IMPROVING THE EFFICIENCY AND THE STABILITY OF DYE-SENSITIZED PHOTOCHEMICAL SOLAR CELLS AND WATER SPLITTING SYSTEM

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Abstract

Dye-sensitized solar cells (DSSCs) are promising solar energy conversion devices because of the low cost of their components. However, there are several challenges that must be overcome for their commercial development. The energy conversion efficiency of dye cells is still far below the level of silicon photovoltaic cells despite an enormous worldwide effort over the past two decades. The widely used N719 dye absorbs the light weakly in the 550 – 700 nm region. If red photons that are not absorbed by the dye can be utilized in DSSC, it will be possible to achieve a much higher efficiency. Several dyes with strong red absorbance have been reported, but because they have lower excited-state excess free energy, they typically have a lower quantum yield for charge injection. Instead of developing additional dyes, this dissertation introduces a novel way to enhance the device efficiency by designing a DSSC with a layer of titania inverse opal photonic crystals (PCs) that enhances light collection. The efficiency of DSSCs increased from 6.5 to 8.3% using titania PCs. This improvement derived from increases in both the short circuit photocurrent and open circuit photovoltage of the cell. Additionally, the enhancement is very sensitive to the degree of physical contact between the PC and nanocrystalline titania layers, and a few hundred nm gap between the layers is sufficient to decouple the two layers optically.

Another issue that prevents DSSCs from commercialization is the use of volatile solvents in the electrolyte. This presents challenges for manufacturing and long term stability for outdoor applications. Hence, a novel solvent system, phosphazene-based nonvolatile electrolytes is examined to replace volatile solvents. Electrolytes based on
hexa [methoxyethoxyethoxy cyclophosphazene] (MEE trimer) with dissolved LiI, NaI, NH₄I, and 1-methyl-3-propylimidazolium (PMII) and I₂ were examined. The anion conductivities were highest in the PMII system and decreased in the order PMII > NH₄I > NaI > LiI. Photovoltaic measurements of DSSCs containing these electrolytes agree with the anion conductivity measurements. In addition, polyphosphazene-plasticizer blends with a dissolved PMII/I₂ electrolyte gave better performance in DSSCs than equivalent poly(ethylene oxide)–plasticizer electrolytes. The efficiencies of these DSSCs are currently low (~1.9%) mainly due to a slow mass transport of I⁻/I₃⁻. This dissertation addresses the primary loss mechanisms and proposes possible ways for improving polyphosphazene-based cells.

The structure of the dye-sensitized solar cell can be modified to carry out the photoelectrolysis of water, producing H₂ and O₂. However, the quantum efficiency of the current dye-sensitized water splitting system is quite low, mainly due to fast charge recombination between photoinjected electrons in TiO₂ and the oxidized dye at the surface. This study assesses the limitations of the current system, and investigates different insulating materials as a thin overlayer, for instance ZrO₂ and Nb₂O₅ on the TiO₂ electrode to improve the efficiency of the system. Having a thin layer of insulating materials increased the photocurrent and slowed charge recombination as confirmed by flash photolysis/transient absorption measurements.
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<th>Description</th>
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<tbody>
<tr>
<td>AM</td>
<td>air mass</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett, and Teller</td>
</tr>
<tr>
<td>Black dye</td>
<td>tri(cyanato)-2,2′′-terpyridyl-4,4′4″-tricarboxylate)ruthenium(II)</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammogram</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>EBG</td>
<td>bandgap energy</td>
</tr>
<tr>
<td>ECb</td>
<td>conduction band edge</td>
</tr>
<tr>
<td>Evb</td>
<td>valence band edge</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>fcc</td>
<td>face-centered cubic</td>
</tr>
<tr>
<td>FESEM</td>
<td>field emission scanning electron microscopy</td>
</tr>
<tr>
<td>ff</td>
<td>fill factor</td>
</tr>
<tr>
<td>FTO</td>
<td>fluorine doped tin oxide</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HPC</td>
<td>hydroxypropyl cellulose</td>
</tr>
<tr>
<td>HRTEM</td>
<td>high resolution transmission electron microscopy</td>
</tr>
<tr>
<td>IPA</td>
<td>isopropanol</td>
</tr>
<tr>
<td>IPCE</td>
<td>incident photon to current efficiency</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>Symbol</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>--------</td>
<td>--------------</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>short circuit photocurrent density</td>
</tr>
<tr>
<td>LHE</td>
<td>light harvesting efficiency</td>
</tr>
<tr>
<td>LPD</td>
<td>liquid phase deposition</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbitals</td>
</tr>
<tr>
<td>MEEP</td>
<td>methoxyethoxyethoxy polyphosphazene</td>
</tr>
<tr>
<td>MEE trimer</td>
<td>hexa (methoxyethoxyethoxy) cyclotriphosphazene</td>
</tr>
<tr>
<td>NHE</td>
<td>normal hydrogen electrode</td>
</tr>
<tr>
<td>OPV</td>
<td>organic photovoltaics</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>$\eta$</td>
<td>efficiency (%)</td>
</tr>
<tr>
<td>nc-TiO$_2$</td>
<td>nanocrystalline titania</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>Ru(bpy)$_3^{2+}$</td>
<td>Ru-tris(bipyridyl)</td>
</tr>
<tr>
<td>SCL</td>
<td>scattering layer</td>
</tr>
<tr>
<td>TCO</td>
<td>transparent conductive oxide</td>
</tr>
<tr>
<td>TON</td>
<td>turnover number</td>
</tr>
<tr>
<td>Ti(i-OPr)$_4$</td>
<td>titanium isopropoxide</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>open circuit voltage</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
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Chapter 1
Introduction

1.1 Renewable Energy

1.1.1 Solar Electricity

Global average energy consumption is increasing rapidly every year. In 2004, the reported energy consumption was 15 terawatt-years (TWh) and is expected to reach 30 TWh by 2050. The greater amount of energy comes from burning fossil fuels, which raises concerns because of finite amount of fossil reserves and climate change caused by greenhouse gas emission from burning fossil fuels. This has motivated the scientific community to find alternative energy sources that are cleaner, greener and more abundant, such as renewable energy sources. There are many options for renewable energy sources such as wind energy, nuclear energy, geothermal energy and solar energy just to name a few. Among these options, solar energy is one of the more attractive alternative energy sources that can provide a solution to a current energy crisis. Roughly 125,000 TW of solar power reaches the earth everyday, and that is more than enough to meet the current energy demands. There are many approaches to utilize solar energy, and one approach is to convert solar energy into electricity using photovoltaics (PVs). However, it is too premature to rely solely on PVs for all our energy needs because of their high processing cost. Solar cell cost can be estimated by Eq. 1.1. Based on Eq. 1.1,
if the materials and processing cost are lowered, and the device efficiency can be improved, it will reduce the solar cell cost. Hence, there is a tremendous amount of effort that has been put into producing solar cells with a high efficiency at lower cost.

One of the major factors contributing to the high cost of PVs is high processing cost because the semiconducting materials being employed in solar cell production must be highly pure and defect-free. The reasons for requiring high purity materials can be explained by understanding the operating mechanism of the PVs.

PVs are made of semiconducting materials such as silicon, cadmium telluride, or copper indium diselenide. Typical pn-junction silicon solar cells consist of n-type and p-type materials that are in intimate contact to each other. Once the pn-junction is formed as shown in Fig. 1.1, some of the electrons in the n-type semiconductor diffuse to the p-type semiconductor leaving positively charged ions at the pn-junction. Also, holes from the p-type semiconductor diffuse to the n-type semiconductor, leaving negatively charged ions at the pn-junction. As a result, a space charge region, or a depletion region is formed at the junction in which a small charge unbalance is created. When photons are absorbed by the semiconductor, charge carriers are generated near the depletion region, and diffuse into the depletion region. This process leads to freeing an electron and a hole while an electron and a hole can also recombine. When the external load (a forward bias) is applied, it provides an alternate current path, and current flows from the pn-junction solar cells. For PVs to achieve high power conversion efficiency, high current and voltage must be generated. These parameters are strongly affected by the surface condition of the

\[
\text{Solar Cell Cost (}/W\text{)} = \frac{\text{Materials & Processing Cost (}/m^2\text{)}}{\text{Conversion Efficiency} \times \text{Manufacturing Yield} \times \text{Insolation}}
\]

1.1
semiconductors. Defects in the materials cause the premature recombination of electrons and holes before they generate any current. As a result, defect-free semiconducting materials with high purity are required to minimize the energy loss due to premature recombination but this concurrently increases manufacturing costs of silicon PVs. Furthermore, this draws more attention to different PVs with lower manufacturing cost.

In general, single-crystal Si-based PVs are considered 1st generation photovoltaic technology. They are single junction cells that have been proven to be more reliable, and are currently dominating the PV markets. However, as mentioned previously, the manufacturing process of these cells is energy- and labor-intensive, and the cost is too high. Additionally, the power conversion efficiencies of these cells are already close to the maximum theoretical efficiency, which is approximately 31% (but is less than 31% due to a mismatch of the bandgap with solar spectrum, as well as parasitic losses). Recently, Sanyo reported an efficiency of 23% for their Si heterojunction cell with
intrinsic thin layer (HIT). Hence, the efficiency of silicon cells is unlikely to improve substantially in the future and the focus of R&D now is to reduce the manufacturing cost.

Second generation photovoltaic technology include amorphous Si (a-Si), CdTe, and Cu(In,Ga)Se₂ (CIGS). Because these thin film solar cells are not made from silicon wafers, the production cost is lower compared to the 1ˢᵗ generation PVs. For instance, First Solar reported the manufacturing cost of $1.25/Wₚ for their CdTe solar cells, which is significantly lower than the current cost of ~$4/Wₚ for single crystalline Si solar cells. Additionally, these cells can be Building Integrated Photovoltaics (BIPVs) and made into shingles for the rooftop. They demonstrate outdoor durability and stability with <1% degradation per year and they are being sold with a 20 year warrantee. However, the device efficiencies of these cells are far below their theoretical limits. Most of the thin film based solar cells have lower open circuit voltage (Vₒc) than the theoretical limits due to Shockley-Read-Hall recombination in the space charge region because of a high density of defects which give rise to energy states within the bandgap. This recombination also lowers the fill factor of the cells. A typical fill factor of one of these cells is below 0.72. However, it can be improved to 0.77, or higher by reducing the recombination and defects through modification of the growth process or performing post-growth passivation. While the efficiencies of these solar cells can be further improved in efforts to lower the solar cell cost, the toxicity of Cd creates certain health and environmental concerns. This problem is now being tackled by First Solar’s “cradle-to-grave” approach in which Cd is sourced from mining byproducts through recovery, and is recycled from used solar cells. These thin film based solar cells have some
significant cost advantages over the 1st generation PVs, and their future in the PV markets is very promising.

Third generation photovoltaic technology is known as an “ultimate” thin film solar cell technology made with abundant, nontoxic, and durable materials, and are not limited by the theoretical maximum efficiency of the single junction device.\textsuperscript{1b} They usually consist of organic photovoltaics (OPV), quantum dots solar cells, dye-sensitized solar cells (DSSC), and multijunction concentrator cells. Because these solar cells are not operated on the principle of the single junction cell, some of these cells can achieve efficiency between 30 – 40 %. For instance, a triple junction InGaP/GaAs/Ge cell demonstrated an efficiency of 36 % (AM 1.5, 100-500x concentration) in 2003 and currently it has increased above 40 %.\textsuperscript{6} Such high efficiency of multijunction cells can be obtained by using semiconductors with different bandgaps. Each semiconductor absorbs different parts of the solar spectrum, and by increasing the number of the semiconductor layers with different bandgap, more photons can be captured. In theory, the maximum efficiency that multijunctions solar cells can attain is 86 %.\textsuperscript{7} Multijunction cells can improve the power conversion efficiency beyond the Shockley-Queisser limit, but the manufacturing cost is very high, so these efficient cells must be used in combination with concentrator optics. As for other types of the 3rd generation PVs, OPVs and DSSCs are emerging as low cost (but currently lower efficiency) alternatives to the 1st and 2nd generations PVs. OPVs are based on organic semiconductors, and these cells and modules can be produced on the roll-to-roll process. The highest reported efficiency of the OPVs is currently ~ 8 % (Plextronics) while most of OPVs are in the range of 4 - 5 %\textsuperscript{8}. 


Dye sensitized solar cells (DSSCs) have higher demonstrated efficiencies than OPVs. The major advantage of DSSCs is low cost production because the anode is made of a wide bandgap semiconductor, TiO$_2$ which is widely available. Other advantages that DSSCs have over Si PVs are summarized in Table 1.1.

Table 1.2: Si p-n-Junction Solar Cells vs. Dye-Sensitized Solar Cells

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Si p-n Junction Solar Cell</th>
<th>Dye-Sensitized Solar Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Conversion Efficiency.</td>
<td>✓</td>
<td>✓ Low Fabrication Cost.</td>
</tr>
<tr>
<td>Robust system for outdoor application.</td>
<td>✓</td>
<td>✓ Transparency of the device.</td>
</tr>
<tr>
<td>Disadvantages</td>
<td>High manufacturing Cost</td>
<td>Lower Conversion Efficiency</td>
</tr>
<tr>
<td>Decrease in performance due to a heat build-up</td>
<td>✓</td>
<td>than Si Solar Cells.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sealing/leakage problem for outdoor application.</td>
</tr>
</tbody>
</table>

Since the first report of 7.1 - 7.9 % efficiency in 1991, the best reported efficiency of DSSC rose rapidly to 10 – 11 % and there has been only incremental improvement since 1993. A maximum efficiency of 11.5 % was recently reported. However, these cells are laboratory scale, and their active area is very small. As the size of the cell increases, the device efficiency decreases as a result of an increased resistive loss in the substrate. The reported efficiency of a 100 cm$^2$ sized module with 59 cm$^2$ active area is 4.9 % at 1000 W/m$^2$. The most recent reported conversion efficiency of the DSSC submodule (Aperture area = 25.45 cm$^2$) is 8.2 %. While DSSCs’ efficiencies are still low compared to Si-wafer based PVs, they are comparable to other thin film based PVs,
and there are possible routes to improve their efficiency. In theory, an efficiency of 15 % is feasible. Because sensitizer molecules act as light absorbing materials, their absorption spectra determine the photocurrent action spectrum of the device, and play a major role determining the device efficiency. Synthesizing novel dye molecules with broader absorption spectrum is one strategy to enhance the photovoltaic performance of these devices. Another strategy to increase the photocurrent is to optically manipulate the photons to increase their interaction with dye molecules and increase the absorption pathlength. In Chapter 3, TiO$_2$ inverse opals are employed in DSSCs to optically enhance the red absorption of the spectrum in which the N719 dye absorbs weakly. The anode of DSSCs is prepared as bilayers of inverse opals and nanocrystalline (nc)-TiO$_2$ a higher photocurrent is observed relative to conventional DSSCs without TiO$_2$ inverse opals. A detailed discussion on the configuration of bilayers, and enhancement mechanism is described in Chapter 3.

There are also some drawbacks with DSSCs that prevent them from commercialization. The major one is the stability issue for outdoor applications. DSSCs are photoelectrochemical cells that contain liquid electrolytes with redox couple between the electrodes to complete the circuit. DSSSs must sustain their performance for at least 20 years in different climates. However, the use of organic solvent based electrolytes complicates the long term stability of DSSCs. In efforts to avoid evaporation and leakage of the liquid electrolytes, a glass frit sealing method has been implemented instead of using polymeric sealing materials. In this study, DSSCs sealed with a glass frit showed an overall degradation of less than 5 % in device efficiency under accelerated ageing tests at 85°C. Also, it was recently confirmed that the N719 dye-adsorbed TiO$_2$ electrode and
carbon counter electrode were stable for ~2.5 years using polyolefin based sealant.\textsuperscript{14} Another approach to improve the stability of the DSSCs is to replace liquid electrolytes with a nonvolatile solvent or organic/inorganic hole conducting materials. However, the power conversion efficiencies of DSSCs with these electrolytes are relatively low. In Chapter 4, the use of phosphazene based nonvolatile electrolytes in DSSCs is discussed in details. Electrochemical characterization and photovoltaics measurements were carried out to elucidate the limitation of phosphazene based electrolytes and to provide ways to improve the performance of these cells.

1.1.2 Solar Fuels

Another approach of utilizing solar energy is to convert sunlight to generate chemical fuels such as H\textsubscript{2}. H\textsubscript{2} has an energy density of 140 MJ/kg as compared to the energy density of liquid fuel, ~50 MJ/kg.\textsuperscript{15} The most ideal way to generate H\textsubscript{2} would be using only sunlight as a driving force to split water because it would be a most clean way to produce hydrogen. H\textsubscript{2} is an energy carrier that can electrochemically react with oxygen in atmosphere inside fuel cells to produce water and electrical energy.\textsuperscript{16}

As shown in Eq. 1.2, water splitting reaction is a thermodynamically uphill reaction that requires an energy input of 1.23 V. This indicates that direct water splitting using either visible or near-infrared light is achievable. Since water does not absorb photons, light absorbing materials such as semiconductor and molecular sensitizers are required to convert photons to H\textsubscript{2} and O\textsubscript{2}. 
According to Bolton et al., the theoretical maximum efficiency of water splitting using visible and near infrared photon absorbers is approximately 31 % when quantum yield is 1. However, it is almost impossible to achieve a quantum yield of unity in reality. When an energy loss of 1V is assumed, an efficiency of 12 % can be obtained as indicated in Fig. 1.2.

\[
\begin{align*}
\text{hv} & \quad 2\text{H}_2\text{O}^{(l)} \rightarrow 2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \quad E^\circ = 1.23 \text{ V} \\
4\text{H}^+ + 4\text{e}^- & \rightarrow 2\text{H}_2\text{(g)} \\
2\text{H}_2\text{O}^{(l)} & \rightarrow \text{O}_2\text{(g)} + 4\text{e}^- \\
\end{align*}
\]
The first demonstration of photocatalytic water splitting system was carried out by Fujishima and Honda in 1972. The Fujishima-Honda cell consists of TiO$_2$ photoanode, and Pt counter electrode as shown in Fig. 1.3. When a TiO$_2$ photoanode is irradiated with UV photons, electrons and holes are generated. When an external bias is applied to the system, electrons can reduce water to produce hydrogen in counter electrode, and holes oxidize water to produce oxygen. However, the system is not relevant in practical applications since sunlight that reaches the earth is mostly composed of visible photons and near infrared. Hence, it is vital to find efficient water splitting systems that operate under visible light irradiation.
There have been a number of reports on overall water splitting, and thus far photoelectrochemical cells based on semiconductors show the most promising results. For instance, a monolithic GaInP$_2$/GaAs photovoltaic-photoelectrochemical device by John Turner et al. demonstrated an efficiency of 12.4 % (Fig. 1.4 (a)), and 18.3 % conversion efficiency was also reported on AlGaAs/Si RuO$_2$/Pt$_{\text{black}}$ photoelectrolysis cell by Licht, S. et al.\textsuperscript{19} However, the major drawback of these cells is a high manufacturing cost. Domen et al. recently reported a visible light driven overall water splitting system based on a powder photocatalyst, (Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$) that is modified with Rh/Cr$_2$O$_3$ core-shell cocatalyst (Fig. 1.4 (b)).\textsuperscript{20} The reported quantum efficiency of the system was 2.5 % at 420 – 440 nm which was later improved to 5.9 % at 420 – 440 nm by post calcining the photocatalyst.\textsuperscript{21} Because this system absorbs only at the blue edge of the visible spectrum, its power conversion efficiency is very low.
In addition to the previously mentioned water splitting systems, molecular-semiconductor hybrid water splitting systems are another way to produce H₂ and O₂. These molecular-semiconductor hybrid systems are inspired by nature’s photosynthesis. As shown in the (as yet experimentally unrealized) schematic in Fig. 1.5, a rapid energy transfer from antenna molecules to sensitizer molecules that are bound to semiconductor surfaces excites the sensitizers, leading to electron injection from excited state of sensitizer to semiconductor. These injected electrons are then supposed to be transported.

Figure 1.9: Schematic illustrations of (a) monolithic PV-PEC device for photoelectolysis of water, and (b) metal-Cr₂O₃ core-shell catalyst for photocatalytic water splitting.
to catalytic sites in which water reduction occurs; regeneration of the reduced form of the sensitizers by an electron donor is supposed to result in water oxidation.

This biomimetic hybrid system is conceptually appealing for several reasons. First, the electron transfer process at the interface of sensitizers and semiconductors has been well studied, and kinetics of the process can be manipulated by tailoring the chemistry between semiconductor and molecule sensitizers to optimize the system. Moreover, the system can be assembled with inexpensive components unlike most semiconductor-liquid junction photoelectrolysis cells.

In our laboratory, we have taken a molecular-semiconductor hybrid approach to tackle the challenges of designing an overall water splitting system. Recently, we reported a dye sensitized photoelectrochemical water splitting system incorporating an oxygen evolving photocatalyst such as IrO$_2$, coupled to sensitizer molecules that are anchored onto TiO$_2$ surface to produce oxygen in the anode compartment of the cell. In the other compartment of the cell, hydrogen is produced at a Pt counter electrode. While the quantum yield of the system is low, $\sim 0.9\%$ at 450 nm, different means to improve the

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Figure 1.10: Hypothetical visible light driven molecular-semiconductor hybrid system for overall water splitting.$^{23}$

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current system are being investigated. Additionally, a novel hybrid water splitting system based on layer-by-layer assembly is currently being explored.\(^{25}\)

1.2 Overview of Research

1.2.1 Preparing Dye-Sensitized Solar Cells (DSSCs) & Coupling Photonic Crystals (PCs) to nc-TiO\(_2\) Films in the DSSCs

Chapter 2 introduces the basic operating principle of the dye-sensitized solar cells (DSSCs) and discusses how each major component of the cells affects the photovoltaic performance of the devices. It also describes the experimental procedure on how to prepare nc-TiO\(_2\) colloidal solution and how to assemble the DSSCs in three different ways. It should be noted that each step along the way to assembling the final device has an effect on the power conversion efficiency of the cell and should be well-controlled.

In Chapter 3, DSSCs with bilayers of nc-TiO\(_2\) and titania inverse opal photonic crystals (PCs) in different configurations are compared quantitatively to conventional DSSCs without titania inverse opal. Previously, we reported that coupling the PCs to DSSCs results in a 26 % enhancement of red photon absorption in the visible spectrum.\(^{26}\) As a follow up study, we prepared DSSCs with bilayers in different configurations to understand the effects of coupling PCs to the nc-TiO\(_2\) films and we recognized that the configuration of bilayers had a strong influence on the enhancement mechanism. The bilayer cells were fabricated with PC/nc-TiO\(_2\) and nc-TiO\(_2\)/PC bilayer films on glass/tin oxide anode of the cell, as well as in a split configuration in which the nc-TiO\(_2\) and PC layers were deposited on the anode and cathode sides of the cell, respectively. The
results of the photoaction spectra, short circuit current densities, and power conversion efficiencies of these cells support a model proposed by Miguez and coworkers, in which coupling of the low refractive index PC layer to the higher index nc-TiO$_2$ layer creates a standing wave in the nc-TiO$_2$ layer, enhancing the response of the DSSC in the red region of the spectrum.\textsuperscript{27} In our study, we have found that this enhancement is very sensitive to the degree of physical contact between the two layers. A gap on the order of 200 nm thick, created by a polymer templating technique, is sufficient to decouple the two layers optically. The coupling of the nc-TiO$_2$ and PC layers across the gap could be improved slightly by treatment with TiCl$_4$ vapor. In the bilayer configuration, there is an enhancement across the visible spectrum, which is primarily caused by defect scattering in the PC layer. There is also an increase of 20-50 mV in the open circuit photovoltage of the cell. With anode side illumination, the addition of a PC layer to the nc-TiO$_2$ layer increased the efficiency of DSSCs from 6.5 to 8.3% at a constant N719 dye loading of 155-160 nmol/cm$^2$.\textsuperscript{28}

1.2.2 Phosphazene-based Non-Volatile Electrolytes for the DSSCs

While DSSCs may have promising future due to their low production cost and their comparable power conversion efficiencies to amorphous silicon solar cells, the use of liquid electrolytes in DSSCs present problems for manufacturing and long term stability. To improve the stability of DSSCs, different alternatives to liquid electrolytes, such as polymer electrolytes, and organic hole materials have been investigated by different research groups. In Chapter 4, phosphazene-based non-volatile electrolytes are
characterized electrochemically, and investigated as an alternative solvent to replace volatile organic solvent based electrolytes in DSSCs. The limitations of phosphazene-based electrolytes are described, and ways to improve the current system are suggested.

