m\(^2\), but is attenuated by nearly 30 % inside the Earth’s atmosphere from Rayleigh and Mie scattering back into space, and absorption by molecular gases in the atmosphere. The *optical air mass* is the minimum path length of light through the atmosphere to the Earth’s surface and can be defined by Eq. 1.1. AM1 radiation is the incident radiation intensity on the Earth’s
surface when the sun is directly overhead whereas AM1.5 has been taken as the U.S. government terrestrial standard for incident light hitting the Earth (37° tilt, 48.19°s latitude), normalized to a total power density of 1 kW/m².

\[
\text{Air mass} = \frac{1}{\cos \theta}
\]

Along with direct incidence, diffuse radiation must be taken into account when examining the makeup of sunlight. Although highest on cloudy days, 10-20 % of solar irradiance on clear days is diffuse and 50 % on days that are between clear and cloudy. Diffuse sunlight is often wasted in solar tracking systems since the concentrator modules must always be normal to the direct radiation. Integration of novel optical designs, such as birefringent concentrators, could lead to the capture of otherwise wasted diffuse light, thereby increasing the efficiency of these expensive systems.

Using the sun for solar cell testing is possible, but not always practical given the intensity and spectral variations that occur over the Earth’s surface as well as daily and seasonal weather changes in a given location. For this reason, solar simulators are often used to mimic the solar spectrum. These simulators typically consist of a Xe arc lamp housing with a variety of filters to mimic the spectrum at a variety of air mass densities. The units also contain a beam homogenizer that assures equivalent incident power densities across the irradiation spot. Xe arc lamps are used exclusively for solar simulators as they most closely match the solar spectrum, compared to metal halide lamps (Figure 1.1), and in most cases can be used without additional filters other than a low density heat absorbing filter (KG, Schott).
1.1.1 Solar Efficiency

Initially reported by Becquerel in 1839, the photovoltaic effect is the mechanism by which all solar cells function. Observations demonstrated that voltage could be produced by placing two metal electrodes in a redox electrolyte and irradiating with light. When incident photons hit the electrodes, some electrons break loose from the delocalized metal framework, leaving behind a hole. As electrons and holes move in opposite directions from one another, a small current is established that can drive a load. This effect was further seen in nearly all solid-state materials of the time. It was not until 1954, however, that an efficient silicon cell, a forerunner to today’s silicon technology,
was produced. During the 1960’s and 1970’s silicon cell technology emerged as a useful source for alternative energy. The increase in production has lead to a decrease in cost, thereby furthering the utility of silicon cell technology.

Like the microelectronics industry, solar technology is constantly striving towards a better device. Rather than minimizing size, the motivation is higher efficiency and lower cost. Since the advent of solar as a feasible technology for energy production, there have been three movements, or generations, of solar technology. First generation cells were based almost solely on silicon technology, specifically single-crystal silicon, but also included GaAs and InGaP. The technology is obviously the most mature, with theoretical efficiencies of 27 %, but is hampered by the costs of materials processing. It is estimated that materials contribute to 70 % of the total cost of 1st generation photovoltaics with little room for a decrease in production costs or increases in solar conversion efficiency beyond 16 %. This naturally led to less expensive thin film materials, known as second generation. These low-cost materials consist of amorphous silicon (a-Si), and polycrystalline CdS, InSe, CuInSe2, and CdTe. Cells of this nature, produced by CVD or other film growth methods, are much less costly than single crystal materials. Although these materials are currently less efficient than first generation cells, typically <15 %, with a reported 18 % maximum for Cu(In,Ga)Se2, continued research is expected to bring these cells to a competing level while also decreasing manufacturing costs and increasing cell manufacturing sizes from ~100 cm² to 1 m². At some point in the future, second generation cells will reach a maturity plateau and will no longer advance in technology or cost savings. Solar technology will then iterate to a system with higher solar conversion efficiencies, the third generation cell. What is this cell? As
of yet, it is everything that is not first or second generation. Third generation cells are marked by low-cost thin film technology and high efficiency. Figure 1.2 shows an estimated representation of technology generation with an efficiency vs. cost analysis, illustrating that in 2003 prices, 1st generation has a manufacturing cost of $3.50/W with a minimum cost of $200/m² and 20% efficiency, 2nd generation costing a minimum of $0.50/W and ~$25/m² at 15% efficiency, and 3rd generation operating at $0.15/W and $50/m² at 60% efficiency. High efficiency and low costs are undoubtedly needed for solar to become a mainstream energy source, which requires efficiencies to double or triple with respect to 1st generation cells. Unfortunately, direct solar energy conversion has a theoretical limit of 31%, much lower than the 95% thermodynamic limit of a Carnot engine operating with a heat source at the blackbody temperature of the sun. The Shockley-Quiesser 31% maximum is only valid for single-junction cells with 1.25 to 1.45 eV bandgaps operating at AM1.5 global conditions. The limit increases dramatically with multi-junction concentrator cells which could theoretically utilize the entire photon energy flux from 0.5 to 3.5 eV. Third generation cells focus on efficient utilization of the entire solar spectrum with multi-junction cells to increase efficiency to values closer to the 68% multi-absorber thermodynamic limit.
Since the sun is a nearly perfect black body emitter at 6000 K, it follows that a solar cell operating as a black body absorber under ambient conditions (300 K) would be most efficient, reaching the Carnot limit. This only holds true, however, if the conversion of the sun’s energy to work produces zero entropy gain, but as stated by Planck in the 1959 English translation, this would be impossible to achieve when the two black-bodies are at different operating temperatures, since there would not be a net energy gain. Assuming an infinitesimally small entropy gain, only an infinitesimally small amount of work can be performed. A more realistic efficiency limit of 85.4 % can be deduced for a black-body thermovoltaic or thermal electric device, which accounts for the inherent entropy gain by a source and converter operating at 6000 K and 300 K, respectively. For a single device to approach this limit, photon energy absorption must be optimized over all wavelengths of light. This is not possible with a single junction cell, such as silicon.

Figure 1.2: Efficiency-cost trade-off for the three generations of solar cell technology; wafers, thin films, and advanced thin films (2003 dollars).
As previously mentioned, silicon has an indirect bandgap of 1.1 eV, meaning energies lower than this are not absorbed whereas energies higher are absorbed, with the excess energy resulting in rapid lattice thermalization. Since only 52% of the solar energy flux is in the infrared to near-infrared and 43% is in the visible (5% UV), a large portion of the spectrum is wasted in single-junction silicon cells. This is where the idea of tandem cells utilizing individual portions of the black-body spectrum becomes so important in so-called third generation solar cell technology. The theoretical limits of efficiency are summarized in Table 1.1 (adapted from Green).

<table>
<thead>
<tr>
<th>Efficiency limit</th>
<th>Direct</th>
<th>Global</th>
<th>Devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multicolor split cell</td>
<td>86.8 %</td>
<td>68.2 %</td>
<td>Hot carrier Tandem cells</td>
</tr>
<tr>
<td>Black-body</td>
<td>85.4 %</td>
<td>53.6 %</td>
<td>Thermal electric Thermophotovoltaic</td>
</tr>
<tr>
<td>2 cells</td>
<td>55.7 %</td>
<td>42.9 %</td>
<td>2 cell stack</td>
</tr>
<tr>
<td>Single junction</td>
<td>40.8 %</td>
<td>31.0 %</td>
<td>Single junction</td>
</tr>
<tr>
<td>Best Laboratory</td>
<td>34 %</td>
<td>30 %</td>
<td>3 cell tandem</td>
</tr>
</tbody>
</table>

1.2 The Dye Sensitized Solar Cell

The dye cell has emerged as one of the primary alternatives to solid-state semiconductor PV cells such as Si, GaAs, and tandem cells such as copper indium gallium selenide (CIGS). The motivation has been low cost materials with ease of fabrication. At the time of this writing, over 1500 articles have been written on this topic, including an educational article for cell fabrication in the undergraduate or high school
lab that has been used by The Penn State MRSEC Summer Teacher Workshop.\textsuperscript{11}

Although a number of issues plague this device design, it is remarkably efficient considering the low manufacturing costs and simplicity. The most common design is a cell fabricated on conductive glass, but new approaches of fabricating these cells on flexible materials, such as ITO coated polymer sheets,\textsuperscript{12} lead to new potential uses of the cell. As these materials are in the early development stages, the architecture used in the highly efficient cell from 1991 has not changed appreciably other than modifications of the absorbing dye.\textsuperscript{13} The caveat of selecting the proper sensitizer dye lies in sacrificing low photocurrents for longer wavelength absorption. An alternative to chemical modification of the dye cell is to alter the optical geometry of the cell, relying on internal reflection and scattering to increase photon absorption at wavelengths of low optical density, typically 540 – 800 nm.

Chapter 2 discusses the use of photonic crystals for photocurrent enhancement in this region by combining TiO\textsubscript{2} inverse opals and porous disordered structures with standard nanocrystalline TiO\textsubscript{2} films. Bilayers of these structures have shown a 26 % quantum efficiency enhancement in the visible spectrum by tuning the stopband of the photonic crystal to the red of the dye absorbance maximum.\textsuperscript{14} Quantitative experimental data reveals that both the ordered photonic crystal and disordered structure yield enhancement through photon localization, a synergistic enhancement of back and forward scattering and slowing of the group velocity of low light energy. Though the overall performance of these cells is lower than the standard Grätzel cell, the modification of geometry reveals a new area for photocurrent enhancement that can be further engineered to maximize photon-to-electron conversion efficiency. In Chapter 3, the modification of
the dye cell discussed in Chapter 2 is further embellished through the fabrication of a more simplistic enhancement architecture that again utilizes a photonic stopband tuned to the red of the dye maximum, but with only a single fabrication step, and allows for dye-side illumination, rather than the cathodic side required for cells in Chapter 2.

1.2.1 Tandem Cells

As first proposed by Jackson in 1955, a spectrum splitting device could be used to reduce the thermalization of high energy photons and increase overall photon-to-electron conversion. These proposed devices direct light towards a cell with a well-matched bandgap by selective mirrors or spectral filtering. The design published by Moon et al. was much like that in Figure 1.3, where mirrors selectively filter light onto a semiconductor device that efficiently uses that portion of the spectrum. Single junction cells are most efficient when the bandgap is matched to the intermediate photon energy (1.4 eV) of the solar spectrum. This has to be balanced, however, with the spectral energy flux of the sun in order to achieve maximum power between bandgap photons and high energy photons. If only a wide bandgap material is used, very little of the solar spectrum can be utilized effectively. The tandem cell does not suffer from this compromise since high energy photons can be absorbed by a high bandgap material and the remaining lower energy photons are directed further down the device to a lower bandgap material. In collaboration with Greg Barber, we have adopted the concentrator design in Figure 1.4 mainly for logistical reasons, but stacked semiconductor cells are another promising tandem cell design for both solid-state PVs and dye cells.
physically stacking lower bandgap films behind higher ones, spectral filtering is accomplished in much the same way by using mirrors, but without the need for individual electrical connections, making this device less bulky and easier to manufacture. These films must be current matched but this can be achieved by proper selection of adjoining semiconductor materials and proper engineering of material thicknesses. For the stacked cell design, there is an additional constraint of epitaxial growth, which is not possible in certain types of cells, such as the dye cell. For either type of cell, the theoretical limiting efficiencies increase with the number of stacked cells. An increasing number of bandgap materials leads to more efficient utilization of the solar spectrum with less loss from phonon decay. The maximum obtainable efficiencies for direct and diffuse irradiation have been calculated and increase from 31% diffuse, 40.8% direct for a single cell device up to 58.8 % diffuse, 74.4 % direct for a 6 cell device.\textsuperscript{18,19} As the number of cells approaches an infinite stack, the efficiency reaches a maximum of 68.2 % diffuse and 86.8 % direct. This represents the upper photovoltaic limit of a tandem cell and though it is below the Carnot limit, it is much higher than the 31 % achievable by a single junction cell.
Figure 1.3: Spectrum splitting tandem cell by spectrally filtering with dielectric mirrors and directing onto differing energy bandgap materials.
The field of third generation photovoltaics aims at increasing efficiency with low cost materials, a merger between 1st and 2nd generation devices. Though this current work is limited to tandem cells, others are researching a variety of architectures that go beyond the traditional single crystal device and beat the 31% limit imposed by such devices. Hot carrier cells, based on hot electron injection, offer similar efficiencies as tandem stacked cells by avoiding thermalization of high energy photons, but without the fabrication complexity. Cells comprised of up and down converters are an interesting approach as they are made to modify the incident light to match the semiconductor bandgap of choice. Two low energy photons can be converted into one high energy photon, and likewise, one high energy photon can be down converted to 2 lower energy...
photons. The more accurate matching of the semiconductor bandgap yields a calculated maximum efficiency of ~60 % with 1.1 eV bandgap under direct sunlight. Luminescent quantum dots (QDs) are one proposed method for achieving this architecture since they can be synthesized to match nearly the entire solar spectrum. Incorporation of QDs as a sensitizer into Grätzel cells has also been proposed since they could produce higher conversion efficiencies and offer greater tunability over the commonly used ruthenium dyes. The tandem cell reported by Dürr et al. uses two dye cells connected in parallel to extend the absorption region and maximize $J_{sc}$, yielding an overall efficiency of 10.5 %.\textsuperscript{17}

In the tandem cells developed in Chapter 4, the visible portion of the solar spectrum is directed to Grätzel cells while the under-utilized red portion of the spectrum is directed to a silicon concentrator cell by using reflective mirrors. The efficiency of Si cells is relatively poor in the visible portion of the spectrum compared to the NIR, and is in fact comparable to the efficiency of the less expensive Grätzel cell. Although this work is only in the early developmental stages, the proof-of-principle data demonstrate that there is no loss in efficiency by the Grätzel cell when the NIR light is deflected to an efficient Si solar cell. Work proposed by our group aims at further improving the efficiency of the Grätzel cell beyond the 10 % maximum, potentially making this tandem geometry more efficient than either individual cell while maintaining a low materials and fabrication cost.

The field of education is very important to both the author and advisor of this dissertation. The undergraduate chemistry lab is not unique to only chemistry majors, but incorporates a variety of other disciplines such engineering, physics, and materials
science. However, the required lab courses rarely have a component that is immediately relevant to the coursework of the non-chemistry student. The modular lab presented in Chapter 4 is relevant for both chemists and non-chemists alike since it utilizes a variety of cross-discipline techniques, including synthesis, microscopy, and self-assembly as a means to introduce materials chemistry at any level of undergraduate education, from first-year through senior level laboratory courses. Photonic crystals incorporate several conceptual intricacies of atomic crystallization such as thermodynamics, kinetics, and defects on a somewhat more macroscopic scale, observable by optical and electron microscopies. From the synthesis of colloidal particles to their characterization and assembly, students are led through a set of exercises that build on first-principle concepts. Cooperative learning environments are fostered by the number of components that can be varied throughout the lab, yielding observable trends and effects for the student. This approach has been proven to be effective in incorporating idea from a number of scientific disciplines and a somewhat unique application of modern materials chemistry.

1.3 References


2. NREL Geothermal Technologies Program. http://www.nrel.gov/geothermal/ (August 8),


Chapter 2
Photonic Crystals for use in Dye Sensitized Solar Cells

2.1 Introduction

2.1.1 Dye Sensitized Solar Cells

The increasing need for energy has driven research towards the goal of low emission, safe, and abundant renewable sources. The desire to convert solar to electrical energy has been spearheaded by photovoltaic devices such as silicon and other semiconductor cells, but the high production costs have motivated newer strategies that are more mimetic of photosynthesis. Since the first reports of 1-2 % efficient dye-sensitized solar cells (DSSCs) in the 1960’s and 70’s,1-3 a dye cell based on nanocrystalline TiO₂ cell was produced by Grätzel et al. with reported >10% efficiency.4 Since then, a large body of research and a number of reviews have been written concerning the operation and efficiency of this particular cell.5-8 The primary advantages of this excitonic cell over a standard PV device are the inexpensive fabrication and materials cost for a relatively efficient cell. Currently, the maximum reported efficiency is 10.6% for the N719 dye,9 however the typical efficiency is less than half that of a single-crystal silicon cell. If the efficiency of Grätzel cells approaches the theoretically predicted 20 % mark, these devices could significantly lower the price/peak watt compared to single crystal Si or GaAs PVs.10
A typical DSSC suffers from semiconductor-liquid junctions and therefore electrolyte volatility and breakdown are concerns for future development. Solid electrolyte junctions and low viscosity non-volatile ionic salts are alternatives to the currently used organic liquid electrolytes, but cells containing them are plagued by low efficiency from slow diffusion kinetics.\textsuperscript{11, 12} Carrier recombination is also an issue within the DSSC since all of the components can theoretically interact and cause electron-hole recombination. As these alternative electrolytes continue to be developed, a means of decreasing electron recombination needs to be developed. Practical DSSCs require recombination be kept to a minimum. This may come at the expense of electron injection kinetics which only need to be fast compared to the excited state decay, typically 100 ps – 1 ns.\textsuperscript{13} To overcome this problem, a variety of potential architectures, including columnar networks, can be used to facilitate charge transport of both electrons and holes in the z-direction while controlling charge separation in the x-y direction. The Grimes group has studied tubular TiO\textsubscript{2} architectures demonstrating high efficiency UV photoassisted water electrolysis\textsuperscript{14} and our group is currently studying DSSC behavior of rod-like TiO\textsubscript{2} structures developed by the Horn group (see Chapter 4).\textsuperscript{15} Molecular mediators can then be attached to the columnar structure by covalent or layer-by-layer assembly, followed by dye sensitization. Intercalation of a 2-5 nm molecule should minimize charge recombination if the redox potential is intermediate of the hole-transport electrolyte and sensitizer dye. A substantial increase in charge separated lifetime has been demonstrated using phenothiazine and triarylamine by moving the hole one molecule away from the TiO\textsubscript{2} surface.\textsuperscript{16, 17}
The five components of the cell are the conductive anode support, wide bandgap semiconductor oxide film, sensitizer dye, redox electrolyte, and platinized conductive counterelectrode. The anode and cathode supports are generally a transparent conductive oxide (TCO), such as fluorine-doped SnO$_2$ on glass (FTO). FTO is preferred over indium doped tin oxide (ITO) because of its greater electrochemical stability and low dopant mobility. The TiO$_2$ semiconductor film is typically comprised of a 10 $\mu$m thick mesoporous network of 10-20 nm anatase particles, which has sufficient surface area to allow a single monolayer of dye molecules to absorb nearly all incident photons with energies above the maximum dye absorbance. The sintered film is then sensitized by a Ru dye, generally a Ru (II) polypyridyl derivative. The $d^6$ metal centers have octahedral geometry and the complexes have both $\pi$ to $\pi^*$-ligand and metal to ligand charge transfer electronic transitions. These Laporte spin-allowed energy transitions are easily modified by ligand substitution of various $\pi$-accepting and $\sigma$-donating molecules and can extend the absorption range over most of the visible region with absorption coefficients on the order of $10^4$ M$^{-1}$cm$^{-1}$. Polypyridine Ru complexes have been extensively studied due to the luminescent and photoredox properties, the most studied being the Ru(bpy)$_3^{2+}$ molecule. Both the N3 and doubly-deprotonated N719 ruthenium bipyridyl dye molecules have been used extensively in Grätzel cell research, but the N719 dye has a higher efficiency and extended $V_{oc}$ at a slightly lower $I_{sc}$.$^{13}$ Ligand deprotonation shifts the conduction band edge potential of the TiO$_2$ by approximately $\sim$60 meV per pH unit,$^{18}$ resulting in higher $V_{oc}$.

This sensitizer dye is the primary means for harvesting solar energy and injecting electrons into the semiconductor film. The LUMO of the dye must be sufficiently
negative to inject an electron into the conduction band of the TiO₂. After injection, the oxidized dye is reduced by I⁻ in the I⁻/I₃⁻ electrolyte. Electrons percolate through the TiO₂ film through a series of trapping-detrapping events¹⁹-²² and transport through the FTO glass and a load. Upon returning to the cathode, the electron is used to reduce the I₃⁻ back to I⁻ and the cycle is repeated as shown in Figure 2.1. This process has been shown to be stable over 9600 hours or 10⁷ – 10⁸ turnovers.⁹ Total power from the cell is determined from the open-circuit voltage (V₉), the short-circuit current (Iₛ), and the fill-factor (ff). V₉ for the photoelectrochemical cell is defined as the voltage difference between the quasi-Fermi level of the illuminated semiconductor and the redox potential of the electrolyte. The sensitizer light absorption efficiency, or difference of the HOMO-LUMO gap, and electron injection efficiency determine the short-circuit current. Fill-factor, or maximum power under the i-V curve, is improved by decreasing recombination and minimizing TCO sheet resistance.

