Utilization of TiO_2 Molecular Organic Framework in Dye Sensitized Solar Cells to Increase Thermal Energy Absorption

Introduction:

Increased energy production is a growing necessity for the global community. Most of the world's energy today and over the past few millennia have come from the "big three" fossil fuels – oil, coal, and natural gas. This is an issue as known sources for these fuels are decreasing, thereby steadily raising their costa. In order to combat this imminent threat to the loss of sustained energy production, the global scientific community has begun research into renewable sources of energy. The most promising source of renewable energy that has had the most growth in energy production over the past two decades has come in the form of solar energy.

Solar energy is not only one of the most efficient and clean renewable energy sources available to us, but the amount of energy that the human population has access to from the sun is unmatched by any other source of energy. If we were able to harness the full amount of solar energy that hit a $500{,}000 km^2$ (smaller than the size of Texas) area of the earth over the course of a day, it would be equivalent to over 250 times the total energy output of all the earth's power plants over an entire year. However, with the present capabilities of high efficiency solar cells that utilize TiO_2 and are doped with high thermal efficiency fluorescent dyes, being able to harness 100% of solar energy is a long way off. The majority of the leading solar cells are able to reach about 30% solar efficiency over an area of about $3m^2$. Improving already established techniques to convert solar energy into usable potential energy is the goal of this research.

In order to increase the overall potential energy created in a solar cell this research will focus in on the thermal efficiency of the materials used in the solar cell materials. Standard solar cells use the doped TiO_2 in metallic form; this is a crude use of a costly and highly thermally efficient material. In this research project, we intend to utilize TiO_2 in a Metallic Organic Framework (MOF) format which will in turn increase thermal activity of TiO_2 by reducing bond strain from the lattice framework of a standard metallic structure. Moreover, replacing the solar cell's structure with a semi-rigid organic linker will more effectively transfer this increased energy to the voltaic component of a standard solar cell. The use of organic carbon linkers will also increase the surface area of the cell while simultaneously decreasing the overall density of the structure. This lattice also allows for an increased permittivity of light through the structure, allowing for high intensity light to penetrate through additional layers of TiO_2 and producing more thermal energy. Furthermore, the MOF will still allow for an equivalent energy output as compared to current high efficiency solar cells under low light intensities.

Preliminary research has shown solar efficiency increases when TiO_2-MOFs contain a standard poly-carbon linker with no functionality as compared to a doped TiO_2 metallic solar cell. We intend to take this one step further and functionalize the carbon linkers, thereby allowing for various fluorescent dyes to directly bind to the structure of the MOF. This increased efficiency is obtained through doping, whereas normal cells simply form surface level interactions with dyes. In doing so, this will increase the amount of solar energy available for conversion into thermal energy, which is usable in redox voltaic reactions. These reactions can then be used for usable energy for world consumption.

The significance in doing so will increase the amount of energy created from solar energy, putting less of a dependence on other energy sources, some of which, will not be available in the near future. Eventually, solar energy will become the most prevalent energy source for earth, so improving techniques such as this will become mandatory. Furthermore, unlike other proposed methods concerning renewable energy, solar energy has little to no ethical problems associated with it, and the only current roadblock standing in its way is the cost. Using MOF's as part of the solar cells will help decrease this cost and make solar energy accessible to people worldwide.

Goal Statement:

If successful, the proposed experiments will result in a method to create a higher efficiency solar cell by using TiO_2-MOFs (UiO-67). This will reduce overall cost per solar cell as MOF integration of TiO_2 allows for maximum thermal efficiency while using less TiO_2 than standard solar cells.

Background:

Recently, metal–organic frameworks (MOFs) have shown promise for use in many practical applications such as gas storage and separation, electro- and photo-catalysis, electrical and optical sensing, and photovoltaic applications.[1] Furthermore, MOFs containing photoactive ligands, such as TiO_2, have been designed and characterized as potential materials for photovoltaic applications, such as solar cells. These molecules can also be used as a base structure on to which fluorescent materials and dyes can be attached, which increases the efficiency of high power solar cells.[1] Dye Sensitized Solar Cells (DSSCs) are a more efficient method for utilizing solar technology due to properties such as low weight, flexibility, transparency, and varied colors. Additionally, DSSCs display increased efficiency in low light conditions[2] compared to traditional solar cells, thereby allowing the cells to produce energy for a larger portion of the day and on days with less direct sunlight.