To optimize the phosphazene based electrolytes in DSSCs, phosphazene-based electrolytes containing different iodide salts were studied. Electrolytes based on hexa[methoxyethoxyethoxy cyclotriphosphazene] (MEE trimer) with dissolved LiI, NaI, NH₄I, and 1-methyl-3-propylimidazolium (PMII) and I₂ were examined by AC conductivity and steady state voltammetry. These measurements gave the individual conductivities of I⁻, I₃⁻, and cations in each electrolyte as a function of salt concentration. The anion conductivities were highest in the PMII system and decreased in the order PMII > NH₄I > NaI > LiI. Photovoltaic measurements of DSSCs containing these electrolytes showed the same order of performance. Electrochemical impedance spectra (EIS) under open circuit and forward bias conditions was used to study the separate impedance components of the cells. Polyphosphazene-plasticizer blends with a PMII/I₂ electrolyte gave better performance in DSSCs than equivalent poly(ethylene oxide)–plasticizer electrolytes. Although the efficiencies of these DSSCs were relatively low (1.9%), this study identified the primary loss mechanisms and suggested possible avenues for designing more efficient polyphosphazene-based cells.²⁹

1.2.3 Photoelectrochemical Water Splitting System

In Chapter 5, overall water splitting systems that incorporate molecular photosensitizers as visible light absorber with oxygen evolving catalyst is discussed.
These photosensitizers also act as a linker to couple catalytic nanoparticles with semiconductor films to build an organic-inorganic hybrid photocatalytic water splitting system. Previously, it was demonstrated in our laboratory that IrO$_2\cdot$nH$_2$O (1-3 nm diameter) nanoparticles that are stabilized by malonate or succinate ligands of Ru-tris(bipyridyl) complexes can perform as oxygen evolving photocatalysts. These results led us to construct an overall water splitting dye-sensitized cell using mesoporous TiO$_2$ and Pt as anode and cathode materials, respectively. However, the quantum efficiency of the system is quite low (0.9%) due to rapid back electron transfer from the TiO$_2$ to the oxidized sensitizer. To retard the back electron transfer rate of the system, we incorporated composite (core-shell) metal oxide films as the photoanode. In DSSCs, it is demonstrated that coating TiO$_2$ films with a thin layer of insulating oxides retards the rate of back electron transfer between the conduction band electrons of TiO$_2$ and the HOMO of the dye by creating a tunneling barrier. Hence, we employed the same idea to the water splitting system, and investigated whether core-shell electrodes can reduce the back electron transfer rate to achieve a higher quantum efficiency.
1.3 References


Chapter 2
Dye-Sensitized Solar Cells

2.1 Introduction

2.1.1 Operating Principle of Dye-Sensitized Solar Cells

In 1985, a group of scientists led by Michael Grätzel introduced dye-sensitized solar cells (DSSC)\(^1\) and later an efficiency of 11.5\% was reported for cells with active areas less than 1 cm\(^2\).\(^2\) In conventional pn junction silicon solar cells, a semiconductor absorbs light generating charge carriers. Then, the charge carriers are separated by the built-in electric field at the p-n junction and are transported via a conductive contact through the external circuit. In DSSCs, light is absorbed by a monolayer of dye adsorbed chemically at a mesoporous nc-TiO\(_2\) semiconductor surface. These dye molecules are electronically excited by absorbing photons, and the excited state dye molecules are able to transfer electrons to the conduction band of TiO\(_2\). Because the interface is bathed in a strong electrolyte (~ 1M LiI) the Debye screening length is very small, and hence there is no electric field driving charge separation. This is a fundamental difference between pn junction cells and dye cells. The electrons are transported across the TiO\(_2\) film to a fluorine-doped tin oxide (FTO) transparent conductor. After having lost an electron to TiO\(_2\), the dye is oxidized but is regenerated by receiving one electron from I\(^-\), which reacts with a second I\(^-\) ion to rapidly generate I\(_2^--\). These radical species combine in
solution to form $I_3^-$, which is the stable form of $I(0)$ in this medium. At the counter electrode, $I_3^-$ is reduced back to $I$ by an electron that travels through the external circuit of the device (Fig. 2.1). In DSSCs, all the components are regenerated during the cycle.

To ensure high photocurrent from the DSSCs, the charge injection process from the sensitizer to TiO$_2$ must be efficient. There has to be a strong electronic coupling between the sensitizers and the semiconductor. In DSSCs with N3 and N719 dyes, the sensitizers are anchored onto the semiconductor surface covalently via carboxyl groups promoting an ultrafast electron injection to the TiO$_2$ and contributing to high power conversion efficiency. In addition, the theoretical maximum voltage in the DSSCs is determined by the Fermi level of TiO$_2$ and the redox potential of $I/I_3^-$ in the electrolyte. The maximum voltage that can be achieved in the DSSCs is approximately 0.9 V, but this value depends on the electrolyte composition since the Fermi level of the semiconductor varies with composition of the electrolyte and the concentration of ions in it.

In the DSSCs, there are two major recombination pathways that affect the photovoltaic performances. One of these processes is recombination between injected electrons and oxidized sensitizer molecules (Fig. 2.1 R1). However, this process has little effect in the DSSCs because charge recombination between injected electrons and the oxidized dye occurs on the timescale of micro- to milliseconds whereas dye regeneration by $I$ happens on the nanosecond timescale. The major recombination pathway is actually between injected electrons and $I_3^-$, and this reaction is responsible for the dark forward-bias current in the cell. The dark current is mainly attributed to electron capture in regions of the TiO$_2$ surface that are not completely covered by the sensitizer molecules, which can be physically accessed by triiodide. In order to realize efficient DSSCs, the dark
current must be minimized. A loss of the $V_{oc}$ in the DSSCs due to a dark current is described by the Eq. 2.1,

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{\eta \Phi_0}{n_0 k_{et} [I_3^-]} \right) \quad 2.1$$

where $k$ is the Boltzmann constant, $q$ is the magnitude of the electron charge, $T$ is the absolute temperature, $n_0$ is the electron density in the conduction band of TiO$_2$ in the dark, $\eta$ is the quantum yield for photogenerated electrons, $\Phi_0$ is the incident photon flux, $k_{et}$ is the rate constant for recombination, and $[I_3^-]$ is the concentration of triiodide.$^5$

Figure 2.1: Principle of operation and energy level scheme of dye-sensitized solar cells. The energy levels drawn for the sensitizer and the redox mediator are the redox potentials of the sensitizer (S) ground state and the iodide/triiodide couple. R1 and R2 represent recombination pathways in DSSCs, although R1 is not kinetically important in an efficient DSSC. The timescales of these recombination reactions are shown.
2.1.2 Components of DSSCs

2.1.2.1 Transparent Conducting Oxide Substrate

Transparent conducting oxide (TCO) substrates such as fluorine-doped tin oxide (SnO$_2$:F; FTO) and indium tin oxide (In$_2$O$_3$:Sn; ITO) are used in many different applications such as optoelectronic devices, flat-panel displays, photovoltaics and gas sensors. In DSSCs, they are used as substrates to deposit nc-TiO$_2$ films and also as a current collector. Generally, FTO is preferred in DSSCs over ITO mainly because ITO has a thermal instability issue due to oxygen interstitial formation during the annealing process. It is reported in the literature that FTO is thermally stable up to 650 °C, which makes it more suitable substrate for DSSCs since nc-TiO$_2$ films are calcined at 450-500 °C. Although ITO has better transparency and conductivity, an increased sheet resistance from undergoing multiple annealing processes in DSSCs leads to a significant loss in device efficiency.

In selecting the TCO, its optical and electrical properties must be considered. However, a compromise must be made since TCOs with low resistivity also have low transmittance (Fig. 2.2). In our laboratory, generally Hartford TEC 8 (8 Ω/sq) is used for the working electrode (photoanode) and Hartford TEC 15 (15 Ω/sq) for the counter electrode. We also have used FTO substrates from Nippon Sheet Glass (a gift from Nippon Sheet Glass Co., Ltd., Japan) as the photoanode for making DSSCs for outdoor testing. These FTO substrates have a better transmittance than Hartford TEC 8.
2.1.2.2 Metal Oxide Semiconductor Electrodes

The metal oxide semiconductor is a very important component of DSSCs since it must harvest as many photons as possible and transport the electrons to the electrode very efficiently. Early studies of dye-sensitization to convert sunlight to electricity were done using single crystal substrates. With a single crystal substrate, there is only monolayer coverage of dye molecules on the surface and the device cannot absorb more than about 1% of the incident light. When a mesoporous TiO$_2$ film is employed instead, more dye molecules can be immobilized on the surface due to an increase internal surface area of the film. These films are composed of TiO$_2$ nanoparticles (20-30 nm diameter) that are sintered together, and the films have good optical transparency. In the DSSC the film

Figure 2.2: Optical transmittance of FTOs with a different sheet resistance and from a different manufacturer.
thickness is usually between 10-14 µm. In addition, a scattering layer (SCL) that is made of large TiO₂ particles (300 - 400 nm diameter) is applied on top of the mesoporous TiO₂ film to scatter longer wavelength photons back to the sensitized film. The scattering layer enhances the absorption of photons at the red end of the visible spectrum, where the dye does not absorb as strongly as it does in the blue.

While other types of metal oxide semiconductors such as Nb₂O₅, SnO₂ and ZnO have been studied in the DSSCs, TiO₂ is the most widely used because it makes the most efficient DSSCs.¹¹ Among three different crystalline forms of TiO₂, anatase, rutile, and brookite, anatase TiO₂ films give the highest device efficiency. Because rutile typically has a smaller surface area per unit volume than anatase, it has lower dye loading leading to a lower photocurrent. It has also been shown that the electron transport in rutile is slower due to differences in the interparticle connectivity, which is associated with the particle packing density.¹²

In DSSCs, TiO₂ nanoparticles are usually prepared via sol-gel and hydrothermal methods. A titanium alkoxide precursor is added dropwise to an aqueous solution that contains an acid catalyst, usually either acetic acid or nitric acid either at a room temperature or at 0 °C, while the solution is vigorously stirred. The mixture undergoes hydrolysis and a white precipitate is instantly formed in the solution. After the hydrolysis, the solution is heated to complete the peptization process, which breaks up the aggregates and re-disperses them into smaller primary particles. The solution goes through a hydrothermal process at a temperature between 200 - 250 °C for 12 hrs. During the hydrothermal process, the TiO₂ particles grow up to 10 – 25 nm by Ostwald ripening, in which the primary particles dissolve and re-precipitate into larger particles that are
thermodynamically more stable.\textsuperscript{13} The solution is then redispersed by ultrasonication and concentrated down to a desired level by using a rotary evaporator. Finally, the binder is added to the TiO\textsubscript{2} solution to control the thickness of the film and also to keep the film from cracking during drying and calcination.

It has been shown that the size and shape of TiO\textsubscript{2} nanoparticles have a strong influence on the electronic transport properties of the films, and also on electrolyte transport within the film, which ultimately affects device performance. Each synthetic parameter must be well controlled to produce a high quality TiO\textsubscript{2} colloidal solution for DSSCs with high power conversion efficiency. The procedure used to prepare TiO\textsubscript{2} colloidal solutions is described in 2.2.1.

2.1.2.3 Dye Sensitizers

Because TiO\textsubscript{2} is a wide bandgap material (\(E_g = 3.2\) eV) that does not absorb visible photons, dye molecules adsorbed to the surface are used for light harvesting. The sensitizer molecules are anchored onto the semiconductor surface covalently through carboxylate, phosphonate or hydroxamate groups.\textsuperscript{14} Since the solar irradiance reaching the earth is composed mostly of visible and near-infrared (IR) photons, the sensitizer should have strong absorption in visible and near-IR to utilize more photons and thus generate a higher photocurrent. Additionally, the energetics of the dye molecules and semiconductor must be well-matched. The excited state redox potential of dye molecule must be more negative than the conduction band edge potential of the semiconductor. Also, its ground state redox potential should be sufficiently positive so that regeneration
of oxidized dye molecules by the redox couple in the electrolyte can occur in an efficient manner. The dye molecules should also be stable enough to sustain about $10^8$ turnover cycles, corresponding to about 20 years of exposure to natural light.\(^{15}\)

Ruthenium polypyridyl based dyes, which exhibit strong absorption in the spectral region of the interest due to their MLCT (metal-to-ligand charge transfer) transitions in which an electron localized on the metal atom is transferred to a ligand-centered $\pi^*$ orbital, are widely used in DSSCs. These Ru-based molecules can be easily tailored by substituting different ligands to extend the absorption range and to increase the electronic coupling to the semiconductor. Unfortunately, spectral tuning of the dye to absorb more strongly in the infrared comes at the cost of reducing the driving force for its photoredox reactions, and thus there is a long history of dye optimization that has led to relatively small gains in DSSC efficiency. Both the N3 dye, which is fully protonated, and N719 dye, which is doubly-deprotonated (Fig. 2.3 (a)) are commonly used sensitizers in DSSCs. These dyes absorb weakly in the red region of the visible spectrum and in the near-IR. To improve light harvesting, in 2001 the “black dye” with a broader absorption spectrum that extends to ~920 nm was synthesized.\(^{16}\) With the black dye, a device conversion efficiency of 10.4\% was achieved. Another strategy to achieve higher photocurrent is to use a cocktail of different sensitizers with different absorption spectra that complement each other. Although in principle such multi-dye cells could exploit energy transfer cascades to achieve higher efficiency, the device conversion efficiency remains low compared to a single dye.\(^{17}\) The major problem of co-sensitization is disorder of the sensitizer molecules on TiO\(_2\), which results in dye aggregation and self-quenching.\(^{18}\) This effect lowers the photocurrent and overall device efficiency.
There are also metal-free organic dyes that have been explored for use in DSSCs. For large scale development of dye cells, there is a need to avoid ruthenium, which is a rare element that is expensive. Ruthenium-based dyes, which usually have more than one ligand type in the coordination sphere of the metal, require very careful synthesis and purification that can be time-consuming and expensive.\textsuperscript{19} There have been numerous reports on organic dyes in the DSSCs, including coumarin, squarane, indoline, hemicyanine and other conjugated donor-acceptor organic dyes.\textsuperscript{20} Thus far, the highest device efficiency achieved with an organic dye is 8\%.\textsuperscript{21}

As for the stability of the DSSCs, a recent test showed that the DSSCs do not suffer from any instability issue after being exposed to continuous full intensity light for 12000 hr.\textsuperscript{22} This represents a potential advantage of DSSCs over amorphous silicon which undergoes photodegradation due to the Stabler-Wronski effect.\textsuperscript{23} With DSSCs however there can be other sources of instability, such as leaking or evaporation of the liquid electrolyte. Thus while properly sealed devices have good photoelectrochemical stability, there are practical issues associated with manufacturing solar cells that contain volatile liquid electrolytes.
The electrolyte in the DSSC consists of iodide (I⁻), triiodide (I₃⁻) and other additives. The redox couple (I⁻/I₃⁻) in the electrolyte is a key component of the DSSC because it regenerates the oxidized dye. The redox couple should be highly soluble in the solvent to produce a high concentration of charge carriers and both halves of the redox couple should have high diffusion coefficients in the solvent for efficient mass transport.²⁴ Inorganic and organic compounds such as LiI, NaI, KI and alkylimidazolium iodide are dissolved in the solvent with iodine. The device performance of DSSCs is
strongly affected by the counter cations of iodides because these cations adsorb on the 
TiO$_2$ surface causing a shift of the conduction band edge of the TiO$_2$. The general trend 
is that as the size of the cation decreases, the photocurrent increases. The smallest cation, 
for example, Li$^+$ can intercalate into a lattice of the TiO$_2$ surface to shift the conduction 
band edge potential to more positive values, increasing the driving force for the injection 
of an electron from the excited state of the dye, and thus resulting in an increase of the 
photocurrent.

Thus far, the redox couple (I$^-$/I$_3^-$) is the most effective system that regenerates the 
oxidized dye molecules at a faster time scale than a charge recombination process 
between injected electrons and triiodide. However, I$^-$/I$_3^-$ redox couple also has a few 
disadvantages. Iodine is detrimental to grid metals such as Ag and Pt, causing them to 
corrode. Additionally, I$^-$/I$_3^-$ absorbs at the short wavelength (~430 nm) of visible region 
which lowers the photocurrent of the devices. More importantly, a photovoltage of 
DSSCs can be enhanced if I$^-$/I$_3^-$ are replaced by alternative one electron outer-sphere 
redox couple with a more positive oxidation potential. Hence, it is essential to find an 
alternative redox couple that does not suffer from the drawbacks of I$^-$/I$_3^-$ and can improve 
the efficiencies of DSSCs. There have been many reports on the alternative redox 
systems such as Co(III)/Co(II)(dbbip)$_2$ (dbbip = 2,6-bis(1/-butylbenimidazole-2'-yl)pyridine), quinone/hydroquinone, (SCN)$_2$/SCN$^-$, (SeCN)$_2$/SeCN$^-$, and Fc/Fc$^+$ 
(ferrocene/ferrocenium) redox couples. However, the reported efficiencies of these 
redox couples are still lower than I$^-$/I$_3^-$ mainly due to large dark currents caused by 
enhanced recombination rate and a slow diffusion of theses redox couples in the solvents.
The highest power conversion efficiency was recently reported using a disulfide/thiolate redox couple which was 6.4% under 1 Sun.\textsuperscript{28}

Other additives are typically dissolved in the electrolyte to enhance the performance of the DSSC. Pyridine and guanidium derivatives are used to suppress recombination processes. When 4-\textit{tert} butylpyridine adsorbs onto the TiO\textsubscript{2} surface, it binds to the bare surface that is not covered with dye molecules, inhibiting the recombination reaction between electrons in the TiO\textsubscript{2} and I\textsuperscript{3−} in the electrolyte. It thus acts as a passivation layer to physically separate the TiO\textsubscript{2} and the electrolyte. Guanidinium thiocyanate suppresses the recombination rate by a factor of 20 and is frequently used in electrolytes along with 4-\textit{tert} butylpyridine.\textsuperscript{29}

Organic solvents such as acetonitrile, valeronitrile, methoxyacetonitrile, methoxypropionitrile, ethylene carbonate, and propylene carbonate have been used as solvents since the dye molecules desorb from the TiO\textsubscript{2} surface in water. The most commonly used solvent among these is acetonitrile because of its low viscosity. However, encapsulating devices that contain organic solvents such as acetonitrile becomes problematic because of its high volatility (b.p. = 81.6 °C). Replacing acetonitrile with other organic solvents with low volatility does not solve the problem since those solvents generally have higher viscosity which leads to lower diffusion coefficients of the redox-active ions in the electrolyte. Currently, there is ongoing research to replace organic solvent-based electrolytes with room temperature ionic liquids, organic hole transport materials, inorganic hole conductors, and polymer/redox couple blends.\textsuperscript{30}
2.1.2.5 **Platinum Counter Electrode**

The major role of a counter electrode in the DSSC is to regenerate $\Gamma^-$ from $I_3^-$ efficiently, i.e., at low overpotential. In absence of catalysts, this process is kinetically slow and degrades the performance of the cell. Therefore, a thin layer of Pt layer is deposited onto the FTO cathode to catalyze the reaction. A Pt layer can be deposited electrochemically and also via sputtering, vapor deposition and other methods. The thermal preparation of Pt nano-cluster catalysts is the preferred method since the process produces a catalytic site that is made solely of Pt metal with possibly some physically- and chemically- adsorbed oxygen. These Pt nano-clusters have superior kinetic properties, resulting in low charge transfer resistance. Additionally, they are electrochemically stable. The experimental procedure for preparing the Pt counter electrode is described in 2.2.3.

Alternative catalytic materials such as carbon black, single wall carbon nanotubes, poly(3,4-ethylenedioxythiphene) (PEDOT) doped with $p$-toluenesulfonate (PEDOT-TsO) and polystyrenesulfonate (PEDOT-PSS) have been investigated in order to address the high cost of Pt and its corrosion problems with $I_3^-$. These lower cost materials have resulted so far in higher overpotentials, so Pt is still generally used in DSSCs.
2.2 Experimental

2.2.1 Synthesis of TiO$_2$ colloidal solutions

After trying several different published synthetic methods and many failures to produce DSSCs with high efficiencies, with help from Dr. Paul Hoertz, a post-doctoral fellow in our laboratory and Dr. Nathan Neal at the National Renewable Energy Laboratory, we have found a synthetic method that gives us reproducible results. The experimental procedure is described in detail in the following section.

First, 80 mL of acetic acid and 250 mL of nanopure H$_2$O are measured and poured into a 500-mL 2-neck or 3-neck round-bottom flask. The solution must be pre-chilled to 0°C with a dry ice/acetone bath before the titanium alkoxide precursor is added. Using a thermometer and thermometer adapter, the temperature of the solution inside the round-bottom flask is constantly monitored. Small pieces of dry ice are slowly added to the acetone bath to adjust the temperature. The acetic acid/H$_2$O mixture is continuously stirred with a magnetic stir bar while the temperature is adjusted. Because the mixture can freeze, it is important not to stop stirring the mixture at any point in time. After keeping the H$_2$O/acetic acid solution at 0 °C, 35.52 g of titanium isopropoxide, Ti(i-OPr)$_4$ (Aldrich, 205273-500 mL) is weighed in a disposable 40 mL vial and is poured into a 125-mL separatory funnel. 7.86 g (10 mL) of anhydrous isopropanol that is pre-weighed in a 20-mL scintillation vial is used to transfer the entire amount of Ti(i-OPr)$_4$ to the separatory funnel. Anhydrous IPA is added to the vial that contained the Ti(i-OPr)$_4$ and swirled around to dissolve any minimal amount of Ti(i-OPr)$_4$ that is still remaining in the vial. The solution is then gently shaken with a stopper on the top of the separatory funnel.
until it becomes homogenous and still remains clear. The Ti(i-OPr)$_4$/IPA is then added dropwise over period of 30 min to the acetic acid/H$_2$O. While the Ti(i-OPr)$_4$/IPA solution is being added, colloidal TiO$_2$ starts to form and the solution becomes slightly less transparent.

Figure 2.4: Titanium precursor is added dropwise using a separatory funnel to the solution of nanopure water and acetic acid at 0 °C, using an acetone bath that is chilled with dry ice.
The solution is then heated to 80°C with a reflux tube using an oil bath on a hot plate and rapidly stirred the entire time. Upon heating to this temperature, the reaction solution becomes a thick gel (the stir bar stops stirring during gelation but the stirring should not be turned off) and then later becomes a loose, white colloidal solution (The stirring resumes). While the reaction solution is heated at 80°C for 8 hours, it is important to make sure the portion of the solution that is exposed to heat is stirred consistently with
a stir bar to prevent TiO$_2$(s) from being deposited onto the side of the glass. During the heating process, parafilm is used at the top of a reflux tube to minimize vapor loss.

At the end of the 8 hours, the reaction solution is cooled to room temperature. The solution can be left to reach to room temperature overnight. When it is cooled down, the total volume of the colloidal solution is measured by transferring the solution to a graduated cylinder and back to the round bottom flask. The total volume is recorded and the amount of the TiO$_2$ per unit volume in the solution is calculated based on amount of TiO$_2$ precursor used in the synthesis. From the total solution, only 80-mL is taken out to a 250-mL beaker and is ultrasonicated (Level 8, 50% Duty-cycle) for five minutes to break up TiO$_2$ aggregates. Upon ultrasonication, the colloidal solution becomes clearer with hints of blue color.

Figure 2.6: After the sonication, the colloidal solution has no visible aggregates and is clear with a hint of blue indicating that the TiO$_2$ colloid in the solution consists mainly of small particles that scatter primarily blue light.
80 mL of the colloidal solution was then placed in a Teflon cup which in turn was placed in an acid digestion bomb and autoclaved for 12 hr at 230°C at a ramp rate = 5 °C/minute using a Lyndberg/Blue M furnace. In this furnace, the programmed temperature is 250 °C, and there is a temperature difference between the place where the sample is placed and where the furnace thermocouple is. The bomb is placed in the back of the furnace directly below the thermocouple and is not elevated. After cooling the bomb to room temperature, the TiO₂ colloid (white solid + colloidal solution) is transferred to a clean 250-mL beaker for ultrasonicating for 5 minutes under the same conditions described previously. The resulting white solution is transferred to a 250-mL one-neck round bottom flask to be rotovapped to concentrate the TiO₂ to a final concentration of 12 wt%. For example, if 80 mL of a total of 370 mL TiO₂ colloid is autoclaved, this gives 2.16 g/80 mL TiO₂ post-autoclave. Hence, the 80 mL colloidal TiO₂ solution should be concentrated until the entire solution weighs 18 g. It is important to minimize the amount of TiO₂ that is “lost” during the process. Also, during the rotovappping, the water bath temperature must be maintained at approximately 30 °C. A higher temperature seems to cause formation of TiO₂ aggregates. Also, concentrating the solution to dryness or partial dryness (i.e. allowing a significant amount of TiO₂ to precipitate out of solution) must be avoided. This seems to significantly lower the performance of the DSSCs.

After acquiring a 12 wt% colloidal solution, the solution is transferred to 30-mL amber vial and a binder such as hydroxypropyl cellulose (Aldrich 435007, Avg. M₆₆ ~80,000) is added slowly over 3-5 minutes while the solution is rapidly stirred. The HPC concentration is 6 wt% with respect to the total weight of solution and 50 wt% with
respect to TiO$_2$ weight. The solution is stirred very fast for 24 hours and then stirred less rapidly for 3-5 days. The stirring rate is lowered to avoid forming bubbles in the solution. A bubbly solution makes it difficult to make smooth films. The TiO$_2$ paste is continuously stirred until it is all used up. The paste appears as a semi-viscous white fluid.

2.2.2 Preparing TiO$_2$ Photoanodes

2.2.2.1 nc-TiO$_2$ Films.

Tape casting is used to deposit TiO$_2$ films using Scotch® Magic™ tape (3M, Cat. 810, Thickness = 50 µm). The thickness of the film depends on the number of pieces of tape stacked on either side of the exposed substrate surface (e.g. four layers of tape give ~11-14 µm thick films by profilometry after sintering the films). TiO$_2$ paste is applied to the substrate by a glass rod and spread using a razor blade. The thin film is allowed to air dry at room temperature for 10-20 minutes; the films should be crack-free and fairly transparent. The films are then sintered by heating the films at a rate of 5 °C/min to a final temperature of 450 °C and maintaining this temperature for 30 minutes using a Lyndberg/Blue M furnace; the programmed temperature was actually 475 °C due to a temperature difference between the place where the sample is placed and the furnace thermocouple. The films are then cooled at a rate of 10 °C/min.

