Dye-Sensitized Solar Cells

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Abstract - Dye sensitized solar cells are a type of thin film solar cell used to convert sunlight into electrical energy. These devices use a different mechanism than conventional solar cells and can be made from materials which are biocompatible and biodegradable. The simplicity of design and small environmental impact of these devices make them a likely candidate for replacing conventional PV devices. Since these solar cells are thin film cells, they can be made to be transparent and can be printed on flexible substrate, allowing their incorporation into many household objects such as windows, backpacks, walls, and other objects which would otherwise not be used for energy generation. A wide variety of fabrication techniques and device designs exist for DSSCs, each having its benefits and deficiencies; it is the purpose of this paper to evaluate some of these design variations, including different semiconductor and dye types and scaffolds, as well as semiconductor surface treatment.

I. Introduction

In today's modern society, energy has become an imperative part of daily life. As the population of the world increases, so does the demand for energy. In the next 30 years, worldwide power consumption is expected to double. With the inevitable acceleration in demand for energy, fossil fuel resources will eventually be depleted. 68% of energy used globally is currently derived from oil and coal [1]. Additionally coal combustion produces toxic nitrogen oxides and sulfur oxides as well as airborne particles [2]. Fossil fuels are also greenhouse gas emitters [3]. The greenhouse effect is the gradual heating of the earth due to increases in the concentration of a small portion of atmospheric gasses. These gasses, including water vapor, certain organic halides, and most crucially carbon dioxide, absorb reflected incident solar radiation that would otherwise pass back into space, and reemit the energy in the form of infrared radiation. With the irresponsible or ignorant overuse of fossil fuels such as oil and coal in the last two centuries, the concentration of these gasses, as well as the earth's average temperature, have increased [4]. Nuclear power, though able to provide large scales of power generation, has proven to have substantial safety and waste management issues. Leaving us with the option of renewable energy sources for meeting long term demand.

The goal of this work was to provide an evaluation of different fabrication methods and DSSC device designs. Three types of experiment were conducted to: 1) determine the effect of semiconductor surface modification on efficiency, 2) determine the influence of semiconductor scaffolding on efficiency, and finally, 3) to determine the effect of using different natural dyes. First, an overview of current fabrication techniques and device designs will be presented.

Competing Alternative Energy Technologies

Upon realizing the myriad environmental dangers and unsustainability associated with fossil fuel power, the scientific and industrial communities proposed many promising alternative energy technologies including hydroelectric, nuclear, wind, solar, tidal, and biological sources of electricity. Each technology has advantages as well as disadvantages, therefore it has been recognized that future energy stability is dependent upon using a blend of these technologies. Each technology has developed independently but with the common goal of achieving maximum efficiency and minimum production and implementation costs. Only after these goals are achieved will these technologies be accepted into the modern market as a viable replacement for fossil fuels. Among all the unrestricted and non-polluting renewable resources (solar, wind, and water) one of the most feasible choices is solar energy as the earth receives 1000 watts of energy per square meter per hour, most of which is untapped [5]. While the sun can provide the

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energy, we are steadily working on methods of conversion, storage, and distribution of this energy.

DSSC Working Principles

Traditional solar (or photovoltaic) devices exploit the photoexcitation of bandgap materials such as doped silicon of gallium compounds. This leads to the creation of an electron-hole pair available for conduction [6]. A p-n junction within these devices creates an electric field capable of separating the pair creating an electrical potential. A more recent trend in photovoltaic research is the investigation of so-called dye-sensitized solar cells (DSSCs), a class of photovoltaics that were first proposed around 1990 by Gratzel [7]. In these devices a dye is adsorbed onto a wide bandgap semiconducting material. The dye molecules are capable of absorbing light in the visible spectrum, leading to excitation of electrons from the highest occupied molecular orbital to the lowest unoccupied molecular orbital (i.e. HOMO-LUMO excitation) resulting in the net transfer of an electron to the semiconductor's conduction band and formation of a transport hole within the dye material. An electrolytic redox couple is also needed in these devices; in a closed circuit, the excited electron flows back to the redox couple which transports it to the dye where electron-hole recombination occurs [8]. The working principles of such a cell are illustrated below in Fig. 1.