Using MOFs or MOF-like frameworks in conjunction with DSSCs could both increase the cost efficiency as well as the energy absorbed by DSSCs, specifically by introducing the highly customizable nature of MOFs to the structure. This will allow the high thermal capacity of TiO2 dyes to be reacted directly into a MOF structure, producing low weight-high efficiency solar cells. Moreover, the use of three-dimensional perovskite structures in contact with the highly porous TiO2–MOF coatings will provide several major advantages, such as a large absorption coefficient, high carrier mobility, and high stability.[3] Perovskite structures include any materials with the same physical structure as calcium titanium oxide. These structures are highly effective in ultrathin films of 500nm and can be optimized for the solar spectrum by altering the halide content in the film.

To produce these new, MOF-based cells, uniform thin films of fluorescent dye will be deposited via the spin coating method, which encompasses products such as thin and ultrathin polymer films. Procedures on the spin coating will include deposition, spin-up, spin-off, and evaporation.[2] This method works by applying a thin layer of desired substrate, such as a fluorescent dye, to a flat surface, such as a crystalline MOF, through use of centripetal force. This method maximizes the dispersion of the dye across the MOF surface. After dye application, the MOF will be crushed into a uniform sheet for use in DSS cells to maximize the thermal energy potential of the cell.

Proposed Research:

1. Materials

In this experiment, TiO_2 MOF's will be used as the basis for the solar cell. These metal frameworks will be constructed from 2-bromo-1,4-dimethyl-benzene and $Ti(OC_3H_7)_4$. A fluorescent dye solution consisting of magnesium and ruthenium dyes obtained from Sigma-Aldrich will be used in order to enable the cell to have a high thermal efficiency. A spin coating apparatus will be required to allow the reaction to take place and will be ordered online from MTI corporation. In order to mimic the effect of sunlight, a Meiji FL154 Single Arm Fiber Optic Illuminator will be obtained from the New York Microscope Company. A hydraulic press will be required to compress the MOF dye into granular solids. This will be obtained from the University of San Diego. A high efficiency solar cell will be used to insert the TiO_2 MOF, which will be acquired from Sun Power INC. The brand name specifically that will be used is the Ultra-Premium Performance. Furthermore, in order to monitor the temperature of the cell, an Infrared Laser Thermometer will be purchased from Bulk Apothecary. Lastly, in order to measure the energy production within the new solar cell, a capacitor, also obtained from the University of San Diego, will be used to quantify the energy.

2. Procedure

2.1 : Synthesis of the Functionalized MOF

The first goal of this research project is to develop a TiO_2 molecular organic framework that can be used in high efficiency solar cell. To optimize the reactivity of the MOF cell, it will need to be able to react with fluorescent dyes that are able to absorb the maximum amount of solar energy and convert it into thermal energy. To do this, the carbon linker between each MOF must be stable, which is achieved through the addition of an aromatic ring. Moreover, the carbon linker must have reactive selectively with the target dye, which is achieved through brominating one of the carbons of the aromatic ring and adding a sterically hindered group to the side of the ring opposite the bromo group, such that the dye interacts with each MOF linker in the same way.

This type of reaction with a TiO_2 MOF has been achieved already by the Vinogradov research group, but never with the added stereo-hindrance, which ensures a uniform binding of the dye to promote further efficiency in the conversion of solar to thermal energy. The formation of the TiO_2 framework will be done using the 1,4-dimethyl-phenyl functional group linkers in a solution containing $Ti(OC_3H_7)_4$ in a limiting amount of HPLC-grade ultrapure water to obtain the non-functionalized MOF. This will then be further reacted to brominate the aromatic ring while adding a tert-butyl group opposite the brominated site.

2.2 : Determination of Fluorescent Dye

The two most commonly used dyes that increase the efficiency of modern day solar cells are dyes that consist of either a ruthenium base or a manganese base. In modern solar cells these dyes are added as a secondary layer behind the TiO_2 to absorb any residual solar energy; in the MOF model of the solar cell, the dye instead will be chemically bound to the linkers between the TiO_2 metal ions as well as in solution instead of in the solution alone. Both manganese and ruthenium dyes have their distinct advantages. Manganese is a more readily available chemical and as such has a lower cost while still offering a stable and efficient transfer of energy; however, it has an incident-photon-to-carrier conversion-efficiency (IPCE) of 68-80% in the optimal range of 7.5% Mn^{2+} in solution, although it does not increase with a higher concentration of Mn^{2+}.[7] Ruthenium, in contrast, bears a bigger financial cost but offers a better IPCE of 78-92% in a Ru^{2+} concentration range of 5.0-6.2% and is highly stable once bound.