For sensitizing films with the N719 dye purchased from Solaronix, 9 mg of N719 is added to 40 mL 1:1 acetonitrile/tert-butanol (0.2 mM) and the solution is sonicated in
an amber vial for 30 minutes. After sintering the TiO$_2$ films at 450 °C for 30 min, the films are cooled to 150 °C and sensitized. The TiO$_2$/FTO samples are slowly submerged into the N719 solution to avoid breaking the substrates. Sensitization for 2 days seems to give the best results. After sensitization, the electrodes are taken out of the staining jar and rinsed with acetonitrile. The films are dried in the air. Once the sensitized film is dried, the ground state absorbance for N719/TiO$_2$/FTO is measured via UV-Vis and the absorption at $\lambda_{\text{max}}$ should be between 1.75 and 2.0 at 535 nm. A blank FTO slide is used as a background sample.

2.2.2.2 Applying the Scattering Layer

A scattering layer (Solaronix, Ti-Nanoxide 300, 10g) is also applied on the nc-TiO$_2$ film using a doctor blade technique after the nc-TiO$_2$ films are calcined. 1 layer of Scotch tape is used to control the thickness and it usually gives a 4-5 µm thick film. After applying the scattering layer, the tape is carefully removed and the films are placed on the heating plate at 150 °C for 30 min. Then, these films are calcined at 450 °C (actual programmed temperature: 475 °C).

2.2.2.3 TiCl$_4$ Treatment

The 1-mL mark is indicated on a Pasteur pipette using a marker. 1 mL (1.73g) of TiCl$_4$ is added to 5 g of ice water slowly to make a 1.82 M stock solution. Preparing the stock solution must be carried out in the hood since a large amount of HCl(g) is generated.
The stock solution can be stored in the refrigerator at 4 °C. 1 mL of the stock solution is diluted to 40 mL (M_f = 0.046M) in a staining jar. Before diluting the TiCl_4 solution, a small amount of water is added to the dessicator. The water level should be about 1 inch. The cover is placed on top of the dessicator and placed in the oven at 70 °C to create a humidified environment. After the TiCl_4 solution is diluted, the nc-TiO_2 films are immersed in the solution and placed inside the dessicator that is already at 70 °C inside the oven. These films are taken out after 30 min, and rinsed with a small amount of water to remove any salt. The films are air-dried and calcined at 450 °C for 30 min.

2.2.3 Pt Counter Electrodes

There are two kinds of Pt counter electrodes used in my research: transparent nano-Pt clusters on FTO and reflective Pt coated FTO with nano-Pt clusters. In order to prepare a reflective Pt coated counter electrode, a layer of Pt (~150 nm) is evaporated onto 15 Ω/sq FTO substrates after approximately 5 nm of Cr is evaporated as an adhesion layer. The E-beam evaporator at the Penn State Materials Research Institute was used instead of the sputtering system at the Materials Research Laboratory because multiple FTO substrates could be fitted into the E-beam evaporator whereas only one FTO substrate can be loaded into the sputtering system. After evaporation, the Pt films have a mirror finish. On top of the Pt layer, 2-3 drops of 5 mM of H_2PtCl_6 in anhydrous IPA is then applied. The H_2PtCl_6/IPA solution is slowly and evenly evaporated by placing the substrates to ensure an even distribution of nano-Pt clusters on the Pt surface. Uneven and an excess amount of nano-Pt clusters affect the fill factor of the DSSC. The samples
are then heated at 380 °C for 15 minutes (ramp rate = 5 °C/min; Lyndberg/Blue M furnace at a programmed temperature of 405 °C).

The same procedure is used to prepare transparent Pt counter electrodes. Briefly, TEC 15 samples are first cleaned by sonicating in IPA and EtOH for 20 min each and rinsing with nanopure water. They are dried completely in air and a few drops of the H$_2$PtCl$_6$/IPA solution are dropped onto the TEC 15 surface, then slowly evaporated, and the Pt nano-cluster film is thermally activated at 380 °C for 15 minutes.

### 2.2.4 Electrolytes

The electrolyte solution consists of 0.1 M LiI, 0.05 M I$_2$, 0.5 M 1,2-dimethyl-3-propylimidazolium iodide$^{35}$ or 0.5 M 1,2-dimethyl-3-hexylimidazolium iodide (Solaronix), 0.5 M tert-butylpyridine, 0.1 M guanidinium thiocyanate dissolved in anhydrous acetonitrile. The electrolyte is sonicated for 30 min in an amber vial covered with parafilm and stored in the same amber vial. The electrolyte is good for one month and should be replaced with a new electrolyte every month due to loss of iodine and increasing water content. The age of the electrolyte will affect the fill factor and the $V_{oc}$ of the device.
2.2.5 Assembling the DSSCs

2.2.5.1 Sealing the Cells with Parafilm and Binder Clips

The excess amount of sensitized TiO$_2$ is scraped off the FTO substrate to make an active area of 0.25 cm$^2$ (0.5 cm x 0.5 cm), measured by using graphing paper. The active area should be close to the top of the FTO substrate as shown in Fig 2.7. A stretched piece of parafilm is used as a spacer between the photoanode and counter electrode. A small piece of parafilm is cut off and stretched out by placing two thumbs on the center of the parafilm. The protective liner is peeled off of the parafilm and that previously unexposed side of the parafilm is placed on the top of the FTO. The parafilm is gently pressed onto the FTO and the excess parafilm is trimmed off. Using a razor blade, a small piece of parafilm is cut off to expose the active area of sensitized TiO$_2$ electrode. It is advised to minimize the exposure of bare FTO when cutting the parafilm around the active area. A drop of electrolyte is placed on the active area. Spreading of the electrolyte under the parafilm should be minimized to the extent possible. Then, a Pt counter electrode is placed on top of the anode. The two electrodes are firmly held by hand while two binder clips are placed on each side of the electrode to secure them and prevent leakage of the electrolyte. However, there will be a small leak of electrolyte and that can be wiped off by an acetonitrile-wetted Kimwipe.
2.2.5.2 Sealing the Cells with Surlyn and Filling the Electrolyte by Capillary Action.

The excess sensitized TiO$_2$ is scraped off of the FTO electrode to make a 0.25 cm$^2$ active area. The active area is at the center of the FTO. Surlyn is cut into two small pieces as shown Fig. 2.8. Surlyn must be placed on a clean surface while it is being cut into small pieces and kept away from dirt so that it will adhere to the FTO surface securely during heat pressing. After placing the Surlyn pieces on the anode and arranging them around the active area, the Pt counter electrode is placed on top of the anode and taken to the heat press. The heating plates are pre-heated to reach 100-110 °C. The sample is placed on the heating plate and the top plate is lowered to seal the cell. It takes about 5-7 minutes. If the electrodes are heat-pressed too long, the Surlyn will over-melt and the slits where the electrolyte is introduced will be closed.

After heat pressing, the cell is held and approximately 200 μL of electrolyte is added through the slit using a 1-mL disposable syringe. The electrolyte fills the cell very
quickly. Then, the slits on both ends are sealed by applying white epoxy (McMaster Carr, Loctite 1C Hysol).

2.2.5.3 Sealing the Cells for Outdoor Measurements

First, a thin strip (1.2 cm x 0.1 cm) of Ag paste (Ferro, CCL-166, lead-free) is applied via tape casting to the edge of FTO using a clean-room swab to make an electrical contact after the cell is assembled. Enough Ag paste should be applied (it should be 10-20 µm thick after the annealing step) so that one cannot see through the paste. Ag paste/FTO is heated at 500°C (ramp rate = 5 °C/min) for 10 minutes and cooled to room temperature at 10 °C/min.

Before preparing the TiO₂ photoanode, holes on the counter electrodes are drilled to vacuum fill the electrolyte. A hole is drilled through the Pt/FTO electrode using a 1/8”
carbide-tipped drill bit (McMaster Carr). The FTO side of the counter electrode is first drilled a quarter of the way through with the Pt side up. Then, the other side of Pt/FTO electrode is drilled until the hole is complete. The Pt side of the electrode should be protected by placing it on a Kimwipe while it is being drilled.

TiO$_2$ paste is applied to FTO using a tape-casting and doctor blade technique. The Ag paste should be protected with tape during application. After sintering and sensitization, an active of area of the desired size is defined with a razor blade. Using a Kimwipe, the edges around the TiO$_2$ are cleaned prior to applying Surlyn for better adhesion and sealing of the DSSCs.

To seal the cell, 60 µm thick sealing sheets from Solaronix (SX 1170-60) are used. Using an Exacto-knife, a “window” of hot-melt polymer is cut out while it is placed on a clean surface. The area of the window should be preferably ≤1 mm larger than the sensitized TiO$_2$ area on all four sides. The sealing sheet is then placed on top of the anode and the Pt/FTO counter electrode is then carefully placed on top of the anode. The electrodes are placed on a hot plate that was pre-heated to 105 °C. Pressure is applied immediately and is held for 30-60 seconds. The polymer is more fully melted by flipping the sandwich over and applying heat for one more minute. This process is repeated until the polymer has completely melted. After the electrodes are cooled to room temperature, the polymer border area was examined to confirm that a good enough seal had been made to prevent the electrolyte from leaking and evaporating.

In order to infiltrate the cell with the electrolyte, Teflon tape is wrapped around the sandwich cell to cover the Ag paste but leave the hole in the Pt/FTO electrode exposed. The cell is then placed into a small, custom-built vacuum chamber that could be
sealed with a rubber septum. The cell is centered by placing it in the middle of a rubber ring that hugs the inside of the container. Vacuum is applied via a vacuum pump until a pressure of 0.1 atm is reached. Approximately 200 µL of redox electrolyte solution is then added using a 1 mL disposable syringe by puncturing the rubber septum and placing the needle in the hole in the Pt/FTO. The chamber is then returned to atmospheric pressure. The Teflon tape is removed and the Ag paste and Pt are then carefully wiped with Kimwipes wetted with acetonitrile to remove electrolyte contamination, in order to enable a good electrical contact. The back side of the Pt/FTO electrode is also cleaned. A small clean piece of Kapton tape is placed over the hole and UV-Epoxy (Epotek # OG116-31) is applied on top of the Kapton tape to seal the hole with a small piece of microscope cover slip (which is pre-cleaned by sonicating in IPA for 10 min). The sample is then placed under a UV lamp (> 100 mW/cm²) for 5 minutes to cure the epoxy. The sample becomes slightly warm while the epoxy is being cured, therefore the exposure to the UV lamp should be limited to 5 minutes.

As a last step, electrical contact is made to the photoanode and counter electrode using Sn-coated copper wires and Alusol solder (Farnell). Fig. 2.8 shows the final assembly of the cell after vacuum sealing and making electrical contacts.
2.2.6 Photovoltaic Performance Testing

2.2.6.1 iV/IPCE Measurements

Because the solar radiation that reaches the Earth is greatly affected by the atmosphere and the path length of the light through the atmosphere, the solar radiation can be calculated by Eq. 2.2 and is defined as air mass (AM). Air mass 0 (AM0) radiation is defined to be the solar radiation outside of the Earth’s atmosphere and its accepted...
value is 1.353 kW/m$^2$. However, it is attenuated by at least 30% by Rayleigh scattering by molecules and aerosols in the atmosphere, and by absorption by gases such as oxygen, ozone, water vapor, and CO$_2$ in the atmosphere. Values of AM can be calculated by using the Eq. 2.2, where $\theta$ is defined as the angle between the sun and the vertical.

$$AM = \frac{1}{\cos \theta} \quad 2.2$$

To measure the efficiency of the solar cells and compare cells from different locations systematically, there is a defined terrestrial standard condition for the measurements. The most widely used standard is AM1.5. It is the light power reaching the Earth at 37° tilt, and the zenith angle is 48.19°. The total power density of 1 Sun at AM1.5 is defined as 1000 W/m$^2$.\textsuperscript{36}

For performing photovoltaic measurements in the laboratory, solar simulators are often used to mimic the solar spectrum. The solar simulator consists of a light source which is usually a Xe lamp because it matches the solar spectrum reasonably well, with various filters to better simulate the power spectrum of sunlight. In our laboratory, a 150 watt Xe lamp is used as our light source with AM filters (Solar light, www.solarlight.com) to simulate the solar spectrum, as shown in the Fig. 2.10. The Xe lamp is calibrated with a reference Si solar cell (Burdick Technologies Unlimited, $A = 0.9790$ cm$^2$) that is certified by NREL. After prolonged use of the lamp, the spectrum of the Xe lamp changes, hence, the calibration is done routinely every 3 months.
Additionally, the spectral distribution of our Xe lamp has been measured using a spectral photometer by Dr. Greg Barber. Fig. 2.11 shows the spectral distribution of the Xe lamp with AM filters, compared to the standard AM1.5 spectrum.

After the Xe lamp is calibrated, the iV measurement of the device is carried out. Electrical contacts on the DSSCs are made by using two alligator clip end cables from the Keithley source meter. The applied bias and measured cell current are collected by using LabView VI, which controls the starting and ending voltage of the sweep, and the voltage increment.
Apart from the efficiency measurement, the spectral response of the cell can also be measured. The incident photon-to-current conversion efficiency (IPCE) is defined as the number of electrons generated by light in the external circuit divided by the number of incident photons. Using a steady-state source of monochromatic light from a monochromator as shown in the Fig. 2.13, the spectral distribution of the electrons generated from the cell can be determined.

Figure 2.11: Solar simulator and AM 1.5 Spectrum. ASTM E-892 represents the standard solar spectral irradiance at AM 1.5 for global at a 37 degree tilted surface. The spectral distribution of the solar simulator is measured by Dr. Greg Barber.
The DSSCs are placed after the monochromator as shown in Fig. 2.12 (d), and the short circuit current at each wavelength is measured. The incident photon intensity is measured with a Si photodiode (Hamamatsu S1226-44BK, A=0.1296 cm$^2$). In both cases, the dark current is measured in the beginning of the IPCE measurements and subtracted.

![Figure 2.12: Experimental setup for IPCE measurements.](image)

Figure 2.12: Experimental setup for IPCE measurements. (a), (b) AM filters are placed in front of the solar simulator. Then, monochromatic light is produced by white light going through a monochromator. (c) After the monochromator, a focusing lens is placed to illuminate the whole area of the sensitized electrode. (d) Monochromatic light overfills the sensitized area of the electrode.

2.3 Results and Discussion

2.3.1 Characterization of nc-TiO$_2$ Mesoporous Films

After synthesizing the TiO$_2$ colloidal solution, nc-TiO$_2$ films are prepared. XRD analysis was performed on these films to determine the crystal phase of the TiO$_2$ and also
to calculate the crystallite size using the Scherrer equation, Eq. 2.3. The XRD pattern (Fig. 2.13) shows that the film (black line) is composed of anatase and there was no rutile found. However, there are other peaks in the pattern that are assigned as the tin oxide from FTO.

![XRD spectrum](image)

**Figure 2.13**: XRD of nc-TiO$_2$ films on FTO after calcination. Reference patterns of anatase and rutile phase TiO$_2$ are also shown along with a reference pattern of SnO$_2$.

Using the Eq. 2.3 where $D$ is the crystallite (or particle) size in angstroms, $k$ is a shape factor (0.94), $\lambda$ is the wavelength of the X-ray (1.54056 Å), $\beta$ is the width of a single XRD peak at half its height in 2θ (radians) and $\theta$ is position of that peak, the crystallite size is calculated. The average crystallite size is approximately 17 nm, which is close to reported values.$^{13a}$

$$D = \frac{k \cdot \lambda}{\beta \cos \vartheta}$$

**Equation 2.3**
The surface area and porosity of the films are important parameters that determine the performance of the DSSC. A larger surface area is necessary to have sufficient dye loading. The porosity of the films and interconnectivity between the particles also affects the electron transport property of the TiO$_2$ films and infiltration of the electrolyte. The surface area and the porosity of the TiO$_2$ films are measured by the nitrogen absorption/desorption technique using a Micromeritics ASAP 2010 instrument. TiO$_2$ films are prepared on FTO or glass slides and after calcination, the films are scraped off and collected. The collected sample was evacuated at 120 °C for 12 – 16 hrs. At least 0.1 g of sample is needed for an accurate measurement. During the BET (Brunauer-Emmett-Teller) analysis, a known amount of nitrogen gas at the temperature of liquid nitrogen adsorbs and is then desorbed from the sample surface, and the amounts of adsorbed and desorbed nitrogen are measured. The surface area was calculated by determining the monolayer volume of adsorbed gas from the isotherm data, and the pore volume, and pore size distribution are calculated by fitting the nitrogen adsorption/desorption isotherm using BJH (Barret-Joyner-Halenda) adsorption/desorption analysis. The results show that the surface area of the films is 57.7±0.8 m$^2$/g and the mean pore diameter is 16.3 nm. Fig. 2.14 shows the distribution of the pores. Although the results are somewhat model-dependent, in this fit most of the pores diameters are between 10 – 20 nm. It is known that the surface area and pore size distribution are sensitive to the calcination temperature and the amount of binder used. We have chosen conditions (sintering temperature and the amount of binder) that are described in the literature.$^{13}$
The sintered TiO$_2$ films were also characterized by FE-SEM. Fig. 2.15 shows that the film is composed of nano-TiO$_2$ particles and densely packed.

Figure 2.14: The pore distribution of nc-TiO$_2$ films is determined by N$_2$(g) adsorption measurement.

Figure 2.15: FE-SEM images of sintered nc-TiO$_2$ films.
2.3.2 Photovoltaic Performance Measurements

Generally, the efficiency of the cell is expressed as the device conversion efficiency as shown in Eq. 2.4. \( J_{sc} \) is the short circuit current density and is recorded at a 0 V with illumination over the active area of the device. \( V_{oc} \) is the voltage across the cell when there is no current flow. It represents the difference in electrical potential between two terminals of a cell under illumination when the circuit is open. \( P_{in} \) is the incident power and is generally 100 mW/cm\(^2\), which is the 1 Sun condition.

\[
\eta = \frac{J_{sc}V_{oc}FF}{P_{in}} \times 100 = \frac{P_{out}}{P_{in}} \times 100
\]

Equation 2.4

Another good indicator of the cell efficiency is the fill factor (FF). FF is the ratio of the maximum power (the maximum product of voltage and current) over the product of open circuit voltage and the short-circuit current. FF for solar cells with reasonable efficiency is usually between 0.7 and 0.85 (Fig. 2.16).37
The performance of the cell can be also measured as the incident photon to current conversion efficiency (IPCE). IPCE is the efficiency at which monochromatic photons are converted into electrons. It is simply the ratio of the number of electron flowing through the circuit over the number of incident photons. It can be calculated by using Eq. 2.5,

$$IPCE(\lambda) = \frac{1240(eV \cdot nm) \cdot J_{sc} (mA/cm^2)}{\lambda (nm) \cdot P (mW/cm^2)}$$

Equation 2.5

where \( J_{sc} \) is the short circuit current density for monochromatic irradiation, \( \lambda \) is the wavelength, and \( P \) is the monochromatic incident light intensity. It should be noted that the IPCE is usually measured at low light intensity using monochromatic light, whereas the power conversion efficiency is typically measured under AM 1.5 conditions.

IPCE can be also expressed by Eq. 2.6,
where LHE is the light harvesting efficiency, \( \Phi_{\text{inj}} \) is the quantum yield of electron injection and \( \eta_c \) is the collection efficiency of the injected electrons. In general, it is assumed that \( \Phi_{\text{inj}} \) and \( \eta_c \) reach unity, and LHE depends on the amount of dye adsorbed on the \( \text{TiO}_2 \). As shown Fig. 2.3, the dye molecules effectively absorb visible light photons and Fig. 2.18 shows that the IPCE of DSSCs sensitized with the N719 dye reaches almost 70% at 550 nm. The IPCE between 450 and 650 nm is also close to 60%. While the literature reports an IPCE of 80% at 550 nm and 70% between 450 and 650 nm, the DSSCs from our laboratory have slightly lower IPCE at 550 nm. Considering light loss due to reflection at the FTO interfaces, the internal quantum yield of the best DSSCs is close to 90 – 100%.

Fig 2.17 shows typical photovoltaic performance data of DSSCs from our laboratory. Devices with and without the scattering layer were prepared and their performances are compared. The performance of the DSSC is closely related to the thickness of the nc-TiO\(_2\) film. As the film thickness increases, the dye loading on the film also increases and a higher \( J_{\text{sc}} \) is expected. However, the rate of recombination between \( \text{I}_3^- \) and the electrons in the conduction band of the TiO\(_2\) film also increases, since its rate is proportional to the total surface area of TiO\(_2\). Thus, very thick films result in less efficient electron collection and lower \( J_{\text{sc}} \). Thicker films also result in a lower \( V_{\text{oc}} \) because of charge recombination and mass transport limitations.\(^{38}\) Without increasing the nc-TiO\(_2\) film thickness, \( J_{\text{sc}} \) can be improved by using a scattering layer. Scattering layers are commonly used in DSSCs to enhance the absorption of red light for a higher \( J_{\text{sc}} \). It is
generally known that particles with \( D \approx 300-400 \text{ nm} \) effectively scatters the longer wavelength photons where the dye absorption is weak.\(^{39}\) Hence, a scattering layer made of large TiO\(_2\) particles is deposited on top of the nc-TiO\(_2\) film. To reduce backscattering and for all photons to penetrate the device, transparent nc-TiO\(_2\) must be deposited onto the FTO first, followed by the scattering layer. The optimized thickness of nc-TiO\(_2\) films for N719 dye is reported in the literature as 10 – 18 \( \mu \text{m} \).\(^{40}\) In our laboratory, we generally use 10 – 12 \( \mu \text{m} \) thick anode layers with the N719 dye.

Fig. 2.17 and Table 2.1 summarize data from DSSCs with and without the scattering layer. The data show a remarkable improvement in \( J_{\text{sc}} \) and the device conversion efficiency.

![Figure 2.17](image_url)

**Figure 2.17:** J-V characteristics of the DSSCs with and without scattering layer (SCL). The devices with SCL exhibit higher photocurrent than the ones without the SCL.
Table 2.1: The values represent average of 3 samples. They were measured on March 8th, 2008.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$ff$</th>
<th>Power (mW)</th>
<th>$Ƞ$ (%)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.77±0.02</td>
<td>13.9±0.5</td>
<td>0.679±0.002</td>
<td>1.8±0.1</td>
<td>7.2±0.4</td>
<td>10.3±0.8</td>
</tr>
<tr>
<td>TiO$_2$/SCL</td>
<td>0.744±0.006</td>
<td>15.6±0.5</td>
<td>0.65±0.02</td>
<td>1.9±0.1</td>
<td>7.6±0.5</td>
<td>15.2±0.3</td>
</tr>
</tbody>
</table>

To verify that the increase in $J_{sc}$ is caused by better red photon absorption, the IPCE of the cells was measured. Fig. 2.18 shows that use of a scattering layer results in a significant improvement beyond 580 nm. Because of the small surface area of the SCL relative to the nc-TiO$_2$ films, the small amount of dye adsorbed in the SCL does not contribute to the photocurrent.

![Figure 2.18: IPCE of samples with and without a SCL. In both figures, the devices with a SCL show red enhancement in the action spectrum due to efficient scattering at longer wavelengths.](image)

Another approach to improve the photocurrent of the DSSCs is chemical deposition of TiO$_2$ from TiCl$_4$. O’Regan et al. demonstrated that the TiCl$_4$ treatment causes a ~80 mV positive shift of the TiO$_2$ conduction band edge potential, reducing the
recombination rate constant between the electron in the conduction band and the electrolyte by a factor of 20 and increasing the quantum efficiency of charge separation at the interface to produce a higher $J_{sc}$.\textsuperscript{41}

DSSCs with the TiCl$_4$ treatment show a higher $J_{sc}$ compared to the DSSCs without it, as shown in Fig. 2.19. In addition to applying a SCL to the DSSC, TiCl$_4$ treatment enhances $J_{sc}$ even further. However, TiCl$_4$ treatment did not always result in a higher $J_{sc}$. Some samples had no improvement in $J_{sc}$ with TiCl$_4$ treatment and had similar $J_{sc}$ to samples without the TiCl$_4$ treatment.

![Figure 2.19](image.png)

**Figure 2.19**: J-V characteristics of DSSCs with/without SCL and also with/without TiCl$_4$ treatment.

Table 2.2 is a summary of DSSC performance demonstrating the effects of TiCl$_4$ treatment. Incorporating a scattering layer and adding the TiCl$_4$ treatment both resulted in a higher $J_{sc}$. 
2.4 Conclusion

In summary, the performance of DSSCs is affected by many different factors. The synthesis of the TiO$_2$ colloidal solution must be carefully monitored to produce high quality TiO$_2$ films. The crystal phase, particle size and the porosity of the TiO$_2$ and TiO$_2$ films are some of the major parameters that have strong effects in determining the efficiency of the device. Based on the experimental data obtained in this work and the literature, high quality of mesoporous TiO$_2$ films and an optimized TiO$_2$-electrolyte interface are needed to realize efficient devices. Such devices must have excellent electron transport through the TiO$_2$ network and a low recombination rate at the TiO$_2$-electrolyte interface.