Figure 2.1: Energy diagram of a DSSC.
Efficiency is most directly affected by recombination processes in the cell. Direct recombination of injected electrons in TiO$_2$ with the Ru center is minimized by physically separating them through ligand fixation on the TiO$_2$. Also, electron injection has been found to occur on the femtosecond to picosecond timescale and reaches near unity efficiency$^{23}$ whereas I$^-$/Ru$^{3+}$ dye recombination is on the millisecond to minute timescale and is considered to be nearly negligible$^{24}$. Recombination of electrons in the TiO$_2$ film is minimized by the slow recombination reaction of the I$_3^-$/$I^-$ redox couple and fast electron transport through the semiconductor film$^{25}$. In the case of a DSSC, dark current occurs by recombination of electrons with I$_3^-$ molecules at the electrocatalytic TCO substrate. This can be minimized by incorporating a blocking layer that is less electrocatalytically active than the TCO or by chemically blocking with molecules such as pyridine derivatives$^{5,26}$. As shown in Figure 2.2, typical dye molecules absorb strongly over a small section of the solar spectrum. An obvious improvement would involve extending the dye absorption into the red portion of the spectrum, but these low energy photons do not have enough energy to promote electron injection in the TiO$_2$ conduction band. Although photons matching the peak absorption edge of the dye are absorbed within the first 2-3 $\mu$m, the remaining photons are not. Thicker films would promote absorption to combat the dye low extinction coefficient, but recombination kinetics would compete with electron percolation in the film. Several approaches are used to optimize the characteristics of the Grätzel cell, focusing on either the kinetic ($I_{sc}$) or thermodynamic ($V_{oc}$) aspects of cell. Not only are these studies often empirical in nature,$^{13}$ but the reported gains in either $I_{sc}$ or $V_{oc}$ are typically inverse to the other.
To work around the issue of low dye absorption, our group has been investigating scattering and localization in DSSC structures. By altering and scattering the path of non-absorbing photons there is an increased chance of the dye absorbing in the low extinction region. This is done without any decrease in cell performance characteristics since the optics, and not the electronics, are being modified. We have the incorporated TiO$_2$ photonic crystals and other scattering structures that have led to a $\sim$25% IPCE increase in the 500-800nm region.$^{27}$ The work performed in this chapter was a collaboration between Professor Lara Halaoui of the The American University of Beirut and the author. Experiments, characterization, and results were evenly split and the discussion section was largely and gratefully attributed to analysis by Dr. Halaoui.

Figure 2.2: Absorption spectrum of (■) N719 dye versus (─) AM1.5 global irradiance.
2.1.2 Bilayer Structures

Recently, our group reported an experimental enhancement in the light conversion efficiency of RuL2(SCN)2-sensitized TiO2 solar cells by coupling a conventional nanocrystalline TiO2 film to a TiO2 inverse-opal with a stop-band centered at 610 nm (as measured in ethanol).27 When illuminated from the electrolyte side of the TiO2 film (hereinafter referred to as frontwall illumination), this bilayer resulted in a 26% increase in the IPCE relative to a nanocrystalline film of the same overall thickness, in the 550-800 nm spectral range, where IPCE is represented in Eq. 2.1. The improved conversion efficiency was thought to arise from localization of heavy photons at the edges of the photonic stop band,12-15 and from Bragg diffraction and scattering within the photonic crystal (PC),16 but the contributions of these different mechanisms were not quantified. An increased absorbance was found for dye adsorbed on titania inverse-opals at energies to the red edge of the stop-band. This phenomenon, which has also been observed by Asher et al. in silver silica colloidal crystals,28 is attributed to the slowing of the group velocity of light near the edges of a photonic gap.13-15 The observation of increased red absorbance suggested that photon localization was the primary reason for the increase in IPCE.

\[
IPCE \, (\%) = \frac{1240(eV \, nm) \times J_{sc} (\mu A / cm^2)}{\lambda (nm) \times P(\mu W / cm^2)} \times 100
\]

2.1

The mechanism of enhancement in solar energy conversion in structures where a degree of light localization is in effect is further explored in this work. Monochromatic IPCE measurements at dye-sensitized TiO2 inverse-opals of varying stop band wavelengths were compared to IPCEs at bilayers of inverse opal/nanoTiO2 films, and at
nanoTiO₂ films. The mechanism of light propagation and the resulting extent of localization and hence the cell conversion efficiency were found to depend on both order and disorder in the photonic crystals. In addition to Bragg reflection by the ordered lattice, localization of heavy photons at the edges of the photonic gap, and particularly multiple internal scattering events at disordered regions ultimately leading to enhanced backscattering, appear to explain the increased IPCE at inverse opal/nanoTiO₂ bilayer photoelectrodes. Similar improvement in the long wavelength spectral region was also achieved by coupling disordered titania films to a conventional nanocrystalline TiO₂ layer. Other groups have subsequently used similar single-layer opal films as materials for dye-sensitized solid-state solar cells, but have obtained very low efficiencies and, unlike our work, report no enhancement due to the photonic crystal. This improvement is believed to result from multiple scattering events in the disordered bilayer films possibly leading to weak localization of light as recently modeled by Mihi and Miguez.

2.1.3 Theory of Photonic Structures

Photonic crystals (PCs) consist of a periodic array of alternating high and low refractive index materials that result in a set of unique optical properties. These crystals can exist in a 1, 2, or 3 dimensional structure and can be fabricated in a variety of manners, including lithography, holography, direct write laser, and self-assembly. The existence of a photonic bandgap, or stopband, originates from the alternating dielectric medium and is analogous to the electronic bandgap in a semiconductor. Devices such as optical waveguides and perfect dielectric mirrors are a result of the
photonic stopband, whereas optical waveplates and reflective polarizers as a result of birefringent dispersion. Nonlinear dispersion results in the so-called superprism effect and can be utilized in highly scattering geometries for the localization of light. In a photonic structure, photons with frequencies corresponding to the bandgap are not allowed to propagate within the crystal and diffract according to Bragg’s Law much like the interaction of X-rays with atomic structures. The first proposed three dimensional photonic structure was reported independently by Yablonovitch and John in 1987 and observed in colloidal crystals by Asher in 1984. Diffraction of these crystals occurs most effectively when the periodic spacing in the crystal is half the wavelength of incident light. Self assembly and other methods allow the size regime for photonic crystals to be in the visible and near infrared (NIR) region, bringing the utility of these materials into the realm of optical filtering and transmission.

If the difference in refractive indices (defined as the square-root of the dielectric constant or dielectric contrast) between the two materials is low, only a partial bandgap is present in the structure. By increasing the dielectric contrast of the photonic crystal, a complete stopband can be formed. This is often done by inverting the structure with high dielectric materials such as TiO₂, GaAs, or Si. Once the structure has been inverted, the low-index templated material, typically silica or polymer, can be removed through chemical or thermal means. The remaining structure is a skeleton of high index material with holes of air. Also, altering the geometry of the crystal from fcc to one such as the diamond structure will exhibit a full bandgap at lower dielectric contrast as compared to an fcc structure. Although full bandgap materials were not produced as a part of this thesis, the potential applications, such as communications and sensing, are worth noting.
2.2 Experimental

2.2.1 General Synthesis of Photonic Crystals and their Replicas

Photonic crystals are generally synthesized from monodisperse colloids, typically silica or polymer, such as polystyrene. Silica sphere synthesis proceeds via the controlled hydrolysis of tetraethoxysilane (TEOS), first described by Stober et al.\textsuperscript{46} Briefly, TEOS is added to a solution of ammonium hydroxide in ethanol and shaken for 12 – 24 hours. Hydrolysis takes place via the following reaction:

\[
\text{Si(OR)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{ROH}
\]

\[
n\text{Si(OH)}_4 \rightarrow n\text{SiO}_2 + 2n\text{H}_2\text{O}
\]

Figure 2.3: General synthesis of 200 – 1000 nm monodisperse silica spheres

Synthesis of silica spheres smaller than 200 nm takes place via a water-in-oil reverse emulsion synthesis.\textsuperscript{47,48} The synthesis of polystyrene spheres can take place via several synthesis routes,\textsuperscript{49} but most commonly through an emulsifier-free emulsion polymerization.\textsuperscript{50} Silica and polymer spheres can also be purchased including polymeric spheres with a variety of surface chemistries such as amine and carboxyl derivitizations and fluorescent tags. Companies include Bangs Labs, Duke Scientific, and Seradyn Inc. Once purchased or synthesized, monodisperse spheres can be easily crystallized via the convective self-assembly strategy developed by Jiang.\textsuperscript{33} Briefly, spheres are dispersed in ethanol or water and sonicated to break up any agglomerates. Cleaned substrates are immersed in the solution of spheres and left to evaporate at room temperature or at slightly elevated temperatures as pictured in Figure 2.4. According to work done by
Nagayama\textsuperscript{51} and adapted by Colvin,\textsuperscript{33} colloidal crystal multilayer thickness can be calculated by Eq. 2.2,\textsuperscript{50}

\[
k = \frac{\beta L \varphi}{0.605d(1 - \varphi)} \tag{2.2}
\]

where \( k \) is the number of layers, \( L \) is the meniscus height, \( \beta \) is the ratio between the colloidal particle in solution and fluid velocity, assumed to 1, \( d \) is the particle diameter, and \( \varphi \) is the particle volume fraction in solution. Energy minimization drives the spheres to crystallize in a close packed geometry, generally hexagonal close packed (hcp) or face-centered cubic (fcc).\textsuperscript{52, 53} If the lattice constant of the crystal is on a similar size scale to the wavelength of light, the crystal will exhibit a photonic bandgap.
2.2.2 Photonic Crystals for use in Grätzel Cells

2.2.2.1 TiO$_2$ Inverse Opals

In order to couple the effects of photonic crystals with typical DSSC structures, TiO$_2$ inverse opals, or photonic crystals were fabricated from polystyrene spheres. Carboxylated polystyrene spheres were purchased from Seradyn, Inc. Ammonium hexafluorosilicate, boric acid, poly(ethylene glycol), poly(ethylene oxide), and titanium
isopropoxide were purchased from Aldrich. Acetic acid was purchased from Fisher Scientific. Fluorine-doped tin-oxide (FTO) glass (TEC 8 or 15) was purchased from Hartford glass. The sensitizer dye, (RuL$_2$(NCS)$_2$:2TBA, L = 2,2′-bipyridyl-4-4′-dicarboxylic acid, TBA = tetrabutylammonium), (N719, Ruthenium 535-bisTBA) and Iodolyte TG-50 were purchased from Solaronix S.A. (Switzerland). All reagents were used without further purification. Deionized water was acquired from a Nanopure system (Barnstead) with 18 MΩ-cm resistivity.

2.2.2.2 Photonic Crystal Fabrication

A 0.1 wt% solution of carboxylated polystyrene spheres and 0.003 wt% Igepal CO-520 in water was sonicated for 30 minutes. FTO glass was cleaned by sonication in water followed by ethanol and then rinsed with water and dried in a nitrogen stream. The FTO substrates were immersed in the sphere solution and placed in a 55°C oven until evaporated, approximately 3 days. Once evaporated, a strong diffraction peak was observed at wavelength, $\lambda_p$, according to Eq. 2.3,

$$\lambda_p = 2d \sqrt{n_s^2 f + n_v^2 (1 - f)}$$

where $n_s$ is the refractive index of polystyrene (1.6) and $n_v$ is the refractive index of air (1.0). The fill-fraction ($f$) was assumed to be close-packed, 74% filling. A strong Bragg reflection was observed at 520 nm, corresponding to diffraction from the (111) face of the crystal. Using geometric relations, lattice spacing, $d$ is related to sphere diameter, D, by $d = (\sqrt{2/3}) \cdot D$, resulting in a sphere size of 217 nm. This result indicates a 10%
sphere shrinkage in drying and has been confirmed by SEM. Although many cracks are apparent in the optical image (Figure 2.5a), electron microscopy reveals relatively large areas of three-dimensional ordering (Figure 2.5b). Peeling and delamination was sometimes observed from the photonic crystals, but can be minimized with thinner films.

![Image]

Figure 2.5: A) Optical microscopy and b) SEM images of a photonic crystal from 243 nm polystyrene spheres.

After evaporation, the polystyrene PC was seeded with TiO₂ by soaking the films in a 1.2 % (w/v) solution of Ti(O'Pr)₄ and 0.12 % HNO₃ for five minutes. After soaking, the films were left to dry for 20 minutes. No visible shift in the bandgap was observed.

To infiltrate the PCs, aqueous solutions of 0.2 M (NH₄)₂TiF₆ and 0.25 M HBO₃ were combined at 51 ± 2 °C and pH was adjusted to 2.9 with 1 M HCl. The films were immersed in the solution for 20-25 minutes and rinsed with copious amounts of water. The films appeared orange/green, demonstrating a shift in the photonic bandgap. The dried films were then calcined in air at 400°C (Lindberg, 51894) for 8 hours. If the films were calcined in a lower oxygen atmosphere, pyrolysis occurred and the films appeared
brown in color and exhibited a smaller bandgap. To ensure complete combustion, ovens with poor seals or additional air intake were used.

The titania inverse opal showed (Figure 2.6a) a strong bandgap at 488 nm in ethanol. Assuming constant $d$ spacing from the original polystyrene lattice, the refractive index of the deposited titania was calculated by infiltrating the inverse structure with solvents of varying refractive indices (ethanol, $n = 1.36$ and toluene, $n = 1.50$) and measuring the stopband. The average refractive index of TiO$_2$ was found to be 2.4, slightly lower than the 2.5 known for anatase ($E_g = 3.2$ eV).$^{27}$ Since crystal diffraction reports 100% anatase (Figure 2.7), this index difference has been attributed to microporosity in structure.

Figure 2.6: Inverse TiO$_2$ structure obtained from a) an ordered opal film from 243 nm spheres and b) a disordered film from a ½ mixture of 150/243 nm spheres.
In order to shift the stopband further to the red and increase the filling fraction of titania, a second LPD was performed according to the conditions detailed in the first LPD. As previously reported, the stopband can be shifted from 10 to 20 nm by increasing deposition time up to 30 minutes. For these DSSC structures, the bandgap was fixed at 610 nm in ethanol, corresponding to a filling fraction of 43%.

### 2.2.2.3 Disordered Structures

Disordered films of titanium dioxide were grown by filling the voids of a disordered template of latex spheres by the same LPD protocol as described above, with calcination of the latex spheres in air at 400 °C for 8 hours. Disordered templates were assembled on FTO glass by evaporating a sonicated 0.08 wt% suspension of polystyrene
spheres of 243 nm diameter mixed with 150 nm diameter spheres in a 2/1 ratio, at 55°C under ambient conditions. Igepal was similarly added to the suspension at 0.003 wt% prior to sonication (30 min). To vary the void fraction, the prepared titania films thus prepared were subjected to a second LPD for 30 min by the same procedure reported above, after calcination of the latex spheres (Figure 2.6b). These films are termed disordered TiO_2_2 in reference to the second LPD step.

2.2.2.4 Bilayer Structures

Grätzel cells based on bilayer photonic crystals or disordered porous TiO_2/nanocrystalline TiO_2 structures were fabricated on FTO substrates. Once the TiO_2 inverse PC was fabricated on the substrate, nanocrystalline TiO_2 was applied to the top of the film, resulting in a bilayer structure. Nanocrystalline TiO_2 was synthesized according to previously published methods by the controlled hydrolysis of Ti(OiPr)_4 in acetic acid. Briefly, Ti(OiPr)_4 is slowly dripped into an 0°C solution of H_2O and acetic acid. The solution is then refluxed for 4 hours followed by autoclaving at 200°C for 12 hours. The solution is then concentrated to 12% TiO_2 and PEG/PEO block co-polymers are added. This synthesis results in 15-20 nm crystallites as calculated by the Scherrer equation.

The TiO_2 nanocrystalline slurry is applied to the top of the film via a doctor blade method (Figure 2.8). In general, two pieces of Scotch tape (3M) on either side of the substrate will result in film thickness of 10µm after calcination as seen in Figure 2.9. The film is then left to dry, tape is removed, and the film is calcined in air at 400°C for 1 hour. To prevent excess cracking, the film is sintered face-down on an FTO substrate
and to prevent Na\(^+\) or other ion migration from soda-lime or borosilicate glass into the TiO\(_2\) film.

Figure 2.8: Doctor-blade method for applying nanocrystalline TiO\(_2\) paste.

Figure 2.9: SEM image of a bilayer TiO\(_2\) photonic crystal/nanocrystalline TiO\(_2\) structure
2.2.3 Grätzel Cell Assembly and Testing

Prior to dye sensitization, titania films were dehydrated at 120 °C for 1 hour. Films were immersed at this temperature in a 0.3 mM solution of N719 dye in dry ethanol for 12-24 hours. Sensitized-electrodes were stored in dry ethanol in the dark. The amount of dye adsorbed onto the different structures was determined spectrophotometrically (by UV-vis absorption) after desorption in 3.8 M NaOH solution.

To assemble the Grätzel cell, a 50 µm PET spacer is sandwiched between the nanocrystalline/PC film and FTO counter electrode. Ohmic contact is made by soldering indium onto both the anode and cathode substrates followed by copper wire leads (24 gauge). The film is then infiltrated with iodide/triiodide redox electrolyte (Iodolyte TG50) by capillary action and held together with small binder clips. Short-circuit photocurrent measurements were made in a 3-electrode configuration using a Ag/AgCl reference electrode, by scanning between –5 mV to 5 mV at 1 mV/s (BAS electrochemical workstation, Bioanalytical Systems, BAS-100B/W) or in a two electrode system (Pine, AFRDE4) by holding the potential at 0 mV. Photoelectrodes were irradiated from a Xe lamp operated at 140 W (Oriel instruments, 6256, 150 W) and equipped with a monochromator (Oriel instruments, Model 77250); either in frontwall (through the electrolyte) or backwall (through the TiO₂ electrode) illumination modes. Short-circuit photocurrents (Isc) are reported after subtraction of dark currents. The lamp spectrum was acquired using a thermopile light detector (Ophir Optronics, Thermal surface absorbing head 2A-SH with NOVA-display) with 10 s average light measurements.
2.2.4 Characterization

UV-visible absorption and transmission spectra were collected using a diode array spectrophotometer (Hewlett-Packard, HP8452A). Absorption spectra of films on FTO were measured against the FTO substrate as a blank. Scanning electron micrographs were collected using a JEOL JSM5400 or JEOL 6700F FESEM microscope operated at 20 kV or 5kV, respectively, after sputtering a thin gold film. For thickness measurement, the surface was cut with a sharp surgical blade, and SEM images were acquired with tilt angles taken into consideration for the thickness calculation. A profilometer (Tencor Instruments Profilometer, Alpha 3.7-2) was also employed for routine thickness measurements. PXRD patterns of the TiO$_2$ inverse-opal (scraped off the FTO surface) were acquired using a Philips X-Pert MPD diffractometer (Cu K$_\alpha$ anode, operated at 40 kV, 40 mA) at a scan speed of 0.030 °2θ/s. High-resolution TEM images were acquired using a transmission electron microscope (JEOL 2010F) operated at 200 kV with a point-to-point resolution of 1.9 Å. TEM samples were deposited on Lacey carbon on copper grids.

2.3 Results

SEM imaging of colloidal crystals assembled from 243 nm polystyrene spheres showed the latex particles arranged in an fcc lattice, having undergone shrinkage to 215-217 nm during solvent evaporation (Figure 2.5b). The film had a stop-band in air centered at 520 nm, which corresponds to 217 nm polystyrene particles according to the Bragg equation applied to the close-packed crystal (26% void). Replication of this latex
colloidal crystal film with titanium dioxide resulted in the inverse-opal structure shown in Figure 2.6a. The titania inverse-opal had a stop-band centered at 488 ± 2 nm in ethanol \((n = 1.36)\), and 524 ± 2 nm in toluene \((n = 1.50)\). PXRD (Figure 2.7) showed the TiO₂ to be predominantly in the anatase crystal phase \(E_g = 3.2 \text{ eV}\), and HRTEM imaging (inset) showed nanocrystalline domain sizes of the order of 10 nm.

