Dye-Sensitized Photovoltaic Cells: A coordination chemistry approach in light harvesting as an alternative energy source

Gratzel et al. have proposed an alternative and possibly more efficient means of harvesting energy from the sun compared to traditional amorphous silicon solar cells. The Gratzel group is calling these new solar cells “dye sensitized photovoltaic cells” (DSC). They have demonstrated the use of anatase phase of TiO$_2$ as a wide band gap semiconductor derivatized with various Ru(II) bipyridyl dyes to act as the photo-reactive media for electron conduction. These dyes are sensitive in the UV/Vis range and when excited with light, inject an electron into the mesoscopic semiconductor, which acts as the conducting anode. The oxidized dye is then reduced by a “coupled redox system” which is regenerated by the cathode. Light harvesting efficiency, incident photon to current conversion efficiency, electron recombination, and overall cell efficiency were tested$^1$. The electrochemical behavior of DSC’s will be described and rationalized using molecular orbital theory. Moreover, the electronic structure of the Ru(II) complex will be discussed in relation to electron absorption spectroscopy and ligand field theory, as well as the overall impact of the paper evaluated.

Background

There is approximately $3 \times 10^{21}$ KJ of energy delivered to the earth from the sun each year. This is approximately 10000 fold of what the world’s population presently consumes. If each country in the world were willing to contribute to covering 0.1% of the earth’s surface with solar cells at their present efficiencies (10-24%) there would be an abundance of energy available at the present global energy consumption rate$^1$. Such an initiative hasn’t been realized yet. Solar power has only been widely researched since the first oil panic in the 1970s that catapulted government funding into the search for alternative forms of energy$^2$. Out of that surge of research came the first generation of commercial grade photovoltaic solar cells available to the consumer. These first photovoltaic cells harvested light utilizing the semiconducting abilities of n/p doped amorphous or crystalline silicon. When light strikes the doped silicon an electric potential is created by the development of “electron-hole pairs” at the intersection of the silicon and doping material, usually boron and/or phosphorous.

While these first photovoltaic cells employed principles of solid-state chemistry, the evolution of photovoltaics has followed Edmond Becquerel who first discovered the photoelectric effect in an electrolyte solution, a metal halide, between to platinum electrodes. Photography employed the metal (Ag) halide solution as an emulsion in the first films. However, a deficiency in the mid-late visible spectrum was consistently observed. Vogel, in 1883, discovered that dyes, namely erythrosine, sensitive to this region of the visible spectrum could be implemented into the emulsion to increase the picture quality. Then in1964, at the conference for photosensitization, it was demonstrated that dyes adsorbed to electrodes as a thin film increased efficiency in photoelectrochemistry. Consequently, Hauffe, Tributsch, and Gerishcier established that it was indeed electron transfer occurring from the dye sensitization.

These advances in photoelectrochemistry a long with nanoscience have inspired Michael Gratzel, a chemist at the Swiss Federal Institute of Technology, to take a cue from early work in sensitization and create a new photovoltaic cell. In his article “Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells”, Gratzel explains in detail the chemical principles of the dye-sensitized photovoltaic cell (DSC). The DSC’s employ three main types of chemistry: solid-state semiconductors in nanochemistry, photoelectrochemistry/inorganic photocatalysts, and redox
coupling chemistry. He also demonstrates the DSC cannot only compete with over all efficiency of solid-state photovoltaics, but is also less expensive in energy and materials costs, and are poised to replace solid state cells completely.

This review of the Gratzel DSC will explain the operational chemical principles of the cell, characterization of the various components, methods that the research group used for cell efficiency characterization, as well discuss the implications of Gratzel’s paper.

**DSC Functional Basis**

The basis of the DSC relies upon the implementation of a nanocrystalline semiconductor that is sensitized with a monolayer of a ruthenium dye coordination complex of various derivatizations. The sensitization is important in that these semiconductors have wide band-gaps and require UV to near UV light to excite electrons into the conducting band. Thus, with the ruthenium dye complexes the sensitivity is increased to the outer visible spectrum.