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Table 2.2: The measurements were done on June 4$^{th}$, 2009. The values represent an average of 2 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$ff$</th>
<th>Power (mW)</th>
<th>$Ƞ$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.721±0.004</td>
<td>11.2±0.3</td>
<td>0.65±0.01</td>
<td>1.31±0.07</td>
<td>5.3±0.3</td>
</tr>
<tr>
<td>TiO$_2$/SCL</td>
<td>0.727±0.004</td>
<td>12.2±0.3</td>
<td>0.655±0.009</td>
<td>1.46±0.06</td>
<td>5.8±0.3</td>
</tr>
<tr>
<td>TiO$_2$/SCL/TiCl$_4$</td>
<td>0.740±0.008</td>
<td>13.4±0.1</td>
<td>0.662±0.004</td>
<td>1.64±0.03</td>
<td>6.6±0.1</td>
</tr>
</tbody>
</table>
2.5 References


Chapter 3

Coupling of Titania Inverse Opals to Nanocrystalline Titania Layers in Dye-Sensitized Solar Cells

3.1 Introduction

Dye-sensitized solar cells (DSSCs) were first introduced by Gratzel and coworkers in the mid-1980’s and have since been studied extensively. DSSCs represent a promising alternative to photovoltaic cells because they can be fabricated using inexpensive materials and processes. While energy conversion efficiencies as high as 10.6% have been reported, more typical values are below 8%, and higher efficiencies (especially for large area cells) are needed for DSSCs to become practical. The poor photoresponse of DSSCs in the red and near infrared is one of the most important factors contributing to their low efficiency, since over 60% of the AM 1.5 solar power spectrum comes from wavelengths beyond 600 nm. The widely used $(\text{Bu}_4\text{N})_2[\text{Ru(dcbpyH)}_2(\text{NCS})_2]^2^-$ (N719, dcbpy = 4,4’-dicarboxy-2,2-bipyridine) dye absorbs light weakly in the 600 – 750 nm region. Chemically related black absorber dyes have more recently been developed to extend the action spectrum of the DSSC further into the red with concomitant gains in efficiency.

A complementary approach, which in principle can be used to extend the photoresponse of any dye, is to modify the optics of the DSSC. In the DSSC, the optically transparent anode is coated with a film of 15-20 nm diameter nanocrystalline $\text{TiO}_2$ (nc-$\text{TiO}_2$) particles. The nc-$\text{TiO}_2$ layer scatters light only weakly. However, when
larger particles of TiO$_2$ are added, they increase the effective path length of light in the film through scattering. In 1997, Usami proposed a bilayer in which an overlayer of larger TiO$_2$ particles confined light to a thin nc-TiO$_2$ film on the DSSC anode through multiple scattering and total internal reflection. Ferber et al. simulated light scattering effects in DSSC using Mie theory and the radiative transfer equation. Their simulations showed that a mixture of small (D = 20 nm) and large particles (D = 125 ~ 150 nm) can enhance photon absorption in DSSC. However, the ratio of the small particles and the large particles must be optimized since too many large particles increase the back-scattering and diminish the enhanced absorption. Rothenberger et al. performed simulations for the optimal optical design of the DSSCs and experimentally demonstrated that films made of a mixture of 65% small and 35% large TiO$_2$ particles (total thickness = 10 µm) and a double layer film composed of a 5 µm nc-TiO$_2$ film and a 5 µm scattering layer both resulted in a 6% increase of absorbed photon flux, mainly in long wavelength region (560~750 nm). Several experimental studies have verified that the inclusion of such scattering centers or layers can increase the short circuit current density and power conversion efficiency of the DSSC.

We have previously found that photonic crystal (PC) scattering layers are effective in enhancing the red response of the DSSC. In our initial studies, we fabricated titania inverse opals on the anode electrode of the cell and covered them with nc-TiO$_2$ films, which were sensitized with the N-719 dye. This arrangement allowed us to study the effect of light localization in the bilayer but required an unconventional illumination of the cell through the cathode and electrolyte, which significantly reduces the performance of the cell. We postulated that the enhancement of incident photon current
efficiency (IPCE) in the long wavelength region was induced by a standing wave effect in
the photonic crystal. This effect has since been investigated by Ozin and coworkers as a
means of enhancing the light absorbing properties of TiO$_2$ inverse opal photocatalysts.$^{16-18}$

While this model correctly predicted changes in the absorption spectrum of dye
molecules confined to a TiO$_2$ inverse opal, the photonic crystal/nc-TiO$_2$ bilayer structure
is more complex. In the bilayer film, resonant modes lead to enhanced absorbance by dye
molecules in the nc-TiO$_2$ layer. Mihi and Miguez modeled the propagation of light in
such bilayers and were able to reproduce the enhancement effect we observed in the
IPCE.$^{19}$ According to their model, most of the photon absorption enhancement arises
from light absorption in the nc-TiO$_2$ layer,$^{20}$ where most of the dye is adsorbed, and this
is consistent with our observations.$^{21}$ Mihi et al. later verified experimentally that dye-
sensitized TiO$_2$ inverse opals had poorer light absorption properties than single-layer nc-
TiO$_2$ electrodes, consistent with their model, and showed that multiple inverse opal layers
on nc-TiO$_2$ could provide spectral enhancement at multiple wavelengths.$^{22}$

Although there have been subsequent reports of using colloidal crystals in
different geometries as scattering layers for DSSCs, in general the performance of these
cells has been poor.$^{22,23}$ These studies have therefore failed to address the question of
whether a photonic crystal scattering layer will substantially improve the light-harvesting
ability of state-of-the art DSSCs. Such DSSCs are illuminated from the anode side, and
they contain nc-TiO$_2$ layers of optimized thickness. One goal of this study was therefore
to fabricate nc-TiO$_2$/PC bilayer structures that could be illuminated through the anode,
and to quantify the effect of the added PC layer in optimized nc-TiO$_2$ cells. A second
goal was to test an interesting prediction made by Mihi and Miguez,$^{19}$ that the
introduction of a gap between the PC and nc-TiO₂ layers should disrupt the optical coupling of the two layers, thereby diminishing the enhancement of the IPCE in the spectral region to the red of the PC stop band.

Fig. 3.1 shows the schematic structure of a dye cell containing a single nc-TiO₂ layer on a glass/fluorine-doped tin oxide (FTO) anode and the bilayer arrangements investigated in this work. The bilayers in (a-c) involve fabricating the titania inverse opal directly on the transparent conductor/glass substrate and then depositing a nc-TiO₂ layer, either on top of the PC layer or on the opposite electrode. Arrangements (b) and (c) allow us to test predictions of the Mihi-Miguez model. The structure in (d) is more difficult to make, because it entails the fabrication of a titania inverse opal on top of the nc-TiO₂ layer without filling the interstices in the latter. We describe a new method for realizing this structure and compare the performance of such cells, illuminated from the anode side, with nc-TiO₂ cells that contain equivalent amounts of dye.
Figure 3.1: Configurations of DSSCs investigated in this work. Top: FTO/nc-TiO$_2$, illuminated from the anode side of the cell. (a), (b) Previously studied configuration in which a titania inverse opal PC was fabricated on the anode and a nc-TiO$_2$ film was deposited on top of the PC layer. In (a) and (b), this structure is illuminated from the cathode and anode sides, respectively. (c) Split configuration with the PC and nc-TiO$_2$ layers deposited on the anode and cathode, with the cell illuminated from the cathode side. (d) Bilayer configuration in which nc-TiO$_2$ film was first deposited on the anode, and a PC layer was added by polymer templating. The thicknesses of the PC and nc-TiO$_2$ layers are typically 5-10 µm.
3.2 Experimental

3.2.1 Materials

Suspensions of monodisperse carboxylate-modified polystyrene spheres ($d = 243, 291, 304$ and $327$ nm; 30, 10, 10 and 2 wt %, respectively, in water) were purchased from Seradyne, stored at 4 °C and used without further purification. Ammonium hexafluorotitanate ($\text{(NH}_4\text{)}_2\text{TiF}_6$, 99.99%, Aldrich), titanium isopropoxide (Aldrich), boric acid ($\text{H}_3\text{BO}_3$, 99.5% Alfar Aesar), $\text{cis}$-$\text{bis(isothiocyanato)bis(2,2'}$-$\text{bipyridyl-4,4'}$-$\text{dicarboxylato)}$ ruthenium(II) bis(tetrabutyl ammonium) (RuL$_2$(NCS)$_2$2TBA also known as Ruthenium535 bis-TBA, or N719, Solaronix), acetonitrile and tert-butanol were used as purchased. The nc-$\text{TiO}_2$ particle slurry was synthesized according to published procedures but hydroxypropylcellulose [Aldrich, Average $M_W = 80,000$] was used as a binder instead of Carbowax.\textsuperscript{25} Titanium isopropoxide ($35.52 \text{ g}$) and 10 mL of anhydrous isopropanol were added to a separatory funnel and mixed well. The Ti(\text{-OPr})$_4$/isopropanol solution was then added dropwise to 80 mL of acetic acid/250 mL of deionized H$_2$O in a round-bottom flask that had been pre-chilled to 0 °C in a dry ice/acetone bath. As the Ti(\text{-OPr})$_4$/isopropanol solution was added over a period of 20-30 min, the mixture was stirred rapidly with a magnetic stirring bar. The reaction solution was then heated to 80 °C and stirred rapidly for 8 hr. After the solution was cooled down to the room temperature, it was sonicated using a cell disrupter for 5 minutes. The solution was then autoclaved at 230 °C for 8 hours and then sonicated again for 5 minutes. The final concentration of TiO$_2$ was adjusted to 12 wt % with respect to total weight of solution. Hydroxypropylcellulose (HPC) was then added over 3-5 min to the
rapidly stirred solution. The final HPC concentration was 6 wt% with respect to total weight of solution. The TiO$_2$ paste was first rapidly stirred for 24 hours to dissolve HPC and the paste was continuously stirred less rapidly until its use. Electrodes were fluorine-doped tin oxide coated glass substrates (FTO-glass, TEC8, Hartford Glass Co., IN, 8Ω/sq). All aqueous solutions were prepared with deionized water of resistivity ≥18.3 MΩ·cm.

3.2.2 Preparation of Bilayer Electrodes.

FTO substrates (1 in X 1 in) were cleaned by sonication for 20 min in isopropanol and for 20 min in ethanol, followed by rinsing with deionized water and drying with air.

3.2.2.1 FTO/PC/nc-TiO$_2$ Configuration (Scheme 3.1 (a), (b))

Colloidal crystal films were grown following a modification of the method of Jiang et al.$^{26}$ Suspensions of carboxylate-modified polystyrene (PS) spheres in 60 mL of water were sonicated for 30 min to break up aggregates of particles. Before sonication, 0.3 g of a 0.5 wt % stock solution of non-ionic surfactant, Igepal, was added to the PS suspension for better formation of a meniscus at the interface between the FTO and the solution. The FTO-glass substrates were immersed vertically in the PS suspension and the solvent was allowed to evaporate at 55 ºC for 48 h. A 0.1 wt % PS suspension in water resulted in a 7-9 µm thick colloidal crystal film. Thinner films could be prepared by starting with lower PS concentrations in proportion to the desired thickness. The PS film
was scraped off the back of the FTO-glass samples and kapton tape was applied to prevent TiO$_2$ deposition during the subsequent seeding and liquid phase deposition (LPD) steps. In the seeding step, the samples were immersed in a solution of 1.2% (weight/volume) of titanium isopropoxide and 0.12% HNO$_3$ in ethanol for 5 min at room temperature to grow a thin surface layer of titania on the polystyrene colloidal crystal. Following this step, the samples were held vertically and dried in air for several hours. In the subsequent LPD step, the samples were immersed vertically in an aqueous solution of 0.25 M boric acid and 0.20 M ammonium hexafluorotitanate for 30 min at 51 °C. The pH of the solution was first adjusted to 2.9 with 1 M HCl. During the LPD process, fluoro-complexes of titanium undergoes an equilibrium exchange with water ligands in presence of a fluoride scavenger such as BF$_4^-$ to produce TiO$_2$ as a final product (Eq. 3.1). The process is usually carried out at a moderate temperature (25-60 °C).

$$\text{TiF}_6^{2-} \text{(aq)} + 2 \text{H}_2\text{O} \leftrightarrow \text{TiO}_2\text{(s)} + 4 \text{HF} \text{(aq)} + 2 \text{F}^- \text{(aq)} \quad 3.1$$

$$\text{H}_3\text{BO}_3 \text{(aq)} + 4 \text{HF} \text{(aq)} \to \text{BF}_4^- \text{(aq)} + 3 \text{H}_2\text{O} \text{(l)} + \text{H}^+ \text{(aq)}$$

After 30 min, the samples were rinsed thoroughly with deionized water and dried in air at room temperature. They were then calcined at 400 °C for 8 hours to remove the PS spheres and create the inverse opal structure. The position of the stop band could be tuned by thickening the walls of the inverse opal in a second LPD step. The deposition time for this step, which typically shifted the stop band to the red by 10-20 nm, was approximately 30 min. Following this step, nc-TiO$_2$ paste was applied by the doctor-blade method. A few drops of nc-TiO$_2$ paste were deposited and spread onto the conductive side of the FTO/glass. Cellophane tape spacers with a thickness of 50 µm
were applied to opposite edges of the electrode to control the thickness of the doctor-bladed nc-TiO₂ films. The samples were then calcined at 475 ºC for 30 minutes.

3.2.2.2 FTO/nc-TiO₂ and FTO/nc-TiO₂/PC Configurations (Fig. 3.1 (c), (d))

To obtain the FTO/nc-TiO₂ structure for conventional DSSCs and the split bilayer structure shown in Scheme 1c, nc-TiO₂ paste was applied to the FTO-glass slide by the doctor blade method and cellophane tape was used to control the film thickness. The nc-TiO₂ films were heated in air at 5 ºC/min to 405 ºC for 30 min and then cooled to room temperature. For the FTO/nc-TiO₂/PC structure, two layers of a poly[(methyl methacrylate)-co-(methacrylic acid)] (80:20 and 75:25 = MMA: MA) copolymer, synthesized as described in the literature [T_g = 140 ºC, Avg. M_w = 129,000, Avg. M_n = 58,000, M_w/M_n = 2.2 ].² Briefly, methyl methacrylate (23.25 g), methacrylic acid (5 g), dry isopropanol (21.20 g) and benzoyl peroxide (282.5 mg) were placed in a 250 mL round bottom flask and heated at 70 ºC for 15-17 hr with stirring. The round-bottom flask was connected to a condenser, and a rubber septum was placed at the top of the condenser to prevent moisture in the air from entering the system. During heating, the reaction solution solidifies due to polymerization process, and the stir bar was no longer able to stir. After 15-17 hr, anhydrous isopropanol (100 mL) was added to the flask and heat is applied to bring the isopropanol with partially dissolved polymer to boil. Anhydrous IPA with dissolved polymer was then poured into a clean 100-mL Erlenmeyer flask to recrystallize the polymer by slowly cooling to room temperature. This process was repeated until the majority of polymer from the reaction solution was dissolved and
recrystallized. A final recrystallization in the 1000 mL Erlenmeyer flask was then performed by heating the contents to a boil and slowly cooling to room temperature. The polymer was obtained via vacuum filtration using a large Buchner funnel with filter paper. The solid was then dried in a vacuum oven at 80°C overnight. The 5 wt% copolymer solution in N,N-dimethylformamide was dropped onto the substrate and spread evenly over the surface. After 1 min, excess solution was spun off the sample at 1600 rpm for 30 s. The substrates were heated at 150 °C for 30 s and allowed to cool before applying the second layer of copolymer. This copolymer layer prevents infiltration of the nc-TiO₂ film during the seeding and LPD steps. PS colloidal crystal layers were then grown, followed by TiO₂ seeding and a single LPD step as described above. The samples were then calcined in air at 400 °C for 8 hours. During the calcination, the copolymer layer and the PS spheres are both burned away, leaving a TiO₂ inverse opal layer on top of nc-TiO₂ layer.

3.2.3 Electrode Assembly

Bilayer structures (FTO/nc-TiO₂/PC and FTO/PC/nc-TiO₂) were heated to 475 °C for 15 min, taken out of the furnace at 180°C, then sensitized. The samples were slowly immersed into a 0.3 mM solution of N 719 dye in a mixture (50:50) of acetonitrile and tert-butanol to prevent cracking of TiO₂ and the substrate. All samples were sensitized for 48 hours. The standard DSSC electrodes without PC layers underwent the same heating and sensitization steps.
After sensitization, the active area of the TiO₂ film was made to be 0.25 cm² by scraping away the excess. Stretched parafilm was used as a 20-30 µm spacer between the anode and platinum counter electrode. A drop of the redox electrolyte (see below) was placed on top of the active area and a platinized FTO-glass counter electrode was placed on it and secured using binder clips. For counter electrode, a thin layer of Cr was first evaporated as an adhesion layer, then a 100 nm film of Pt was evaporated by e-beam onto 15-Ω/sq FTO. A few drops of 5mM hexachloroplatinic acid in anhydrous isopropanol were then deposited on the platinized electrode, which was dried and calcined at 385 °C for 15 min. For cells that were illuminated from the cathode side, the hexachloroplatinic acid solution was deposited on a bare FTO substrate and calcined at 385 °C for 15 minutes. The age of the Pt electrodes affects the fill factor of the cells significantly, so this step should be done shortly before assembly of the cell.

The redox couple/electrolyte solution consisted of 0.1 M LiI, 0.05 M I₂, 0.6 M 1,2-dimethyl-3-propyl-imidazolium iodide, 0.5 M tertbutylpyridine, and 0.1 M guanidinium isothiocyanate, which were dissolved in acetonitrile and sonicated for 30 min before use. 1,2-dimehtyl-3-propyl-imidazolium iodide was prepared according to the literature method.²⁸

3.2.4 Photoelectrochemical Measurements

Electrical contact was made at the ends of the electrodes using alligator clips and the cell was connected to a source meter (Keithley, Model 2300). All current-voltage curves were obtained at 100 mW/cm² using AM 1.5 filters. A 150 W Xe Lamp (Oriel,
Model 77250) was used as the light source. For incident photon current efficiency (IPCE) measurements, the short circuit current at each wavelength was obtained by passing light from the Xe lamp through a monochromator (Oriel 77250), which was scanned from 350 to 800 nm. A Si photodiode (Hamamatsu, S1226-44BK) was used to measure the spectral distribution of the incident power.

3.2.5 Dye Desorption

The amount of dye adsorbed onto the electrodes was determined spectrophotometrically (by UV-Vis absorption) after desorption in 10mL of 0.1M NaOH in water:ethanol (50:50) solution for 5 h. Before the measurement, several drops of 0.2 M NH$_4$F$_{(aq)}$ were added to dissolve any TiO$_2$ residue from the film and thus eliminate the scattering background in the absorption spectra.

3.2.6 Analytical Instrumentation

UV-visible absorption and transmission spectra were collected using a diode array spectrophotometer (Hewlett-Packard, HP8452A). Scanning electron micrographs were collected using a JEOL 6700F FESEM microscope operated at 5 kV, after sputtering a thin Ir film. A Tencor Instruments Alpha 3.7-2 profilometer was used to measure the thickness of the nc-TiO$_2$, copolymer, and bilayer films.
3.3 Results and Discussion

3.3.1 Fabrication of FTO/nc-TiO$_2$/PC Electrodes.

In order to realize PC-coupled DSSCs that give red photocurrent enhancement without absorption losses in the blue, one must fabricate FTO/nc-TiO$_2$/PC bilayers that can be illuminated from the anode side. Unfortunately, any conformal deposition method that can convert the close-packed polystyrene sphere layer to a TiO$_2$ inverse opal can fill the mesoporous nc-TiO$_2$ layer as well. This can be prevented by first covering the nc-TiO$_2$ layer with a thin polymer film, as illustrated in Fig. 3.2. In this scheme, a ~200 nm thick layer (as measured by profilometry) of 80:20 or 75:25 MMA:MA copolymer caps the nc-TiO$_2$ layer and prevents it from being infiltrated during the LPD process. The composition of the capping polymer is important in the deposition and LPD filling of the PS film. The water contact angle of the 80:20 copolymer surface was approximately 53°. If the copolymer is too hydrophilic, it is unable to protect the nc-TiO$_2$ layer during the LPD step.
When a more hydrophilic commercial copolymer (40:60 = MMA:MA, Fluka) was used, the aqueous borate/hexafluorotitanate solution penetrated the polymer layer, causing the nc-TiO$_2$ film to delaminate. Fig. 3.2 also shows an FE-SEM image of the final bilayer structure. The thickness of the inverse opal TiO$_2$ layer was typically 5-7 µm; this thickness can be easily adjusted by changing the concentration of PS spheres used in the growth of the film.

Fig. 3.3 (a) shows transmission spectra of the unsensitized bilayer structures in ethanol ($n = 1.36$), which has a similar refractive index to the solvent (acetonitrile, $n = 1.34$) used in the electrolyte of the DSSCs. All three spectra show pronounced stop bands, although the bands are broad because of the relatively small crystal domains in the
PC structure. The small domain size, which is also evident in Fig. 3.2, is most likely a consequence of the polydispersity of the PS spheres, which were 291±1 nm, 304±5, and 327±5 nm, respectively. Because the lattice contracts approximately 30% during the PC fabrication and LPD processes, the diameters of the cavities formed from 291 and 327 nm PS spheres were 200~210 and 230~240 nm, respectively. These 291, 304, and 327 nm templates gave stop bands centered at 580, 605, and 650 nm, respectively which matched well to the calculated stop band maximum ($\lambda_s$) according to Bragg’s law (Eq. 3.2),

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

Equation 3.2

where $n_s$ is the refractive index of the surrounding medium (1.34), $n_v$ is the refractive index of TiO$_2$ (2.54), the filling fraction (f) of TiO$_2$ is 26% for a closed-packed inverse opal structure, and d is the interlayer spacing, which is 0.87 times the diameter of the cavity. When these samples were sensitized with N719 dye, the absorption spectra shown in Fig. 3.3 (b) were obtained. As we previously observed with FTO/PC/nc-TiO$_2$ films, there is an enhancement in the apparent absorbance at the red edge of the stop band, resulting in a peak that shifts progressively to longer wavelengths with larger size PS template spheres.$^{15,21}$ This enhancement is visibly apparent in the reddish and dark brown to black appearance of sensitized FTO/nc-TiO$_2$ and FTO/nc-TiO$_2$/PC bilayer films, respectively. A strong scattering background is evident in all the spectra as a decreasing transmittance in the blue. Because this background is present in the FTO/nc-TiO$_2$ sample, it must arise primarily from the nc-TiO$_2$ layer. The bilayer structures have an
additional diffuse scattering background in the red that apparently originates from the inverse opal layer.

Figure 3.3: (a) Transmission spectra of unsensitized FTO/nc-TiO$_2$/PC bilayer structures made from 291 (open circles), 304 (dashed line), and 327 nm (crosses) PS spheres. Spectra were recorded in ethanol. (b) Normal incidence UV-visible absorption spectra of a sensitized nc-TiO$_2$ film (solid line) and sensitized FTO/nc-TiO$_2$/PC bilayer structures made from 291 (open circles), 304 (dashed line), and 327 nm spheres (crosses), recorded in acetonitrile. The background spectrum of an FTO-glass slide was subtracted to obtain the spectra shown in Figure 3.2 (a) and (b). The absorbance spectra are measured in the
transmittance mode. Inset shows sensitized FTO/nc-TiO\(_2\) (left) and FTO/nc-TiO\(_2\)/PC bilayer (right) electrodes viewed from the back (i.e., the anode side).

DSSCs fabricated from FTO/nc-TiO\(_2\)/PC bilayer anodes showed consistently higher short-circuit current densities (\(J_{sc}\)) than did FTO/nc-TiO\(_2\) DSSCs without scattering layers (Fig. 3.4 and Table 3.1). An increase in open circuit photovoltage (\(V_{oc}\)) of 20-30 mV was also consistently found with the bilayer electrodes. Fill factor and power conversion efficiency comparisons tended to be more variable, because they were more dependent on the quality of the counter-electrodes used.
Figure 3.4: (a) Photocurrent vs. photovoltage and (b) short circuit IPCE vs. wavelength for FTO/nc-TiO₂ and FTO/nc-TiO₂/PC DSSCs with anode-side illumination (Scheme 1d): FTO/nc-TiO₂ (solid line), FTO/nc-TiO₂/PC (291 nm) (open circle), and FTO/nc-TiO₂/PC (327 nm) (crosses). The dotted line in (b) represents the transmittance of the...
blank FTO-glass. IPCE was not corrected for reflectance or scattering losses of the FTO-glass. (c) IPCE spectra normalized to the maximum value, showing slight enhancement in both the blue and red spectral regions for the FTO/nc-TiO$_2$/PC cells, and (d) enhancement factor (the ratio of the IPCE to that of the FTO/nc-TiO$_2$ DSSC) vs. wavelength. The bilayer resembles configuration (d) in Fig. 3.1.

Table 3.1: Summary data from FTO/nc-TiO$_2$ and FTO/nc-TiO$_2$/PC DSSCs with anode-side illumination. Each entry represents the average of two cells. For each type of cell, a total 6–11 cells were prepared. The total number of samples for each type of cell is shown in parentheses in the first column. Because of the large sample-to-sample variation in dye adsorption, representative cells containing similar dye coverage were chosen for this comparison.