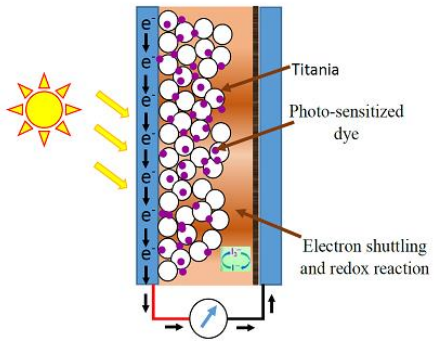

Figure 1. Working principle of a DSSC. Excitation occurs among the electrons of a dye, the excited electrons are transferred to a semiconductor and then to an outer circuit. Returning electrons are carried via a catalyst and electrolyte back to the oxidized dye.

The glass housing of these devices is coated with a conductive material such as indium or fluorine-doped tin oxide which allows incorporation into circuits for powering other electronic devices.

Components of the DSSC

In addition to the glass housing, there are four main components of a DSSC: the semiconductor material, the dye, the redox couple, and the redox catalyst. Recent developments in each of these components are analyzed in the forthcoming paragraphs.

The semiconductor material is fundamental to the function of any PV device, as the nature of this material determines the kinetics of exciton generation and separation, electron flow, controlled or uncontrolled electron recombination, and device stability and cost. For this reason, much emphasis has been placed on photoactive semiconductor research within the field of DSSCs. While the use of multilayered (heterojunction) devices which incorporate a range of materials with differing bandgaps corresponding to the incident solar spectrum into one device have produced excellent conversion efficiencies, they generally are too expensive to currently manufacture on the industrial scale . Because of this situation, TiO_2 (titania) and ZnO have become the semiconductors of choice for much of recent DSSC research. Titania is a widely-used nanomaterial with a bandgap 3.05eV [9]. One of the key features of titania, in addition to thermal and chemical stability, is its ease of morphological conversion; titania can be formed into nanospheres, nanorods, and nanotubes all of controlled diameter and/or length. The shape of the individual titania nanostructures determines the active surface area, electron path, and thus is related directly to the power conversion efficiency of the device. It was proven, for example, that the high surface area of devices fabricated with titania nanorods performed with greater efficiency than those made with standard P25 titania spheres [9]. Recent work by Giannouli [10] illustrated the potential increases in efficiency associated with using composite semiconductor materials by testing a blend of ZnO and TiO_2 active material sensitized with simple organic dyes. Devices made with a 90:10 ratio of ZnO to TiO_2 resulted in energy conversion efficiencies higher than that of ZnO alone and with higher material stability. The use of pure ZnO as the photo anode has led to significant power conversion efficiency but reduced stability [10]. For example, it has been demonstrated that the sensitizing time of the cell must be limited due to the potential formation of Zn^{2+}-dye complexes [10]. Work by N.R. Matthews, et al, revealed important morphological changes associated with the annealing

temperature of the semiconductor when using an organotitanium solution [11]. The conclusion was that particle size and density increase with annealing temperature. All such factors are capable of reducing the dye-semiconductor interface and must be considered when choosing the semiconducting material used in the device.