The absorption spectrum of the Ru-complex dissolved in ethanol or adsorbed on a nanoTiO₂ film is characterized by two absorption peaks of similar extinction coefficients at \(\lambda = 400\) nm and 535 nm (Figure 2.10). Adsorbing the dye onto a mesoporous titania photonic crystal with a stop-band centered at 488 nm results in an enhancement of absorbance at the red edge of the stop band, and an attenuation of absorbance at the blue edge. When the position of the stop-band was tuned to the red, the same effect was observed.\(^{27}\) This phenomenon is attributed to the appreciable bending of the photon dispersion curve at the edges of the photonic gap, and therefore the slowing of the group velocity of light (heavy photons) in photonic crystals at wavelengths near the gap.\(^{27, 56-59}\) At the red edge of the stop-band, the standing photon wave, or heavy photon, becomes localized in the high dielectric part of the photonic crystal, and at the blue edge the heavy photon is localized in the low dielectric part.\(^{27}\) This manifests itself by an increase in the absorbed light intensity by dye molecules localized in the high dielectric part of the structure. The same effect has been reported by Asher \textit{et al.} to result in increasing the plasmon absorbance of silver nanoparticles embedded in a silica photonic crystal.\(^{28}\) Vlasov \textit{et al.} also observed that femtosecond light pulses significantly slow down at the photonic band edges of a photonic crystal of 254 nm silica particles; delays as long as 100-150 fs have been reported.\(^{59}\)
When a dye-sensitized 6-µm thick TiO$_2$ inverse-opal with a 486 nm stop band was coupled to a 5-µm nanoTiO$_2$ film, the photoaction spectrum exhibited two maxima in accordance with the absorption spectrum of the photosensitizer, but a higher IPCE was observed at the bilayer compared to a 10-11 µm nanoTiO$_2$ film in both frontwall and backwall illumination in the 550-800 nm spectral region (Figure 2.11a and 2.11b, i and ii). This is consistent with our previous observation of IPCE enhancement for a photonic crystal (610 nm stop-band)/nanoTiO$_2$ bilayer in frontwall illumination. The low conversion efficiency at 400-450 nm results from attenuation of light by triiodide, which absorbs strongly at these wavelengths. The dip in the IPCE of the PC-TiO$_2$ bilayer at
480-500 nm in backwall illumination is caused by a lower light intensity reaching the nanoTiO₂ layer because of significant Bragg reflection at these wavelengths. Scattering at disordered regions in the photonic crystal and the higher amount of I₃⁻ in its open structure could account for the lower IPCE at the photonic crystal/TiO₂ bilayer relative to the nanoTiO₂ film at wavelengths shorter than 450 nm in backwall illumination.

To assess the role of internal light propagation and energy conversion in the photonic crystal itself, the IPCE at the dye-sensitized TiO₂ inverse-opal (stop band at 486 nm) in Figure 2.11 (iii) was compared to the IPCE of nanoTiO₂ films. Variations in IPCE at photonic crystal structures were 10-20% within one standard deviation of the mean value at different wavelengths, while the IPCE at nanoTiO₂ photoelectrodes varied by 7-10% within one standard deviation of the mean. The effective surface area of the 6-µm PC was found by dye adsorption measurements to be comparable to that of a 1.4-1.6 µm nanocrystalline TiO₂ film. At the peak wavelength of 540 nm, the short-circuit photocurrent density (J_sc) at a 10 µm nanoTiO₂ film was a factor of 2.9 (backwall) or 2.5 (frontwall) higher than the J_sc generated at the photonic crystal. Because of the high extinction coefficient of the photosensitizer at this wavelength, there is an inner filter effect in the nanocrystalline TiO₂ film, causing most of the incident light to be absorbed in the first few microns. On the other hand, at 680 nm where the dye has a low extinction coefficient, light is homogeneously absorbed and therefore the short circuit photocurrent increases in proportion to the nanoTiO₂ film thickness (or surface area).
Figure 2.11: Photoaction spectra in a) backwall illumination and b) frontwall illumination of a dye-sensitized (i) TiO$_2$ disordered inverse opal film/nanocrystalline TiO$_2$ bilayer, (ii) a nanocrystalline TiO$_2$ film, and (iii) the disordered TiO$_2$ inverse opal film. The TiO$_2$ nanocrystalline film and the bilayer structure are 10-11µm thick. Panel c) shows the IPCE (frontwall) normalized at 540 nm.
An enhancement factor (in the conversion efficiency) can be computed for the inverse opal titania structures relative to the nanocrystalline TiO$_2$ film as the ratio of surface area to IPCE at 680 nm. These results are summarized in Table 2.1. The monochromatic IPCE at 680 nm of the nanocrystalline film in frontwall illumination was a factor of 7.2 higher than that measured at the inverse opal, which is proportional within experimental error to its 7-times higher surface area. The linear dependence of IPCE on surface area at this wavelength indicates that this PC is converting light at the same efficiency per molecule of adsorbed dye as a nanocrystalline TiO$_2$ film, thus showing the absence of enhancement in light-harvesting due to internal multiple scattering in the PC in the red spectral range.

The improved light conversion at the bilayer at 550-800 nm is therefore a result of enhanced beam intensity at the nanocrystalline film due to its proximity to the PC, rather than to photon localization in the crystal. The increase in $I_{sc}$ at the photonic crystal/nanoTiO$_2$ bilayer at 680 nm relative to a nanoTiO$_2$ electrode was larger than the photocurrent generated at the photonic crystal itself, further supporting this conclusion. The photocurrent at the bilayer was also larger than expected from the contribution of the two layers if uncoupled. The synergistic effect on the light conversion efficiency resulting from the coupled architecture is summarized in Table 2.2. In this case, the monochromatic IPCE at 680 nm equals 25% at the bilayer in frontwall illumination compared to a mere 1.9% at the PC. Since the $J_{sc}$ at 680 nm is proportional to the thickness of the nanoTiO$_2$ film, a 5 µm thick layer would convert 680 nm light with a ~7% efficiency. This therefore constitutes a 16% enhancement in efficiency at this wavelength that is a direct result of the coupled architecture. It is believed that disorder,
originating possibly from template disorder caused by stacking faults and the sphere size
distribution, and from the chemical infiltration process, causes light scattering at the PC
thus enhancing the beam intensity at the nanocrystalline layer. This is discussed in
section 2.4 below.

To elucidate the role that ‘heavy’ photons at the edges of a photonic gap play in
determining the light conversion efficiency, the photonic crystal stop-band was shifted to
582 nm so it was positioned to the red of maximum dye absorption. Coupling this
sensitized 6-µm thick PC to a 5-µm nanoTiO$_2$ film resulted in a 36 % increase in the total
conversion efficiency in frontwall illumination relative to a nanoTiO$_2$ film of the same
thickness (Figure 2.12). The enhancement was predominantly in the spectral region of
580-800 nm (amounting to 94% of the energy gain). In backwall illumination, however,
the total light conversion efficiency at the bilayer was appreciably lower than at the
nanoTiO$_2$ film. This loss is attributed to attenuation of the incident light by scattering
and Bragg reflection at the photonic crystal. Nevertheless, a higher IPCE was still
achieved at the bilayer at wavelengths to the red of the photonic crystal stop-band.
Figure 2.12: Photoaction spectra in (a) backwall illumination and (b) frontwall illumination of a dye-sensitized (i) TiO$_2$ inverse opal (stop band at 580 nm)/nanocrystalline TiO$_2$ bilayer, (ii) a nanocrystalline TiO$_2$ film, and (iii) the TiO$_2$ inverse opal. The inverse-opal film is 6 $\mu$m thick, and the TiO$_2$ nanocrystalline film and bilayer structure are 10-11$\mu$m thick. The absorbance spectrum of this photonic crystal with ethanol filling the void is presented (right axis, panel a), showing the stop-band centered at 580 nm. Panel (c) shows normalized IPCE (frontwall), with spectra (iv) and (v) corresponding respectively to the sensitized PC of stop band at 488 nm, and the same PC coupled to a nanocrystalline TiO$_2$ film, presented for comparison.
If light localization in the photonic crystal does not play a major role in enhancing the IPCE, then enhanced scattering in disordered TiO$_2$ structures coupled to nanoTiO$_2$ films could also improve the light-conversion efficiency of the dye-sensitized cell. To test this hypothesis, disordered templates were assembled from mixtures of different size polystyrene particles (e.g., 150 nm and 243 nm) and were replicated with TiO$_2$. An SEM image of the resulting 4.5 µm-thick structure is shown in Figure 2.6b, revealing the level of disorder and the nanoparticulate nature of the film. When the cell was operated in frontwall illumination, this disordered titania structure (LPD1) coupled to a nanoTiO$_2$ layer resulted in a 10% photocurrent gain compared to a nanoTiO$_2$ film of the same thickness (10 µm), as shown in Figure 2.13. The gain was mainly measured in the 580-800 nm spectral range, amounting to a 24% higher efficiency relative to the nanoTiO$_2$ film (Table 2.2). When operated in backwall illumination, however, a lower total IPCE resulted at the bilayer, as a result of scattering at the disordered layer, which reduces the intensity of the light reaching the nanocrystalline TiO$_2$ film. Pronounced scattering at the disordered structure compared to the transparent nanoTiO$_2$ film was further evidenced by UV-visible transmission spectra in ethanol, shown in Figure 2.14. Despite the lower efficiency in backwall illumination, an improvement in IPCE was still measured at the bilayer electrode in the 600-800 nm spectral range. Interestingly, recent simulations have predicted a decrease in light harvesting efficiency if only a photonic crystal layer was present, since the gain in enhancement would be less than the attenuation from middle-gap reflections.$^{30}$
Figure 2.13: Photoaction spectra in (a) backwall illumination and (b) frontwall illumination of a dye-sensitized (i) TiO$_2$ disordered inverse opal film/nanocrystalline TiO$_2$ bilayer, (ii) a nanocrystalline TiO$_2$ film, and (iii) the disordered TiO$_2$ inverse opal film. The TiO$_2$ nanocrystalline film and the bilayer structure are 10-11µm thick. Panel (c) shows the IPCE (frontwall) normalized at 540 nm.
An enhancement factor of 1.5 in the conversion efficiency at 680 nm resulted in this disordered film relative to a nanoTiO₂ film of the same surface area, which is attributed to multiple internal scattering in the disordered film. The longer pathlength of light in the disordered structure however cannot account for the entire energy gain at the bilayer electrode. For example, the IPCE at 680 nm at the 4.5 µm disordered titania (equivalent to 2.8-3.1 µm thick nanoTiO₂) in frontwall illumination equaled 6%.

Therefore, based on an estimated 8 % conversion efficiency at a 6 µm thick nanoTiO₂ film at this wavelength, a 7% additional enhancement in IPCE at 680 nm at the bilayer can be attributed to enhancement from interfacial scattering.

When the disordered structure was subjected to a second LPD filling, the red-light conversion efficiency was increased beyond that of the original disordered film, with an enhancement factor of 2.6 at 680 nm relative to a nanoTiO₂ film of the same area.
(Table 2.1). Furthermore, a significantly higher enhancement resulted when this disordered TiO$_2$ film was coupled to a nanocrystalline TiO$_2$ layer. This gave more than an 80% increase in the conversion efficiency in the 580-800 nm spectral range in frontwall illumination relative to a 10 $\mu$m nanoTiO$_2$ film (Figure 2.15b). In this case as well, a conversion efficiency of 12 % at the 4.5 $\mu$m film at 680 nm did not account for the entire 35% IPCE at this wavelength. A synergistic effect of 15% IPCE is attributed to scattering at the interface of the coupled architecture. Normalized IPCE spectra yield equivalent red enhancement for both the photonic crystal (280 nm stopband) and disordered TiO$_2$ film, demonstrating the pronounced effects of scattering and localization versus purely photonic effects (Figure 2.16). A summary of these results comparing the gains of the different structures is presented in Tables 2.1 and 2.2.
Figure 2.15: Photoaction spectra in (a) backwall illumination and (b) frontwall illumination of a dye-sensitized (i) TiO$_2$ disordered inverse opal film (LPD 2) /nanocrystalline TiO$_2$ bilayer, (ii) a nanocrystalline TiO$_2$ film, and (iii) the disordered TiO$_2$ inverse opal film. Panel (c) shows the IPCE (frontwall) normalized at 540 nm.
Figure 2.16: Normalized frontwall photoaction spectrum of a dye-sensitized (i) TiO$_2$ inverse opal bilayer (580 nm stopband), (ii) nanocrystalline TiO$_2$, and (iii) disordered inverse opal TiO$_2$. Absorbance curves for (iv) the inverse opal photonic crystal and (v) the disordered inverse TiO$_2$ structure are present on the right hand axis.
Table 2.1: IPCE ratio at a nanocrystalline TiO$_2$ film and photonic crystal (PC) or disordered titania inverse opal, compared to the ratio of respective surface areas, and the corresponding enhancement factor in the conversion efficiency in the red.$^{a,b}$

<table>
<thead>
<tr>
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<th>Surface area ratio</th>
<th>IPCE ratio</th>
<th>Enhancement factor</th>
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<tr>
<td><strong>TiO$_2$ to PC (486 nm)</strong></td>
<td>7</td>
<td>7 at 680 nm</td>
<td>1 at 680 nm</td>
</tr>
<tr>
<td><strong>TiO$_2$ to PC (582 nm)</strong></td>
<td>4.8</td>
<td>3.8 at 680 nm</td>
<td>1.3 at 680 nm</td>
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<tr>
<td></td>
<td></td>
<td>3.3 at 640 nm$^c$</td>
<td>1.5 at 640 nm</td>
</tr>
<tr>
<td><strong>Disordered TiO$_2$ (LPD1)</strong></td>
<td>3.5</td>
<td>2.3 at 680 nm</td>
<td>1.5 at 680 nm</td>
</tr>
<tr>
<td><strong>Disordered TiO$_2$$_2$ (LPD2)</strong></td>
<td>3.4</td>
<td>1.3 at 680 nm</td>
<td>2.6 at 680 nm</td>
</tr>
</tbody>
</table>

$^a$ Frontwall illumination

$^b$ The enhancement factor resulting from the internal localization in the PC or disordered inverse opal film is computed as the surface area ratio to the IPCE ratio.

$^c$ Reported at 640 nm, close to the red edge of this PC stop band (at 582 nm)
2.4 Discussion

Nanocrystalline TiO$_2$ films are transparent because the particles are very small ($d = 10$-30 nm) and the films have a high packing density. Monte Carlo simulations based on solutions of the Maxwell equation revealed that about 99% of the incident light penetrates a TiO$_2$ film of 30 nm particles without scattering.$^{61}$ Ferber and Luther$^{62}$ predicted that addition of larger titania particles will appreciably increase solar absorption because of enhanced multiple scattering in the film. They showed (using a numerical solution to the radiative transport equation) that adding 250-300 nm TiO$_2$ particles at 5 wt% to 20 nm particles results in a 27% energy gain in the solar absorption of a 10 µm

<table>
<thead>
<tr>
<th></th>
<th>IPCE of PC or disordered</th>
<th>IPCE of nanoTiO$_2^{b}$</th>
<th>IPCE for bilayer</th>
<th>Synergistic enhancement</th>
<th>Gain at 580-800 nm$^{c}$</th>
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<tr>
<td>6 µm PC (486 nm)</td>
<td>2 %</td>
<td>7% (5µm)</td>
<td>25%</td>
<td>16%</td>
<td>29 %</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>61 %</td>
</tr>
<tr>
<td>6 µm PC (582 nm)</td>
<td>4 %</td>
<td>7% (5µm)</td>
<td>27%</td>
<td>16%</td>
<td>38 %</td>
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<td></td>
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<td></td>
<td>70 %</td>
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<td>24 %</td>
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<td></td>
<td></td>
<td></td>
<td>26 %</td>
</tr>
<tr>
<td>4.5 µm TiO$_2$ disordered 2</td>
<td>12 %</td>
<td>8% (6µm)</td>
<td>35%</td>
<td>15%</td>
<td>71%</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>83 %</td>
</tr>
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</table>

$^{a}$frontwall illumination
$^{b}$computed from a 14-15% IPCE measured at 10 µm TiO$_2$ film at 680 nm, based on the homogeneous light absorption at this wavelength.
$^{c}$First row computed from IPCE data normalized at 540 nm for the bilayer relative to the nanoTiO$_2$ film of same thickness. Second row (in italics) computed from measured % IPCE.
film, calculated to be predominantly in the 550-750 nm spectral range where the dye extinction coefficient is low. A similar gain in light absorption was obtained for a 2 µm scattering layer of 270 nm TiO₂ particles applied onto an 8 µm nanocrystalline TiO₂ film. The same approach was predicted by Usami to improve light-harvesting at these films. The structures studied in this work constitutes a geometrically similar bilayer architecture with comparable sphere size (e.g., 217 nm holes in the single LPD inverse opal), and the gain in the light conversion efficiency at long wavelengths agrees well with the theoretical prediction of enhanced absorbance as a result of scattering. Nevertheless, a marked difference is observed because of the different internal geometry of the bilayer photonic crystal TiO₂/nanoTiO₂ arrangement. Mihi and Miguez have found that a bilayer structure induces photon localization for specific frequencies within the nanocrystalline portion of the bilayer structure, therefore increasing the probability of photons in this frequency range being absorbed.

With a high enough degree of scattering in disordered media, light transport is halted as a result of interference of waves that have undergone multiple scattering events, making the elastic mean free path on the order of the wavelength of light. This regime of strong light localization, known as Anderson localization of light, is a similar phenomenon to the Anderson localization of electron waves, which yields a transition from a conducting state to an insulating state in highly disordered semiconductors. Anderson localization of light has been reported for several systems, such as films of highly disordered GaAs powders (e.g., 1 µm and 300 nm diameter), and macroporous GaP structures. It was also predicted by John that disorder at photonic crystals can lead to Anderson localization of light in these media, in what he
described as a “delicate interplay between order and disorder”. Before the onset of strong localization, enhanced backscattering, also known as the weak localization regime, takes place as a result of constructive interference between counterpropagating waves in disordered media. Disorder is common in self assembled photonic crystals as a result of the sphere size distribution, stacking faults, and the chemical infiltration processes, and models have shown positive contributions to photocurrent enhancement as a result of scattering in these disordered regions. Koenderink et al. reported enhanced backscattering from photonic crystals of polystyrene opals and air spheres in titania, with enhancement factors between 1.2 and 1.85 depending on the crystal. To study localization of light in disordered media, the backscattered intensity can be measured as a function of the angle above the diffuse background, and the width of the cone exhibiting a maximum in the back scatter direction is taken as a measure of the degree of localization, the width being inversely proportional to the transport mean free path. The backscattering cone was shown to be wider at wavelengths to the red of the stop band, indicating a shorter mean free path and a higher degree of scattering, and to narrow within the stop band from the red to the blue edge. Backscattering in this medium was modeled by diffusion theory in disordered media after incorporating the effect of the photonic band.

Accordingly, and in addition to Bragg diffraction by the periodic lattice, other mechanisms of light propagation in effect at photonic crystals and at disordered titania structures affect the light-conversion efficiency of these bilayer photoelectrodes. The first mechanism is the localization of light near a photonic gap, whereby light waves with wavelengths at the red edge of the stop band have higher amplitude in the medium with
the higher refractive index and nodes in the medium of the low refractive index. This mechanism can be maintained in the presence of disorder in a photonic crystal, as an amorphous semiconductor retains the existence of an electronic mobility gap or pseudo gaps. The second mechanism consists of multiple scattering at disordered regions in the structure; internal multiple scattering can cause an increase in the pathlength of light, and if the magnitude is high enough it will result in weak localization and enhanced backscattering (and ultimately in Anderson localization). Enhanced backscattering coupled with diffusely scattered background and forward scattering where present, will affect the absorption of light at the coupled nanocrystalline film in the bilayer, onto which the scattered beam is directed; this will be manifested in a strong dependence on the direction of illumination.