Based off the IPCE data and the equivalent dye-linker reactivity of both ruthenium and manganese, both dyes will be bound to the linker through the spin coating method described in the Kagan paper.[3] The spin coating apparatus allows for the dye to be quantitatively administered to the MOF in a uniform manner to ensure that there is not a “hot spot” in the cell, which could throw off the equilibrium of the redox reactions at other parts of the cell. Each dye will be bound to the MOF and subjected to all further steps of the procedure to determine if one dye is more durable than the other. Looking at the extinction rates of the chemical bond between the linkers and the dyes as they are exposed to high levels of solar radiation will allow us to throw out any unforeseen calamities for either dye.

After each dye has been added through spin-coating each MOF will be taken in granular form and compressed into a thin sheet that can then be used in the solar cell apparatus in its most stable form. Compressing the sheet with the dye bound to it also allows for a more precise control of the ratio of TiO_2 to dye. Compressed film granular untreated MOFs, granular dye-treated MOFs, and compressed untreated MOFs will be made into a variant solar cell to account for all necessary controls for the experiment.

2.3 : Mechanical Setup of the MOF Solar Cell

The setup of the MOF cell will be very similar to that of standard high efficiency dye sensitized solar cells that are in production today. The first layer of the solar cell will consist of transparent conducting glass treated with fluorine-doped tin oxide (FTO) to increase compatibility of the glass with the dye layer. The second layer will consist of the TiO_2-MOF-Ru/Mn compound in solution of dye in the optimal concentration ratios stated above. This is where the MOF cell differs from standard solar cells as the dye and TiO_2 layers are separate but sequential. Here they are combined to increase thermal efficiency and reduce heat lost through transfer at each layer of the solar cell. This is visually represented in **Figure 1**.

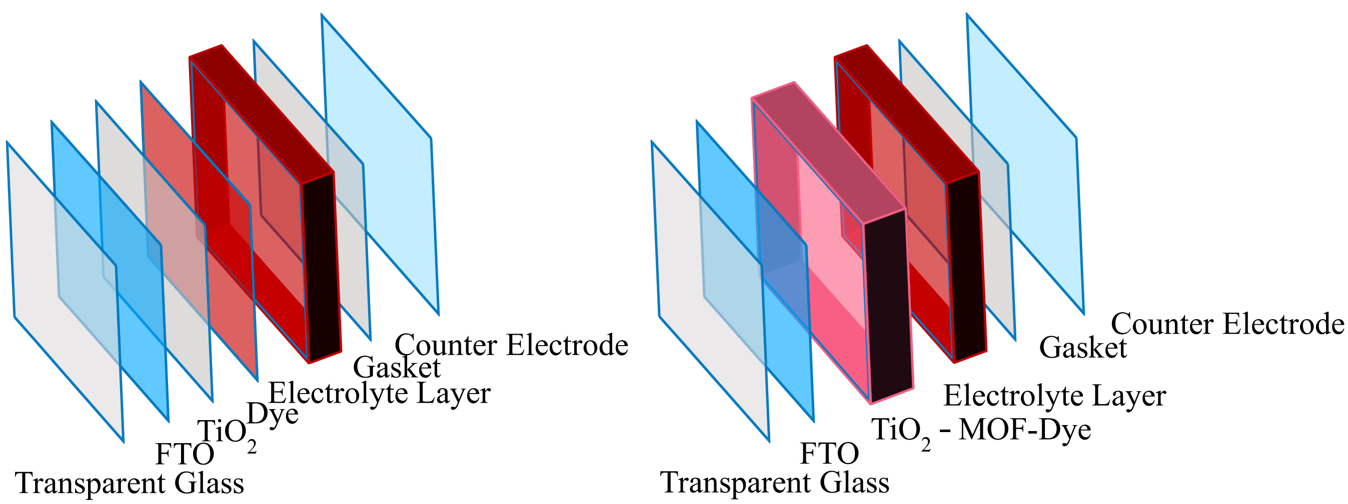

Figure 1. Visual representation of the differences between proposed solar cell (left) and standard high efficiency dye sensitized solar cells (right).

The standard electrolyte layer, which is where the redox reactions convert thermal energy to chemical energy in a voltaic cell reaction, will follow the MOF layer in the high efficiency solar cell. The gasket to seal the system and ensure there is no loss of solution will be located behind the standard electrolyte layer. The counter electrode, which transfers the electrical charge to a capacitor, will form the last layer. Finally, the capacitor allows the charge to be stored in a battery for later use.

2.4 : Testing of MOF Cells

Thermal efficiency of each solar cell will be tested against the current leading dye sensitized solar cell in standard industry tests as well as specialized testing to determine full conversion efficiency. The industry tests are conducted by subjecting each cell to light testing in a controlled chamber with known light output, which mimics the solar energy that reaches the earth. The chamber will be set to mimic a full week of the solar cycle; going through dark, dim, bright, and intense light conditions to mimic night, dawn, day, and high noon for a full week. The energy output of the cells will be recorded and compared using the DSSC cell as the baseline.