In order to complete the circuit in a DSSC, an electrolytic material called a redox couple is needed. This redox couple serves one specific purpose: to reduce the dye molecules which have undergone photoexcitation/oxidation In the case of electrolytes, this is accomplished by the transportation of electrons from the counter electrode to the dye molecules. Alternatively, a hole transport medium (HTM) can be used in the place of the redox couple. The traditional electrolyte of choice has been a solution of iodide and triiodide which has led to devices with efficiencies as high as 12%, but this solution is corrosive towards high performance electrode materials such as silver [12]. Many materials have been tested to replace the iodide electrolyte thereby allowing more freedom of electrode material choice with varying relative power conversion efficiencies. One of the most successful redox couples is that synthesized from 5-mercapto-1-methyltetrazole and its dimer form [13]. Power conversion efficiencies of up to 6.4% were obtained using this material. A variety of HTMs are available too, such as SPIRO-OMeTAD, PEDOT, and P3HT. The former is a wide bandgap small molecule, whereas the latter two compounds are semiconducting polymers.

The purpose of redox catalyst is to facilitate the recombination of electrons which have arrived from the external circuit with the holes left in the oxidized dye molecules [13]. This catalyst material must be highly active, have high conductivity, be physically and chemically stable in the electrolyte solution of choice, and possess a large surface area [14]. Nanoparticulate platinum offers the highest catalytic activity, but fails in other areas such as stability and cost, so carbon-based alternatives have been investigated. Mesoporous carbon black (CB) has offered the greatest potential as a catalytic material because it is inexpensive and more catalytically efficient than other forms of carbon; this is thought to be due to edge-plane irregularities which offer a greater number of active sites for electron transfer. By spin coating the counter electrodes with a variety of thicknesses and particle sizes, J.M. Kim14 showed that a 9µm thick layer of CB with 20nm diameter particle size approached the catalytic efficiency levels of platinum (power conversion efficiency of 7.2% with CB vs. 7.6% with Pt).

A variety of natural dyes can be used in DSSC fabrication. These are extracted from fruits and vegetables and grafted onto the semiconductor thus acting as a sensitizer for converting solar energy into electricity. This widens the photoactive range of the cell by enabling absorption in the visible spectrum. Taya, et al. [15], measured the relative success of twenty-three different dyes extracted from leaves. The dyes used are from cream, apricots, figs, apples, sage, ziziphus jujuba, thyme, mint, oranges, shade tree, basil, mirabelle plums, victoria plums, peaches, mangos, pomegranates, bananas, guava, raspberries, and blackberries. The most efficient dye to have been tested by the group so far is the ziziphus jujuba dye with a power conversion efficiency of 1.077% and the least efficient dye so far is the thyme dye with an energy conversion efficiency of 0.187%.

II. Materials

TiO_2 powder, ZnO powder, and TiO_2 nanoparticles in suspension were purchased for Sigma Aldrich. FTO coated glass substrates and iodide/triiodide electrolyte were purchased from Arbor Scientific. Anhydrous ethanol and glacial acetic acid were purchased from Sigma Aldrich. Soot from a tea candle was used for catalytic cathode preparation.

III. Methods

FTO glass substrates were cleaned in ethanol and deionized water and a sonicator. Anodes were fabricated on the FTO substrates by spin coating a drop of either nanoparticles in suspension as-purchased, or semiconductor powder in a prepared suspension. The spin coating rate was 3000 rpm. The suspension used was 67% ethanol, 31% water, and 1% acetic acid by volume. The spin coater used was made by MTI. Substrates and anode were annealed at 450oC for 30 minutes in air. Scaffolding was accomplished by repeating this process multiple times. The anodes were sensitized by placing a few drops of crushed berry juice on the semiconductor active area. The catalytic cathodes were fabricated by holding the FTO glass in a candle flame for a few seconds. Cathodes and anodes were either clamped

together or sealed together with a Meltonix gasket (Solaronix). Plasma etching was achieved by placing the anode and substrate in a glass flask, evacuating the flask with a vacuum pump, and placing it in a microwave oven.

Cells were evaluated using an Abet Technologies solar simulator at 1 Sun intensity and a Keithley SourceMeter to determine the IV characteristics. This setup is shown below in Fig. 2.