<table>
<thead>
<tr>
<th></th>
<th>N719 Surface Coverage (nmol/cm$^2$)</th>
<th>Total film thickness (µm)</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>V$_{oc}$ (V)</th>
<th>ff</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO/nc-TiO$_2$ (10)</td>
<td>110.0 ± 0.5 (100 ± 20)</td>
<td>10.0±0.4</td>
<td>13.8±0.7</td>
<td>0.75±0.2</td>
<td>0.57±0.04</td>
<td>5.9±0.2</td>
</tr>
<tr>
<td>FTO/nc-TiO$_2$ (9)</td>
<td>154 ± 2 (200 ± 30)</td>
<td>13.8±0.6</td>
<td>14.7±0.1</td>
<td>0.72±0.01</td>
<td>0.612±0.001</td>
<td>6.5±0.2</td>
</tr>
<tr>
<td>FTO/nc-TiO$_2$/PC291 (11)</td>
<td>159 ± 2 (200 ± 20)</td>
<td>15±1</td>
<td>15.9±0.5</td>
<td>0.750±0.004</td>
<td>0.693±0.004</td>
<td>8.3±0.2</td>
</tr>
<tr>
<td>FTO/nc-TiO$_2$/PC327 (6)</td>
<td>155 ± 2 (200 ± 20)</td>
<td>17 ± 3</td>
<td>15±1</td>
<td>0.748±0.001</td>
<td>0.679±0.006</td>
<td>7.9±0.5</td>
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In reporting these data, typical cells were selected that contained approximately equal amounts of adsorbed dye. The thickness of the nc-TiO$_2$ film was optimized at 14-16 µm for FTO/nc-TiO$_2$ DSSCs. Thinner films gave lower dye coverages and lower J$_{sc}$ values. For example, a 10 µm nc-TiO$_2$ film absorbed about 70% as much dye as did a 14 µm film, and consequently had lower J$_{sc}$ (Table 3.1). Because the inverse opal layer was 5-7 µm thick, the nc-TiO$_2$ layer in the bilayer films was 9-11 µm thick. The bilayer cells
and the thinner FTO/nc-TiO$_2$ cell have higher $V_{oc}$ than the thicker FTO/nc-TiO$_2$ cell because there is less recombination between electrons in the TiO$_2$ and I$_3^-$ ions in the electrolyte, as a consequence of the shorter average diffusion distance to the FTO surface. Decreasing the recombination rate results in a higher open circuit voltage.$^{29}$

Fig. 3.4 and Table 3.1 show that the short circuit current density ($J_{sc}$) increased by approximately 16% and 22% with 291 and 327 nm PC layers, respectively, relative to the 14 µm thick FTO/nc-TiO$_2$ DSSC. Surprisingly, this enhancement does not come from the increased red absorbance (Fig. 3.3) of the bilayer electrode, because the shapes of the IPCE curves (Fig. 3.4 (b)) are very similar. By normalizing all the IPCE curves to their maximum value and by calculating the enhancement factor (Fig. 3.4 (c), 3.4 (d)), one can see that the increase in photocurrent comes from both the blue and red regions of the spectrum, implying that scattering enhances light absorption in the nc-TiO$_2$ layer across the spectrum.

Three effects may contribute to the increase in photocurrent. First, the PC layer can act as a dielectric mirror, reflecting light that is transmitted by the nc-TiO$_2$ layer. However, this effect should be most pronounced in the stop band region and cannot explain the increased IPCE in the blue. A more likely effect, especially in the blue spectral region, is multi-directional scattering from defects in the PC layer.$^{30,31}$ Although simple computational models often do not account for the presence of the defects, defects in PCs can cause broadband diffuse scattering.$^{32}$ Both grain boundaries and voids in the PC layer are effective scattering layers. Hore et al. have found that incorporating spherical voids as scattering centers in nc-TiO$_2$ films improved the efficiency of DSSCs by ~24%.$^{11}$ From Rayleigh scattering theory,$^{33}$ the intensity of scattering is inversely
proportional with the fourth power of the wavelength. Hence, photons in short wavelength region should be more efficiently backscattered to the nc-TiO₂ film by defects in the PC layer. The weak enhancement to the red of the stop band is most likely caused by coherent scattering which gives rise to resonant modes in the nc-TiO₂ layer, as predicted in the Mihi-Miguez model.¹⁹

García-Santamaría et al. reported that the surface resonance mode created at the interface of PC layers and dielectric slab can be tuned and even removed by altering the geometry of the bilayer.³⁴ In that study, a high dielectric slab grown on top of opal structures was etched away and its effect on the surface resonance was investigated. As the high dielectric slab was progressively removed, the surface resonant mode was attenuated and finally vanished. By analogy, one should expect that when the nc-TiO₂ and PC layers are separated from each other by a rough interface or a gap on the order of half the wavelength of light, as appears in Fig. 3.2, there should be little optical coupling of the two layers. To demonstrate the importance of the close physical contact of the bilayer, cells with split bilayers were prepared.

### 3.3.2 Spectral Response of Bilayer and Split-Layer FTO/PC/nc-TiO₂ Cells.

Fig. 3.5 compares short-circuit IPCE data for a FTO/nc-TiO₂ DSSC with no scattering layer, and for photonic crystal bilayer cells in the configurations shown in Fig. 3.1 (a) – (c). For the configuration in Fig. 3.1 (a) and (b), PCs were directly grown on the bare FTO electrode and nc-TiO₂ paste was spread on top of PC layers. This procedure results in intimate contact between the two layers as demonstrated previously.¹⁵ For the
PC cells, 243 nm polystyrene spheres were used, and two LPD steps gave a stop band maximum of approximately 585 nm in ethanol. This stop band maximum is 35 nm to the red of the IPCE maximum of the FTO/PC/nc-TiO$_2$ cell. With cathode-side illumination of the bilayer cell (Fig. 3.1 (a)), the photocurrent is markedly enhanced in the spectral region (600-750 nm) to the red of the stop band maximum, as we have reported previously. However, the current is also attenuated in the blue spectral region because of strong light absorption by the I$^-$/I$_3^-$ redox electrolyte. With anode side illumination (Fig. 3.1 (b)), there is a similar red enhancement, but reflection of light from the photonic crystal layer creates a wide notch in the IPCE spectrum in the vicinity of the stop band, as predicted by Mihi and Miguez. Interestingly, the IPCE curve of the split bilayer cell (Fig. 3.1 (c)) closely resembles that of the FTO/nc-TiO$_2$ cell. Additionally, the IPCE of the split bilayer experiment is reminiscent of that of the bilayer configuration in Fig. 3.1 (d) (Fig. 3.2), in which the IPCE increases slightly and across the whole spectrum relative to a FTO/nc-TiO$_2$ DSSC.
Figure 3.5: IPCE data (top) comparing a FTO/nc-TiO₂ DSSC with anode-side illumination (open circles) with the bilayer structures illustrated in Schemes 1a-c. Dashed line: FTO/PC/nc-TiO₂ cell with cathode side illumination (Scheme 1a). Solid line: Same cell, anode-side illumination (Scheme 1b). Crosses: Split bilayer cell, anode side illumination (Scheme 1c). The enhancement factor is shown at the bottom.

The striking difference between the split-layer spectrum (configuration (c) from Fig. 3.1) and those of the coupled bilayer cells (configuration (a) and (b) from Fig. 3.1)
confirms that in the latter case, IPCE enhancement in the red region is not the result of a simple dielectric mirror effect. Intimate physical contact of the two layers is needed for optical coupling of the two layers. Hence, in order for configuration Fig. 3.1 (d) to have the kind of red spectral enhancement as the configurations shown in Fig. 3.1 (b) and (c), the connectivity between the inverse opal layer and the nc-TiO$_2$ film must be improved. In an attempt to improve the connectivity, the bilayer electrodes were treated with 40 mM TiCl$_4$ at 70 °C for 30 min. and then calcined at 475 °C for 30 min. before sensitization. TiCl$_4$ treatment is often used in DSSC fabrication to increase the photocurrent, probably by improving the connectivity of the particle film, and more detailed experimental procedures are described in the literatures. Table 3.2 summarizes the effect of this treatment with FTO/nc-TiO$_2$ and bilayer DSSCs. The bilayer structures have a higher loading of dye molecules than the FTO/nc-TiO$_2$ DSSCs. However, with such thick films, dye molecules anchored at the most outer surface of PC layer do not contribute much to $J_{sc}$ because of the inner filter effect of dye molecules closer to the FTO anode. We again find an increase in the photocurrent and open circuit voltage with the addition of the scattering layer. The increase in photocurrent and power conversion efficiency is not as pronounced as it is without TiCl$_4$, possibly because of overfilling of the nano-TiO$_2$ film. Fig. 3.6 shows that bilayers treated with TiCl$_4$ have a slightly increased red response, consistent with increased connectivity of the layers. However, the effect still appears very small compared with the dramatic increase seen in the intimately coupled FTO/PC/nc-TiO$_2$ bilayer (Fig. 3.2).
Table 3.2: Summary data from FTO/nc-TiO$_2$ and FTO/nc-TiO$_2$/PC DSSCs which were treated with TiCl$_4$ prior to sensitization. Three samples of FTO/nc-TiO$_2$/PC304 (200 ± 20 nmol/cm$^2$) and PC327 (200 ± 10 nmol/cm$^2$) and ten samples of FTO/nc-TiO$_2$ (200 ± 20 nmol/cm$^2$) were prepared. Because of the sample-to-sample variation in the amount of dye adsorbed, cells with similar amounts of dye were compared in each case. Each entry represents the average of two such cells.

<table>
<thead>
<tr>
<th></th>
<th>N719 Surface Coverage (nmol/cm$^2$)</th>
<th>Film thickness (µm)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO/nc-TiO$_2$</td>
<td>195±7</td>
<td>15.6±0.3</td>
<td>14.2±0.2</td>
<td>0.721±0.007</td>
<td>0.66±0.03</td>
<td>6.7±0.4</td>
</tr>
<tr>
<td>FTO/nc-TiO$_2$/PC (304 nm)</td>
<td>210±8</td>
<td>18±4</td>
<td>14.6±0.3</td>
<td>0.747±0.004</td>
<td>0.684±0.004</td>
<td>7.4±0.2</td>
</tr>
<tr>
<td>FTO/nc-TiO$_2$/PC (327 nm)</td>
<td>210±7</td>
<td>19.1±0.3</td>
<td>14.8±0.1</td>
<td>0.740±0.002</td>
<td>0.66±0.04</td>
<td>7.2±0.5</td>
</tr>
</tbody>
</table>
Figure 3.6: (a) IPCE spectra normalized to the maximum value for FTO/nc-TiO$_2$ and FTO/nc-TiO$_2$/PC DSSCs (Scheme 1d) with anode-side illumination, where the anode films were treated with TiCl$_4$ prior to sensitization: FTO/nc-TiO$_2$ (solid line), FTO/nc-TiO$_2$/PC (304 nm) (triangle), and FTO/nc-TiO$_2$/PC (327 nm) (crosses). (b) The enhancement factor is the ratio of IPCE to that of the single-layer nc-TiO$_2$ DSSC. The bilayers are in configuration (d) from Scheme 1.

3.4 Conclusion

The most important conclusion one can draw from this study is that intimate physical contact between nc-TiO$_2$ and TiO$_2$ inverse opal layers is needed to achieve strong red enhancement in the action spectrum of bilayer DSSCs. This effect is evident
when one compares the IPCE spectra of the FTO/PC/nc-TiO$_2$ and split-layer cells (Fig. 3.2). Those experiments are consistent with predictions of the Mihi-Miguez model.$^{19}$

The new polymer templating method we describe allows one to fabricate FTO/nc-TiO$_2$/PC bilayer cells that can be illuminated from the anode side. In this case, a substantial increase in efficiency results from adding the scattering layer. The improvement in efficiency arises from an increase in both the photovoltage and the photocurrent at constant dye loading. Unfortunately, the method appears to result in a rough interface at the bilayer interface, and consequently we do not find a strong red enhancement in the IPCE of these cells. It is interesting that a dielectric band effect is apparent in the absorption spectra of dyes in these bilayers (Fig. 3.3), but not in the IPCE spectra (Fig. 3.6). This implies that the change in the absorption spectrum comes from light localization in the inverse opal layer, but because of poor coupling of the layers, this absorbed light does not contribute to the photocurrent. It will be interesting to explore other methods of fabricating this bilayer structure – for example decal transfer methods – that can give better physical contact between the two layers.

In the poorly coupled FTO/nc-TiO$_2$/PC bilayers we have fabricated, defect scattering appears to play a role in the enhancement of the photocurrent. We have previously found that disordered inverse opal layers in FTO/PC/nc-TiO$_2$ cells are also effective in enhancing the IPCE.$^{21}$ The roles of defects and disorder are still poorly understood and will be investigated in future work.
3.5 References


Chapter 4

Influence of different iodide salts on the performance of dye-sensitized solar cells containing phosphazene based non-volatile electrolytes

4.1 Introduction

Dye-sensitized solar cells (DSSCs) are promising solar conversion devices that can achieve >10% solar conversion efficiency using inexpensive and abundant materials. However, volatile liquid electrolytes, which give the highest efficiency DSSCs, present problems for manufacturing and long term stability. For DSSCs to become competitive with solid state solar cells, critical issues such as the leakage and evaporation of the volatile electrolyte must be addressed and overcome. Several different strategies for replacing organic electrolytes with room temperature ionic liquids, organic hole transport materials, inorganic hole conductors, and polymer/redox couple blends have been proposed. In general, the efficiencies of DSSCs with these alternative electrolytes or hole conductors are substantially lower than those that contain low-viscosity liquid electrolytes.

Polyphosphazenes are inorganic polymers in which the backbone contains phosphorous-nitrogen repeating units. They are thermally and oxidatively stable, and can accommodate a wide variety of functional side groups that enable a broad range of applications. The P-N repeating unit in polyphosphazenes, which is isoelectronic with the Si-O unit in siloxane polymers, confers high chain flexibility, resulting in low crystallinity and in low $T_g$ values. This property leads to high lithium ion mobility with
dissolved Li$^+$ salts, and in fact polyphosphazene derivatives with oligo(ethyleneoxy) side chains show higher Li$^+$ mobility than poly(ethylene oxide) and are promising materials for lithium ion battery applications. Because lithium iodide/triiodide is the most commonly used electrolyte salt in DSSCs, polyphosphazenes are now being investigated as polymer electrolytes for those cells.$^9$

To realize efficient DSSCs, the electrolyte must support the transport of both iodide and triiodide ions, which undergo electron transfer reactions at the porous titania anode and transparent conductor cathode, respectively. Generally, liquid electrolytes in DSSCs are composed of an inorganic or organic iodide salt, iodine and different co-adsorbents such as 4-tert butylpyridine, guanidium thiocyanate and N-methylbenzimidazole. It is also generally known that Li$^+$ cations can intercalate or adsorb on TiO$_2$ surfaces and affect the electron transport within the semiconductor film.$^{10}$ Thus, the ideal polyphosphazene electrolyte system for DSSCs should promote the dissociation of Li$^+$ salts of I$^{-}$ and I$_3^-$, and may also incorporate additives that passivate or modulate the energy of trap states at the TiO$_2$ surface.

In a preliminary study of polyphosphazene-based DSSC electrolytes, we chose methoxyethoxyethoxy polyphosphazene (MEEP, Fig. 4.1(a)), and hexa (methoxyethoxyethoxy) cyclotriphosphazene (MEE-trimer, Fig. 4.1 (b)) and as model systems.$^{11}$ MEEP is a thermoplastic polymer. The MEE-trimer is liquid but has negligible vapor pressure at room temperature. Cells were fabricated and tested with LiI/I$_2$ dissolved in both MEEP and MEE-trimer electrolytes. The performance of these DSSCs was found to depend on both the manner in which the polymer was infiltrated into the porous TiO$_2$ layer and on the microstructure of the TiO$_2$ itself. Not surprisingly, liquid MEE-trimer
gave higher photocurrents than the solid MEEP electrolyte with LiI/I₂ electrolytes. Interestingly, the conductivity of these electrolytes increased with added I₂; the DSSCs nevertheless gave low photocurrents and power conversion efficiencies, consistent with the relatively low ionic conductivity of the polymer/LiI/I₂ system.

In the present study, we examined MEE-trimer electrolytes containing iodine and different iodide salts (LiI, NaI, NH₄I, 1-propyl-3-methylimidazolium iodide). We also performed a comparison study on thermoplastic polymer/plasticizer blends of MEEP (Fig. 4.1(b))/PC and poly(ethylene oxide) (PEO)/PC. The ion transport properties of these electrolytes are characterized by measuring the total ionic conductivity and the mass transport-limited anodic and cathodic current for electrolysis of I⁻ and I₃⁻, which provides a measure of the individual ionic conductivities. These measurements also give by difference the cation conductivity in the MEEP/salt and MEE-trimer/salt systems. These measurements are correlated with the current-voltage behavior of DSSCs containing the same electrolyte/salt mixtures. These measurements give some insight into the factors that limit the photocurrent and efficiency in DSSCs that contain phosphazene-based electrolytes and suggest ways in which the composition of the electrolytes might be optimized for improved cell performance.

![Figure 4.1: Structures of (a) methoxyethoxyethoxy polyphosphazene (MEEP) and (b) hexa[methoxyethoxyethoxy cyclophosphazene] (MEE-trimer).](image-url)
4.2 Experimental

4.2.1 Materials

For all phosphazene reactions, hexachlorocyclotriphosphazene, \((\text{NPCl}_2)_3\) (Fushimi Chemical and Pharmaceutical Co. Ltd., Japan and Nippon Fine Chemicals) was used as the starting material. The small-molecule cyclic intermediate was purified by recrystallization from heptane, and sublimation at 40 °C and 0.05mmHg vacuum. Celite, sodium metal, and di(ethylene glycol)methyl ether were obtained from Aldrich. Diethyl ether, hexanes, tetrahydrofuran (THF), and methylene chloride (CHCl_2) were purchased from VWR. Di(ethylene glycol) methyl ether was purified by vacuum distillation over calcium hydride. The diethyl ether, hexanes, THF, and CHCl_2 were purified through copper/ silica catalytic drying columns. For DSSCs, \(\text{cis-} \text{bis(isothiocyanato)bis(2,2'} \text{bipyridyl-4,4'} \text{dicarboxylato) ruthenium(II) bis(tetrabutyl ammonium)} \) (RuL_2(NCS)_2-2TBA also known as Ruthenium535 bis-TBA, or N719) was received from Solaronix and used without any purification. Lithium iodide (LiI, Aldrich), sodium iodide (NaI, Aldrich), ammonium iodide (NH_4I, Aldrich), 1-propyl-3-methylimidazolium iodide (PMII, \(\text{C}_7\text{H}_{13}\text{IN}_2\), Aldrich), iodine (I_2, Aldrich), 4-\text{tert-Butylpyridine} (C_9H_{13}N, Aldrich), Poly(ethylene oxide) \(((\text{CH}_4\text{O}_2)_n, M_w = 100,000 \text{ and} 600,000, \text{Aldrich})\) and propylene carbonate (anhydrous, Aldrich) were used as received.
4.2.2 Preparation of Electrodes

The nanocrystalline (nc)-TiO$_2$ particle slurry was synthesized according to previously published procedures. Electrodes were fluorine-doped tin oxide coated glass substrates (FTO-glass, TEC8, Hartford Glass Co., IN, 8Ω/sq). FTO substrates (1 in × 1 in) were cleaned by sonication for 20 min in isopropanol and for 20 min in ethanol, followed by rinsing with deionized water and drying with air. A few drops of nc-TiO$_2$ paste were deposited and spread onto the conductive side of the FTO/glass. Cellophane tape spacers with a thickness of 50 µm were applied to opposite edges of the electrode to control the thickness of the doctor-bladed nc-TiO$_2$ films. The samples were then calcined at 450 ºC for 30 minutes. The average thickness of TiO$_2$ film was measured by the profilometer and was between 7-8 µm. After the samples had cooled to 150 ºC, they were taken out of the furnace and immersed slowly into a 0.3 mM solution of N719 dye in a mixture (50:50) of acetonitrile and tert-butanol to prevent cracking of TiO$_2$ and the substrate. All samples were sensitized for 48 hours. After sensitization, the active area of the TiO$_2$ film was made to be 0.25 cm$^2$ by scraping away the excess. Stretched parafilm was used as a 20~30 µm spacer between the anode and platinum counter electrode. A drop of the redox electrolyte (see below) was placed on top of the active area and a platinized FTO-glass counter electrode was placed on it and secured using binder clips. Counter electrodes were made by depositing a few drops of 5mM hexachloroplatinic acid in anhydrous isopropanol onto 15-Ω FTO-coated glass slides, which were dried and calcined at 385 ºC for 15 min. DSSCs samples with electrolytes were assembled in the ambient environment.
4.2.3 Synthesis of MEE-trimer and MEEP

MEE-trimer and MEEP were synthesized using previously published procedures.\textsuperscript{13-15}

4.2.4 Preparation of Electrolytes

4.2.4.1 MEE-trimer

Electrolytes were prepared with different salts at different concentrations, but in all cases the molar ratio of I\textsuperscript{-} to I\textsubscript{2} was kept at 10:1. The salts and MEE-trimer were mixed and stirred at ambient temperature for 24-48 hrs. For LiI and NaI at the highest concentrations tested (1M and 1.5M) the mixtures were heated at ~60 °C to more completely dissolve the salt in the MEE-trimer. The solutions were then allowed to cool to room temperature and iodine was added. Despite the heating procedure, there were still a few crystallites of salts remaining in the MEE-trimer at the highest concentrations. All electrolytes also contained 0.6M 4-\textit{tert} butylpyridine.

4.2.4.2 MEEP/Propylene Carbonate (PC)

1g of MEEP and 1g of propylene carbonate (50:50 wt\%) was first mixed in a vial. PMII (1 M), I\textsubscript{2} (0.1 M) and 4-\textit{tert} butylpyridine (0.4 M) were then added and stirred overnight to ensure homogeneity. The MEEP/PC electrolytes were used within 24-48 hours of preparation.
4.2.4.3 PEO100K(or PEO600K)/Propylene Carbonate (PC)

1g of PEO and 1g of propylene carbonate (50:50 wt%) was first mixed in a vial. PMII (1 M), I₂ (0.1 M) and 4-tert butylpyridine (0.4 M) was then added and the mixture was stirred overnight. (Sonication of the PC/PEO mixtures was avoided because it can cause phase separation of the PEO/PC mixture). These electrolytes were used within 24 hrs of preparation to avoid phase separation.

4.2.5 Photovoltaic Measurements.

Electrical contact was made at the ends of the electrodes using alligator clips and the cell was connected to a source meter (Keithley, Model 2300). All current-voltage curves were obtained at an irradiation of 100 mW/cm² using AM 1.5 filters. A 150 W Xe Lamp (Oriel, Model 77250) was used as the light source and was calibrated with an NREL-certified Si solar cell.

4.2.6 Ionic Conductivity of the Electrolytes

The ionic conductivity of the electrolytes was measured with a HP 4192A impedance analyzer at ambient temperature in a two-point liquid or solid conductivity cell.
4.2.7 Measurement of the Apparent Diffusion Coefficients ($D_{\text{app}}$) of $\Gamma^-$ and $I_3^-$.  

The apparent diffusion coefficients ($D_{\text{app}}$) of $\Gamma^-$ and $I_3^-$ were obtained by measuring steady-state current-voltage curves using a Pt ultramicroelectrode (EE016, Cypress Systems, diameter=10 µm) as a working electrode and a Pt wire as a counter electrode at a scan rate of 10 mV/s on a CH Instruments potentiostat (Model 660). The active radius of the working electrode ($r = 4.67$ µm) was calculated by standardization with 10 mM ferrocene and 0.1 M tetrabutylammonium perchlorate in acetonitrile using a diffusion coefficient of $2.37 \times 10^{-5}$ cm$^2$/s for ferrocene.$^{16}$

4.2.8 Electrochemical Impedance Spectroscopy of DSSCs.

Electrochemical impedance spectroscopy (EIS) on DSSCs was performed under 1 Sun irradiation at the open circuit voltage and in the dark at a forward bias (as indicated in Figs. 4.8 & 4.11) using a Solartron 1260 impedance analyzer in a 2-electrode system. The open circuit voltage was separately measured. The frequency range for the analysis was from 200K to 0.002 Hz and the amplitude of the alternating signal was 10 mV. The impedance spectra were fitted with the Zview program from Scribner Associates, Inc.
4.3 Results and Discussion

4.3.1 Ionic Conductivity and $D_{app}$ of Different Iodides in MEE-trimer

The ionic conductivity of different iodide/tri-iodide salt mixtures in MEE-timer was determined by EIS measurements. The bulk resistance of electrolytes can be obtained from the oblique line at high frequency that intercepts the real axis in the Nyquist plot. The conductivity $\sigma$ is inversely related to the real part of the bulk impedance ($Z$) according to Eq. 4.1:

$$\sigma = \frac{L}{Z \cdot A}$$

Equation 4.1

where $L$ is the thickness of the electrolyte layer between the two electrodes and $A$ is the cross-sectional area.