Thermal efficiency will then be calculated using the equations depicted in the Maza paper.[2] First the Energy interface between the MOF and the solar energy will be determined through the exterior temperature of the MOF as determined by a laser thermometer. This will be plugged into the equation below to show loss of energy in the interface.

$$(\tau'' obs)^{-1} = k_r + k_{nr} + k_{hop} + k_{inj}$$

After this the electron injection efficiency at the interface will be determined by the equation below. This will show the energy loss after each electron jump in the MOF.

$$\Phi_{inj} = \tau''_{obs} k_{inj}$$

The average distance of each electron hop will be computed to show which cell has the least distance covered per jump and relate the ratio of energy per jump and jump distance to show which cell loses the least amount of energy within the MOF/TiO_2 layer of the solar cell. This will be calculated through the following two equations:

Determination of Electron Hopping Distance

$$k_{hop} = \frac{mD_{RET}}{R_{hop^2}}$$

Determination of Electron Transfer Efficiency

$$\Phi_{RET} = 1 - \frac{\tau'_{obs}}{\tau_o} = \frac{1}{1 + (\frac{r}{R_{hop}})^3}$$

Finally, from the determined thermal efficiency, the cell that has the smallest loss of energy between the solar and thermal energy transitions will be selected to move on for further experimentation and for future experiments after the conclusion of this experiment.

2.5: Production of Voltage from MOF Solar Cell

The transfer of thermal energy obtained from the TiO_2 electrode and its accompanying dye solution to chemical energy via the standard electrolyte layer, which is where the redox reactions will occur, is the determinant of the efficiency of the MOF cell. The solar cell that minimizes energy loss to the greatest extent will be utilized in this part of the experiment. Due to the photoactive TiO_2 ligand in the MOF structure, charge separation will start to occur due to the formation of metal cations from the framework of the MOF. In the electrolyte layer of the MOF solar cell, an iodide-based electrolyte is present in order to convert the thermal energy generated from the injection of electrons into the conduction band of TiO_2 into chemical energy.[8]

To do this, the electrolyte is oxidized from I^- to I_3^- by regenerating oxidized dye molecules. This oxidation occurs on the counter electrode side of the MOF solar cell, which transfers the electrical charge to the capacitor, where it is then stored and can be saved for electrical output through the use of a battery. During this process, charge recombination can occur, which greatly inhibits the production of electrical charge as a means of usable chemical energy. In order to enhance the MOF solar cell's ability to separate charge, the number of pores can be increased, as this will result in a higher rate of charge flow in the system. Also, the degradation of the MOF structure into a more amorphous structure has been noted to contribute well in electrochemical processes. Overall, the redox reactions that take place in the MOF solar cell explains the mechanism of how thermal energy obtained from shining light onto the photoelectrode is converted to chemical energy, which can be used for electrical purposes.

2.6: Testing MOF Cell Configurations for Voltage Production

The efficiency of converting the thermal energy into electrical energy via redox reactions in the voltaic cell will be tested by using three different variations of the MOF cell. These tests will be carried out by exposing each of the configurations to conditions that imitate the solar energy that reaches the earth, as described in Section 2.4; the light source will be the Meiji FL154 Single Arm Fiber Optic Illuminator with a known output of light. This will take place in a controlled chamber to minimize any complications, and it will be subject to light and dark conditions identical to those mentioned in Section 2.4. To determine the efficiency of the conversion of energy, we will begin by testing the granular MOF in a DSSC. An ammeter, which measures the flow of charge delivered to the capacitor, will be used on the new solar cell to determine the photocurrent of each period during the light cycle. In addition, the photovoltage generated by each period of light during this cycle will be determined by using a voltmeter on the new solar cell. Once these data are recorded, three different graphs will be plotted: one of the photocurrent vs. time, one of the photovoltage vs. time, and one of the photocurrent vs. photovoltage. The plot of the photocurrent vs. photovoltage will be used to assess the degree of efficiency of the constructed solar cell. Each minimum or maximum from the measurements will be recorded. These different established relationships will illustrate the amount of voltage that is generated from the light-induced separation of charge.

Next, the configuration of a compressed MOF in a DSSC will be used. The same procedure as listed above will be used, ensuring that the photovoltage and photocurrents are both recorded during the same time periods. The relationships between photocurrent and photovoltage will be established by using the same three graphs. The experiment will be repeated once more with a granular MOF in a fluorescent dye solution in DSSC. The data points with the highest voltage, and the configuration with the highest generation of voltage correspond to the most efficient converters of thermal energy to chemical energy of the three subjects.

Part IV: References

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