The metal oxides used in this DSC are TiO$_2$ of the anatase phase, although other wide band-gap semiconductors were explored including ZnO, Nb$_2$O$_5$, and SnO$_2$. The ruthenium dye is excited by an incident photon and injects its electron into the conduction band of the semiconductor. The sensitizing dye is regenerated by a redox couple (triiodide complex) in an electrolyte solution. The iodide/triiodide couple is then regenerated at the cathode made of platinum mesh-wire. The anode of the circuit is a glass upon which the TiO$_2$ is applied. The glass and TiO$_2$ were overlaid with a conducting material, usually tin-doped indium oxide or a fluorine-doped tin oxide. The electrolyte solution used was a mildly acidic bromide/bromine solution, although organic electrolytes such as EDTA could be used as well.

The iodide/triiodide couple is significant in that it reduces the oxidized sensitizing dye, and if done in time this can prevent the electron in the conduction band of the TiO$_2$ from recombining with the dye. If the electron that was injected into the conduction band of the TiO$_2$ were to recombine with the dye it would prevent current generation, and decrease the efficiency of the solar cell. A schematic of the operation of this cell is given in figure 1.

![Figure 1: Schematic of DSC. NHE is abbreviated for normal hydrogen electrode](image1)

![Figure 2: SEM of anatase TiO$_2$. Particles average 20 nm in size, and are on fluorine-doped tin oxide glass. TiO$_2$ nanoparticles can be synthesized with titanium tetraisopropoxide as a precursor in a solution of water that is acidified with nitric acid. The anatase phase can be achieved by sintering between 160 and 220 degrees Celsius for at least 16 hours](image2)
Nanocrystalline Semiconductor

Nanocrystalline metal oxides have exuded properties that are proving to be quite beneficial in the world of materials chemistry. While it is known that semiconductors such as TiO$_2$ have a large band gaps that can only excite electrons under high-energy visible light there are other benefits as well. Specifically, for DSC’s it means that the semiconducting material, TiO$_2$, is only µm’s thick and has a large surface area due to the number of exposed facets attributed to its mesoporous morphology and small layer. The anatase phase hexacoordinated TiO$_2$ nanoparticles display a distorted octahedral geometric symmetry of tetragonal bipyramidal shape. Figure 2 shows a scanning electron micrograph of anatase TiO$_2$. The coordination of the TiO$_2$ crystal lattice creates a large surface area allowing for maximum adsorption of the dye sensitizer to the semiconductor. This in turn increases the ratio of incident photon: current conversion. Moreover, because of the high ratio of sensitizer adsorbed to the TiO$_2$ facets there is a dipole created between the carboxylate ligands of the ruthenium dye and the oxide. This dipole moment contributes to creating a charge gradient forcing the electrons to move into the conducting glass, and deters recombination with the reduced ruthenium.

The TiO$_2$ complex has an oxidation state of 4$^+$ and a d$^0$ electronic state, although it is coordinated to six other oxygen atoms in the crystal lattice in the anatase phase. The distortion experienced in the geometry is then imposed by the ligands of the metal, and not the electronic structure. The ligand field stabilization energy is 0 dq for the Ti(IV) metal, and is has empty t$_{2g}$ (non-bonding) orbitals representing the conduction band of the mesoscopic oxide.

Ruthenium Dye Complex

As stated above, the ruthenium dye sensitizers are the key component to the photovoltaic cell. The dye, being sensitive to longer wavelengths of visible light than the oxide, is able to insert its excited state electron into the conduction band of the oxide film. It is the metal-ligand charge transfer (MLCT) that begins the process of the of electron dissemination into the oxide. Figure 3 gives three examples of various Ru(II) dye complexes. The dyes carboxylated bypyridines are where it attaches to the oxides exposed facets. The t$_{2g}$ $\pi^*$ orbital of the bipyridyl ligand is the platform for the electron injection into the oxide conduction band. Figure 4 represents a molecular orbital diagram for the M$_{Ru}$ – L$_{bipy}$ interactions with the oxide conduction band.