The results of this study are interpreted based on these light propagation mechanisms. At a photonic crystal with a stop-band centered at 488 nm, localization of heavy photons predicted by the periodicity of the refractive index does not extend to wavelengths of 600-800 nm where absorption of the dye molecule is low. When this photonic crystal is coupled to a nanoTiO₂ film, Bragg diffraction results in a decrease in the IPCE in backwall illumination within the photonic gap. Scattering at disordered regions in the photonic crystal enhances the intensity of light in the nanoTiO₂ film, thus increasing the conversion efficiency in the 550-800 nm spectral region in frontwall and backwall illumination. It appears however from comparison of the spectra in Figure 2.11a and the normalized spectra in Figure 2.11c that neither backscattering nor forward scattering is particularly enhanced in this photonic crystal above diffuse scattering. Enhanced backscattering would be manifested in a higher gain in the light
conversion efficiency in frontwall illumination relative to backwall illumination. The absence of evidence for enhanced backscattering at 550-800 nm is taken as an indication of the lack of any (weak) localization that would be caused by significant internal scattering at disordered regions. This is consistent with the observation that this dye-sensitized photonic crystal electrode converts light in this spectral range at the same efficiency as a nanoTiO$_2$ film of identical surface area.

On the other hand, by shifting the photonic crystal stop band to 582 nm, its light conversion efficiency at 600-800 nm per molecule of adsorbed dye increases beyond that of a nanoTiO$_2$ film. This is attributed in part to heavy photons localized at the edge of the 582 nm stop-band, in a spectral range where the dye has a low extinction coefficient. Furthermore, to re-position the stop-band, the photonic crystal was subjected to a second LPD step, which induces more disorder and causes higher internal scattering. Increased disorder is evident from the increase in the width-at-half-height of the photonic crystal spectral gap region and the higher degree of scattering measured in the UV-visible absorption spectra following the second LPD step (Figure 2.11a and Figure 2.12a, secondary absorbance axes). In the photonic crystal/nanoTiO$_2$ bilayer, the significant attenuation in the conversion efficiency in backwall illumination relative to a nanoTiO$_2$ film at wavelengths falling outside the L-gap can also be attributed to significant scattering caused by a high degree of disorder. In this case, the measured IPCE gain at 680-800 nm (in backwall illumination, beyond the small effect accounted for by internal localization at this photonic crystal) must be caused by diffusely scattered light, or a degree of forward scattering enhancing the light intensity at the nanoTiO$_2$ layer. It follows that the higher gain at 680-800 nm in frontwall relative to backwall illumination
is a result of enhanced backscattering over the diffuse background in the crystal, 
enhancing the light intensity at the nanoTiO₂ layer in frontwall illumination.

Light scattering in the disordered TiO₂ film increasing the pathlength of light 
must have also caused its slightly higher conversion efficiency at 550-800 nm compared 
to a nanoTiO₂ film of comparable surface area (e.g., enhancement factor of 1.5 at 680 
mm). When the disordered TiO₂ structure was coupled to a nanocrystalline TiO₂ film, the 
IPCE was lower at 450-580 nm in backwall illumination relative to the nanocrystalline 
TiO₂ film, consistent with significant scattering in the disordered film. Since the higher 
light conversion in the long wavelength range in backwall illumination compared to the 
nanoTiO₂ electrode must be due to a degree of diffuse or forward scattering, the more 
pronounced attenuation in the IPCE at 450-580 nm relative to the enhancement at 580-
800 nm, and the higher degree of IPCE enhancement in frontwall illumination compared 
to backwall illumination show that backscattering is enhanced over diffuse and forward 
scattering at the disordered film. This is an indication of a degree of weak light 
localization at this structure.

The second LPD step increases the degree of internal scattering by inducing 
further disorder in the structure and a change in the void size. The resulting increase in 
the pathlength of light explains the significant monochromatic IPCE of 12 % at 680 nm at 
this sensitized photoelectrode, appreciably higher than the original disordered film, 
amounting to an enhancement factor of 2.6 relative to a conventional nanocrystalline 
electrode of the same surface area. The measured 80% higher conversion efficiency in 
frontwall illumination when this film was coupled to a nanoTiO₂ film relative to a 
nanoTiO₂ photoelectrode is attributed to significant localization of light and the resulting
scattering at the interface. Furthermore, the higher enhancement in the red spectral region in frontwall compared to backwall illumination, relative to the nanoTiO$_2$ electrode, is indicative of enhanced backscattering over the diffuse or forward background, a manifestation of light localization in the disordered TiO$_2$ film.

2.5 Conclusions

Light propagation in scattering films of titania photonic crystals or disordered scattering titania inverse opal structures was exploited to increase the light conversion efficiency of dye-sensitized nanocrystalline TiO$_2$ solar cells. Higher conversion efficiency in the spectral range of 600-800 nm where the RuL$_2$(SCN)$_2$ dye has a low extinction coefficient was observed at disordered titania structures and inverse-opals with properly positioned stop bands, and at bilayer electrodes of photonic crystals and disordered layers coupled to nanocrystalline TiO$_2$ films. Multiple scattering events at disordered regions in the ordered and disordered inverse opals, and to a lesser extent localization of heavy photons at the edges of a photonic gap, account for the improved light-harvesting behavior of these structures. This approach provides an alternative to re-design of the sensitizer as a means of increasing the efficiency of dye-sensitized nanocrystalline TiO$_2$ cells.
2.6 References


46. Stober, W.; Fink, A.; Bohn, E., Controlled growth of monodisperse silica spheres in the micron size range. *J. Colloid Interface Sci.* **1967**, 26, 62.


Chapter 3

Improved Solar Efficiencies for Photonic Crystal Enhanced Dye Cells

3.1 Introduction

As described in Chapter 2, adding disordered scattering centers into a path of incoming light leads to enhanced photoconversion efficiency in the standard dye cell, or Grätzel cell. The previous work focused on the effect of a photonic crystal or “disordered” photonic crystal coupled to a standard nanocrystalline TiO$_2$ film. Although this bilayer structure provides moderate enhancement to the photoconversion efficiency, it is not an optimal structure for the assembly and practical use of a dye cell. One issue is that of light attenuation in the cell. Our typical structure design is a TiO$_2$ inverse opal grown on top of an FTO substrate, followed by the application of the nanocrystalline film. In this structure, the nanocrystalline film is the main source of photocurrent and amplification,$^1$ but it is not placed in the optimal geometry. In a standard Grätzel cell, irradiation comes from the anode side (“through dye”, or “backside”), directly into the nanocrystalline framework. This is an optimal light path for a number of reasons, including minimizing both the electron diffusion length and absorption of light by the electrolyte and counter electrode, it is not the most effective for photocurrent enhancement by light localization.$^2$ If light were to pass through the cathode side first, the light would undergo attenuation by the cathode, which in this case could not be platinized. This would decrease efficiency by not catalyzing the reduction of the I$_3^-$ ion.
The incoming photons must then pass through the redox electrolyte, which is strongly absorbing in the blue, at wavelengths up to ~450 nm. The remaining photons are then efficiently absorbed by the Ru dye, but farthest from the collecting anode. Since the majority of photons are collected within the first 2-3 µm of the film, the electrons must percolate through the polycrystalline TiO$_2$ network without undergoing recombination with the redox electrolyte. The alternative is to illuminate the bilayer structure through the anode. When the photonic crystal is directly attached to the anode however, light passing through this side is Bragg reflected at the stopband wavelength of the photonic crystal, causing a decrease in the photoconversion efficiency as photons are primarily backscattered out of the dye cell. The influence of this effect can be seen in Figure 3.1, where IPCE is decreased at the exact position of the photonic stopband. As photocurrent conversion is dependent upon distance from the anode the light that is not first Bragg reflected becomes absorbed relatively far from collecting electrode, causing the photocurrent efficiencies to decrease. A possible cell redesign would be to place the photonic crystal on the cathode side, thereby Bragg reflecting any non-absorbed photons back onto the dye-sensitized film. In practice, however, no enhancement was experimentally detected in this structure and was further verified to be ineffective by scattering simulations performed by the Crespi group. A more efficient cell architecture would be to place the nanocrystalline TiO$_2$ layer on the anode followed by growth of the photonic crystal. This allows for anode side illumination while also providing the backscattering amplification from the photonic crystal layer. This design has been experimentally realized by modification of the original bilayer deposition method.
Both the nanoTiO$_2$-on-PC and PC-on-nanoTiO$_2$ bilayer structures are assembled vertically so enhancement arises from vertical backscattering of light. A potentially more efficient means of scattering would be to horizontally assemble layers of nanocrystalline TiO$_2$ and photonic crystals side by side. Scattering would occur at each photonic-nanocrystalline TiO$_2$ interface, thereby increasing localization and photoconversion efficiency in the low extinction portion of the dye absorbance spectrum. In this structure, the photonic crystal is again fabricated from templated colloidal spheres, which are first assembled in lithographically defined channels. The remaining channels are then infiltrated with nanocrystalline TiO$_2$ followed by adsorption of dye. Although this project is not yet complete, a preliminary representation is shown in Figure 3.2.

![Figure 3.1: IPCE spectrum of (—) a bilayer with anode side irradiation and (-□-) corresponding photonic bandgap of the 2nd TiO$_2$ LPD from 243 nm spheres.](image)
Figure 3.2: Image and diagram of a horizontally stacked Grätzel cell scattering structure. The SEM image (a) shows 243 nm spheres crystallized inside 20 \( \mu \)m lithographically defined channels (photoresist borders) and inset shows the extended structure. After this step, diagram (b) illustrates the infiltration with nanocrystalline TiO\(_2\) paste. Anode side illumination results in light scattering and Bragg reflecting horizontally throughout the structure.
3.2 Experimental

Many of the same techniques for fabricating Grätzel cells in Chapter 2 were used in this work with some technical modifications. All materials were used without further purification. Nanocrystalline TiO₂ was synthesized as previously mentioned, but hydroxypropylcellulose was used as a binder rather than PEO and PEG polymers. Film thickness was determined by profilometry (Tencor 500 Alpha Step) or SEM. A 0.05 M TiCl₄ solution (aq) was used as both a blocking layer and to increase surface contact of the nanocrystalline TiO₂ by placing the solution on the TiO₂ film and heating at 70°C for 30 minutes. TEC 15 FTO glass (Pilkington) was used as anode and cathode electrodes. The counter electrode was coated with Pt by first sputtering a 100 nm Cr adhesion layer followed by 600 nm of Pt, unless otherwise noted. To further increase the surface area of the Pt counter electrode, a solution of 5 mM H₂PtCl₆ · 6H₂O in EtOH was dropped on to the electrode followed by heating in air 380°C. A piece of 50 µm thick PET was used as a spacer. It was found that Iodolyte TG-50 (Solaronix, S.A.) was a poor electrolyte and decreased efficiency by 1-2 %, and a I⁻/I₃⁻ redox electrolyte was prepared from the synthesis of 1,2-dimethyl-3-propyl imidazolium iodide according to the literature procedures. The ionic liquid was prepared by equimolar dropwise addition of 3-iodopropene (Sigma Aldrich) to a solution of 1,2-dimethylimidazole (Avocado) in 1,1,1-trichloroethane followed by reflux. After 2 hours, the top yellow solution was decanted off and the remaining brown oily liquid was washed twice with hot trichloroethane to yield a fluffy brown solid in 75 % yield. The electrolyte solution was made from 0.6 M 1,2-dimethyl-3-propyl imidazolium iodide, 0.05 M I₂, 0.5 M t-butyl pyridine, and 0.1 M
LiI in 85:15 (v/v) acetonitrile/valeronitrile. Concentrations were prepared as recommended by researchers Nathan Neale and Jao van de Langemaat at NREL (Golden, CO). Photonic crystals were grown on FTO counter electrodes by using standard evaporation techniques, followed by TiO₂ replication. Platinized PC counter electrodes were produced by first coating the FTO with Pt-Catalyst T/SP (Solaronix, S.A.) and calcining at 200°C for 1 hour followed by growth of the PC and TiO₂ infiltration.

3.2.1 Photonic crystals on nanocrystalline TiO₂

To produce photonic crystals on nanoTiO₂ films, the films had to be first backfilled with polymeric material. Sintered nanocrystalline films of standard thickness (10 µm) were fabricated on FTO glass. The polymer backfiller was synthesized by the copolymerization of methylmethacrylate (0.8 mol) and methacrylic acid (0.2 mol) in 1% (w/v) AIBN at 60°C. The copolymer was dissolved in DMF to final concentration of 1 wt % and acetone was added to the solution to make the final concentration 0.8%. The polymer was spin cast onto the TiO₂ films by first applying the solution to the film and allowing it to wet for 1 minute. The solution was then spun off at 1500 RPM and the film was briefly heated to 150°C for 15 sec. until the DMF was evaporated. This cycle was repeated 4 times and the sample was then immersed in a 0.1 % solution of 291 nm or 243 nm carboxyl modified latex spheres (medium acid content, Seradyn, Inc.) and left to evaporate at 55°C. The deposited colloidal crystal was then infiltrated with TiO₂ by a single LPD step described in section 2.2.2.1. The samples were then calcined in air at 400°C for 8 hours, then sealed with a 0.05 M TiCl₄ solution and sensitized in ethanolic
0.3 mM N719 dye. The scheme is illustrated in Figure 3.3. For comparison, photonic crystal / nanoTiO₂ bilayers were fabricated in the same manner as chapter 2.

![Figure 3.3: Scheme depicting the fabrication and assembly of a TiO₂ inverse opal onto nanocrystalline TiO₂. Only a single LPD step is possible for this cell.](image)

**3.2.2 Indoor Cell Testing**

Current-voltage and IPCE measurements were made in a 2-electrode setup using a Keithley 2400 sourcemeter and controlled by in-house Labview applications. Lamp intensity data was collected using a Molelectron EPM 2000 power meter with PM3 thermopile head. Scans were performed under constant power conditions with a 150W Xe
lamp (Oriel). Current-voltage characteristics were obtained under 1 sun intensity (~100 mW/cm²) unless otherwise noted and intensity adjusted by using neutral density filters along the beam path. A glass cuvette filled with water was used as an IR filter to minimize heating and a UV filter (LP400, Melles Griot) was used to filter UV bandgap irradiation. The cell was placed in the path of the incident light and scanned from $I_{sc}$ (0 mV) to $V_{oc}$ (~ 720 mV) at 68 mV/s with 16 mV increments and 10 point averaging at each increment. To test IPCE performance, the cell was placed on the output side of a monochromator under maximum lamp intensity, typically 5.5 mW at 480 nm. The monochromator was controlled using a stepper motor and in-house Labview software, and slits were fully opened to 3 mm. $I_{sc}$ values were obtained at 5 nm increments from 350 – 800 nm with 10 point averaging at each increment. The lamp spectrum was obtained in a similar manner by placing the thermopile head at the output of the monochromator.

### 3.3 Results

A great deal of effort has been made to synthesize a highly efficient Grätzel cell, typically 10 – 12 % as reported by Grätzel’s group. This proved to be experimentally challenging in our hands as there is little literature that fully details the fabrication process. Our cells have a maximum efficiency of 5.1 % using a Xe light source, and would be approximately the same under AM1.5 sunlight. Although this is lower than the highest reported dye cell efficiency, the results presented here should scale linearly with more efficient cells. Better cells could in principle be produced by further purification of
the N719 dye, using smaller sample areas, and more precise layer thicknesses. Cell efficiency, $\eta$, is defined as see in Eq. 3.1

$$\eta = \frac{V_{oc} \cdot J_{sc} \cdot ff}{E} \tag{3.1}$$

Where $E$ is the irradiation power, and $ff$ is defined as Eq. 3.2

$$ff = \frac{P_{max}}{V_{oc} \cdot J_{sc}} \tag{3.2}$$

Where the maximum power point, $P_{max}$, is the product of $i \cdot V$ at the maximum power point. Ideally, the fill-factor would be unity, but does not occur in real solar cells due to deviation from diode ideality, shunt, and series resistance in the cell. The cells fabricated in our lab suffer from low $I_{sc}$, which could be due to a number of factors including TiO$_2$ impurities and low dye loading leading to poor electron injection.$^9$ Large series resistance, however, would be indicated by not only decreased $I_{sc}$, but also by low $V_{oc}$ and poor fill-factors.$^6$

3.3.1 Photonic crystals on nanocrystalline TiO$_2$

Bilayer DSSCs with the PC structure on top of the nanocrystalline layer should result in an enhancement by anode side illumination similar to the reverse structure irradiated on the cathode side. Attempts to directly fabricate inverse TiO$_2$ photonic crystals on sintered nanocrystalline TiO$_2$ using the standard LPD method are described in Chapter 2. Colloidal crystals from polystyrene spheres deposited very well on the TiO$_2$ film, but in all cases, the nanocrystalline films peeled away from the FTO glass before the LPD procedure was complete. Although decreasing the reaction temperature and
increasing the solution pH helped to prevent the delamination, the films frequently delaminated after sintering and resulted in poor solar performance from low dye uptake. It is believed that the LPD process hydrolyzes TiO$_2$ in the mesoporous structure of the nanocrystalline TiO$_2$, hence lowering the surface area and decreasing dye uptake. To prevent this from occurring and aid in film adhesion, the nanocrystalline film was backfilled with a hydrophilic polymer. The as-cast film allowed minimal dye uptake when placed in an ethanolic N719 solution, suggesting that the LPD process would not infiltrate the microporous TiO$_2$ network. First attempts at backfilling with a polymer solution used a copolymer of poly(styrene/methacrylic acid), but SEM showed a thick polymer layer on top of the TiO$_2$ film and colloidal crystals did not deposit well on the film, presumably due to the hydrophobicity of the poly(styrene) and spin-casting from toluene. A more hydrophilic polymer solution was made from poly(methyl methacrylate/methacrylic acid) in DMF/acetone. The solution appeared to wet the TiO$_2$ film better as water had a lower contact angle (58°) on this film as compared to the poly(styrene/methacrylic acid) copolymer (91°). After colloidal crystal deposition and TiO$_2$ LPD, the films were calcined at 400°C to burn away the PS spheres and the backfilled polymer. Figure 3.4 shows the polymer layer on top of the TiO$_2$ film after spin-casting. Intuitively, one would believe the polymer film would act as a sacrificial spacer and prevent good adhesion of the PC layer to the nanocrystalline TiO$_2$ during calcination, but the films adhered well, even when subjected to a high-pressure air stream. This is presumably due to slight sintering of the deposited TiO$_2$ particles with the nanocrystalline film.
Work in our group has determined that both a photonic crystal and nanoTiO$_2$ films must be present in the Grätzel cell structure to contribute to the IPCE enhancement in the red portion of the dye absorbance spectrum. To better understand the role of the specific placement of these films with respect to one another the PC layer was placed on the counter-electrode side of the Grätzel cell allowing for anode-side irradiation, which contributes to the backscattering necessary for enhancement. This was done by growing a photonic crystal from 243 nm spheres on the FTO counter electrode either with or without a Pt catalyst underlayer. The photonic crystal then underwent 2 LPDs to maximize the IPCE enhancement. The cells were assembled to minimize the space between counter and working electrodes, decreasing attenuation by I$^-$/I$_3^-$ absorption and scattering. The estimated distance from the top of the nanoTiO$_2$ layer to the top of the photonic crystal was 9 µm (Figure 3.5). Although the cells exhibited a strong stopband at

Figure 3.4: Polymer film spin cast on a 10 µm thick nanocrystalline TiO$_2$ film.
580 nm, the IPCE spectra demonstrate a lack of enhancement for a photonic crystal over a standard Pt FTO counterelectrode (Figure 3.6). The maximum IPCEs are nearly equivalent within error and the normalized spectrum shows equivalent spectra, indicating the junction of the photonic crystal and the nanoTiO₂ layer is necessary for photocurrent enhancement.

Figure 3.5: Grätzel cell assembly for a photonic crystal placed on the counter electrode.
Photocurrent enhancement of the visible spectrum was accomplished by setting the stopband of the inverse opal to the red edge of the dye maximum at ~540 nm. The crystallized 291 nm sphere showed a strong stopband at 630 nm. After infiltration and calcination, the bandgap shifted to 581 nm in ethanol (Figure 3.7) and showed a strong orange colored reflectance in ethanol. For comparison, films produced from 243 nm spheres exhibit a narrow strong stopband at 500 nm after a 1st LPD and shifts to a wider FWHM reflection at 580 nm during the 2nd LPD. An image of a typical Grätzel cell film compared to the bilayer qualitatively shows strong red light absorption and appears black compared to the red Grätzel cell (Figure 3.8). The film thickness of the nanocrystalline TiO$_2$ was 13.2 µm and the 291 nm replica was 13.5 µm with pore sizes of 212 nm, as determined by profilometry and SEM (Figure 3.9). The 26.7 µm film had a dye surface
coverage of 114 nmol/cm², comparable to a typical Grätzel cell with 14 µm thickness.