Figure 4.2: Total conductivity of different iodide/I$_2$ salt mixtures (10:1 molar ratio of I$^-$ to I$_2$) in MEE-trimer electrolytes as a function of salt concentration.
Fig. 4.2 shows that for all salts, at very low concentration, the conductivity increases with increasing concentration. In the case of the PMI cation, the increase in conductivity is linear up to about 0.7 M as expected for soluble electrolytes. Above 1.0 M concentration the conductivity begins to saturate, consistent with increased ion pairing, and there is only a small increase in conductivity between 1.5 and 3.0 M. In the case of all the other iodide salts, the conductivity quickly saturates and then decreases at salt concentrations above about 0.5 M. This suggests that, for the smaller cations, ion pairing is significant at relatively low concentrations (0.3-0.5 M). The neutral ion pairs and clusters that form at these concentrations do not contribute to conduction. At higher salt concentration, electrostatic crosslinking of the polymer substantially reduces the diffusion coefficients of free M⁺ and I⁻ ions. NH₄I was not soluble in MEE-trimer beyond the concentration of 1M. For NaI and LiI, the viscosity of the electrolytes increased dramatically above the concentrations of 1M, consistent with the electrostatic crosslinking mechanism. The striking difference between the behavior of PMII and the alkali iodides suggests that the cations interact differently with the MEE-trimer. The smaller cations are likely to coordinate more strongly to oxygen atoms of the ether side chains of the MEE-trimer than the larger PMI cation.

The measured ionic conductivity is determined by both cations and anions in electrolytes, but in the case of the DSSC the transport of the anions (I⁻ and I₃⁻) is the most important factor. The individual conductivities of the electroactive anions can be extracted from the total ion conductivity, in order to provide a better understanding of how each ion influences the photovoltaic characteristics of DSSCs. The total
conductivity can be expressed as the sum of contributions from the individual ions according to Eq. 4.2:

$$\sigma(T) = \sum_i |Z_i|^2 F c_i e D_i \frac{e}{k_B T}$$  \hspace{1cm} \text{Equation 4.2}$$

where $$Z_i$$, $$c_i$$, e, and $$D_i$$ are the charge, concentration, electronic charge and diffusion coefficient of the ith ion, T is the absolute temperature and $$k_B$$ and F are the Boltzmann and Faraday constants, respectively.

In order to calculate the conductivity of individual ions using this equation, the apparent diffusion coefficients of I⁻ and I₃⁻ must be measured.

The apparent diffusion coefficients of electroactive anions can be obtained by measuring electrolysis currents under mass transport-limited conditions. Here, this was done by linear sweep voltammetry using ultramicroelectrodes. Fig. 4.3 shows i-V curves of each electrolyte obtained under quasi-steady state conditions using 10 µm diameter Pt ultramicroelectrodes. The anodic and cathodic plateau currents were used to calculate the diffusion coefficients ($$D_{\text{app}}$$) of I⁻ and I₃⁻ according to Eq. 4.3:

$$D_{\text{app}} = \frac{I_{ss}}{4nCrF}$$  \hspace{1cm} \text{Equation 4.3}$$

where n is a number of electrons per molecule, C is the bulk concentration, r is the radius of the electrode and F is the Faraday’s constant. While the values of $$D_{\text{app}}$$ obtained by this technique assume that C is equal to the analytical concentration of electrolyte (clearly not valid for the alkali halides, which show strong evidence of ion pairing), the product $$D_{\text{app}} C$$ ($$=D_i c_i$$ in Eq. 4.2) can be obtained directly from the current and used to calculate the contribution of each ion to the total conductivity.
From Fig. 4.3 (a), it is evident that the steady state currents for $I^-$ oxidation and $I_3^-$ reduction vary with dramatically with different solvents. LiI/I$_2$ in acetonitrile exhibits the highest steady-state currents, followed by LiI/I$_2$ in propylene carbonate, consistent with the relative viscosities (0.34 and 2.51 cP at 298K, respectively) of the two solvents. LiI/I$_2$ in MEE-trimer shows dramatically lower current for $I^-$ oxidation and $I_3^-$ reduction - about 500 times lower than the current observed in acetonitrile – which is a combined effect of the greater viscosity of the MEE-trimer at high salt concentration and the ion pairing effect noted above. Fig. 4.3 (b) compares on an expanded scale the limiting currents of different iodide salts at same concentrations in MEE-trimer. The currents for both $I^-$ oxidation and $I_3^-$ reduction are highest with the PMI cation, consistent with the total conductivity values shown in Fig. 4.2. Interestingly, higher anodic and cathodic limiting currents are obtained with NaI/I$_2$ and NH$_4$I/I$_2$ than with LiI/I$_2$, despite the fact that the total conductivities are comparable for the Li and Na salts (Fig. 4.2). This is appears to be a consequence of the higher cationic conductivity of Li$^+$ relative to Na$^+$. Again, it is important to note that the performance of the DSSC should depend primarily on the anionic conductivity.
Limiting anodic and cathodic currents were measured at different concentrations in MEE-trimer for each of the iodide salts. Fig. 4.4 shows the data expressed as the apparent diffusion coefficients ($D_{\text{app}}$) of $I$ and $I_3^-$, with the assumption that $I_2$ is quantitatively converted to $I_3^-$. The general trend is that $D_{\text{app}}$ decreases for both $I$ and $I_3^-$ at increasing salt concentration, which is again likely to be a combined effect of increasing ion pairing and viscosity.

Figure 4.3: Steady-state voltammograms of the different iodide salts in MEE-trimer. (a) LiI/I$_2$ in acetonitrile, propylene carbonate, and MEE-trimer. They all contain 1M LiI, 0.1M I$_2$ and 0.6M 4-tert butylpyridine. (b) 1M LiI, NaI, NH$_4$I and PMII, 0.1M I$_2$ and 0.6M 4-tert butylpyridine in MEE-trimer.
From these data and the conductivity data in Fig. 4.2, it is possible to extract the contributions of the anions and cations to the total conductivity. Fig. 4.5 shows that the cations and anions have comparable conductivities, and in all cases (at the 10:1 salt/I\textsubscript{2} molar ratio tested), the transport of I\textsubscript{3} ions is likely to be the limiting factor in MEE-trimer based DSSCs. Interestingly, in this system, LiI is the poorest choice for both I\textsuperscript{-} and I\textsubscript{3} conductivity. NH\textsubscript{4}I and NaI give comparable anionic conductivities, which reach optimum values at about 1.0 M salt concentration. The conductivity of all ions is highest in the PMII/I\textsubscript{2} system, where the I\textsubscript{3} conductivity reaches an optimum value at about 1.5 M salt concentration.

Figure 4.4: Apparent diffusion coefficients of I\textsuperscript{-} and I\textsubscript{3} from mass transport-limited currents of iodide salts/I\textsubscript{2} in MEE-trimer vs. the analytical concentration of I\textsuperscript{-} and I\textsubscript{3}. The salt/I\textsubscript{2} mole ratio was 10:1 in all experiments.
4.3.2 Photovoltaic Behavior of DSSCs with Different Iodide salts in MEE-trimer Electrolytes

Fig. 4.6 (a) and Table 1 show the photovoltaic behavior of DSSCs containing MEE-trimer electrolytes with different iodide salts at 1.0 M. Electrolytes tested concentrations below 1.0 M showed very poor device efficiency and the data are not included here. It is evident that the anionic conductivity results are in qualitative agreement with the photovoltaic measurements. The ordering of current densities (PMII > NH₄I > NaI > LiI) matches the ordering of I₃⁻ conductivities at 1.0 M salt concentration. Increasing the PMII concentration while maintaining the 10:1 PMII/I₂ ratio (Fig. 4.6 (b)) also increases the short circuit current density up to 3.0 M PMII concentration, as anticipated from the trend in anionic conductivity in Fig. 4.5.

Figure 4.5: Individual ion conductivities in MEE-trimer electrolytes as a function of salt concentration. The salt/I₂ mole ratio was 10:1 in all cases.
In contrast to a distinctive trend observed with the J_{sc}, the V_{oc} did not show a clear pattern among different iodides salts except in the case of LiI. In liquid electrolytes and some polymer electrolytes, different cations have different effects on V_{oc}.^{22} Li^{+} can intercalate into the lattice of TiO_{2} causing a positive shift of the conduction band edge potential. This increases the driving force for charge injection and typically leads to a higher photocurrent density at the expense of V_{oc}. The effect of Li^{+} on V_{oc} is evident in Fig. 4.6 (a), but any enhancement in J_{sc} from increased injection efficiency is masked by the lower limiting current of I_{3}^{-} in the LiI electrolyte.

Figure 4.6: J-V characteristics of DSSCs with different iodide salts in MEE-trimer electrolyte under AM 1.5G illumination. All the electrolytes had a 10:1 salt/I_{2} molar ratio and contained 0.6M 4-tert butylpyridine.
The photovoltaic properties of DSSCs containing PMII electrolytes at different concentrations are summarized in Table 4.2. It is clear that $J_{sc}$ increases with increasing concentration of PMII up to 3.0 M, where a power conversion efficiency of 1.3% was observed. $V_{oc}$ starts to drop beyond 1.0M salt concentration as a result of increased recombination between injected electrons and polyiodide species in the electrolyte. While we did not vary the $I_2$ concentration in these cells, the conductivity data suggest that adding more iodine may improve the device efficiency slightly; however, strong absorption of $I^-/I_3^-$ in blue region of the spectrum and increasing recombination will limit the device performance. It has been shown by Grätzel and coworkers that in pure PMII electrolytes, reductive quenching of the sensitizer (S) by iodide (Eq. 4.4) competes with charge injection into TiO$_2$, resulting in a decrease of photocurrent density by about 20%.$^{23}$

$$S^* + 2I^- \rightarrow S^- + I_2^-$$  

Equation 4.4
4.3.3 Electrochemical Impedance Spectroscopy on MEE-trimer Electrolytes.

To further elucidate the photovoltaic performance of DSSCs containing MEE-trimer electrolytes, the electrochemical impedance spectra were measured in the 2-electrode configuration at $V_{oc}$ under 1Sun illumination and under forward bias in the dark. Fig.4.7 shows the equivalent circuit that was used to model the impedance of the cell. This simple RC circuit is commonly used to describe the electrochemical process in DSSCs with liquid, polymer and ionic liquid electrolytes.\(^{24}\) There are typically three arcs in the impedance spectra of DSSCs. The charge transport process at the electrolyte/Pt interface dominates the response at high frequency in the range between 500,000 and 1,000 Hz. The arc in the mid frequency range between 1,000 and 1 Hz describes the charge transport process at the TiO$_2$/dye/electrolyte interface. In the low frequency region between 1 to 0.002 Hz, the arc represents the mass transport resistance of I$_3^-$ in the electrolyte.

### Table 4.2: Photovoltaic parameters of DSSCs with different concentrations of PMII/I$_2$ in MEE-trimer electrolytes under 1Sun (100 mW/cm$^2$). Each entry represents an average of 5 DSSCs.

<table>
<thead>
<tr>
<th>PMII (M)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$ff$</th>
<th>$P_{max}$ (mW)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2.6±0.3</td>
<td>0.655±0.008</td>
<td>0.53±0.02</td>
<td>0.23±0.02</td>
<td>0.92±0.08</td>
</tr>
<tr>
<td>1.5</td>
<td>3.1±0.2</td>
<td>0.633±0.005</td>
<td>0.526±0.008</td>
<td>0.26±0.01</td>
<td>1.03±0.06</td>
</tr>
<tr>
<td>3.0</td>
<td>4.3±0.3</td>
<td>0.63±0.01</td>
<td>0.49±0.02</td>
<td>0.33±0.03</td>
<td>1.3±0.01</td>
</tr>
</tbody>
</table>
Figure 4.8 (a) shows impedance spectra of different iodide salt/MEE-trimer electrolytes at $V_{oc}$ under 1Sun and Table 4.3 lists the fitted values of the resistance associated with each interfacial process in the DSSC. At the $V_{oc}$ under full sun illumination, the device generates no net current since all the injected electrons recombine with $I_3^-$, but the oxidized dye is still regenerated by $I^-$.\textsuperscript{24a} As shown in Fig. 4.8 (a), the charge transfer resistance at the Pt/electrolyte interface, which is the diameter of the first arc, increases in the order $\text{PMI}^+ < \text{NH}_4^+ < \text{Na}^+ < \text{Li}^+$. The high charge transfer resistance at the Pt electrode indicates the slow regeneration of $I^-$ from $I_3^-$, which will then result in low $J_{sc}$. In order to verify that the first arc is indeed caused by charge transfer resistance at the Pt/electrolyte interface, MEE-trimer electrolytes were placed between the two Pt electrodes and EIS spectra were obtained at 0 V in the same frequency range used for DSSCs (Fig. 4.9). Indeed, the arcs in these spectra match quite well with those obtained in the high- and low-frequency regimes of the spectra measured with DSSCs.
Interestingly, the mid-frequency arcs of MEE-trimer electrolytes were hard to distinguish in the spectra. It appears that the charge transfer resistance at the Pt/electrolyte interface overwhelms the charge transfer resistance at the TiO\textsubscript{2}/dye/electrolyte interface. For DSSCs with high efficiencies, the electron transport resistance within the TiO\textsubscript{2} film is much smaller, compared to the recombination resistance at the TiO\textsubscript{2}/dye/electrolyte interface. It is generally assumed that the mid-frequency arc mainly describes the recombination process between electrons in TiO\textsubscript{2} and the electrolyte, and an enlarged mid-frequency arc represents a reduced recombination process. In MEE-trimer electrolytes, because of slow transport of I/I\textsubscript{3}, recombination between the oxidized dye molecules and electrons in TiO\textsubscript{2} may also play a role, resulting in a lower photocurrent yield and \( J_{sc} \). In conventional liquid electrolytes, the major recombination pathway is at the TiO\textsubscript{2}/electrolyte interface since the dye regeneration process is very effective. Hence, in MEE-trimer electrolytes, there may be more than one major recombination pathway that affects the device performance.

The arc observed at a low-frequency region corresponds to the mass transport resistance of I\textsubscript{3} in the electrolyte. In low-viscosity liquid electrolyte systems, because of the high ionic conductivity and mobility of both I\textsuperscript{−} and I\textsubscript{3}\textsuperscript{−} ions, \( Z_N \) is small compared to the other internal resistances of the DSSCs and is hard to observe it in the Nyquist plot.\textsuperscript{25} However, in viscous electrolytes such as MEE-trimer, it is easy to determine \( Z_N \). The arcs of MEE-trimer electrolytes expand in the same order as the charge transfer resistance at the Pt/electrolyte interface. These measurements are consistent with the measurements of individual ion conductivities by linear sweep voltammetry.
Fig. 4.8 (b) and Table 4.4 show the results of impedance measurements and fitted impedance values for DSSCs that were measured in the dark with a forward bias. In the dark, when a forward bias is applied to the DSSC, electrons transport through the TiO$_2$ and react primarily with I$_3^-$ as I$^-$ is oxidized to I$_3^-$ at the counter electrode.$^{24a}$ In the dark, all three arcs of DSSCs are evident in the Nyquist plots of MEE-trimer cells, in contrast to the data obtained at $V_{oc}$ under full illumination. Fig. 4.8 (c) ~ (e) shows Bode plots of these electrolytes under 1 Sun and in the dark and the difference can be very clearly seen. This difference can be explained by comparing the local concentration of I$_3^-$ on TiO$_2$ films at open circuit and under forward bias. Under illumination at open circuit, I$_3^-$ is formed by dye regeneration in close proximity to the TiO$_2$/electrolyte interface, whereas in the dark, I$_3^-$ is generated at counter electrode and diffuses through the electrolyte to the TiO$_2$ film.$^{24a}$ This provides an explanation of a clear distinction of the mid-frequency arc from the first arc at the high-frequency region. At open circuit under illumination, both I$^-$ and I$_3^-$ are present at their bulk concentrations at the TiO$_2$/dye/electrolyte interface. The mid-frequency arc is not distinguishable and sometimes missing from the spectra indicating a small charge transfer resistance at the TiO$_2$/dye/electrolyte interface relative to other impedance components of the cell. Under forward bias in dark, however, the mid-frequency arc expands as the concentration of I$_3^-$ is depleted at the interface.
Figure 4.8: Nyquist plots of DSSCs containing different MEE-trimer electrolytes (a) at $V_{oc}$ under 1 Sun, and (b) under forward bias in the dark. (c) ~ (f) Bode plots of LiI, NaI, NH$_4$I, and PMII in MEE-trimer electrolytes at $V_{oc}$ under 1 Sun and under forward bias in the dark, respectively. All electrolytes contained 1.0 M salt, 0.1 M I$_2$, and 0.6 M TBP.
The photovoltaic measurements together with the impedance spectra demonstrate that the ionic conductivity is not the only factor that determines the performance of DSSCs with the MEE-trimer electrolytes. The impedance spectra suggest that minimizing the recombination process is also an important problem with viscous electrolytes such as the MEE-trimer. To reduce the rate of recombination at the TiO$_2$/dye/electrolyte interface, coating the TiO$_2$ particles with a thin layer of oxides that have a more negative conduction band edge potential than TiO$_2$ can create an energy barrier, which in this case may minimize these recombination reactions and increase the device efficiency.$^{26}$

Figure 4.9: (a) Nyquist plots of MEE-trimer electrolytes between two Pt electrodes at 0V DC bias with 10 mV ac voltage. (b) Enlarged Nyquist plot of NH$_4$I and PMII in MEE-trimer. The same concentrations of redox couples were used as in Figure 4.8.
Table 4.3: Internal impedance components of DSSCs with MEE-trimer based electrolytes at $V_{oc}$ under 1 Sun, obtained by fitting the impedance spectra.

<table>
<thead>
<tr>
<th>$[\Gamma]$</th>
<th>$R_{Pt}$ (Ω)</th>
<th>$R_{TiO2/Dye/el}$ (Ω)</th>
<th>$Z_N$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiI</td>
<td>452.4</td>
<td>-</td>
<td>532.5</td>
</tr>
<tr>
<td>NaI</td>
<td>278.1</td>
<td>63.64</td>
<td>177.6</td>
</tr>
<tr>
<td>NH₄I</td>
<td>116.2</td>
<td>37.43</td>
<td>121.6</td>
</tr>
<tr>
<td>PMII</td>
<td>91.68</td>
<td>-</td>
<td>78.95</td>
</tr>
</tbody>
</table>

Table 4.4: Internal impedance components of DSSCs with MEE-trimer based under forward bias in the dark, obtained by fitting the impedance spectra.

<table>
<thead>
<tr>
<th>$[\Gamma]$</th>
<th>$R_{Pt}$ (Ω)</th>
<th>$R_{TiO2/Dye/el}$ (Ω)</th>
<th>$Z_N$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiI</td>
<td>440</td>
<td>1635</td>
<td>1333</td>
</tr>
<tr>
<td>NaI</td>
<td>298</td>
<td>731</td>
<td>842</td>
</tr>
<tr>
<td>NH₄I</td>
<td>148</td>
<td>495</td>
<td>356</td>
</tr>
<tr>
<td>PMII</td>
<td>101</td>
<td>270</td>
<td>206</td>
</tr>
</tbody>
</table>
4.3.4 Polyphosphazene/Propylene Carbonate vs. Poly(ethylene oxide)/Propylene Carbonate

Having identified PMII as the best iodide salt for MEE-trimer based electrolytes, a high polymertic polyphosphazene thermoplastic gum (MEEP) with a small molecule plasticizer (propylene carbonate, PC) was examined as an alternative electrolyte. It was evaluated against poly(ethylene oxide)/PC with a molecular weight close to the MEEP used in the study. PC was chosen as the plasticizer because of its low volatility relative to acetonitrile. We have found that using acetonitrile to dissolve the electrolyte and polymer, followed by vacuum drying to remove the solvent, gives inconsistent DSSC performance results. This is because of variable loss of the volatile solvent and iodine during the heating/vacuum-drying process. Because the boiling point of propylene carbonate (240 °C) is much higher than that of acetonitrile, it can be used as a plasticizer without complications arising from volatility.

Table 4.5 summarizes the ionic conductivity of MEEP/PC (50:50 wt%) and PEO/PC (50:50 wt%) blends. MEE/PC shows higher ionic conductivity than PEO/PC blends. MEEP/PC forms a homogenous mixture which is stable for at least one month, whereas PEO/PC did not appear to be a homogeneous mixture within a few days after its preparation. The poor phase stability of PEO/PMII/PC relative to the analogous MEEP mixtures may be a result of the tendency of PEO to crystallize.27
Photovoltaic measurements were carried out on these electrolytes (Fig. 4.10) and their photovoltaic parameters are listed in Table 4.6. The MEEP/PC electrolyte shows better photovoltaic performance than the PEOs/PC mixtures. The ordering of $J_{sc}$ values with these electrolytes is in accord with the ionic conductivity measurements. MEEP/PC also gave a higher fill factor than the PEO/PC electrolytes. Electrochemical impedance spectra, Fig. 4.11, reveal that the PEO/PC mixtures have much higher internal resistance compared to the MEEP/PC electrolytes, resulting in a lower fill factor. The Warburg mass transport resistance of the PEO/PC electrolyte in the low-frequency region is significantly higher than that of MEEP/PC. This suggests that the transport of $I_3^-$ in PEO/PC is slower, possibly due to phase separation in the electrolyte. The slow ion transport also affects the dye-regeneration which can lower the $J_{sc}$, and can create a concentration gradient in the electrolyte that results in a concentration polarization loss in the cell. It may be possible to improve the characteristics of the MEEP/PC system by varying amount of $I_2$ and adding inorganic nanofillers such as TiO$_2$ and SiO$_2$ particles to enhance the mechanical stability and the conductivity of the electrolyte. Experiments along these lines are currently in progress.

Table 4.5: Total ionic conductivity of MEEP/PC, PEO (Average $M_v = 100$K)/PC and PEO (Average $M_v = 600$K)/PC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ionic Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEEP/PC</td>
<td>2.7</td>
</tr>
<tr>
<td>PEO100K/PC</td>
<td>1.7</td>
</tr>
<tr>
<td>PEO600K/PC</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Photovoltaic measurements were carried out on these electrolytes (Fig. 4.10) and their photovoltaic parameters are listed in Table 4.6. The MEEP/PC electrolyte shows better photovoltaic performance than the PEOs/PC mixtures. The ordering of $J_{sc}$ values with these electrolytes is in accord with the ionic conductivity measurements. MEEP/PC also gave a higher fill factor than the PEO/PC electrolytes. Electrochemical impedance spectra, Fig. 4.11, reveal that the PEO/PC mixtures have much higher internal resistance compared to the MEEP/PC electrolytes, resulting in a lower fill factor. The Warburg mass transport resistance of the PEO/PC electrolyte in the low-frequency region is significantly higher than that of MEEP/PC. This suggests that the transport of $I_3^-$ in PEO/PC is slower, possibly due to phase separation in the electrolyte. The slow ion transport also affects the dye-regeneration which can lower the $J_{sc}$, and can create a concentration gradient in the electrolyte that results in a concentration polarization loss in the cell. It may be possible to improve the characteristics of the MEEP/PC system by varying amount of $I_2$ and adding inorganic nanofillers such as TiO$_2$ and SiO$_2$ particles to enhance the mechanical stability and the conductivity of the electrolyte. Experiments along these lines are currently in progress.
Figure 4.10: J-V characteristics of DSSCs with MEEP/PC and PEO100K (& PEO600K)/PC blends under the AM 1.5G illumination. All electrolytes contain 1.0 M PMII, 0.1M I₂ and 0.4M 4-tert butylpyridine.