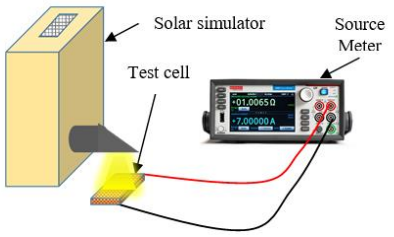

Figure 2. Apparatus for evaluating DSSC performance. Solar simulator at 1 Sun intensity, and SourceMeter for measuring IV curves.

There are multiple equations needed when dealing with DSSC. Current and voltage were measure using the SourceMeter. Power was calculated by multiplying current and voltage at each point. Power is represented by "P" and is measured in watts, voltage is represented by "V" and is measured in volts, and current is represented by "I" and measured in amperes.

$$P = V \times I \qquad 1)$$

The efficiency equation below was used to determine the percentage of solar energy that is converted into electrical energy. Efficiency, η, is the ratio of the max power in the cell to the product of lamp intensity and area of the solar cell. Max power is measured in milliwatts (mW). Lamp intensity is measured in milliwatts per square centimeter, mW cm^{-2}.

$$\eta = \frac{P_{max}}{\frac{mW}{cm^2} \times cm^2} \qquad 2)$$

Fill factor (FF) is the measure of how well the solar cell is performing due to resistances in the cell and resistances in the materials used to measure current and voltage (3). Fill factor is determine by the ratio of max power to the product of open circuit voltage and short circuit current.

$$FF = \frac{P_{max}}{V_{oc} \times I_{sc}} \qquad 3)$$

IV. RESULTS AND DISCUSSION

Multiple scaffolds (layers of semiconductor) were fabricated to determine the effect of semiconductor thickness on efficiency. As seen in Fig. 3 below, the efficiency of the DSSC decreased as the thickness of the semiconductor layer was increased.

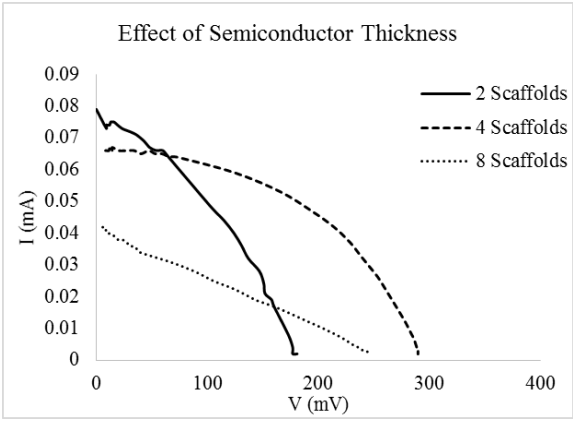

Figure 3. Effect of scaffolding on IV curves. It can be seen that as the semiconductor layer is increased, the efficiency increases initially for 4 scaffolds, and then decreases significantly for 8 scaffolds.

The effect of plasma etching on efficiency is shown below in Fig. 4. For pure semiconductor (ZnO in this case), it is shown that increasing the etching time increases efficiency until a plateau is reached at about 4 seconds. Previous work in this lab has shown that plasma etching serves to remove surface adsorbed molecules which may contribute to complex electron withdrawing mechanisms. It is feasible, based on this result, that most of the withdrawing groups are desorbed by about 4 seconds, and therefore little change occurs thereafter.

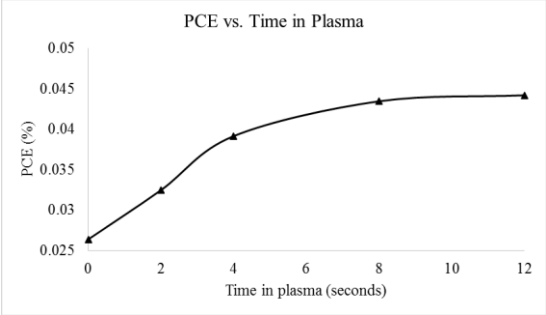

Figure 4. Plasma etching the ZnO0based DSSCs yielded a dramatic increase in PCE at first which then plateaued between 4 and 6 seconds.