This change in absorption directly leads to an increase in efficiency over the red portion of the spectrum since the light that would otherwise pass through the cell is now being absorbed without a large increase in the overall thickness of the cell.

Figure 3.7: Transmittance spectrum of a polystyrene colloidal crystal from 291 nm spheres in air (—) and the crystal after a first (−−−−) and second (—−−−−−) infiltration and calcination (in EtOH).
As seen in Figure 3.10, IPCE measurements yield a 10.5% increase in short-circuit photocurrent integrated over the range from 540 nm – 750 nm and a 2.8% decrease over the 400 – 800 nm range as compared to a standard Grätzel cell. Although the enhancement is negligible in the non-normalized structure, it is apparent that there is a higher photon to current enhancement in the red side of the spectrum. It is not unusual for there to be sample to sample variations with IPCE_{max} differences of up to 20% for equivalent samples and can be attributed to thickness, dye loading, and environmental factors. For that reason, normalized spectra are essential in examining current enhancement in IPCE spectra. Though the efficiency enhancement is lower than that found by Halaoui et al.\textsuperscript{10} for the reverse bilayer structure, these structures do not exhibit the loss in efficiency due to I^-/I_3^- absorption and electron recombination. In fact, efficiency for the 291 nm PC-on-nano cell was recorded as 4.47% whereas the efficiency for the reverse nano-on-PC single LPD structure is only 3.24% most likely due the

Figure 3.8: Optical image of a) a photonic crystal/nano bilayer (114 nmol/cm\textsuperscript{2} dye) and b) standard nanocrystalline film (104 nmol/cm\textsuperscript{2} dye) illuminated through a light box with equivalent dye coverage. The light path is through the nano layer, then the PC.
proximity of dense nanocrystalline close to the anode surface. This demonstrates that there is not only an enhancement in the red portion of the dye absorption, but the overall efficiency is comparable to a standard Grätzel cell, 4.7% for an 8 µm film. Grätzel cell bilayer films from a single TiO$_2$ infiltration of 243 nm spheres resulted in a lack of red enhancement (Figure 3.10) as well as a low photocurrent efficiencies (Figure 3.10, inset), presumably from the stopband being located in the dye absorbance maximum, rather than to the red of it.

Figure 3.9: Single deposition inverse opal structure from 291 nm PS spheres measuring 13.5 µm thick.
Measurement of $i$-$V$ curves with non-platinized electrodes resulted in extremely different cell characteristics, illustrating the problems with using transparent counter electrodes and cathode-side irradiation. Figure 3.11 shows $i$-$V$ curves for Grätzel cells in which unmodified FTO was used for both cathode and anode electrodes, with anode side irradiation. For comparison, the $i$-$V$ curve using a Pt counter electrode is also presented. The lack of catalytic material to aid in the reduction of the $I_3^-$ to $I^-$ creates overvoltage losses that lower exchange current densities and cause reactions at the counter electrode to be rate limiting in the cell.\(^3\) Experimentally, this limits the $I_{sc}$ to 17% of the value obtained in the presence of a Pt catalyst layer. Thus, although cells with bilayer nano-PC layers show increased red enhancement in the IPCE spectra,\(^{10}\) the IPCE values are much lower, 20 % compared to 60% at 540 nm and virtually zero power can be extracted from

![Normalized IPCE spectra](image-url)
this cell configuration. For this reason, anode side irradiation in the presence of a catalytic counter electrode is essential to the proper functioning and efficiency gains expected from bilayer structures.

Figure 3.11: Current-voltage curves for 291 nm bilayer cells without the presence of a Pt counter electrode. Cathode side irradiation (♦) and anode side (-●-) shows similar curves compared to the diode-like behavior of the platinized electrode (-—).

Comparison of IPCE values for bilayers fabricated from 291 nm spheres and 243 nm spheres indicate the similarities of red-side enhancement with equivalent stopbands but different TiO₂ filling fractions. The 581 nm stopband observed in 1ˢᵗ LPD infiltrated structures is identical in position to the 2ⁿᵈ LPD stopband from infiltration of 243 nm structures, and the 581 nm band shifts to 660 nm for a 2ⁿᵈ deposition. The comparative enhancement for equivalent stopbands is shown in Figure 3.12, where the ICPE spectrum has been normalized to a point preceding the stopband. IPCE spectra for 2ⁿᵈ LPD
structures using anode side irradiation were acquired for nanoTiO₂ on both 243 nm and 291 nm sphere templates and demonstrate similar red-side enhancements, with 291 nm templates having a slightly larger integrated IPCE over the 540 – 800 nm region. The 291 nm bilayers have no apparent dip in the IPCE curve from the stopband reflection, which is evident in the 243 nm templated structure (Figure 3.13). The enhancement at >640 nm in the 243 nm bilayer structure is presumably due to the very low extinction coefficient of the dye in this region and incomplete photonic stopband, which allow some of the low energy light to forward scatter into the nanocrystalline layer with little reflection or loss in efficiency. Table 3.1 lists the normalized efficiency enhancements over the 540 – 800 nm range for 291 nm and 243 nm templates. Negative values over the 400 – 800 nm range are attributed to typical cell to cell variations and possible absorption due to the inverse opal pores filled with I⁻/I₃⁻ solution, but improve over the 540 – 750 nm range. It is believed that bilayer cells with maximum IPCE values equivalent to a nanoTiO₂ film can be fabricated, but require iterative synthesis, fabrication, and testing.
Figure 3.12: Through-dye photoaction spectrum normalized at 480 nm (preceeding the stopband) of a) (—) 1st LPD PC on nanoTiO₂ from 291 spheres and b) (■) 2nd LPD nanoTiO₂ on PC from 243 nm spheres. The backscattering in (b) contributes to a large decrease in IPCE in the region of the stopband (580 nm).
Figure 3.13: Anode side irradiation with Pt counter electrode of nano-on-PC 2nd LPD bilayers from 291 nm (—) and 243 nm (■) and a nanocrystalline TiO₂ layer (▲) demonstrating the increased red side enhancement of the bilayers, but in the case of the 243 nm replicas, also a sharp decrease in the efficiency corresponding to the photonic stopband.

Table 3.1: Anode side photocurrent enhancement for bilayer structures compared to a typical single layer TiO₂ film. Non-normalized increases are minimal over the entire spectral region, but demonstrate increased red-side conversion except for 1st LPD 243 structure.

<table>
<thead>
<tr>
<th>Templated structure</th>
<th>400 – 800 nm not normalized</th>
<th>540 – 750 nm not normalized</th>
<th>400 – 800 nm normalized</th>
<th>540 – 750 nm normalized</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st LPD 291</td>
<td>-2.8</td>
<td>10.7</td>
<td>15.9</td>
<td>27.1</td>
</tr>
<tr>
<td>1st LPD 243</td>
<td>-17.27</td>
<td>-13.48</td>
<td>4.98</td>
<td>9.2</td>
</tr>
<tr>
<td>2nd LPD 291</td>
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<td>22.8</td>
<td>4.67</td>
<td>24.0</td>
</tr>
<tr>
<td>2nd LPD 243</td>
<td>-37.8</td>
<td>31.1</td>
<td>3.75</td>
<td>12.33</td>
</tr>
</tbody>
</table>
As a comparison, the calculated IPCE for cathode-side irradiation of structures with nanoTiO₂ on PC is 23.5 % (8% normalized) greater than the 291 nm structure and 18.3 % (8% normalized) greater than the nano structure (Figure 3.14). This results in the 2⁻rd LPD 243 nm conversion efficiency to be greater than the nearly equivalent nanoTiO₂ and 1ˢᵗ LPD 291 nm structures, likely occurring from the higher degree of disorder in 2⁻rd LPD structures. It is obvious that this structure extends the maximum photocurrent past the typical dye absorbance maximum, to nearly 605 nm, but still results in an overall lower IPCE and poor i-V characteristics due to the non-platinized cathode and through-electrolyte irradiation.

![Image](image.png)  
Figure 3.14: Cathode-side irradiation of nano-on-PC (¬) 2ⁿᵈ LPD 243 nm, (--)1ˢᵗ LPD 291 nm, and (▲) nanoTiO₂ films. The extended red-side enhancement can be seen extending past 605 nm for the 2ⁿᵈ LPD structure.
3.4 Discussion

3.4.1 Red enhancement in dye cells on nanocrystalline TiO₂

Previous research has demonstrated enhancement in the red portion of the dye-sensitized solar cell by the addition of a TiO₂ photonic crystal or disordered structure to the standard nanocrystalline TiO₂ film.¹, ², ¹⁰ These cells have utilized a non-optimal structure where the photonic crystal was deposited closest to the anode, followed by the nanocrystalline TiO₂ layer, thus creating a bilayer structure. Illumination through the anode side results in an efficiency loss due to light reflection by the stopband of the photonic crystal whereas illumination through the cathode side suffers from blue light attenuation by I⁻/I₃⁻ absorption. Modeling has shown placement of the PC on top of the nanocrystalline TiO₂ layer still provides enhancement on the red side of the dye maximum by improving backscattering in the bilayer structure.¹ This has been experimentally verified by physical juxtaposition of the two layers, and has been compared to placement of the PC layer on the counter electrode. Titania inverse opals were replicated from 243 nm spheres, followed by a second TiO₂ deposition to shift the bandgap to the red of the dye maximum. The lack of photocurrent enhancement by separation of photonic crystal layer from nanocrystalline TiO₂ layer can be understood by examining light propagation at the PC/nanoTiO₂ interface. The majority of amplification takes place at the interface of the nanocrystalline TiO₂ and disappears as the distance from the photonic crystal junction is increased, with the extreme being the complete separation of the photonic layer from the absorbing layer. As mentioned in Chapter 2, localization of resonant modes in the TiO₂ dielectric slab are caused by the Bragg mirror
effect of the photonic crystal. Localization effectively slows the propagation of incident light, increasing the probability of absorption.\textsuperscript{1} Examination of anode-side illumination IPCE values for the 2\textsuperscript{nd} LPD 291 nm structure indicates equivalent enhancements as the 243 nm. Placement of the stopband at 660 nm, in the region of low dye absorbance, still provides scattering in the structure, but reflection losses are generally less than the enhancement in photon absorption, as demonstrated by a lack of IPCE attenuation in the stopband region. Comparison of the 291nm 2\textsuperscript{nd} LPD and 1\textsuperscript{st} LPD structures, however, reveals greater red side enhancement for the 1\textsuperscript{st} LPD structure predicted by the composite effects of scattering and localization (Figure 3.15).\textsuperscript{1,11-13} There is a small increase in enhancement near 725 nm, but it is nearly negligible when compared to the far greater enhancement in the 540 – 750 nm region. Both of these structures provide a greater photocurrent enhancement than a standard Grätzel cell, 10.7 \% for the 1\textsuperscript{st} LPD and 22.8 \% for the 2\textsuperscript{nd} LPD.
By reversing the nanoTiO$_2$/PC bilayer, only a single TiO$_2$ deposition from 291 nm spheres was used since the mesopores in the nanoTiO$_2$ would be filled, decreasing dye uptake and efficiency. This single deposition does not induce as much disorder as the two deposition method in the nano-on-PC bilayer and limits the increased enhancement effects of scattering,$^{10}$ as observed by the FWHM in Figure 3.16. A 291 nm structure fabricated by a single LPD would not be expected to produce as much red side enhancement, yet it provides a nearly equivalent normalized IPCE and Bragg reflection (581 nm vs. 580 nm) with a lower filling fraction and effective refractive index. Comparison of two normalized IPCE spectra at 480 nm under anode illumination reveals
nearly identical efficiencies except for the marked decrease at the stopband in the 243 nm 2nd LPD structure (Figure 3.12). In the case of the 1st LPD 291nm structure, placement of a TiO$_2$ inverse opal on top of the nanocrystalline layer prevents first surface Bragg reflection at 580 nm and provides an internal reflectance within the structure and increased conversion efficiency in the red.

The normalized cathode-side IPCE spectrum reveals a nearly equivalent percentage of red enhancement, indicating that refractive index is equally important as pore size, supported by previous work in our group (Figure 3.14). The degree of backscattering that occurs in both structures must be nearly equivalent in order to obtain similar IPCE values in the Bragg scattering region. Work by Ferber and Luther$^{12}$ indicate that the addition of 5 wt% pores with sizes in the region of 250 – 300 nm gave increased enhancement while work by Mihi and Miguez$^1$ predicts an optimal pore size of 210 nm. Structures obtained from 291 nm spheres result in pore size of 212 nm by SEM, experimentally verifying the prediction of red-side enhancement for photonic structures from slow group velocity and localization in the nanocrystalline titania film. The number of resonant modes in this bilayer structure is relatively large compared to thin dielectric structures.$^{11}$ Disorder and thickness variations eliminate specific high transmittance peaks and effectively smear out the decreased group velocity over the spectral region.
Utilizing high-refractive index materials with optimal pore sizes would maximize the effect of photocurrent enhancement in photonic crystal-based Grätzel cells. Though an optimal 210 nm pore size is predicted for such effects, work by Mihi et al. have based their modeling on 224 nm pores, but also declare work by Nishimura et al. to have the same optimal structure when the experimentally determined pore size was 182 nm. Mihi et al. have modeled extracted experimental data from Nishimura et al. and indicate a larger pore size than that used by Nishimura would yield further enhancement on the red side of the dye absorbance maximum. Despite this, utilizing pores in the predicted size regime (160 – 270 nm) has yielded normalized enhancements (27 %) that are equivalent to those reported by Nishimura or Halaoui. The width of the backscatter cone, which is inversely proportional to the transport mean free path, is smaller for the 1st LPD.

Figure 3.16: Photonic stopband of TiO$_2$ replicas in EtOH from (--) 1st LPD 291 nm and (♦) 2nd LPD 243 nm spheres. The larger FWHM for the 2nd LPD indicates increased scattering over a single LPD.
presented by comparatively less disorder in the structure. There is an increased amount of internal reflection in the 1st LPD 291nm compared to the 243nm 2nd LPD structures but decreased scattering due to the smaller backscatter cone of the 291 nm template structure.

3.5 Conclusions

Light harvesting efficiency can be effectively increased through the use of photonic crystal layers coupled to nanocrystalline TiO₂. By placing the stopband of the photonic crystal to the red-side of maximum dye absorption, weakly absorbing light becomes localized at the bilayer junction. Previous work focused on nanocrystalline TiO₂ layers fabricated on photonic crystals, but suffered from attenuation either by reflections from the photonic crystal layer or by light absorption by the electrolyte. More efficient cells have been produced by placing the photonic crystal layer directly on top of the nanocrystalline TiO₂ film and irradiating through the anode. This was accomplished by polymer infiltration of the porous TiO₂ film, followed by evaporation of the photonic crystal and liquid phase deposition. The polymer infiltration prevents delamination of the nanoTiO₂ layer as well as LPD inside the mesoporous structure. Photoaction spectra indicate nearly equivalent efficiencies for cells with equivalent stopbands produced from a single LPD (291 nm spheres) compared to the previously studied second LPD (243 nm spheres). Eliminating the bilayer junction by moving the photonic crystal layer to the counter electrode of the cell eliminates any photocurrent enhancement, matching well with theoretical models based on this work. The enhanced photocurrents and assembly
into a typical Grätzel-like architecture further the possibilities for increased conversion efficiencies without altering the delicate electrochemical balance of the cell components.

3.6 References


Chapter 4

Light Manipulation in Tandem Silicon-Dye Sensitized Solar Cells

4.1 Introduction

Another driving force of this research has been to couple dye cells to silicon cells. Although silicon solar cell research is comparatively mature, costs of silicon itself in cell fabrication are in the range of $3.50/watt for single cells and $0.90 for concentrator cells. Production costs have dropped over 90% since 1976, but it is doubtful that they will drop much further. Single crystalline silicon is a superior material for solar cells as there is a very low rate of electron-hole recombination, because the material has few grain boundaries. The theoretical maximum efficiency for silicon is 28% in AM1.5 sunlight. Recent field tests show that single crystal Si modules rated at ~17% efficiency actually operate in the range of 11-13%, and that polycrystalline Si cells operate at 8-11%.\(^1\)

What is not often discussed outside the solar community is the fact that no solar products operate at ‘ideal’ efficiencies, which are typically measured at 25°C and under a flash of light. In the real world, many Si PV devices operate at 60°C or more where their efficiency degrades because of the decrease in $V_{oc}$ and voltage at the maximum power point ($V_{mp}$) with increasing temperature,\(^2\) which can be quite large. For example, a theoretically 24% efficient Si PV cell operating at 100°C has a loss of roughly 40%, meaning that it operates at ~14% efficiency.\(^3\) The heating arises from internal loss mechanisms and is exacerbated by poor heat rejection from the cell. This internal heating
limits the practical concentration ratio of Si concentrator cells to 20-25x (~2 W/cm²) with 19+ % efficiencies. Reports of concentrator cells working at 100-125x (~10 W/cm²) with efficiencies as high as 26%, using integrated high thermal conductivity packaging under flash lamp-25 °C conditions, are unfortunately irrelevant to use in the real world.

A large portion of excess heating originates from thermalization of high energy photons. Since the energies are larger than the bandgap, the excess energy undergoes phonon decay, heating the material and decreasing the bandgap. This in turn decreases $V_{oc}, ff$, and overall efficiency. Attempts at circumventing the high manufacturing cost of single crystal silicon have been made with polycrystalline and amorphous silicon and, though these materials are much less expensive to produce, they suffer from poor efficiency and high electron-hole recombination rates. Alternatives such as direct bandgap GaAs cells have a more ideal bandgap and are more efficient, but the scarcity of Ga and toxicity of As are concerns for practical use. Although Si is nearly 26 % efficient in the NIR portion of the spectrum, it is only 13% efficient in the visible range. This is comparable to the best reported Grätzel cells and inferior to the Grätzel cells in the visible portion of the spectrum. It follows that Grätzel cells could be coupled to silicon cells to maximize incident light efficiency for both cells.

The volatility of liquid electrolytes in the Grätzel cell will always be problematic in the manufacturing and widespread substitution of these cells, relative to more expensive but robust solid-state semiconductors. Attempts at circumventing the some of the problems of the liquid electrolyte have been made by substitution of hole-conducting polymers, semiconductor CuI and CuSCN materials, and electrolyte gels, but all suffer low efficiency due to poor electrolyte-semiconductor interaction. Solid-solid interfaces
are difficult to fabricate because of the intercalating structure required with the typical mesoporous TiO$_2$ network. A 2-dimensional TiO$_2$ architecture proposed in this research offers an improved contact area, efficient donor-acceptor charge separation by segregation of electron mobility from the redox electrolyte, and an insulated transparent conductive oxide TCO interface.

Rapid interfacial recombination results from architectures that use redox mediators with faster kinetics than the kinetically slow triiodide complex, such as the ferrocene/ferrocenium couple. As the recombination rate increases with light concentration, it is advantageous to decrease potential recombination pathways by altering the porous TiO$_2$ geometry. Increased porosity of the mesoporous network increases surface area, but also leads to more dead-end particles (TiO$_2$ crystallites without adjoining particles) and a longer, more tortuous path. Though increasing the film porosity from 50 % to 75 % creates larger pores for interaction, it increases the electron pathlength 10 fold. High surface areas are necessary to maximize dye-loading and light-harvesting efficiency, but negatively influence recombination. Ambipolar diffusion in liquid electrolyte cells will likely be quite different in solid-state polyelectrolyte hole carriers, limiting physical diffusion to negligible levels and thereby increasing recombination. Molecular blocking layers such as $t$-butyl pyridine are often used to prevent recombination of conduction band electrons with I$_3^-$, but this could become problematic in the solid-state cell. Direct fabrication of the TiO$_2$ film on the TCO by sputtering or evaporation should eliminate the pinholes normally present from squeegee printed nanoTiO$_2$ films. Frank and coworkers have determined that ultrafast electron injection is not the most important factor in the fabrication of efficient solid state dye
cells. Rather, the physical separation of hole conductors from the TiO$_2$ film determines the greater efficiency. A potential method for charge separation is the incorporation of a 2-5 nm thick conductive molecular mediator, but is difficult to incorporate into the current mesoporous TiO$_2$ network. More open structures such as periodic arrays of nanorods and nanowires offer similar crystallite grain size as nanoTiO$_2$ films with the ability to covalently attach a mediator and decrease charge recombination. These structures have demonstrated enhanced photocatalytic surface reaction efficiency and dye-cell activity. Initial $i$-$V$ and monochromatic current efficiencies with sculptured TiO$_2$ films (STFs) offer promise for 2D architectures, but suffer from low dye loading due to low film thickness. More promise for using these STFs in localized and scattering DSSC architectures results from the circular Bragg phenomenon behaving as a Bragg grating. Research in this area has been performed in collaboration with the Horn group in Engineering Science and Mechanics, in which films have been grown by graduate student Sean Pursel and MRSEC REU student Joy Gallagher, and characterization was performed by Neal Abrams and Gallagher. This work is far from complete, but the promising results to date demand further experiment and explanation.