Table 4.6: Photovoltaic parameters of DSSCs with MEEP/PC vs. PEO/PC under 1Sun (100 mW/cm²). All entries are average values of multiple samples: MEEP/PC (4 Samples), PEO600K/PC (4 Samples), PEO100K/PC (3 Samples).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>$ff$</th>
<th>$P_{max}$ (mW)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEEP/PC</td>
<td>5.4 ± 0.2</td>
<td>0.640 ± 0.004</td>
<td>0.55 ± 0.02</td>
<td>0.471 ± 0.007</td>
<td>1.88 ± 0.03</td>
</tr>
<tr>
<td>PEO100K/PC</td>
<td>4.4 ± 0.1</td>
<td>0.63 ± 0.01</td>
<td>0.52 ± 0.02</td>
<td>0.36 ± 0.01</td>
<td>1.44 ± 0.06</td>
</tr>
<tr>
<td>PEO600K/PC</td>
<td>3.0 ± 0.2</td>
<td>0.58 ± 0.01</td>
<td>0.47 ± 0.05</td>
<td>0.21 ± 0.04</td>
<td>0.8 ± 0.2</td>
</tr>
</tbody>
</table>
4.4 Conclusions

A series of phosphazene based non-volatile electrolytes with different iodide salts was examined by linear sweep voltammetry and electrochemical impedance spectroscopy. The results illustrate that the conductivity of individual anions (I and I$_3$) in MEE-trimer based electrolytes is strongly cation-dependent. A high concentration of iodide salt and I$_2$ is needed to lower the electrolyte impedance and also to efficiently regenerate the oxidized sensitizer, but it also increases the recombination rate. We find that PMII is a better iodide source for MEE-trimer electrolytes than LiI, NaI, or NH$_4$I. Interestingly, this is the opposite of the trend observed with the more widely studied PEO polymer electrolytes for DSSCs. MEEP polymer/PC-based DSSCs containing the PMII electrolyte have transport behavior that closely resembles that of the MEE-trimer/PMII DSSCs. Although the power conversion efficiency is currently low, the amorphous
nature of the MEEP polymer and the improved photovoltaic performance relative to PEO are encouraging. Because it is easy to vary the side groups of polyphosphazenes, these polymers can be easily redesigned for DSSCs applications. Understanding the loss mechanisms in polyphosphazene based DSSCs should inform future studies in which oligomeric or monomeric phosphazenes are used as non-volatile liquid electrolytes. We are currently investigating the possibility of making room temperature ionic liquids based on phosphazenes that could serve as both the solvent and the iodide salt in DSSCs.
4.5 References


Chapter 5

Core-Shell Structuring of Nanocrystalline Titania Electrodes and its Effects in a Photoelectrochemical Water Splitting System

5.1 Introduction

5.1.1 Operating Principle of Dye-Sensitized Water Splitting Photoelectrochemical Cells

Photocatalytic water splitting has been one of the grand challenges of chemical research for over three decades. The photoelectrolysis of water using solar radiation to drive either the anode or cathode process is an interesting alternative to pairing photovoltaic cells with a water electrolyzer. While there are numerous reports on semiconductor-liquid junction water splitting systems, there had been little progress on molecular-semiconductor hybrid water splitting systems that incorporate molecular photosensitizers as visible light absorbers. However, since the first hybrid molecular-semiconductor photoelectrochemical system for water splitting was reported in 2009,\(^1\) a number of other papers that are exploring the similar concept have been published.\(^2\)

In a conventional photoanode-based semiconductor-liquid junction water splitting system as shown in Fig. 5.1(a), the semiconductor acts as the light absorbing material. For efficient light absorption, the bandgap (\(E_{BG}\)) of the semiconductor must be less than 2.0 eV.\(^3\) Moreover, in order to effectively split water into \(\text{H}_2\) and \(\text{O}_2\), the edge potentials of the conduction band (\(E_{CB}\)) and valence band (\(E_{VB}\)) of the semiconductor must be properly situated relative to the \(\text{H}_2\) and \(\text{O}_2\) evolution potentials. Specifically, \(E_{CB}\) must be
more negative than the H₂ evolution potential, and E_{VB} must be more positive than the O₂
evolution potential. To build a robust system, the materials also must be photochemically
stable in an aqueous environment. In general, early transition metal (Ti, Nb, W, Ta, etc.)
oxides are reasonable candidates for photoanodes because of their stability in water.
However, they are also wide bandgap materials, and thus they are not effective light
absorbers in the visible region of the solar spectrum. Oxides that contain later transition
metals do absorb visible light but their excited states tend to be localized and hence the
efficiency of devices based on them is low. Recently, research on early transition metal
oxynitrides has provided a new way to extend the spectral response of early transition
metal oxides. However, the efficiency of such systems remains low because the
absorption is typically at the blue end of the solar spectrum and because charge
recombination reactions are difficult to control. On the other hand, molecular sensitizer
systems are well understood, are accessible across the visible and near infrared regions of
the spectrum, and achieve reasonably high quantum yields and power conversion
efficiencies in devices such as dye sensitized solar cells (DSSCs). Hence, employing
molecular sensitizers as the light absorbing materials for water photoelectrolysis can in
principle address the problems of inefficient light absorption and poor control of charge
recombination reactions.
In molecular-semiconductor hybrid systems, a wide band gap (>3.0 eV) semiconductor is sensitized with a visible light absorbing dye, and the role of the semiconductor in the cell is to collect photogenerated electrons. Ideally, $E_{\text{CB}}$ of the semiconductor should be more negative (more reducing) than the potential of the hydrogen-water couple, $E^0(\text{H}^+/\text{H}_2)$, for unassisted water electrolysis. The molecular sensitizers should have strong visible absorption, and ideally their absorption spectrum should extend into the near infrared. The excited state lifetime of the sensitizer should be sufficiently long for charge injection into the oxide semiconductor. In conventional (non-aqueous) DSSCs, charge injection is very fast, so long excited state lifetimes are not

**Figure 5.1:** (a) Photoanode based semiconductor-liquid junction cell. When photoanode is illuminated, electron-hole pairs are generated. The Fermi level of semiconductor is raised towards the flat band potential of semiconductor by photogenerated potential. However, if the Fermi level ($E_F$) lies below a reduction potential of hydrogen, an external bias must be applied to produce hydrogen on metal counter electrode. (b) Dye-sensitized semiconductor based photoelectrochemical cell. When a dye-sensitized photoanode is illuminated, there is an electron transfer process from an excited state of the dye to semiconductor. These electrons travel through an external circuit to a metal (Pt) counter electrode to reduce water producing hydrogen. The oxidized dye molecules are then regenerated by oxygen evolving photocatalysts, and this process leads to water oxidation to produce oxygen. $R_1$ represent the major recombination path of the system between electrons of the $E_{\text{CB}}$ and the oxidized dye molecules.
needed; however, charge injection tends to be slower in aqueous systems, which are needed for water splitting. The excited state oxidation potential must be more negative than $E_{CB}$ of the semiconductor for efficient electron injection. The ground state oxidation potential of the dye, $E^0(S/S^+)$ must be more positive than potential of water oxidation, $E^0(H_2O/O_2)$.

Additionally, hydrogen evolving or/and oxygen evolving photocatalysts are generally needed in the system for fast and efficient $H_2/O_2$ production. Fig. 5.1(b) shows a schematic representation of a molecular-semiconductor hybrid water splitting system with an oxygen evolving photocatalyst. In our laboratory, we are taking a molecular-semiconductor hybrid approach to tackle the challenge of a visible light driven water cleavage.

Comparing the two half reactions, $H_2/H^+$ and $H_2O/O_2$, water oxidation is more difficult to achieve because it requires four electrons whereas reduction of $H^+/H_2$ is a two electron process as illustrated in Eq. 5.1. It is difficult to find a water oxidation catalyst that is composed of abundant elements, is efficient (i.e., turns over rapidly at low overpotential), and can also withstand the harsh oxidizing conditions of water electrolysis. Although it is convenient for proof-of-concept purposes to operate the system at neutral or slightly acidic pH, i.e., under conditions that are compatible with currently available system components, a practical and efficient water photoelectrolysis system would likely need to run at either low (pH <2) or high (pH>13) pH in order to avoid polarization and membrane losses.

$$O_2 + 4e^- + 4H^+ \leftrightarrow 2H_2O \quad E = 1.23 \text{ V} \ (E^0(H_2O/O_2)) - 0.059(pH) \text{ V}$$

$$4H^+ + 4e^- \leftrightarrow 2H_2 \quad E = 0 \text{ V} \ (E^0(H^+/H_2)) - 0.059(pH) \text{ V}$$

5.1

$$2H_2O \rightarrow O_2 + 2H_2 \quad E^0 = -1.23 \text{ V}$$
5.1.2 Sacrificial Water Oxidation Systems

5.1.2.1 Sacrificial Water oxidation with Ru(bpy)_3^{2+}, S_2O_8^{2-} and Metal Oxide Photocatalysts

In efforts to constructing an overall water splitting system, our group first re-examined the established water oxidation reaction of Ru-tris(bipyridyl) complexes (Ru(bpy)_3^{2+}), and S_2O_8^{2-} as a sacrificial electron acceptor using IrO_2·nH_2O as an oxygen evolving catalyst. Harriman and coworkers previously tested different metal oxides including IrO_2, Co_3O_4, RuO_2, NiCo_2O_4, Rh_2O_3, and Mn_2O_3 and reported that IrO_2 and its amorphous, hydrated form exhibited a high photocatalytic activity. According to Harriman et al., the criteria for O_2 evolving electrocatalysts also apply to metal oxide photocatalysts. As an effective oxygen evolving catalyst, metal oxides must have multiple oxidation states near the potential of the oxygen/water couple, and they must have good stability in their highest oxidation states.

In the sacrificial water oxidation cycle, Ru(bpy)_3^{2+} absorbs the photon energy and an electron is transferred from the excited state Ru(bpy)_3^{2+} molecule to the sacrificial electron acceptor, persulfate (S_2O_8^{2-}). Eq. 5.2 shows that with a suitable metal oxide photocatalyst, Ru(bpy)_3^{2+} is regenerated, and water oxidation occurs. However, when an oxygen evolution photocatalyst is absent, Ru(bpy)_3^{3+} decomposes, and little or no O_2 is formed.

\[ [\text{Ru(bpy)}_3]^2+ + \text{hv} + [\text{S}_2\text{O}_8]^{2-} \rightarrow [\text{Ru(bpy)}_3]^3+ + \text{SO}_4^{2-} + \text{SO}_4^{2-} \]

\[ [\text{Ru(bpy)}_3]^2+ + \text{SO}_4^{2-} \rightarrow [\text{Ru(bpy)}_3]^3+ + \text{SO}_4^{2-} \]

\[ 4[\text{Ru(bpy)}_3]^3+ + 2\text{H}_2\text{O} + \text{Catalyst} \rightarrow 4[\text{Ru(bpy)}_3]^2+ + \text{O}_2 + 4\text{H}^+ + \text{Catalyst} \]
Our group previously reported an improved sacrificial water oxidation system using IrO$_2$·nH$_2$O after investigating different buffer solutions.\textsuperscript{6} It was found that O$_2$ evolution strongly depends on the composition of the buffer solution. When sodium hexafluorosilicate and sodium bicarbonate (Na$_2$SiF$_6$-NaHCO$_3$) at pH 5.8 was used to minimize the pH change due to release of H$^+$ from O$_2$ formation, it effectively maintained the pH of the solution. Additionally, the turnover number of Ru(bpy)$_3^{2+}$ appreciably improved from Harriman’s work in which a phosphate buffer was used to control the pH. The improved turnover number (TON) was explained by a decreased decomposition rate of the Ru(bpy)$_3^{3+}$ in Na$_2$SiF$_6$-NaHCO$_3$ buffer (Fig.5.2).

![Figure 5.2](image)

Figure 5.2: Schematic of sacrificial photocatalytic water oxidation of Ru(bpy)$_3^{2+}$ and IrO$_2$·nH$_2$O. This also shows the decomposition of oxidized dye molecules, which competes with water oxidation.

To further our understanding of sacrificial water oxidation, we prepared IrO$_2$·nH$_2$O nanoparticles stabilized by different organic ligands, and studied their performance as oxygen evolving photocatalysts.\textsuperscript{7} We have found that using dicarboxylate
capping ligands such as butylmalonate and succinate during the particle synthesis resulted in well-dispersed nanoparticles (1-3 nm diameter), however, citrate stabilized \( \text{IrO}_2 \cdot n\text{H}_2\text{O} \) particles underwent some aggregation. It was hypothesized that two carboxylates of the citrate ligand bind to the surface of \( \text{IrO}_2 \cdot n\text{H}_2\text{O} \) particle, and a third carboxylic group that orients away from the surface of \( \text{IrO}_2 \cdot n\text{H}_2\text{O} \) binds to neighboring \( \text{IrO}_2 \cdot n\text{H}_2\text{O} \) particle resulting in an aggregation of particles. Based on these results, \( \text{Ru(bpy)}_3^{2+} \) with malonate and succinate ligands were synthesized and also used as a stabilizer for 2 nm diameter \( \text{IrO}_2 \) particles. In presence of the sacrificial electron acceptor, persulfate, these dye-\( \text{IrO}_2 \) diads showed reasonable photocatalytic activity (TON = 150) for oxygen evolution. This study provided us with valuable information to design a heteroleptic Ru-dye with appropriate surface anchoring groups that bound orthogonally to the \( \text{IrO}_2 \) water oxidation catalyst and to the \( \text{TiO}_2 \) semiconductor, allowing the dye to be employed in a visible light driven molecular-semiconductor water splitting system.

### 5.1.3 Non-Sacrificial Overall Water Splitting System

5.1.3.1 Overall Water Splitting in a Dye-Sensitized Photoelectrochemical Cell.

Based on the previous results, we synthesized the heteroleptic Ru-dye containing malonate and phosphonate groups as shown in Fig. 5.3. The phosphonate group was chosen as the anchoring group for \( \text{TiO}_2 \), because it provides a stable linkage to the oxide surface, as opposed to carboxylic groups which desorb from the semiconductor at pH>4. After synthesizing the heteroleptic Ru-dye, we constructed an overall water splitting dye-
sensitized cell using mesoporous TiO$_2$ and Pt as anode and cathode materials, respectively.\textsuperscript{1} Fig. 5.3 shows a schematic of the overall water splitting system. These Ru-photosensitizers act as linkers to couple photocatalytic nanoparticles with the TiO$_2$ film to build an organic-inorganic hybrid photoelectrode. The photoelectrochemical cell was designed in an H-configuration. The compartment with a flat window contains the working electrode, a TiO$_2$ film sensitized with the dye-IrO$_2$·nH$_2$O colloid and a reference electrode. A Pt wire counter electrode was placed in the other compartment of the cell in which H$_2$ was generated. The two half reactions were separated from each other by a coarse glass frit, and all three electrodes were immersed in a buffer solution (pH 5.75) of 37.5 mM Na$_2$SiF$_6$/NaHCO$_3$ (1:1.5).
Under 450 nm illumination, the cell produces O$_2$ at the anode and H$_2$ at the Pt counter electrode with an applied bias $\geq$ 350 mV. The quantum efficiency of the system is quite low (0.8%), mostly due to rapid back electron transfer from TiO$_2$ to the oxidized sensitizer. To improve this system, a strategy is needed for slowing the back electron transfer reaction and/or for increasing the rate of sensitizer regeneration by electron transfer from the water oxidation catalyst.

Figure 5.3: Schematic of the overall water splitting dye-sensitized photoelectrochemical cell.
5.1.3.2 Effects of Core-Shell Electrodes on Back Electron Transfer Kinetics

In an effort to improve the quantum efficiency of the system, we employed core-shell oxide semiconductor electrodes. In DSSCs, core-shell electrodes are used to slow down charge recombination between $e^-$(TiO$_2$) and I$_3^-$, resulting in a higher open circuit voltage, $V_{oc}$\(^8\). Applying the same idea to the water splitting system, we investigated whether core-shell electrodes could retard the back electron transfer process between $e^-$(TiO$_2$) and the oxidized dye in the aqueous medium of the water-splitting dye cell. If the rate of this process could be decreased while maintaining the quantum yield for charge injection, we would expect the quantum efficiency of water oxidation to increase. We thus compared different shell materials and studied their effects on the interfacial electron transfer rates in the system.

Figure 5.4: Schematic of core-shell electrode sensitized with dye-IrO$_2$·nH$_2$O. Shell materials are made of a wide bandgap material with a more negative conduction band edge than TiO$_2$. 
5.2 Experimental

5.2.1 Heteroleptic Ru-Dye Synthesis.

The heteroleptic dye was synthesized by Dr. W. Justin Youngblood, and Dr. Landy K. Blasdel using the procedure we previously reported.\textsuperscript{1}

5.2.2 Heteroleptic Ru-Dye-IrO\textsubscript{2}·nH\textsubscript{2}O Synthesis.

K\textsubscript{2}IrCl\textsubscript{6} (6 mg, \textasciitilde 13 \textmu mol), heteroleptic Ru-dye (139.4 mg, \textasciitilde 128 \textmu mol), and water (11 mL) were added to a 100 mL 3-neck round bottom flask. The pH was adjusted to 7.5 with 0.25 M NaOH before the mixture was heated from room temperature to 90 °C and held it at 90 °C for 30 min. The reaction mixture was then cooled in an ice bath, and the pH was readjusted to 7.5. After a second 30 min heating at 90 °C, the mixture was cooled in an ice bath and the pH was readjusted to 7.5. All the pH measurements were done with a pH meter. The mixture was then refluxed for 2 hr while air was bubbled through it. The mixture was then removed from the heat and cooled down to room temperature. The mixture was chromatographed over Sephadex LH-20 using water as the eluent. The first band (dark red-brown) was collected. Both synthesis and purification were carried out on the same day.
5.2.3 IrO$_2$·nH$_2$O Particle Characterization

The IrO$_2$·nH$_2$O particles stabilized with dye molecules were characterized by TEM. TEM samples were prepared by dipping a copper grid supported by lacy carbon film directly into the dye-colloidal solution and drying the copper grid overnight. TEM images were obtained on a JEOL EM-2010.

5.2.4 TiO$_2$ and Core-Shell Photoanode Preparation

A TiO$_2$ colloidal solution was prepared by the method previously reported. TiO$_2$ films were deposited on fluorine-doped tin oxide coated glass substrates (FTO-glass, Nippon Glass, Japan, 10Ω/sq) as electrodes using Scotch Tape spacers to adjust the film thickness. The films were then sintered at 450 °C for 30 min and sensitized overnight at room temperature.

The sintered TiO$_2$ films were coated with ZrO$_2$ and Nb$_2$O$_5$ by dipping them in solutions of zirconium and niobium precursors for 15 min and 30 seconds, respectively and were then rinsed with distilled water. The 0.15 M zirconium and 5 mM niobium precursors were prepared from zirconium butoxide in dry 2-propanol and niobium(V) chloride dissolved in dry ethanol, respectively. The resulting ZrO$_2$ and Nb$_2$O$_5$ films were then sintered at 435 °C and 500 °C for 30 min in air, respectively. To maintain similar conditions between the uncoated and coated electrodes, the TiO$_2$ films without ZrO$_2$ and Nb$_2$O$_5$ coating were sintered with the coated ones. The electrodes were sensitized in either dye or dye-IrO$_2$·nH$_2$O aqueous solutions overnight. For sensitization, the concentration of dye and dye-IrO$_2$ solution was adjusted to 0.15 mM with water after...
they were purified from Sephadex LH-20 column (The Ru concentration in the dye-IrO$_2$

solution was determined by UV-vis, assuming the molecular extinction coefficient is

same as Ru(bpy)$_3^{2+/3+}$, $\epsilon = 14600$). After the sensitization, the absorbance of the

sensitized films was measured and the absorbance of sensitized films at 464 nm was

approximately 1.4 – 1.8 using a blank FTO as a reference. During sensitization, the

electrodes were kept in the dark.

5.2.5 Nanosecond Transient Absorption Spectroscopy

For transient absorption measurements of TiO$_2$ and core-shell films at open
circuit, sensitized films were prepared on microscope slides to eliminate light scattering

from the rough FTO layer. They were irradiated with a 300 W Xe arc lamp as the

analyzing light source, and photoexcited with a 532 nm Nd:YAG Spectra-Physics

Quantum-Ray laser (~150 mJ/pulse, pulse width 15 ns). The analyzing light with a 410

nm long-pass filter and a water filter were placed before the sample. The analyzing light

then passed through the sample and a monochromator (Spectral Products), and reached

the PMT detector (Products for Research, Inc). A bandpass filter, ~450 nm and two laser

line filters were placed in the beam path before the PMT. Each kinetic trace was recorded

by using a Tektronic oscilloscope TDS 540A and approximately 40-60 shots were

averaged at each wavelength. The experimental setup for the transient absorption

measurements is shown in Fig. 5.5. All the samples were purged with Ar for 15 min

before the measurements.
5.2.6 Photoelectrochemical Measurements

Insulated copper wires were connected to the sensitized TiO$_2$ film on FTO glass using silver paste and the electrical contact was sealed with epoxy (Hysol-C, McMaster-Carr). After attaching the wires, the electrodes are sensitized and the electrodes were kept in the dark before use. The sensitized working electrode was then placed in an H-shaped quartz cuvette cell. A Pt-wire counter electrode was placed in one side of the cell and other side of the contained the Ag/AgCl reference electrode and working electrode.
(sensitized TiO$_2$ film on FTO). Each side of the apparatus was filled with 37.5 mM Na$_2$SiF$_6$-NaHCO$_3$ buffer (pH 5.75), containing 0.1 M LiClO$_4$ as supporting electrolyte. The buffer solution was prepared the day before and aged overnight. The buffer solution was also filtered through syringe filters ($D_{\text{pore}} = 0.2 \, \mu\text{m}$).

The wires were fed through both septa on each side of the apparatus to connect to a potentiostat (Bioanalytical Systems 100A). The apparatus was sealed with rubber septum, and was degassed with Ar gas before the measurement. A 150 W Xe lamp was used as the light source with a 410 nm long-pass filter and a water filter. The photocurrent of the system was measured by scanning from -500 mV to 0 mV vs. Ag/AgCl at a scan rate of 0.5-2 mV/s.

5.2.7 Amperometric Detection of O$_2$ Generated at the Photoanode.

Pt film electrodes were prepared by Emil Hernandez-Pagan and Dr. Yixin Zhao. First, 10 nm of Ti was sputtered on glass slides as an adhesion layer, and 200 nm of Pt was sputtered. More Pt was deposited by electroplating for 30 min and the current density reached 1.6 mA/cm$^2$. The insulated wires were then attached onto the Pt film electrodes with silver paste (DuPont 4922N) and epoxy (Hysol-C, McMaster-Carr) was applied to protect the electrical contact. Also, a thin layer of epoxy was applied around the edge of the electrodes as a spacer. The height of a spacer was approximately 1.5 – 2 mm. The electrodes are then electropolished in 0.5M H$_2$SO$_4$ by holding the potential at 2 V vs. SCE for 1 min (Applying the 2V potential for longer than 1 min caused Pt films to delaminate from the substrates) to form an oxide layer on Pt. The oxide layer was then
removed and the electrode roughened by scanning from -0.3 V to 1.1 V vs. SCE at 100 mV/s in 0.5M H₂SO₄ multiple times until the peaks of hydrogen adsorption and stripping became pronounced.

The setup for amperometric detection of dissolved O₂ is shown in Fig. 5.6. It is a 4-electrode system in which a bipotentiostat (Pine Instrument Company, AFCBP1 Bipotentiostat) is used to apply different potentials, relative to the Ag/AgCl reference electrode, to two working electrodes (W1 and W2). The collection efficiency was calibrated by using two Pt electrodes, with W2 held at -500 mV vs. Ag/AgCl. It was found that oxygen generated at W1 could not be completely reduced at potentials positive of -450 mV in the pH 5.8 silicate buffer. The current efficiency for water oxidation at the illuminated dye-IrO₂-TiO₂ anode was then measured with W1 at 0 and W2 at -500 mV vs. Ag/AgCl.
Figure 5.6: Schematic of amperometric detection of dissolved O₂. The calibration and detection were performed in an H-cell sealed with rubber septa. (a) Calibration setup. First, two Pt film electrodes, one being an O₂ generator and the other as an O₂ collector were used to calibrate the collector electrode and the efficiency of the collector electrode was calculated. (b) O₂ detection setup. The O₂ generator electrode is replaced by a sensitized photoelectrode and the incident light is illuminated through a FTO side. Before calibration and measurements, the cell was purged with Ar for 20 – 30 min. Pt mesh was used as a counter electrode and Ag/AgCl sat’d was used a reference electrode.
5.3 Results and Discussion

5.3.1 Characterization of Heteroleptic Ru-Dye-IrO$_2$·nH$_2$O Diads

The particle size of dye-IrO$_2$·nH$_2$O diads was measured by using HRTEM after the synthesis. Fig. 5.7 shows HRTEM images of these particles, and it is apparent that the particles are approximately 1-3 nm in diameter, and well-dispersed.

Figure 5.7: High resolution HRTEM images of IrO$_2$·nH$_2$O nanoparticles synthesized with heteroleptic dye molecules. This batch of IrO$_2$·nH$_2$O was prepared by Dr. Landy K. Blasdel.
5.3.2 Characterization of Core-Shell Electrode

The core-shell electrodes were characterized by HRTEM and X-ray photoelectron spectroscopy (XPS), which confirmed the presence of thin insulating layers on the TiO$_2$ films. All XPS samples were prepared on either FTO glass slides or microscope glass slides and calcined. Fig. 5.8 shows the XPS spectra of TiO$_2$ and TiO$_2$/ZrO$_2$ core-shell electrodes with different thicknesses of ZrO$_2$. As shown in Fig. 5.8 (b), the Zr 3d peak was not observed in the TiO$_2$ film, however, the intensity of the Zr 3d band in the core-shell electrodes increased with the number of coatings. Concurrently, the Ti 2p band was seen in the spectra of all samples (Fig. 5.8 (a)). This suggests that the ZrO$_2$ layers that are less than 2 nm thick in all samples, or that the thickness of the film varies enough to expose some Ti at the photoelectron escape depth. The intensity of the Ti 2p band decreased with increasing number of ZrO$_2$ layers, as expected for the core-shell geometry. A thin overlayer of Nb$_2$O$_5$ (1 coating) was also confirmed by XPS as shown in the spectra, Fig. 5.8 (c).

The morphology of the core-shell film was also characterized by HRTEM. TiO$_2$/ZrO$_2$ and TiO$_2$/Nb$_2$O$_5$ films were fabricated on glass substrates and scraped off mechanically. The powders were re-dispersed in ethanol by sonication. A drop of each suspended sample was placed on the TEM grid and dried overnight before being imaged. The HRTEM images in Fig. 5.9 show the crystalline portion of TiO$_2$, and the thin amorphous ZrO$_2$ and Nb$_2$O$_5$ layers on TiO$_2$. The thicknesses of these overlayers are approximately 1 nm which is in rough agreement with the XPS measurements.
Figure 5.8: XPS spectra of TiO$_2$/ZrO$_2$ and TiO$_2$/Nb$_2$O$_5$ in the (a) Ti 2p, (b) Zr 3d, (c) Nb 3d band regions.
The HRTEM images show that the TiO$_2$ surface is covered with the oxide films, but that they are not uniform and that the morphology is different for ZrO$_2$ and Nb$_2$O$_5$. The amorphous ZrO$_2$ film varies in thickness between about 1 and 3 nm and appears rough on the 1 nm length scale. The Nb$_2$O$_5$ film is less uniform, showing hemispherical features that are 2-3 nm in diameter and some uncoated areas of TiO$_2$. 
Figure 5.9: (a) High resolution TEM images of TiO$_2$-ZrO$_2$ 1 coating electrode, and (b) TiO$_2$-Nb$_2$O$_5$ 1 coating electrode
5.3.3 Charge Separation and Recombination in the Dye-Sensitized Water Splitting System

From our initial studies, it was evident that the quantum yield of the water-splitting DSSC was limited by fast recombination between electrons in TiO$_2$ with the oxidized dye, which was not kinetically competitive with dye regeneration by IrO$_2$·nH$_2$O. However, a more detailed study of this system was needed to quantify the factors that contribute to the low quantum yield, including the charge injection process. In order to achieve a highly efficient dye-sensitized water splitting system, there are several requirements that must be fulfilled.