The effect of different dyes can be seen below in Fig. 5. Many papers, some of which are described in the introduction, have shown that the type of dye source used has a profound influence on DSSC performance. This case is no exception, with blueberry extracts performing much better than blackberry dye. In this case, the blueberry dye yielded a PCE of 4.6% while blackberry yielded about 0.2% efficiency.

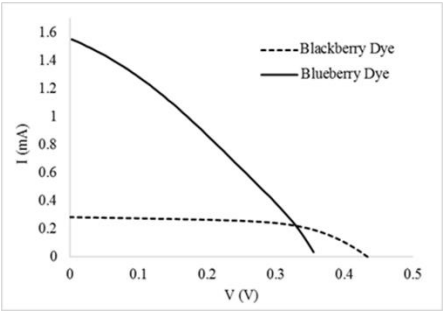

Figure 5. The use of blueberry dye as a sensitizer greatly improved PE over the use of blackberry dye.

The effect of blending semiconductors and plasma etching can be seen below in Fig. 6. Plain TiO_2 with blackberry dye as used as a control and performed as expected and indicated in the experiment above. When TiO_2 was blended with ZnO of various morphologies, however, the efficiency decreased significantly. Strangely, the efficiency was decreased in all cases when the blends were plasma etched. This indicates that plasma etching may only have a positive impact when used on ZnO semiconductors. More experimentation is needed to determine the effect of plasma etching on a pure TiO_2-based DSSC.

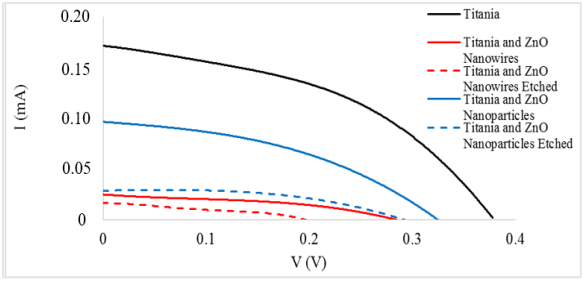

Figure 6. Using DSSCs made with blends of TiO_2 and ZnO yielded PCEs less than that of pure TiO_2. Etching the blends decreased efficiency.

The efficiencies and fill factors of all of the cells described here are tabulated below in Table 1.

Table 1. Summary of PCE values

Description	PCE %
ZnO with 0 sec plasma etch	0.02
`` 2 sec plasma etch	0.03
`` 4 sec plasma etch	0.04
`` 8 sec plasma etch	0.04
`` 12 sec plasma etch	0.04
ZnO 1 scaffold	$7.45x10^{-4}$
2 scaffold	0.02
3 scaffold	0.017
4 scaffold	0.05
Transparent TiO_2 blackberry dye	0.22
Transparent TiO_2 blueberry dye	4.61
Powder TiO_2 blackberry dye	$5.37x10^{-2}$
TiO_2 and ZnO nanowires	$5.19x10^{-3}$
TiO_2 and ZnO nanowires etched	$2.22x10^{-3}$
TiO_2 and ZnO nanoparticles	$2.41x10^{-2}$
TiO_2 and ZnO nanoparticles etched	$8.89x10^{-3}$

V. CONCLUSIONS

In this work, a large number of variations on DSSC fabrication parameters were explored. The impact of plasma etching was shown to positive in the case of pure ZnO, but detrimental in the case of composited ZnO and TiO_2 semiconductors. The impact of semiconductor thickness was also explored by scaffolding experiments; it was shown that efficiency was optimized at four scaffolds, but decreased dramatically at eight scaffolds. It was shown that TiO_2 composited with ZnO of different morphologies resulted in mixed efficiency, with ZnO nanowires outperforming ZnO nanoparticles. Finally, it was shown that blueberry dyes resulted in a much higher PCE than did blackberry-based dye.

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