4.2 Experimental

4.2.1 Tandem cells

Hot mirror coatings were fabricated on the non-conductive side of TEC 15 glass by Evaporated Coatings, Inc. (Willow Grove, PA) with 750 nm normal incidence cutoff.
Before the nanocrystalline TiO<sub>2</sub> film was applied to the evaporated hot mirror/FTO slides, the conductive side was polished with 1 µm alumina paste until the conductivity reached 30 ohm/sq. A silicon concentrator test cell (1.44 cm<sup>2</sup>) was donated by Sunpower Corporation (Sunnyvale, CA). Neutral density filters were acquired from Melles Griot and hot mirrors (not evaporated on FTO) were acquired from Edmund Industrial Optics.

4.2.2 Tandem Cell Module

A multi-DSSC with single Si cell tandem module was constructed by fabricating 12 individual Grätzel cell with a total active area of 4.3 cm<sup>2</sup>. Cells were produced in the same manner as described in the previous sections followed by dicing into individual 0.4 cm<sup>2</sup> cells. 1 mm holes were drilled into platinized counter electrodes using a water-cooled diamond core bit (Lunzer) attached to a Dremel tool. The cells were then heat sealed with Surlyn tape to the counter electrode at 100°C for 15 seconds in a standard laboratory press (Carver). Redox electrolyte was vacuum infiltrated into the cell area by injection through the pre-drilled hole and sealed with another piece of Surlyn tape. The cells were then assembled onto a wooden parabolic frame and masked with electrical tape to cover any areas without active DSSC. The Grätzel cells were individually positioned with modeling clay and focused on the Si concentrator cell that was suspended 5 cm above the array by the 4-point electrode connections. Grätzel cells were connected in parallel to eliminate current matching without individual cell characterization. Testing was performed on the observation deck of the Chemistry Research Building on August
17, 2005 with a reported sun altitude of 61.91°, 187.65° azimuth at 77.87° West, 40.8° North at 2 pm under clear skies at 26° C.

4.2.3 Indoor Cell Testing

4-point measurements were performed on the silicon concentrator cell and showed a dramatic increase in ff compared to the 2-electrode setup. No gains in Jsc or ff were seen in 4-point Grätzel cell measurements and were therefore not performed. Scans under visible, NIR, and white light were done under constant power conditions with a 150W Xe lamp (Oriel). Current-voltage characteristics were obtained under 1 sun intensity (~100 mW/cm²) unless otherwise noted. Lamp intensity was adjusted using neutral density filters along the beam path. A glass cuvette filled with water was used as an IR filter to decrease heating and a UV filter (LP400, Melles Griot) was used to filter UV bandgap irradiation. IPCE and i-V scans were performed as described in section 3.2.2. All efficiencies are reported using the standard “external” efficiency, whereby attenuation from the glass electrode is not subtracted from the incident power density. Experiments using only NIR light were performed by reflecting the incident light 90° from the incident light using the hot mirror evaporated FTO. Except for Voc vs. time data, all Si characterization experiments were performed after a 10 minute soak at the desired incident power.
4.2.4 Sculptured TiO$_2$ film Grätzel cells

Sculptured films of TiO$_2$ were fabricated by electron beam (e-beam) evaporation of amorphous TiO$_2$ onto an FTO substrate at a variety of glancing angles and rotation speeds, resulting in columnar and helical films (see figure 4.8). Films are masked to a specified area using Kapton tape. The e-beam evaporation was performed in a Semicore instrument in the Class 10 Penn State Nanofabrication Facility with runs typically lasting 12-24 hours under constant monitoring. Due to the low volume of source material in the evaporation chamber, film thicknesses were typically 2-3 µm, but were doubled by “second round” evaporation, resulting in 5-6 µm films. Films were then sintered in air at 425 °C for 12 hours and sensitized with 0.3 mM N719 dye. Assembly and testing was performed using previously mentioned procedures. Dye surface coverage was determined by dye desorption in 0.1 M NaOH in a mixed solvent (1:1 ethanol/water) and monitored by UV-vis absorption at 515 nm with an extinction coefficient of $1.41 \times 10^4$ M$^{-1}$cm$^{-1}$. The cell was probed with a weak laser pulse at 532 nm (Nd:YAG, 10 ns) on a relatively large background bias illumination at 632 nm (HeNe diode laser, 50 mW). Both probe pulse and background were illuminated on the working electrode side of the cell. The current transients were measured by connecting the electrode leads to a 10Ω shunt resistor and corresponding voltage was measured with a Tektronix TDS540A 500MHz oscilloscope.
4.3 Results

4.3.1 Dye/silicon tandem cells

Efficiencies in visible, NIR, and white light were acquired using Grätzel cells made in-house. Table 4.1 lists the characterization data for the best performing cell we have produced to this date. Since the start of this research, efficiencies have increased from 1.8 % up to 5.0 % by optimizing a variety of experimental parameters. For the most part, this involved the synthesis and fabrication of all components of the dye cell. The only purchased item was the N719 dye, but it could be synthesized according to published procedures if necessary. The modifications involved using an evaporated Pt film with reduced Pt nanoparticles as counter electrode, the synthesis of nanocrystalline TiO₂, sealing by the hydrolysis of TiCl₄, and most importantly, a 2.5% gain by use of a freshly synthesized triiodide redox couple. Although the efficiency is not as high as reported in the literature, we believe that our values are comparable to most researchers working on dye cells and consistently compare our values to “standard” Grätzel cells synthesized in our laboratory. The Iₘ for our cells is consistently lower than those reported by other prominent researchers in the field, but both Vₘ and ff are in the typical high performance range. All of the necessary electrochemical processes appear to be taking place in the Grätzel cell, but low Iₘ values lead us to think electrons are not percolating through the TiO₂ film. This could be due, in part, to impurity-driven recombination in the film as well as poor adhesion to the substrate. Work by Hagfeldt and Nelles have indicated physical compression of the film leads to higher Iₘ values by increasing contact with the substrate and improved necking in the TiO₂ particles.
Using this approach along with purified materials should lead to increased photocurrent and efficiencies.

<table>
<thead>
<tr>
<th>$V_{oc}$</th>
<th>0.672 V</th>
<th>Lamp power</th>
<th>102 mW/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{sc}$</td>
<td>5.53 mA</td>
<td>Area</td>
<td>0.48 cm$^2$</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>11.51 mA/cm$^2$</td>
<td>$ff$</td>
<td>0.656</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>4.98</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reflection accounts for up 30 % light loss on polished silicon and 4 % on glass. This also translates to a loss of efficiency due to the lack of light being absorbed by the semiconductor. This loss can be decreased through the use of anti-reflective (AR) coatings, typically $1/4\lambda$ dielectric films. In the case of hot-mirror coated FTO glass, the dielectric hot mirror is an inherent AR coating, not only maximizing NIR light reflection, but also minimizing visible light reflection more so than the glass itself. The hot mirror coatings used in the tandem cells have a spectral cutoff beginning at 675 nm under normal irradiance whereas typical FTO absorption begins at 700 nm, continuing past 2300 nm (Figure 4.1). The evaporated hot mirror coating reflects this NIR irradiation, preventing absorption as well as minimizing IR heating. Utilizing a NIR mirror, light attenuation by the FTO float glass is reduced from ~16 % to 5%. The N719 dye has an absorbance maximum near 540 nm and quickly drops off to only 13.6 % of the absorbance maximum by 650 nm as seen in Figure 2.2. This translates to an inherent loss of photon absorption to the red of the dye maximum that could be otherwise utilized by the more efficient silicon cell. Coupling these two cells together into a single module maximizes the efficiency in each independent spectral range.
4.3.1.1 Dye cell with hot mirror anode

Efficiencies of the Grätzel cell over the visible and full white light spectrum were calculated using hot-mirror coated FTO glass as the anode. In traditional Grätzel cells, FTO glass attenuates incident light due to reflection, impurities, and NIR absorption by about 26 %, but when evaporated with a hot mirror coating, nearly all of the light that is normally absorbed by the FTO coating is reflected along with all light above 675 nm. The hot mirror coating is fabricating by a series of 23 layers of high ($n_H$) and low ($n_L$)
index materials all $1/4$-$\lambda$ thick, where $\lambda$ is center wavelength. A phase shift of 180° results as light passes from $n_L$ to $n_H$ and is reflected off of the stack with the remaining light decreasing in intensity as it travels through the stack. The width of the high-reflectance zone increases with increasing ratio of $n_H/n_L$ and the % reflectance increases with the number of layers (Figure 3.1). Over the entire 300 nm – 3 $\mu$m region, only 5 % of the incident light is lost due to scattering and absorption. In this case, the light that reaches the dye-sensitized titania is nearly equivalent to the incident light on the FTO glass. For example, although the hot mirror FTO anode is irradiated with 100 mW of white light, only 20.7 mW is transmitted through the cell. The hot mirror reflects 74.6 % of the incident power away from the cell, resulting in an internal incident power of 25.4 mW and 4.7 % white light attenuation (Figure 3.4). Our experiments using a Grätzel cell on a hot mirror anode resulted in a maximum efficiency of 2.10 % at 115 mW/cm², but this is actually only 24.8 mW/cm² once NIR reflection is taken into account. Over just the visible range of 400 – 700 nm, Grätzel cell i-V measurements demonstrate drastically improved efficiency from 2.10 % in white light to 7.42 % in transmitted visible light, a factor of 3.53 over full spectrum light. The decrease from a factor of 4 can be assumed to result from hot mirror reflections in the visible portion of the spectrum, decreasing the incident photon flux in that region below the LHE of the dye. If the incident light through the hot mirror is increased to 100 mW/cm² (approximately 4 sun concentration) visible light cell efficiency remains nearly constant with external efficiency increasing by a factor of 3.1. According to the efficiency data presented in Figure 3.7, the maximum concentration the Grätzel cell can attain is near 2x without any loss in efficiency. Concentration is detrimental towards efficiency and a challenge in the current design of
the Grätzel cell. By splitting light and directed it to the more efficient silicon cell, an overall more efficient solar module can be constructed. Although our Grätzel cell does not perform as well as the best recorded at NREL, one can assume that a cell of 10.4% efficiency under AM1.5 sunlight, which is frequently reported by Grätzel and Arakawa,\textsuperscript{15,22} would undergo a 3.5-fold increase and have an efficiency near 33% in visible light with these hot mirror coated anodes. As discussed in section 4.3.1.2, this value is much higher than the efficiency of silicon in the same spectral range, which is only 12.49% with 100 mW/cm\textsuperscript{2} visible light.

![Diagram of a hot mirror coating fabricated by alternating layers of high index (n\textsubscript{H}) and low index (n\textsubscript{L}) materials where the number of layers is proportional to the % reflectance and the ratio of n\textsubscript{H}/n\textsubscript{L} indicates the width of the reflectance zone.](image)

Figure 4.2: Diagram of a hot mirror coating fabricated by alternating layers of high index (n\textsubscript{H}) and low index (n\textsubscript{L}) materials where the number of layers is proportional to the % reflectance and the ratio of n\textsubscript{H}/n\textsubscript{L} indicates the width of the reflectance zone.
Figure 4.3: Visible light transmission and NIR reflection on a hot mirror coated FTO anode.

Figure 4.4: Two sets of data reporting concentration efficiency for a Grätzel cell with hot-mirror coated anode. The cell efficiency has a maximal increase of 3.5 once the hot mirror is placed in the beam path.
4.3.1.2 Efficiency for silicon cells

The bandgap of silicon is 1.1 eV, so light with energy higher than this is absorbed and converted to electron-hole pairs. Much of this higher energy light, however, results in efficiency losses due to band-gap relaxation and internal diode thermalization effects, which have been estimated to contribute to 45-50% of power conversion loss in the cell.\textsuperscript{23} By directing only near-bandgap light, or near infrared (NIR), at the Si cell, the internal losses from heating by high energy photons can be eliminated. The hot mirror coating reflects 90% of the light from 700 – 1150 nm, or 27% of the total incident power (E > \( E_{\text{gap, Si}} \)) and 44% of the light, or 8.6% of the spectral energy from 1150 – 1500 nm, where E < \( E_{\text{gap, Si}} \). Characterization of a silicon concentrator cell produced by Sunpower Corporation demonstrates the advantage of eliminating visible light from the silicon PV and the results are shown in Table 4.2.

<table>
<thead>
<tr>
<th>Spectral Range</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmitted (visible)</td>
<td>12.49</td>
</tr>
<tr>
<td>Reflected (NIR)</td>
<td>23.70</td>
</tr>
</tbody>
</table>

Table 4.2: Efficiency data for the Sunpower silicon concentrator cell. Rows list efficiencies for the cell at 100 mW for the specified spectral ranges.

At 100 mW/cm\(^2\) white light intensity, the Si cell has an overall efficiency of 19.53%, which is comparable to the value of 25% reported by the manufacturer at 5 W/cm\(^2\). As light intensity increases, Si PV modules becomes more efficient at constant
temperature according to Eq. 4.1, and this cell would be expected to increase in efficiency with increased light intensity. By using the evaporated hot mirror on FTO as a filter/mirror, the cell efficiency decreases to 12.49% when visible light is transmitted through the hot mirror, but jumps to 23.70% with reflected NIR light. In this case, 73% of the incident white light is reflected as a combination of visible and NIR light. When NIR light of 1 sun intensity (140 mW/cm² white light) is incident on the Si cell, its efficiency increases to 4% higher than in white light at 1 sun intensity and 11.2% higher than 100 mW visible light efficiency. At a little over 2 sun NIR intensity, 244 mW/cm² (340 mW/cm² white light), the Si module performs at 22.7%, translating to an efficiency gain simply by removing the visible portion of the solar spectrum.

\[ V_{oc,n} = V_{oc} + m \frac{kT}{e} \ln X \]

The increase in open-circuit voltage with concentration where \( m \) is the diode ideality factor, \( n \) is the concentration level, and \( X \) is given by

\[ \left( \frac{I_L}{I_0} + 1 \right) \]

where \( I_L \) is light-generated current and \( I_0 \) is the saturation current density.

Heat dissipation is essential to the efficient operation of silicon PVs. The decrease in \( V_{oc} \) over time was measured at one sun intensity (100 mW/cm²) incident power density (IPD) over 10 minutes using white, visible, and NIR light, \( V_{oc} \) loss is approximately constant, 9 mV. The \( V_{oc} \) of 1 sun visible light is lower than the other two by 24.3 mV for white light and 24.8 mV for NIR light. At 100 mW white light intensity, NIR light has a higher \( V_{oc} \) loss (5 mV vs. 1.5 mV), but the IPD is higher than for visible light, 48.6 mW compared to 28.9 mW and 44.6 mV higher \( V_{oc} \) under NIR incidence than
visible light. For the equivalent IPDs, white light and NIR light have approximately the same $V_{oc}$ and loss over time, but visible light has a much lower $V_{oc}$ (Figure 4.5). This translates to an overall higher power that can be drawn from the cell.

Figure 4.5: Open circuit voltage vs. time for (top) a Si PV concentrator cell operating at 100 mW/cm$^2$ for each respective incidence range and (bottom) 1.2 W incident light split into the corresponding white, visible, and NIR ranges.
4.3.2 Silicon/dye cell module

The real-world behavior of a Grätzel cell/Silicon cell tandem module was tested using true a true solar environment. Although testing conditions do not precisely mimic the standard AM1.5 global irradiance, a sunny day in the summer in Central Pennsylvania is not far from these values. The cell module pictured in Figure 4.6 was qualitatively aligned to reflect NIR irradiation on the central Si cell. Attempts were made to use the output current of the Si cell as a measure of alignment, but minute solar irradiance fluctuations made this task exceedingly difficult. As a point of reference, however, the $I_{sc}$ improved from 4 mA to 34 mA by adjusting the DSSC angles from normal to the specified angles, proving NIR reflection was the cause of the observed photocurrent.

Figure 4.6: Tandem cell module consisting of (a) 12 individual Grätzel cells connected in parallel and focused on (b) a 1.44 cm$^2$ Si concentrator cell. The Grätzel cells were masked with black electrical tape prior to alignment and testing.
In the device geometry pictured above, the Grätzel cell had a measured efficiency of 2.93 % under white light illumination, but a calculated 9.38 % internal efficiency under incident light with a $J_{sc}$ of 1.7 mA/cm$^2$. The 16.4 % efficiency observed for the Si concentrator cell was obtained by dividing the cell output power by the product of the reflected incident power area (4.3 cm$^2$) and 75 % of the incident light (28.3 mW). A module efficiency of 12.5 % is calculated by dividing the total output power per incident area of the tandem cell by the incident solar power. Table 4.3 below lists characterization data for the tandem cell module.

Table 4.3: Characteristics for 12 parallel connected DSSCs and reflected NIR light on a single Si concentrator cell.

<table>
<thead>
<tr>
<th></th>
<th>Silicon concentrator</th>
<th>Grätzel cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{oc}$ (V)</td>
<td>0.600</td>
<td>0.660</td>
</tr>
<tr>
<td>$I_{sc}$ (mA)</td>
<td>33.4</td>
<td>7.27</td>
</tr>
<tr>
<td>$J_{sc}$ (mA/cm$^2$)</td>
<td>23.2</td>
<td>1.69</td>
</tr>
<tr>
<td>$I_{max}$ (mA)</td>
<td>30.8</td>
<td>7.91</td>
</tr>
<tr>
<td>$V_{max}$ (V)</td>
<td>0.495</td>
<td>0.525</td>
</tr>
<tr>
<td>Max power (mW/cm$^2$)</td>
<td>10.6</td>
<td>0.966</td>
</tr>
<tr>
<td>Solar power (mW/cm$^2$)</td>
<td>64.6</td>
<td>7.92</td>
</tr>
<tr>
<td>Area (cm$^2$)</td>
<td>1.44</td>
<td>4.30</td>
</tr>
<tr>
<td>Fill factor</td>
<td>76.1 %</td>
<td>86.5 %</td>
</tr>
<tr>
<td>Efficiency (calculated)</td>
<td>16.4 %</td>
<td>9.38 %</td>
</tr>
<tr>
<td>Module efficiency</td>
<td></td>
<td>12.5 %</td>
</tr>
</tbody>
</table>

4.3.3 Sculptured films

Depending on evaporation conditions, a variety of nanorod architectures can be produced using e-beam evaporation. Parameters such as thickness, film density, porosity, and radius of curvature can all be varied by both rotation speed and deposition angle. The as-evaporated films resulted in moderately reflective gray colored films and resulted
in very poor efficiencies (Table 4.4), but dramatically improved by calcination. As expected by evaporation from an amorphous source, PXRD reports a phase change upon calcination from amorphous to anatase (Figure 4.7) with 27 nm crystallites and a preferred (004) orientation compared to (101) for bulk anatase. This differs from the strong (101) reflection reported by both Kiema\textsuperscript{12} and Gomez,\textsuperscript{11} potentially due their rutile source. The films change to a reflective white after calcination and in the case of certain helical structures, exhibit a stopband coinciding with the z-direction periodicity (Figure 4.8). Maximum film thickness was restricted by instrumental parameters, which directly influence dye loading. The calculated IPCE is consistently lower than expected, presumably due to low dye loading and light not being fully absorbed within the thickness of the film. IPCE is expressed by the product of the three terms in Eq. 4.2:

\[
IPCE(\lambda) = LHE(\lambda)\varphi_{inj}\eta_c
\]  

4.2

where LHE is the light harvesting efficiency, \( \varphi_{inj} \) is the quantum yield of charge injection, and \( \eta_c \) is the efficiency of collecting the injected charge at the back contact.\textsuperscript{16} To account for poor loading and determine conversion efficiency, the LHE must be calculated for the film, Eq. 4.3:

\[
LHE(\lambda) = 1 - 10^{-A(\lambda)}
\]  

4.3

where \( A \) is the optical absorbance of the N719 dye on the TiO\textsubscript{2} film. The product of \( \varphi_{inj} \) and \( \eta_c \) is the APCE, or absorbed photon to current efficiency, which determines the cell efficiency based solely upon the photons that can be absorbed by the film rather than the integrated input power. APCE can then be calculated by Eq. 4.4:
from the calculated IPCE value and measured surface coverage from dye desorption.

\[ APCE(\lambda) = \frac{IPCE(\lambda)}{1 - 10^{-\Delta(\lambda)}} \]

Table 4.4: Characterization results of an STF before and after calcination

<table>
<thead>
<tr>
<th></th>
<th>Dye loading (nmol/cm²)</th>
<th>IPCE₅₄₀ nm (%)</th>
<th>APCE₅₄₀ nm (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-calcination</td>
<td>10.9</td>
<td>3.22</td>
<td>19.8</td>
<td>0.075</td>
</tr>
<tr>
<td>Post-calcination</td>
<td>7.35</td>
<td>16.40</td>
<td>77.3</td>
<td>0.831</td>
</tr>
</tbody>
</table>

Figure 4.7: Powder XRD pattern of a TiO₂ STF before and after calcination at 425°C for 12 hours. Crystallite size is calculated to be 27 nm by the Scherrer equation.