1. Electron injection from the excited state of the dye to the semiconductor must be fast enough to compete with other excited state decay processes, including quenching by IrO$_2$ and radiative decay.

2. The charge recombination process between electrons in the TiO$_2$ and oxidized dye molecules must be slow relative to dye regeneration by electron transfer from IrO$_2$.

3. The subsequent elementary processes of water oxidation, including proton diffusion out of the porous TiO$_2$ film, should be fast enough to prevent electrode polarization.

4. The regeneration of the dye must also be much faster than the irreversible decomposition of the oxidized dye.
To study the charge injection process of the heteroleptic dye molecules into TiO$_2$, a control experiment with I$^{-}$/I$_3^-$ in acetonitrile in place of IrO$_2$·nH$_2$O in pH 5.8 buffer was performed. I$^-$ is a well-known hole scavenger that is commonly used in DSSCs. The standard potential of the I$^-$/I$_3^-$ redox couple is 0.35 V vs. NHE in acetonitrile, and the oxidation potential of Ru(dcbpy)$_2$(NCS)$_2$, a commonly used Ru-dye in DSSCs is 1.1 V, providing 0.75 V of driving force for regeneration of oxidized dye. First, TiO$_2$ films were sensitized with heteroleptic dye molecules, assembled into DSSCs and their current-voltage behavior was tested using I$^-$/I$_3^-$ in acetonitrile as the electron donor in a 2-electrode system. Although the oxidation potential of heteroleptic dye used in the study is more close to the oxidation potential of Ru(bpy)$_3^{3+/2+}$ which is 1.29 V, it still provides sufficient driving force to regenerate oxidized dye molecules. Fig. 5.10 shows J-V characteristics of DSSCs with heteroleptic dye molecules. The low device efficiency compared to conventional DSSCs sensitized with N3 or N719 dyes is expected because the heteroleptic dye absorbs weakly at wavelengths longer than about 520 nm. The photocurrents observed – in the range of 2 mA/cm$^2$ - demonstrate that in acetonitrile the charge injection efficiency of the heteroleptic dye itself is fairly high (Table 5.1).
One of the reasons for the high photocurrent observed with heteroleptic dye molecules in DSSCs can be explained by the facile dye regeneration by $I^-/I_3^-$. In DSSCs, the recombination between the electrons in trap states below the conduction band edge and oxidized dye molecules is multiphasic, but the major component is in the microsecond to millisecond range.\textsuperscript{12} The dye regeneration process by $I^-$ occurs on a much faster (nanosecond) timescale.\textsuperscript{13} The dye regeneration process in DSSCs is thus much faster than the millisecond timescale electron transfer between $\text{IrO}_2\cdot n\text{H}_2\text{O}$ and the oxidized dye in the water splitting DSSC.\textsuperscript{1}

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**Figure 5.10:** J-V Characteristic of DSSCs sensitized with heteroleptic dye molecules under 1 Sun.

**Table 5.1:** Photovoltaic parameters of DSSCs sensitized with heteroleptic dye molecules.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$ff$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.6 ± 0.1</td>
<td>2.1 ± 0.2</td>
<td>0.60 ± 0.01</td>
<td>0.7 ± 0.1</td>
</tr>
</tbody>
</table>
While this result confirms that Ru(bpy)$_3$-based sensitizers such as the heteroleptic dye can inject electrons efficiently into TiO$_2$ in non-aqueous media, it raises several questions that need to be addressed. First, the effects of the solvent in electron injection dynamics must be understood. In DSSCs, organic solvents such as acetonitrile, and 3-methoxy-propionitrile (MPN) are generally used, and the electron injection in these solvents is ultrafast, resulting in high quantum yields. One major difference between DSSCs and the water splitting system is the solvent used. Solvents with different dielectric constants have different solvent reorganization energies, which in turn affect the rate of outer-sphere electron transfer. Additionally, the energetics of the dye molecules and the semiconductor both vary with the solvent used. The band edge potentials of TiO$_2$ are sensitive both to the solvent and to solutes that can adsorb on the surface, as well as to the pH in aqueous systems. Hence, it is possible that the electron injection process between the heteroleptic dye molecules and TiO$_2$ in an aqueous environment would be different from the process in an organic solvent.

To study the effects of water on the electron injection and recombination process, the photocurrent of TiO$_2$ electrodes sensitized with the heteroleptic Ru(bpy)$_3$ dye was measured as a function of the amount of water in the system. These measurements were carried out in a 3-electrode cell with NaI as an electron donor (no I$_2$ was used in the measurements). Fig. 5.11(a) shows that the initial photocurrent density decreased by a factor of $\sim$6, and that the steady state current decreased by a factor of $\sim$15 in aqueous silicate buffer relative to pure acetonitrile. As shown in Fig. 5.10(b), the photocurrent in acetonitrile does not decay with time, but the photocurrent in the aqueous buffer decays from an initial value of about 180 to $\sim$ 50 $\mu$A/cm$^2$. The low photocurrent can be explained
by examining the energetics of semiconductor, sensitizers, and the iodide redox couple in acetonitrile and also in a buffer solution.
Figure 5.11: (a) Photocurrent density of sensitized TiO₂ electrodes in three different solvents were measured as function of applied bias. An area of electrode is ~ 2 cm² (b) Photocurrent density of sensitized TiO₂ electrodes under 0 V vs. Ag/AgCl potential with [NaI] = 0.7 M as an electron donor in neat acetonitrile and pH 5.8 silicate buffer under ~100 mW/cm² illumination.
At pH 5.8, the conduction band of TiO$_2$ is positioned at -0.45 V vs. NHE.$^{15}$ The excited state (LUMO) levels of the dye is estimated qualitatively using the excited-state energy $E_{00}$, and ground state redox potential and it is approximately -0.802 vs. NHE at pH 5.8.$^{16}$ Although this estimation contain uncertainties of 100 mV or more, previous reports on water splitting system using the heteroleptic dye show that there is still a negative enough driving force for fast electron injection into the conduction band of TiO$_2$ in an aqueous environment. Hence, we can postulate that the dye regeneration by $\Gamma$ is very slow in the aqueous environment, relative to the analogous nanosecond process in acetonitrile. It is reported in the literature that $E^\circ (\Gamma'/\Gamma)$ in acetonitrile is +1.23 V, however, $E^\circ (\Gamma'/\Gamma)$ in water shifts 100 mV positively, becoming +1.33 V.$^{17}$ Fig. 5.12 shows the cyclic voltammetric (CV) curves for the heteroleptic dye in pH 5.8 buffer solution and water, and its oxidation potential is at 1.19 V vs. NHE. A positive shift of the $\Gamma'/\Gamma$ one-electron redox potential in water was observed resulting in a decrease of the driving force for charge regeneration. As a result, lower photocurrents and photovoltages would be observed in an aqueous environment.
The oxidized dye regeneration process with an iodide in an aqueous environment was further investigated by performing a linear sweep scan of heteroleptic dye sensitized electrodes in water containing different concentration of iodide. The results are shown in Fig. 5.13. As the iodide concentration was increased from 50 mM to 0.1 M, the photocurrent increased. However, increasing the iodide concentration from 0.1 M to 0.7 M did not result in higher photocurrent.

Figure 5.12: Cyclic voltammogram of a heteroleptic dye in Nanopure water and pH 5.8 silicate buffer solution containing 0.1 M KNO₃ as supporting electrolyte. A bare FTO (Nippon) was used as a working electrode.
To monitor the dye regeneration dynamics by iodide in water, dye sensitized TiO$_2$ films were immersed in water of different iodide concentrations. The results are summarized in Fig. 5.14. As the concentration of NaI increases, the dye regeneration rate becomes faster. However, no significant difference in dye regeneration kinetics is observed for 0.1 and 0.7 M NaI, which is consistent with the photocurrent measurements.

Figure 5.13: Photocurrent density of heteroleptic dye sensitized TiO$_2$ electrodes in water containing different concentration of NaI and 0.1M LiClO$_4$. Photocurrent density of sensitized TiO$_2$ electrode with 0.7M NaI in CH$_3$CN is also shown as a comparison.
Figure 5.14: (a) Quenching of oxidized heteroleptic dye with different iodide concentration in water containing 0.1M LiClO₄ was monitored at 460 nm with 532 nm excitation. (b) A plot of log (Δ OD) vs. time of quenching of oxidized heteroleptic dye with different iodide concentration. The values of excited state lifetime of sensitizers with different iodide concentrations are also shown.
Since a change in the solvent reorganization energy could affect the electron injection process and the quantum yield, solvent effects on the electron transfer processes in the water splitting system must be understood. As previously demonstrated, the photocurrents of heteroleptic dye sensitized electrodes are noticeably higher in acetonitrile when either I\(^{-}\) alone or both I\(^{-}/I_3^-\) are employed as an electron donor than in water. However, due to a positive shift in iodide redox potential in water, measuring the photocurrent with iodide in water vs. acetonitrile would not be a fair comparison. Hence, additional electron transfer kinetic studies using transient absorbance spectroscopy was performed to determine the injection yield in different solvents. Sensitized TiO\(_2\) films of similar absorbances were immersed in acetonitrile and water in the absence of iodide, with both containing 0.1 M LiClO\(_4\), and the bleaching and recovery process was monitored. The amplitude of ∆A at time zero at the dye absorbance maximum (460 nm) can be used to estimate the injection quantum yield.\(^{18}\) Interestingly, the amplitude of ∆A at time zero in water and acetonitrile did not vary much, however the recovery rate of oxidized dye from injected electrons in water were slightly faster than in acetonitrile as shown in Fig. 5.15.
Figure 5.15: Oxidized heteroleptic dye molecules and injected electron recombination kinetics in (a) CH$_3$CN and (b) H$_2$O monitored at 460 nm. The data are fit to a single exponential decay ($y = A_1 e^{-x/t_1} + y_0$) and had a lifetime of 0.86 ms and 0.60 ms, respectively.
We previously reported that approximately 15 dye molecules are chemisorbed on each IrO$_2$ particle and postulated that only a few of the bound dye molecules could coordinate both the IrO$_2$ and TiO$_2$ surfaces. Because the geometry of TiO$_2$-dye-IrO$_2$ cannot be easily controlled, the fraction of excited state dye molecules that are quenched by electron injection into TiO$_2$ is also uncontrolled, but the similarity of ΔA values at t=0 in Fig. 5.15, combined with the relatively high photocurrent obtained with the heteroleptic dye alone in acetonitrile/ꞏ solutions (see Fig. 5.16) suggests that almost all of the excited states in the dye-IrO$_2$ diad are quenched by electron transfer to TiO$_2$. In order to gain more insight into electron injection processes of the water splitting system, TiO$_2$ electrodes sensitized with the heteroleptic dye alone and dye-IrO$_2$ diads were prepared, and the photocurrents of these films were measured at 0 V vs. Ag/AgCl in the presence of 0.7 M NaI. Fig. 5.16 shows that the peak photocurrent of the electrode sensitized with the dye-IrO$_2$·nH$_2$O diad is ~30% lower than the electrode sensitized only with dye molecules; however, the photocurrent measured with iodide is an order of magnitude larger than the photocurrent measured in absence of iodide. These results indicate that the majority of excited state dye molecules in the water splitting systems are injecting effectively, and that the primary reason for low photocurrent in the water splitting system is fast back electron transfer from TiO$_2$ to the oxidized dye.
Fig. 5.17 shows the photocurrent and dark cathodic currents of a sensitized TiO$_2$ electrode with dye-IrO$_2$·nH$_2$O diads at 0 V vs. Ag/AgCl. As the electrode was exposed to the light, the photocurrent density increased but decayed rapidly to a steady value of ~15-30 µA/cm$^2$. When the light was turned off, dark cathodic current was observed. This dark cathodic current represents interfacial hole accumulation, implicating inefficient dye regeneration by IrO$_2$·nH$_2$O. All of these data support the idea that the dye-sensitized water splitting system could be significantly improved by slowing down charge recombination and increasing the rate of dye regeneration by IrO$_2$·nH$_2$O.
The effect of the core-shell electrode structure on charge recombination was investigated by monitoring the bleaching recovery of the dye at 460 nm, which corresponds to the ground state absorbance maximum of the dye-IrO$_2$nH$_2$O diad. Data were acquired with TiO$_2$, TiO$_2$/ZrO$_2$, and TiO$_2$/Nb$_2$O$_5$ films. During the transient measurements, no voltage was applied to the samples. The $E_{BG}$, $E_{CB}$, and $E_{VB}$ of TiO$_2$ and shell materials are listed in Table 5.2.

**Figure 5.17:** Photocurrent density transient of a TiO$_2$ electrode sensitized with dye-IrO$_2$nH$_2$O diads at 0 V vs. Ag/AgCl at ~ 100 mW/cm$^2$. The change in the photocurrent and dark cathodic current were monitored as the light was turned on and off.

### 5.3.4 Core-Shell Electrodes in Dye-Sensitized Water Splitting System

The effect of the core-shell electrode structure on charge recombination was investigated by monitoring the bleaching recovery of the dye at 460 nm, which corresponds to the ground state absorbance maximum of the dye-IrO$_2$nH$_2$O diad. Data were acquired with TiO$_2$, TiO$_2$/ZrO$_2$, and TiO$_2$/Nb$_2$O$_5$ films. During the transient measurements, no voltage was applied to the samples. The $E_{BG}$, $E_{CB}$, and $E_{VB}$ of TiO$_2$ and shell materials are listed in Table 5.2.
In Fig. 5.18, the recombination kinetics of dye-IrO$_2\cdot$nH$_2$O on TiO$_2$, and the core-shell (TiO$_2$/ZrO$_2$ and TiO$_2$/Nb$_2$O$_5$) electrodes are compared. The kinetic parameters of these samples are summarized in Table 5.3. The data were normalized to the transient absorbance ($\Delta A \sim 0.06$) of the sensitized TiO$_2$ film to compensate for the fact that different amounts of dye adsorb to the core-shell films. It is apparent that the core-shell electrodes showed slower back electron transfer. We previously observed a multiphasic decay on the $\sim$0.1-0.4 ms timescale with the dye-IrO$_2$ on TiO$_2$ alone, and in that case the back electron transfer from TiO$_2$ to the oxidized dye was an order of magnitude faster than the forward electron transfer from IrO$_2\cdot$nH$_2$O to the oxidized dye.$^1$ When an overlayer of insulating material is deposited onto the TiO$_2$, the timescale of back electron was slower by a factor of 2-3. With two coatings of ZrO$_2$, a slower recombination rate was measured than with one coating, and the decay was no longer multiphasic. The kinetic trace for TiO$_2$ films and TiO$_2$ with one layer of ZrO$_2$ overlayer was fitted to double ($y = A_1e^{-x/t_1} + A_2e^{-x/t_2} + y_0$) exponential decay but single ($y = A_1e^{-x/t_1} + y_0$) exponential decay was used to fit the kinetic trace of TiO$_2$ with two layers of ZrO$_2$ overlayer and one layer of Nb$_2$O$_5$ overlayer.$^{13b,18}$

With increasing thickness of the overlayer, the fast component of the recombination process was diminished, and the slow component became dominant. This

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>$E_{BG}$ (eV)</th>
<th>$E_{VB}$ ($V$ vs. SCE at pH 5.8)</th>
<th>$E_{CB}$ ($V$ vs. SCE at pH 5.8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>3.0 – 3.3</td>
<td>2.39</td>
<td>-0.76</td>
</tr>
<tr>
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</tr>
<tr>
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<td>-0.84</td>
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</tbody>
</table>

Table 5.2: The bandgap energy and band edge potentials, $E_{VB}$ and $E_{CB}$ of TiO$_2$, ZrO$_2$ and Nb$_2$O$_5$.$^{8b,8c}$
is consistent with the idea that tunneling through the insulating film becomes slow relative to charge transport within the TiO$_2$, and thus the kinetics of charge recombination are dominated by the tunneling rate.$^{8b}$ We did not investigate thicker layers, because it has been reported in the literature$^{8b}$ and also verified in preliminary experiments that thicker overlayers slow down the charge injection process and result in a loss of cell efficiency.

Table 5.3: Back Electron transfer rates between the oxidized sensitizer-IrO$_2$ diads and TiO$_2$ and core-shell films. The rate constants are obtained by inverse excited state lifetime of the oxidized sensitizer-IrO$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_1$</th>
<th>$R_1$ (ms$^{-1}$)</th>
<th>$A_2$</th>
<th>$R_2$ (ms$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>-0.42 ± 0.02</td>
<td>5.6 ± 0.3</td>
<td>-0.55 ± 0.01</td>
<td>88 ± 12</td>
</tr>
<tr>
<td>TiO$_2$/ZrO$_2$</td>
<td>-0.70 ± 0.01</td>
<td>2.8 ± 0.1</td>
<td>-0.32 ± 0.03</td>
<td>33 ± 5</td>
</tr>
<tr>
<td>1 layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$/ZrO$_2$</td>
<td>-0.92 ± 0.01</td>
<td>1.4 ± 0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2 layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>-0.52 ± 0.02</td>
<td>2.9 ± 0.2</td>
<td>-0.40 ± 0.07</td>
<td>72 ± 20</td>
</tr>
<tr>
<td>TiO$_2$/Nb$_2$O$_5$</td>
<td>-0.74 ± 0.01</td>
<td>1.5 ± 0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1 layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.18: Normalized transient bleaching recovery curve monitored at 460 nm for dye-IrO₂·nH₂O sensitized TiO₂ and core-shell electrodes in pH 5.8 buffer. The slower components of TiO₂ and core-shell electrodes had a lifetime of (a) TiO₂: 0.18 ms, TiO₂/ZrO₂_1 layer: 0.36 ms, and TiO₂/ZrO₂_2 layers: 0.70 ms; (b) TiO₂: 0.34 ms, and TiO₂/Nb₂O₅_1 layer: 0.68 ms.
The slower back electron transfer rate observed with the core-shell electrode is consistent with steady-state photoelectrochemical measurements of these films, which showed an increase in photocurrent relative to unmodified TiO$_2$ films. Fig. 5.19 (a) shows the photocurrent generated from the sensitized TiO$_2$ and core-shell electrodes as a function of applied bias. Although one coating of both ZrO$_2$ and Nb$_2$O$_5$ on TiO$_2$ films resulted in higher photocurrents than a TiO$_2$ film alone, the Nb$_2$O$_5$ overlayer appears to be more effective than ZrO$_2$. The difference may be due to the different morphologies of the overlayer, or to electronic effects. It was has been reported in the literature that Nb$_2$O$_5$ is an exceptional shell material for retarding charge recombination, but that ZrO$_2$ forms a dipole layer at the interface between the electrode and the electrolyte, shifting $E_{CB}$ of the TiO$_2$, either positively or negatively based on the dipole intensity and direction.\textsuperscript{20} Additionally, the photocurrent decayed as the applied potential was scanned positively at a scan rate of 0.5 mV/s. It is suspected that water oxidation competes with nucleophilic attack on the oxidized dyes competes at such a slow scan rate, resulting in a lower photocurrent at longer times (i.e., as the applied potential becomes more positive).

Fig. 5.19 (b) shows the photocurrent of a TiO$_2$ electrode and core-shell electrode sensitized with the dye-IrO$_2$·nH$_2$O diad. Photocurrents of the electrodes with dye-IrO$_2$·nH$_2$O diads increase sharply up to $\sim$40 - 50 $\mu$A/cm$^2$, and decay to stabilize at 15-20 $\mu$A/cm$^2$. The photocurrent of the core-shell electrode also decays at a slower rate than a TiO$_2$ film alone.
Figure 5.19: (a) Photocurrent density of TiO$_2$ and different core-shell electrodes measured as function of applied bias at ~100 mW/cm$^2$. (b) Photocurrent density of TiO$_2$ and TiO$_2$/Nb$_2$O$_5$-$1$ coating electrodes sensitized with dye-IrO$_2$·nH$_2$O diads in pH 5.8 silicate buffer at 0 potential vs. Ag/AgCl.
5.3.5 Amperometric Detection of O₂ Generated at the Photoanode

As O₂ is generated at the anode, a collector electrode, which is a Pt film electrode placed close to and parallel to the anode, reduces the photoelectrochemically generated O₂. By applying a sufficiently negative potential, a mass transfer-limited current of O₂ reduction is measured at the Pt collector electrode, and that current is proportional to the concentration of O₂ in the solution.²¹

To calibrate the collector electrode, the baseline current was first measured after purging the solution with Ar for 20 min. A generator electrode was placed on top of the collector, separated from it at a fixed distance of 1.5 – 2mm. Both electrodes were immersed in pH 5.8 silicate buffer with 0.1M LiClO₄ as supporting electrolyte, in one side of an H-cell. The other side of the cell, separated by a glass frit, contained the counter and a reference electrodes. After Ar purging, a -500 mV vs. Ag/AgCl potential was applied to the collector electrode to record the background current with the generator collector at open circuit (i.e., disconnected from the bipotentiostat). At steady state, the collector electrode generated 7 µA of cathodic current as shown in Fig. 5.20 (a).

After obtaining the background current, the Pt generator electrode was connected to the bipotentiostat and 1200 mV vs. Ag/AgCl was applied, which is positive of the O₂/H₂O formal potential (+1087 mV) in this medium. After 60 seconds, the generator electrode was producing 66 µA of anodic current and the collector electrode, still at -500 mV, was generating 59 µA of cathodic current. The baseline current was subtracted from the collector current and a collection efficiency of 79 % was obtained (Fig. 5.20 (b)).
Figure 5.20: Calibration of the Pt generator/Pt collector electrode system. The system was purged with Ar for 20 min. (a) No current was passed at the generator electrode while the background current was measured at the collector electrode. The collector electrode was held at -500 mV vs. Ag/AgCl sat’d, starting at t=0. (b) Generator electrode was held at 1200 mV vs. Ag/AgCl. Collector electrode was at -500 mV vs. Ag/AgCl sat’d.
After the calibration, the sensitized photoanode was assembled with the Pt collector electrode, in the same configuration as the Pt generator electrode, and connected to the bipotentiostat. As the sensitized electrode was illuminated, the peak current reached approximately 250 µA and it sharply decayed. The photocurrent of the TiO$_2$ electrode and TiO$_2$/Nb$_2$O$_5$ core-shell electrode reached approximately 26 and 44 µA after 40 seconds, respectively as shown in Fig. 5.21. After subtracting the background current, the collector electrode generated 19 and 38 µA at the TiO$_2$ and TiO$_2$/Nb$_2$O$_5$ core-shell electrodes, respectively, giving current efficiencies for oxygen evolution of 93 and 109 %, respectively (i.e., 100% within experimental error). The results confirm that the thin layer of Nb$_2$O$_5$ clearly enhances O$_2$ photoproduction in dye-sensitized photoelectrochemical cells, compared to a TiO$_2$ film alone, and that the current efficiency is near unity in both cases.
Figure 5.21: Photoelectrode is at 0 potential vs. Ag/AgCl and collector electrode is at -500 mV vs. Ag/AgCl. (a) Dye-IrO₂ diads sensitized TiO₂ electrode. An area of the electrode was 2.79 cm² (b) Dye-IrO₂ diads sensitized TiO₂/Nb₂O₅ electrode. An area of the electrode was 2.97 cm². A 150 W Xe lamp was equipped with LP 410 and water filters and the light intensity was ~ 100 mW/cm².
5.4 Conclusion

In this study, we demonstrated that core-shell electrodes help to increase the photocurrent in dye-sensitized solar cells for visible light water splitting. Thin insulating oxide shells slow down the recombination process by factor of 1.5-2, but thicker shells also lower the quantum yield of excited state electron transfer from the dye to TiO₂.

This study also demonstrates the limitations of the current system and shows that there are other important factors that contribute to the overall performance of the dye-sensitized water splitting system besides the fast back electron transfer. Further improvements may be possible using a mixture of acetonitrile and buffer to improve the dye stability, and changing the semiconductor-sensitizer-catalyst geometry to accelerate the regeneration of the oxidized dye, for example by using an electron transfer mediator between the catalyst and sensitizer.
5.5 References


12. (a) Wang, Y.; Lu, H.P.; He, Y. *Abstracts*, 42nd Central Regional Meeting of the American Chemical Society, Dayton, OH, June 16-19, 2010; American Chemical


VITA

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Seung-Hyun Anna Lee was born in 1979 in Republic of Korea. In December of 1994 at age of 15, she came to the states to study abroad. After finishing her high school education in Blacksburg, VA, she attended the Penn State University for her freshman year majoring in materials science and engineering, then transferred to Purdue University to begin her study in chemistry. She completed her bachelor and master degrees at Purdue in 2002 and 2005, respectively. After completing her master thesis in DNA nanotechnology at Purdue, she came back to the Penn State to obtain her PhD in Chemistry under supervision of Dr. Thomas E. Mallouk.