The sensitizers began with simple Ru(II)tris-bypyridine, and have evolved to include isothiocyanate, as well as $\pi$-conjugated structures off the bipyridine ring. These modifications are important factors in dye durability, as well as light harvesting ability. The industry standard for a solar cell would require 50-100 million turnovers for the dye sensitizers, corresponding to the industry standard of serviceability for 20 years.
Methods for Analysis

Experiments were conducted on the dye and nanocrystalline oxide in order to determine the rate for electron excitation to electron injection, but also to determine the recombination rate, or electron injection rate. This was estimated using transient absorption spectroscopy. The dye was adsorbed to the nanocrystalline oxide, and excited using a 535 nm laser, and probed with an 860 nm laser. The cross correlation between the excitation from the higher energy laser and the lower energy probing laser gave a time of 57 femtoseconds (fs). This data provides insight into the injection rates for the electron into the oxide film. Which can be used further to calculate the “quantum yield of charge injection” which provides information on how many incident photons cause electron injection into oxide conduction band.

\[ \phi_{\text{inj}} = k_{\text{inj}}(k_{\text{deact}} + k_{\text{inj}}) \]

Where \( k_{\text{deact}} \) represents the sum of the rates in which the electron is recombined or doesn’t continue conducting through the oxide. \( \phi_{\text{inj}} \) is a needed operator for calculating the light harvesting efficiency (LHE), which is used in determining the incident photon to current conversion efficiency (ICPCE). LHE in terms of wavelength is calculated using the reciprocal absorption length, \( \alpha \), and \( d \) the oxide film thickness.

\[ \text{LHE}(\lambda) = 1 - 10^{-\alpha d} \]

The ICPCE optimal wavelength can be calculated in terms of LHE, \( \phi_{\text{inj}} \) and the electron collection efficiency (\( \eta_{\text{coll}} \)).

\[ \text{ICPCE}(\lambda) = \text{LHE}(\lambda) \phi_{\text{inj}} \eta_{\text{coll}} \]

Electron absorption spectroscopy (EAS) in the late UV – near IR was conducted to determine the absorption maximum as well as ICPCE maximum. Figure 5 provides an absorption spectrum of the ruthenium dye derivatized with (bis) bipyridines and isothyocyanate ligands. Figure 6 provides corresponding ICPCE data at the same range of light.
The EAS show that the ruthenium dyes not only have MLCT regions, two in this case, but that there is also over 80% conversion of incident photons to current. Moreover, there is a large region, virtually the entire visible spectrum and parts of the ultraviolet, where current can be generated efficiently.

Overall DSC efficiency was also determined using the equation: \( \eta_{\text{global}} = \frac{i_{\text{ph}} V_{\text{oc}} (\text{ff})}{I_s} \) where \( i_{\text{ph}} \) represents the photocurrent density measured at short circuit, \( V_{\text{oc}} \) is the open-circuit voltage, \( \text{ff} \) is the fill factor of the cell, and \( I_s \) is the intensity of incident light. Based on these parameters, overall cell efficiencies have been determined as high as over 11% (11.4%)\(^1\).

**Discussion and Conclusion**

Gratzel’s paper presents the ideas, analysis, and future of the DSC clearly. However, there are points of the paper that do lack in either experimental or referential support. Many times the recombination of effect of the electron into either the dye complex, or redox couple is presented. The transient absorption spectroscopy does not fully support these ideas. It is at best his hypothesis into the problem of incident photon to current conversion efficiency. The data do more than hint at these notions, but are definitely not conclusive. His analysis using molecular orbital theory, and conducting attributes related to symmetry are not fully developed as well. Furthermore, when presenting a calculation Gratzel explains the parameters, but does not always explain clearly how they are experimentally determined, for example \( \eta_{\text{coll}} \).

DSC technology is no doubt a large contribution to the development for alternative forms of energy. The fact that it is made of relatively inexpensive compounds such as the ruthenium dyes, the TiO\(_2\) semiconductor, as well as the redox couple and electrolyte, is a significant factor in switching from solid-state silicon based photovoltaic cells to the DSC. That the DSC is able to compete with the solid-state cells in overall efficiency is a vital factor in the push to employ DSC’s in the industrial/commercial markets as well\(^1,2\). DSC technology is in fact already being implemented into the mainstream. The US based company Konarka is currently incorporating DSC technology into the development of new photovoltaic products. Sustainable Technologies International has announced production of glass tiles capable of producing energy via DSC’s. The application of solar energy storage is also of great interest. The reducing potential of the DSC could be used to reduce protons to H\(_2\) for fuel cell technology. The greatest limiting factor in the harnessing of solar energy and storage are the materials we use to achieve this. As research progresses with the discovery of cheaper, more efficient materials, the ability to live life free from fossil fuels will become more of an everyday reality.

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