Trends in efficiency appear to have a dependence on deposition angle, with low \( \chi \) angles of 80-85° performed markedly better than a higher \( \chi \) of 87°. Film density and porosity presumably contribute to the differences in efficiency, but have yet to be fully understood. Film packing density is inversely proportional to deposition angle, and leads
to lower surface coverage from isolated columns. Systematic iteration of fabrication, analysis, and characterization need to be performed before a definitive relation between variable can be made. Increasing film thickness by performing double depositions increases dye loading and doubles IPCE and efficiency, but APCE values remain constant. Ideally, film thicknesses would be on the order of 10-15 µm, but have yet to be experimentally realized. Characterization data for a variety of films is listed in Table 4.5. The maximum efficiency for these cells has been 1.60 % but with a film thickness of only 5.6 µm. This shows promise for continued studies as efficiency doubles with film thickness, demonstrating poor dye loading as a basis for low efficiencies rather than electron transport. Interestingly, APCE and efficiency tend to be inversely related for columnar films, but are directly related for helical structures. The stopband present in helical structures may contribute to increased scattering, thereby increasing the chance for photon absorption by the dye. Current-voltage curves and IPCE spectra reproduce the behavior of standard Grätzel cell architectures including high $V_{oc}$, $ff$, and comparable APCE values, but lower values for $I_{sc}$ and IPCE (Figure 4.9). Initial rudimentary current transient measurements (Figure 4.10) demonstrate efficient electron transport through the TiO$_2$ nanorod network with a time constant $\tau$ of 23.6 ms with a calculated diffusion coefficient, $D$, of $1.28 \times 10^{-6}$ cm$^2$/s (Eq. 3.1) and an $I_{sc}$ of 0.718 mA, consistent with previous reports for the Grätzel cell geometry$^{24}$ and STF network.$^{11}$ Improved measurement using intensity-modulated photocurrent and photovoltage studies need to be performed to definitively analyze transport kinetics, but even at these early stages justify further examination for a 2D nanorod Grätzel cell.
\[
\tau = \frac{(d/2)^2}{D}
\]

Where \(d\) is the thickness of the film, \(\tau\) is the time constant, and \(D\) is the diffusion coefficient.

Figure 4.8: SEM image of a TiO\(_2\) STF on Si with a 95 nm helical periodicity. Inset shows the stopband in EtOH corresponding to a complex set of interference phenomenon from the circular Bragg stack. The peak at 540 nm corresponds to dye absorbance on the film.
Table 4.5: Characterization data for various TiO₂ sculptured films.

<table>
<thead>
<tr>
<th>Angle</th>
<th>Speed (RPM)</th>
<th>Efficiency (%)</th>
<th>FF (%)</th>
<th>Surface coverage (nmol/cm²)</th>
<th>APCE₅₄₀ (%)</th>
<th>Thickness (µm)</th>
<th>IPCE₅₄₀ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>87</td>
<td>0.125</td>
<td>0.470</td>
<td>68.7</td>
<td>15.1</td>
<td>46.3</td>
<td>2.5</td>
<td>15.9</td>
</tr>
<tr>
<td>87</td>
<td>1.5</td>
<td>0.582</td>
<td>70.0</td>
<td>9.54</td>
<td>38.9</td>
<td>2.45</td>
<td>8.95</td>
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<tr>
<td>87</td>
<td>1.5</td>
<td>0.596</td>
<td>71.3</td>
<td>14.4</td>
<td>38.5</td>
<td>5.57</td>
<td>13.3</td>
</tr>
<tr>
<td>85</td>
<td>1.5</td>
<td>0.617</td>
<td>58.4</td>
<td>4.22</td>
<td>76.0</td>
<td>2.62</td>
<td>11.0</td>
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<tr>
<td>84</td>
<td>0.0380</td>
<td>0.658</td>
<td>70.5</td>
<td>13.3</td>
<td>83.0</td>
<td>3.3</td>
<td>26.1</td>
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<tr>
<td>87</td>
<td>1.5</td>
<td>0.697</td>
<td>66.6</td>
<td>17.1</td>
<td>31.1</td>
<td>2.5</td>
<td>11.7</td>
</tr>
<tr>
<td>87</td>
<td>0.125</td>
<td>1.26</td>
<td>71.2</td>
<td>40.7</td>
<td>33.1</td>
<td>5.57</td>
<td>22.9</td>
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<tr>
<td>80</td>
<td>0.0296</td>
<td>1.60</td>
<td>69.4</td>
<td>21.5</td>
<td>61.1</td>
<td>5.57</td>
<td>29.4</td>
</tr>
</tbody>
</table>

Figure 4.9: Current vs. voltage curve for a nanorod network and corresponding IPCE spectrum. The measured dye loading is 13.2 nmol/cm².
4.4 Discussion

An interesting note of efficiency reporting for solar cells is the unstated parameters of acquiring data. As shown in section 4.3.1.2, the $V_{oc}$ of silicon decreases with heating resulting in a poorer efficiency, but data are typically presented using millisecond $i$-$V$ scans, virtually eliminating losses due to heating. In the case of Grätzel cells, sensitized portions of the cell are kept to a minimum, and can be small as 0.1697 cm$^2$, as reported in one of Grätzel’s most efficient cells ($\eta = 10 \%$).\textsuperscript{25} The cell size is kept small to minimize iR drop across the TiO$_2$ film and the poorly conductive FTO glass, but commercial-grade cells would need to have larger surface areas, typically >1cm$^2$ and typically such cells have efficiencies ~5\%. More conductive FTO can be produced, but

![Figure 4.10: Transient photocurrent time trace for a TiO$_2$ STF network. The measured time constant is 23.6 ms with a calculated electron diffusion coefficient of 1.28 x 10$^{-6}$ cm$^2$/s.](image)
this also increases the haze and light attenuation of the anode. The efficiency loss from a more resistive FTO glass is typically equivalent to the light loss of a highly conductive film, so there is little gain in choosing one over the other. Minimizing cell size with a less conductive but more transparent film is the architecture used in these cells. A more conductive, less hazy film would be ideal, but coatings such as indium doped tin oxide (ITO) have increased dopant diffusion upon heating. It has been speculated that an ITO film with a thin FTO coating would result in a more transmissive, highly conductive film with low ion diffusion, but this has yet to be experimentally realized.26

4.4.1 Efficiencies for hot mirror anode Grätzel cells

The dielectric coating of the hot mirror functions not only as an effective reflective coating for NIR light, but also serves as an antireflective coating for the visible light. The spectral region in this work are defined as; visible, 400 – 700 nm; NIR, 700 – 1200 nm; and full region 400 – 3000 nm. Compared to standard FTO glass, the hot mirror coating and FTO glass attenuated light equally in the visible region (8 %), but the hot mirror attenuated much less in the NIR region (8 % vs. 16%) due to the inherent NIR absorption of the tin oxide coating. The 8 % attenuation is primarily due to the impurities of float glass. A more ideal anode would be fabricated from optical glass such as BK7, but this is not commercially available. The hot mirror coating does not increase the amount of visible light transmitted through the anode, but actually decreases it by approximately 25 % due to harmonic reflections from the coating. A majority of this loss (~21 %), however, is recovered by the Si cell in the tandem design. The primary
advantage of the hot mirror coating is that it reflects 89 % of the NIR light away from the Grätzel cell, which is light primary unutilized by the cell, only allowing <4 % of NIR light through the cell. Transmittance, reflectance, and attenuation data are presented in Table 4.6.

Table 4.6: Reflectance, transmittance, and attenuation powermeter data of white light through a hot mirror coated FTO (hot mirror first surface) and FTO.

<table>
<thead>
<tr>
<th></th>
<th>% Reflectance</th>
<th>% Transmittance</th>
<th>% Attenuation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot mirror</td>
<td>75.9</td>
<td>22.8</td>
<td>1.36</td>
</tr>
<tr>
<td>FTO glass</td>
<td>11.91</td>
<td>75.6</td>
<td>12.5</td>
</tr>
</tbody>
</table>

The incident light power on the Grätzel cell decreases to only 24 % of the total white light power when the hot mirror anode is used. A perfect hot mirror coating would reflect all 52% of the IR and NIR light and transmit the 46% of visible light in the solar spectrum. The hot mirror coatings used in this work transmit virtually 23% of the Xe spectrum power into the Grätzel cell, reflecting the remaining 75% towards the Si cell. This increases the fraction of usable light power by about 4x compared to white light and the efficiency of the dye cell by 3.5x compared to the full white light spectrum. Although the visible light transmitted through the glass is slightly lower relative to plain FTO, this is adequately compensated for by referencing only the visible light intensity for efficiency calculations. In typical Grätzel cell efficiency calculations, the entire incident white light spectrum must be taken into account since this is the true photon conversion of the solar spectrum. Reporting only the visible light intensity is typically meaningless in traditional Grätzel cells since a large portion of the spectrum would go unaccounted for, thereby yielding an artificially high efficiency. This becomes important in the dye cells since they are often compared to competing devices such as semiconductor PVs.
which are much more efficient in the NIR and nearly equivalent in the visible. The semiconductor cell will always be more efficient since the lower energy bandgap utilizes both portions of the solar spectrum. Another typically incorrect method for reporting efficiency is using the internal efficiency, or light that actually hits the solar conversion medium (dye coated TiO₂ in the Grätzel cell). This would also result in artificially high efficiencies since glass impurity attenuation and reflection would not be accounted for. Experimentally, this could be done by placing the anode material in front of a power meter and using the measured intensity as the incident power rather than measuring the unfiltered incident intensity. Since we are purposefully dividing the incident light into visible and NIR regions and utilizing each portion in a separate solar device, efficiency calculations are based upon the incident light intensity after reflection from the hot mirror coating. The inherent glass attenuation is taken into account for all calculations in order to prevent false reporting.

Separately, the Si cell is very efficient in the NIR spectrum, up to 30 %, and the Grätzel cell nearly 35 % in the visible. Until this time, a single module utilizing both types of solar cell has yet to be reported. Even though the Grätzel cell is less efficient over the entire spectrum, it is much less expensive to produce since purity is not nearly as important as in silicon-based devices. It is known that the current design of dye cells cannot be concentrated since efficiency decreases dramatically with more than 4 sun concentration, due to resistive and polarization losses in the cell. However, because these cells are inexpensive, large panel arrays are not cost prohibitive. Silicon efficiency, however, benefits from concentration by increasing \( V_{oc} \), thereby resulting in smaller cell areas being able to effectively magnify and utilize light, up to 500 x.²⁷
4.4.2 Grätzel cell/Si PV Tandem Cell Module

Alternatives to our tandem dye cell/silicon cell have been proposed, such as sensitizing with two dyes such as the N719 and N3 dyes. The N719 has a higher $J_{sc}$, but the N3 dye has a larger absorption region. Unfortunately, mixing of these two dyes results in poor efficiency generally due to the more efficient dye overcompensating for the lower efficient one.\textsuperscript{28} DSSCs involving two separately sensitized electrodes also result in low efficiency as the cell is current matched to the lowest performing dye.\textsuperscript{29} To date, only the stacked parallel connected two dye cell has reported a higher efficiency higher than that of the individual components.\textsuperscript{30} Although inexpensive, this cell has drawbacks such as fabrication difficulty and light attenuation from a platinized counter/working electrode. Unfortunately, stacked dye cells cannot compete with new technologies unless better electrode substrates are developed. Since our tandem cell design utilizes optics to reflect light, the transmission losses associated with stacked cells is avoided.

Silicon cell efficiency is maximized by individually focusing NIR reflections from hot mirror-coated Grätzel cells under normal incidence. The 16 % calculated efficiency is likely lower than a true efficiency due to poor alignment of the cell and would likely be as high as the 23 % reported for light reflection from a hot mirror and potentially higher from the increased $V_{oc}$ with concentration (Table 4.2). The primitive cell test used in this set of experimental data does not utilize tracking since the $i-V$ scan for both cells takes less than 60 seconds, but real-world use would likely require module tracking to maintain high efficiencies throughout the day. Proper alignment and NIR
reflection was maintained in this module by independent focusing of the Grätzel cells and off-center vertical alignment of the Si concentrator with respect to the Grätzel cell receivers. In this module, the parallel connection of Grätzel cells assures a maximum photocurrent, but sacrifices high output voltages. Cell fabrication is still in its infancy in our lab and 12 optimally performing cells could not be guaranteed. The connection of a combination of cells will always result in a lower output power than the sum of the individual cells. This mismatch loss is highest for cells connected in series due to poor performance and units with non-uniform area, and could result in overheating and device breakdown. Mismatch losses are minimized by parallel connections, but a combination of series and parallel connections would be most advantageous for a block of Grätzel cells and Si concentrator cell. Once optimum Grätzel cells have been fabricated, a series-parallelizing approach could be used (Figure 4.11) whereby strings of parallel cells are interconnected in series blocks, minimizing cell mismatch. If the Si concentrator cell is then connected to the block of Grätzel cells, parallel connections are used since output currents vary dramatically between the cell types, but photovoltage remains nearly equivalent. This unit-cell of sorts can then be further integrated into a tandem cell networks through another set of series-parallelizing. Bypass diodes can also be integrated into the module to account for any individual device failure.
4.4.3 Direct and Diffuse Radiation

A key factor in concentration is the utilization of direct incident light. Silicon concentrator cells use fresnel or receiver dish architectures that focus and magnify the incident light onto a small cell, but this is only effective with direct incidence light. To achieve the focusing needed, tracking systems can be employed that follow the Earth’s arc throughout the day and year. These systems are expensive to produce and require maintenance, but are beneficial since they maintain a direct incidence on the concentrator cell. It is estimated that 10-20% of light is diffuse even on clear, cloud-free days and increases to 50% on “party-cloudy” days that much of North America is accustomed to. The diffuse light is essentially wasted in concentrator cells and goes unreported in some
silicon cell efficiency data. This diffuse light can be recaptured by non-concentrating device, such as a planar device like the Grätzel cell. A design proposed by Goetzberger\textsuperscript{27} (Figure 4.12) uses a concentrating lens to magnify direct incidence light onto concentrator cells while flat-panel collectors are used to collect diffuse light. This architecture is a tandem cell of sorts, but lacks separation of light in traditional tandem cells. An interesting proposal would be to allow only a specific wavelength range to be concentrated and the remaining unconcentrated wavelengths to pass through onto a flat plate collector. This offers the benefits of concentration as well as the capture of diffuse radiation. As applied to our current tandem cell, an optical device would concentrate NIR light onto a set of small Si cells but normally transmit visible wavelengths onto a Grätzel cell that functions at 1 sun intensities. Although optics with such birefringent capabilities are not yet available, the concept offers motivation towards such a goal.

Figure 4.12: Solar tandem cell concentrator designed by Goetzberger for collecting direct and diffuse irradiation.\textsuperscript{27}
4.4.4 Efficiency losses

Although the efficiency for Si can be calculated theoretically, this differs greatly from what is actually achievable. Calculations show that Si efficiency can reach a maximum of 44 % in AM1.5 concentrated direct light, but Si empirically only achieves 26 % – 29 % at global intensities. Much of the theoretical loss comes from phonon decay, from photon energy being larger than the bandgap. As previously mentioned, this excess energy is thermalized, decreasing cell efficiency. The primary constituent of efficiency loss from thermalization is the decrease in $V_{oc}$, not $I_{sc}$ as illustrated in Eq. 4.6

$$\frac{dV_{oc}}{dT} = \frac{V_{g0} - V_{oc} + \gamma(kT / q)}{T}$$  \hspace{1cm} \text{(4.6)}$$

And the relation of $V_{oc}$ to $I_{sc}$ is given by Eq. 4.7

$$I_{sc} = AT^\gamma (e^{-\frac{E_{g0}}{kT}} e^{\frac{V_{oc}}{kT}})$$  \hspace{1cm} \text{(4.7)}$$

Where $I_{sc}$ is the short circuit current, $E_{g0}$ is the extrapolated zero temperature bandgap of a semiconductor, $\gamma$ is the temperature dependent variable for $I_0$, the diode saturation current. After differentiation and cancellation of terms, Eq. 4.6 demonstrates that as temperature increases, $V_{oc}$ will decrease. Substitution of values for silicon result in a linear decrease of -2.3 mV/°C, or 0.4 %/°C. Since fill-factor is also dependent upon $V_{oc}$ (Eq. 4.8 ),

$$ff = \frac{V_{oc} - \ln(V_{oc} + 0.72)}{V_{oc} + 1} \times \frac{ff_0}{r_{sh}}$$  \hspace{1cm} \text{(4.8)}$$

Where $ff_0$ is the ideal fill factor and $r_{sh}$ is the shunt resistance caused by leakage across the $p$-$n$ junction.
it too decreases with increasing temperature. Temperature plays a small role in \( I_{sc} \) by increasing the Fermi level and decreasing the bandgap. This increases the \( I_{sc} \) slightly, but the effect is small compared to the more detrimental \( V_{oc} \) loss. In the case of solar concentrators, such as the Sunpower cell used in these studies, increased light intensity causes more phonon decay and requires some sort of cooling mechanism. Although passive heatsinks could be used to effectively dissipate thermalized photons, this heat could otherwise be used in a more useful application. For this reason, it is advantageous to remove the high energy portion of the solar spectrum. Diversion of this light will not only increase the overall efficiency on the Si cell, but it can also be directed to a cell that is better suited for this spectral range.

### 4.4.5 Sculptured TiO\(_2\) films

Optimization of device morphology for solid-state Grätzel cells is essential for further commercial development. The use of viscous solid electrolytes in the place of the current liquid \( I^-/I_3^- \) couple requires improved intercalation, something difficult to achieve in mesoporous TiO\(_2\) structures. Rather than an “antfarm” network of porous channels, a 2D architecture can be utilized, and has been shown to be effective in filling pores in alumina membranes with viscous polymers.\(^{32, 33}\) The high-surface area present in the mesoporous channels is sacrificed in 2D geometries, but is maximized by thicker films and bifurcating fiber bundles that increase with growth progress.\(^{12}\) Such structures are obtained by the evaporation of TiO\(_2\) STFs in which the branching, rod diameter, and packing density are determined by experimental parameters. The presence of an electron
mediator is also necessary for effective long lived charge separation in the solid-state dye cell. The 2D architecture exhibits excellent characteristics for modification with the mediator since the packing density can be varied, allowing for a variety of mediator lengths to be incorporated in the structure. Once mediators have been covalently bound to the TiO₂ structure, dye molecules can then be attached or the mediator itself may consist of a sensitizer antenna and would require no further modification. The mediator is necessary as recombination in the Grätzel cell structure is driven by slow electrolyte diffusion kinetics and would likely be an issue with solid-state electrolytes. The cells currently fabricated from STFs have poor efficiencies, but this is primarily due to low dye loading. Current transients predict nearly equivalent electron diffusion through the TiO₂ network, and high APCE values demonstrate efficient electron injection. Even with improved loading by increased thickness, the cell will most likely still perform worse than a typical Grätzel cell due to the lower surface area. A benefit of this cell structure, however, is the direct evaporation of TiO₂ that should minimize recombination with the TCO interface. This is evidenced by equivalent photocurrent efficiencies for TiCl₄ seeded and non-seeded structures. Incorporation of STFs as the bottom layer of a bilayer structure will improve contact with the FTO electrode, but any charge separation advantages gained by the nanorod structure would be lost by inclusion of a nanoTiO₂ layer.

Even the most efficient Grätzel cells operate at half the maximum efficiency when made on a commercial scale, and they cannot be used in the “real world” because of electrolyte volatility and toxicity; this requires a new cell design regardless of current maximum efficiencies. A solid-state cell is needed for commercial production and the
incorporation of 2D networks not only introduces a novel cell design, but provides a more ideal structure for modeling and theoretical cell improvements. Although only nanorods have been examined in this portion of the research, other 2D geometries such as nanotubes provide interesting structures. These micron sized tubes have been grown by the anodization of titanium films and exhibit excellent water-photolysis efficiencies, 12.25 % under UV illumination. Films consisting of highly ordered 3 – 6 μm tubes have been tested as a potential DSSC, but have resulted in very low efficiencies, both IPCE and APCE, to date. This is presumably due to not only the low dye loading contributing to the poor IPCE, but also the presence of a rutile underlayer preventing efficient electron injection into the conductive substrate which has been a titanium foil. Irradiation must also take place from the counter-electrode side as films have not yet been grown successfully from FTO substrates. This architecture could show promise once a purely anatase phase can be grown on FTO since the tubular structure offers increased surface area and dye loading.

4.5 Conclusions

The high visible light efficiency of the Grätzel cell and NIR efficiency of silicon were utilized in a spectrum splitting tandem cell geometry. In this manner, only the wavelengths of light that could be efficiently utilized were transmitted to the Grätzel cell via a dielectric hot mirror coating on the first-surface of the FTO anode. NIR light was then reflected onto a central silicon concentrator cell. Over just the visible spectrum (400 – 700 nm) the Grätzel cell has an efficiency 3.5 times higher than the entire white light
spectrum, and silicon increases in efficiency by 1.15 over the full spectrum. Potentially more important, preventing the absorption of visible wavelengths by silicon decreases thermal losses that are detrimental to $V_{oc}$ and fill-factor. This eliminates the need for cooling and decreases operational costs. Although our reported efficiencies for the Grätzel cell are low, the efficiency over just the visible region is higher than that of silicon. The reported 10.4% efficient Grätzel cells are anticipated to have efficiencies near 33% in the visible and even higher efficiencies by the incorporation photocurrent enhancement structures described elsewhere in this dissertation. These studies are currently underway, including new TiO$_2$ geometries such as nanorod STFs. These films will aid in the future development of solid-state DSSCs by allowing the incorporation of charge separating mediator molecules. Initial studies of these STFs demonstrate equivalent APCE values compared to standard Grätzel cell films, but they suffer from low material thickness and dye loading. Once thicker films are fabricated, efficiencies are expected to compare to the current Grätzel cell architectures.

4.6 References


Chapter 5
Utilizing Colloidal Crystals as Atomic Crystal Analogues

5.1 Introduction

Inorganic crystal chemistry is often underrepresented in the undergraduate laboratory environment due to experimental and characterization logistics. Equipment such as high-temperature furnaces, electron microscopy, and diffraction instrumentation are not frequently encountered by undergraduates and are typically reserved for upper level and graduate laboratories. This is unfortunate since crystal chemistry introduces a geometric basis for many ionic bonding concepts introduced in the first-year undergraduate lecture course. Crystal growth and formation occur by a delicate balance between thermodynamics, kinetics, electrostatics, and packing efficiencies; processes not easily visualized on the atomic scale. Along with these principles, the undergraduate chemistry lab setting is not unique to chemistry majors, but also comprised of other disciplines such as materials science, engineering, and physics that utilize the principles of inorganic crystals. In an attempt to more effectively integrate crystal chemistry into the undergraduate laboratory and to provide a hands-on materials science laboratory for non-majors, a modular series of mix-and-match laboratory exercises has been developed that focus on a modern area of materials chemistry research – self-assembled colloidal crystals. As previously mentioned in Chapter 2, colloidal crystals are periodic arrays of monodisperse spheres that self-assemble into a close packed lattice. These crystals are
analogous to the many of the simple packing structures found in elements and simple molecules. Since colloidal crystals are at least two orders of magnitude larger than atomic crystals, packing geometry can be observed with standard microscopy. In this laboratory experiment, colloidal particles in the size range of 300-800 nm are synthesized, and colloidal crystal films are assembled using these colloids. The crystal structure is then be determined by examining diffraction from visible light sources. Diffraction experiments are easily performed with visible light, lasers, or transmission spectroscopy. Utilizing colloidal crystals as models for atomic crystals introduces a segue between the over-generalized “ball and stick” model and the more conceptual atomic model. For some, an intricate explanation of diffraction and symmetry concepts may suffice as a model for crystal chemistry. In most cases, however, this is not plausible in the already cramped and intensely driven lecture and laboratory courses. The “ball and stick” model of solids offers an easily manipulated visualization of ionic solids. Although these models can be constructed by a student, it lacks experimental cause and effect relationships such as dislocations, anisotropy, and defects common to real crystals. The synthesis of organic or inorganic monodisperse spheres and the corresponding inverse structures provides a rich, yet simple synthetic portion to this modular lab. The application of colloidal crystals in areas such as communications, separations, and photonics also makes this lab very applicable to current technology. Although there are a number of lab exercises devoted to materials science, there are few labs that address so many principles of crystal chemistry, including synthesis and a variety of characterization strategies.
The fundamental mechanisms of sphere synthesis and colloidal crystal assembly have been described in Chapter 2 and will not be discussed here.

5.2 Modular Lab Approach

The design of this laboratory is modular to allow instructors to tailor the synthesis and characterization to the desired level of complexity, length of time, and availability of instrumentation. The modular components of the colloidal crystal laboratory are shown in Figure 5.1. The basic elements involve (1) synthesizing monodisperse colloidal spheres, (2) assembling these spheres into close-packed colloidal crystal lattices, (3) characterizing the local structure of the colloidal crystals by microscopy, and (4) characterizing the long-range order using optical spectroscopy and diffraction.
These experiments have been successfully implemented at The Pennsylvania State University over the past four years with classes of first-year undergraduates majoring in either chemistry or chemical engineering. Class supervision included one laboratory instructor, and collaboration with technicians in an electron microscopy facility, and occasionally a teaching assistant. These experiments were combined as a
long-term team-based laboratory project that typically lasted 4-6 weeks, and included aspects of inorganic and organic synthesis, thin film self-assembly, optical microscopy, scanning electron microscopy, UV-visible spectroscopy, and optical diffraction. By focusing on individual experiments, this laboratory could easily be adapted to shorter modules appropriate for any undergraduate setting.

5.3 Synthesis and Assembly

Inorganic sol-gel or organic polymer synthesis can be used to obtain submicron SiO₂ or microscale polystyrene spheres, respectively. Alternatively, monodisperse polymer spheres can be purchased commercially (e.g. Polysciences, Bangs Laboratories, Interfacial Dynamics Corporation, etc.), which is ideal for facilitating simple observations and lecture demonstrations. Monodisperse SiO₂ spheres are synthesized by the slow, base-catalyzed hydrolysis of tetraethoxysilane (TEOS). In a typical synthesis, ethanol (59 mL), ammonium hydroxide (9 mL), and water (10 mL) are combined in a 250 mL Erlenmeyer flask, and TEOS (4 mL) is added while stirring. Stirring is continued for several hours or days, and spheres are washed with ethanol and separated using centrifugation (1000 – 4000 rpm). Typical results are summarized in Table 5.1. Polystyrene spheres (1 – 10 µm) can be synthesized using several approaches, but the preferred method is the preparation of 3 – 4 µm spheres by dispersion polymerization in ethanol. Typically, 0.4 g of 2,2’- azobisisobutyronitrile (AIBN) and 1.6 g of polyvinylpyrrolidone (PVP) are added to a mixture of 22 mL (0.192 mol) of styrene and 49 mL of ethanol while mechanically stirring (150 rpm) and refluxing at 60 °C under
nitrogen or argon. After 24 h, the spheres are washed with methanol and separated using centrifugation (1000 rpm). Both SiO$_2$ and polymer spheres are dried under ambient conditions.

Table 5.1: Synthesis variables and results for various SiO$_2$ sphere preparations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ethanol (mL)</th>
<th>NH$_4$OH (mL)</th>
<th>H$_2$O (mL)</th>
<th>TEOS (mL)</th>
<th>Size (nm)</th>
<th>Dispersity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>54</td>
<td>8</td>
<td>9</td>
<td>3.5</td>
<td>316</td>
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<td>54</td>
<td>10.5</td>
<td>7</td>
<td>3.5</td>
<td>528</td>
<td>5.4</td>
</tr>
<tr>
<td>C</td>
<td>54</td>
<td>9.5</td>
<td>8</td>
<td>3.5</td>
<td>462</td>
<td>4.9</td>
</tr>
<tr>
<td>D</td>
<td>53</td>
<td>8.5</td>
<td>10</td>
<td>3.5</td>
<td>695</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Microscopy can be used to image the colloidal particles, and then these images can be used to determine their size. For particles larger than 800 nm, a high-magnification optical microscope can be used. For smaller particles, a scanning electron microscope (SEM) will need to be used to image the particles. (Generally speaking, the SEM will give clearer, high-resolution images for submicron particles than an optical microscope.) Most imaging products for SEM come with a scale bar that can be viewed and printed, while not all optical microscopes include a scale bar. A good way of manufacturing a scale bar is to place a ruler with fine increments under the same magnification as the imaged spheres. Using the gradations of the ruler, one can determine the sphere size. This is best done by measuring the length of a row of 5-10 spheres and finding the average diameter per sphere. If a digital SEM image is obtained, software (freeware) such as NIH Image$^6$ (Macintosh), ImageJ$^6$ (Java), and Scion Image$^7$ (Windows) can be used to count and size the spheres.

Colloidal crystallization can be achieved either through convective self-assembly, which takes hours to days, or by simple drop coating, which takes minutes. The highest
quality colloidal crystals of monodisperse submicron spheres are prepared using the thin film convective assembly method developed by Colvin and co-workers. In a general assembly, dry SiO₂ spheres are placed in a 20 mL vial or small beaker along with an appropriate amount of ethanol, and sonicated for 30 minutes to disperse the spheres as a uniform colloidal suspension. A cleaned glass slide (washed with acetone, ethanol, and water) is placed vertically in the colloidal suspension, and evaporation over several days deposits a uniform colloidal crystal film on the glass slide. Spheres larger than 400 nm tend to settle before deposition is complete, so the crystallization process can be accelerated by using a vacuum dessicator or drying oven. Alternatively, a few drops of the colloidal suspension can be placed on a clean glass slide and quickly dried to form a colloidal crystal with localized ordering. Work performed by Ozin and co-workers uses convective heating to maintain a suspended solution of larger spheres, but this procedure is most likely beyond the scope of an undergraduate lab.

5.4 Colloidal Crystal Characterization

To determine the quality of the colloidal crystal films, a few different characterization methods can be employed. Direct imaging of the colloidal crystal can be achieved by SEM, which shows the close-packed assembly of spheres. To do this, a thin conductive film must be evaporated on top of the colloidal crystal to prevent surface charging. When imaging, the (111) crystal face will be the top surface of the crystal. Each sphere should have 6 nearest neighbors in the same plane. To see other crystal faces and neighbors above and below, the substrate must either be cracked or scratched.
before placing into the SEM. By viewing the cross-section of the colloidal crystal, other crystal faces can be seen along with the close-packed neighbors. Students can directly observe several aspects of colloidal crystals that mimic atomic crystals (see Figure 5.2): (a) the colloidal spheres adopt a close-packed lattice, (b) each sphere is surrounded by 12 other spheres (6 in-plane, 3 above, 3 below) in a cubic close packed (face centered cubic) arrangement, (c) defect sites exist, and they cause distortions in the crystal lattice, and (d) domain sizes can vary from 10 µm up to 1 cm, depending on the crystallization conditions. (Regions of hexagonal close packing are also present, but difficult to discriminate.) Cross-sectional views are best achieved by evaporating a conductive coating on the scratched edge and tilting the sample stage in the SEM.
Viewing the crystallization process *in situ* through an optical microscope is also highly instructive, because students can see the spheres move around and adopt an optimized geometry, as well as form and propagate defects in the lattice. By analogy to the diffraction of x-rays by atomic crystal lattices, a colloidal crystal diffracts visible and near-infrared light since its modulated dielectric constant is periodic at optical frequencies. The optical (photonic) properties of colloidal crystals made from submicron
SiO$_2$ spheres are easily observed in the highly reflective and deeply colored films (Figure 5.4a).

### 5.4.1 UV-Visible Characterization

According to Bragg’s law, a crystal will diffract according to Eq. 5.1:

$$\lambda_{peak} = 2n_{eff}d_{111} \sin \theta$$  \hspace{1cm} 5.1

Where the value of $\lambda_{peak}$ yields the expected positions of the absorption peaks that correspond to particular interplanar spacings ($d_{hkl}$), $n_{eff}$ is the refractive index of the material ($n_{eff} = 1.375$ for the optimal volume packing fraction of 74% SiO$_2$ and 26% air), $\theta = 90^\circ$ if the substrate is placed perpendicular to the incident beam, and $d_{111}$ is the interplanar spacing of the fcc colloidal crystal. If the edge length of the crystal unit cell is represented as $a$, the body diagonal length is found to be $a\sqrt{3}$. The unit cell is then split into four (111) planes or three interlayer $d_{111}$ spaces. The distance between spaces is then $(a\sqrt{3})/3$, or $a/\sqrt{3}$. From Pythagorean Theorem, if $D$ is the sphere diameter, the face diagonal is found to consist of a length $2D$ since two full sphere diameters span the diagonal. This is related to edge length $a$ by $a\sqrt{2} = 2D$ or $a = D\sqrt{2}$. Substituting this value into $a$ from the body diagonal, $d_{111} = (\sqrt{2}/3)D$ (Figure 5.3).
To determine the diameter of the spheres from a colloidal crystal, the colloidal crystal is placed in a UV-Vis-NIR instrument to obtain an absorbance or transmittance spectrum. Although absorbance and transmittance are mathematically interconvertible, a photonic stopband results from reflection, rather than from absorption of a particular wavelength. The transmittance minimum corresponds to the diffraction peak of the colloidal crystal. Sphere size is then determined by solving the Bragg equation for $d_{111}$. By accurately varying $\theta$, the stopband will be blue-shifted and an angle dependence on Bragg’s law can be calculated. Thus, absorption spectra obtained using a standard UV-Visible spectrophotometer can be used to analyze both the color and structure of the colloidal crystal films (Figure 5.4b). Note that high quality colloidal crystals are necessary to yield the sharpest, most easily resolved absorbance peaks.
5.4.2 Optical Diffraction

High-quality colloidal crystal films act as diffraction gratings, and diffraction of monochromatic light from a laser pointer can yield a hexagonal diffraction pattern, which can be used to calculate the periodicity of the lattice. In determining sphere size and crystallinity with the conventional spectroscopy, many wavelengths are scanned and the maximum of the absorbance peak corresponds to the wavelength at which Bragg’s Law is satisfied. Utilizing an incident beam with a fixed wavelength will also cause diffraction, but since sphere diameter is fixed, $\theta$ must vary to satisfy the Bragg equation. To determine the $d_{111}$ spacing with optical diffraction, a monochromatic incident beam is directed at the substrate. In this case, the Bragg equation is modified to account for the transmission rather than reflection of the diffracted spots by removing the factor of 2, otherwise known as the Fraunhoffer Law.\textsuperscript{10} The distance between the incident spot and diffraction spots that are displayed can then be measured as well as the distance from the

Figure 5.4: (a) Photograph of self-assembled colloidal crystal film of 236 nm SiO\textsubscript{2} spheres on glass, and (b) its UV-visible transmission spectrum.
substrate to the display surface. The lattice spacing can be calculated using the 
Fraunhofer law and simple trigonometry as seen in Figure 5.5.

Figure 5.5: Experimental setup for lattice spacing calculation. As incident light (from a 
laser pointer) passes through the photonic crystal, it is diffracted according to the 
Fraunhoffer law. The distance from the photonic crystal and the incident spot can be 
measured, as well as the spacing between the incident spot and the 1st order diffraction. 
Trigonometric calculations lead to the lattice spacing, $d$. 

Typical laser sources include gas lasers such as HeNe and Ar-ion, as well as simple handheld red and green laser pointers. To calculate the lattice spacing, the laser wavelength must be known. In the case of a HeNe, $\lambda = 632$ nm. Solving Figure 5.5 for $d$ requires simple trigonometry:

$$\theta = \arctan\left(\frac{l}{l_0}\right)$$

$$\lambda_{632\text{nm}} = d n_{\text{eff}} \sin \theta$$

$$d = \frac{\lambda}{n_{\text{eff}} \sin \theta}$$

5.5 Conclusion

The development of a synthetic lab based on crystal chemistry and self-assembly is a unique addition to the undergraduate curriculum. These experiments have been designed and written for a first year undergraduate chemistry laboratory, but they easily accommodate higher levels of undergraduate education. Since the experiments are highly modular, they can be used at several levels of ability, instrumental availability, and synthetic complexity. The lab is also amenable to cooperative learning, because certain experimental details can be varied to produce distinct, but comparable, results among groups. For example, the concentrations of ammonium hydroxide, ethanol, water, and TEOS can be varied in the synthesis of monodisperse SiO$_2$ spheres to yield different sphere sizes, which will yield colloidal crystal films that have different photonic properties. Through comparison among multiple groups, students can deduce trends and
the effects of these variations. Overall, this laboratory module has proven to be highly effective both at introducing students to crystal chemistry in the laboratory and at providing chemistry majors and non-majors with a modern materials science approach to chemical synthesis and characterization.

5.6 References


VITA

Neal M. Abrams

Neal Mathew Abrams was born on the 30th of November, 1978 in Fall River, Massachusetts to Lisa Abrams and Steven Abrams. With consistent inclination to take dissect and figure out “what makes things work”, Neal found himself attracted to science and getting to the bottom of it all, while also convincing his parents that a 3rd child would be a bad choice. During this scientific discovery process, which ironically included frequent sunlight concentration with a magnifying glass, his teachers inspired him to learn more outside textbooks as well as take an interest in teaching itself. Neal served as a student mentor during his years at B.M.C. Durfee High School and later became certified as a chemistry teacher in New York State. While growing up, Neal’s scientific interests were juxtaposed with music and theatre as Neal became proficient in playing the clarinet, tenor saxophone, bassoon, and bass, and changing his hair color. His technical theatre skills were honed during high school, but also continued into community theatre and college. Upon matriculation, Neal was unsure of not only what major to choose, but also which college. He somewhat randomly chose both- chemistry at Ithaca College. During his beloved time at Ithaca, Neal was the Outreach coordinator for the chemistry department and served as the stage chair for the Bureau of Concerts where he met his future wife, Julie, amongst many other famous people. In the year of 2000, Neal graduated with a B.S. in Chemistry and earned a certification in secondary education. Knowing that he did not wish stop his education, he turned to graduate school and joined the lab of Dr. Thomas Mallouk at The Pennsylvania State University. While there, he gained expertise in the area of materials chemistry doing work in dye-sensitized solar cells as well as being active in the MRSEC Outreach Program and summer science camps. Not wishing to spend all of his time in lab, Neal took to making wheel thrown pottery, making useful, but rarely beautiful pieces. Turning to other hand-crafted arts, Neal took up beer brewing with his friends and produced quite a number of rich and complex ales. In 2005 Neal graduated Penn State with a Ph.D. in chemistry and traveled back up to Ithaca, NY as a postdoctoral researcher to join the lab of Dr. Francis DiSalvo at Cornell University. Neal wishes to continue in the field of education and teach at a small liberal arts college and eventually travel the world with his wife in a Mini Winne.