



Substrate Effects in Hybrid Solar Cells

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Abstract

As the world's traditional energy sources slowly dwindle, many have turned to solar energy as a substitute. Particularly, dye sensitized solar cells (DSSCs) have become a popular topic of study. They differ from other solar devices by having an organic dye as the light collector and an inorganic semiconductor to transfer the excited electrons. Traditionally, TiO_2 has been used as the semiconductor as the highest energy efficiency has been reported in cells using it. Since efficiencies reported with TiO_2 have plateaued recently, many have looked into using other, similar metal oxides as substitutes or even additions to TiO_2 for use as semiconductors. Identical DSSCs with several different metal oxide suspensions were tested, including ZnO , ZrO_2 , and MgO as well as compound semiconductor layers, TiO_2/ZnO and $\text{TiO}_2/\text{ZrO}_2$. Unfortunately, the tested metal oxides and compound metal oxides failed to effectively rival TiO_2 as a substitute. A difference in particle size between the TiO_2 and the other metal particles, however, did keep this this experiment from being completely conclusive. Despite this, the other materials still successfully function as the inorganic components and thus show potential for incorporation into hybrid cells in the future.

Chapter 1. Introduction

Fossil fuels are an important source of energy for the world. However, these resources are defined as nonrenewable, as they are theorized to be produced by millions of years of heat and pressure within the earth's surface. Fossil fuels, including petroleum, coal, and natural gas, were estimated by the Energy Information Administration in 2007 to together amount to an 86.4% share in the primary energy consumption of the world^[1]. In addition, the burning of these

resources for fuel creates harmful by products, including most predominantly CO₂ which is theorized to be a major factor in global warming^[2]. As a result of human CO₂ emissions, the current global CO₂ level is higher than it has been in at least 800,000 years^[2]. Thus, efforts to find reliable alternative and affordable sources of energy have rapidly increased in recent years.

In particular, solar cells have been studied extensively as an alternative option for renewable energy from the sun. They are solid devices that convert light energy collected from the sun into electric current. The cells have two main functions: the capture of light photons to generate electrons and holes and the transferal of these charge carriers to generate electrical current.

Solar energy is particularly attractive for use as it is essentially inexhaustible and can be found around the world, unlike wind and hydroelectric power. The total amount of energy that reaches the Earth's surface is approximately 3,850,000 EJ every year, more energy in one hour than the entire world uses in a year. Finally, the production of solar energy does not produce any harmful waste products^[5].

Currently, the most widely used solar cells are mostly made up of silicon. Within these cells, the silicon semiconductor absorbs photons to generate electrons and holes which then cause the current. In this experiment, the type of solar cell used are dye sensitized solar cells (DSSCs). These hybrid cells are mainly comprised of an organic dye and inorganic semiconductor. They use similar principles to generate electricity but use the organic dye to absorb light (similar to chlorophyll in photosynthesis) and have multiple layers to enhance electron collection efficiency. TiO₂ is the compound that predominantly makes up the semiconducting layer of DSSCs, as the highest electron collection efficiencies (11.18%) have been reported with TiO₂^[6].

However, due to unfavorable electronic recombination researchers, have found a plateau in the efficiencies that TiO₂ based cells can reach^[6]. A further increase in conversion efficiency has been limited by energy loss due to recombination between electrons and either the oxidized dye molecules or electron-accepting species in the electrolyte during the charge transport process^[6]. Specifically, the electron being transported through the semiconductor can short circuit the cell and recombine with the iodine ion mediator (I⁻/I₃⁻) without passing through the load. Similar oxide compounds, including most predominantly ZnO, are predicted to, after further study and optimization, have the potential to be more efficient semiconductors in DSSCs^[4].

Chapter 2. Literature Background

As the electronic short circuiting of the cell via the iodine redox couple is believed to be critically important to efficient device function, much research has gone into investigating possible methods for the retardation of this effect^[6]. ZnO as a substitute has gathered much attention in recent years. In addition to having many of the same electron injection properties as TiO₂, ZnO also has a much greater degree of electron mobility than TiO₂. However, efficiencies of only at most 6.58% have been thus far achieved^[6]. Despite this, ZnO's ease of crystallization has enabled the creation of numerous types of nanostructures to aid in electron injection and transport, including nanoparticles, one-dimensional nanowires/rods/tubes/fibers, and two dimensional nanosheets/belts/plates^[6].

In addition to using ZnO and similar metal oxides, supplementary metal oxide coatings over a TiO₂ layer has also proven to be effective. Oxide coatings consisting of ZrO₂, Al₂O₃, and

SiO₂ were all successful in reducing the degree to which the unfavorable electrolyte recombination occurred^[4].

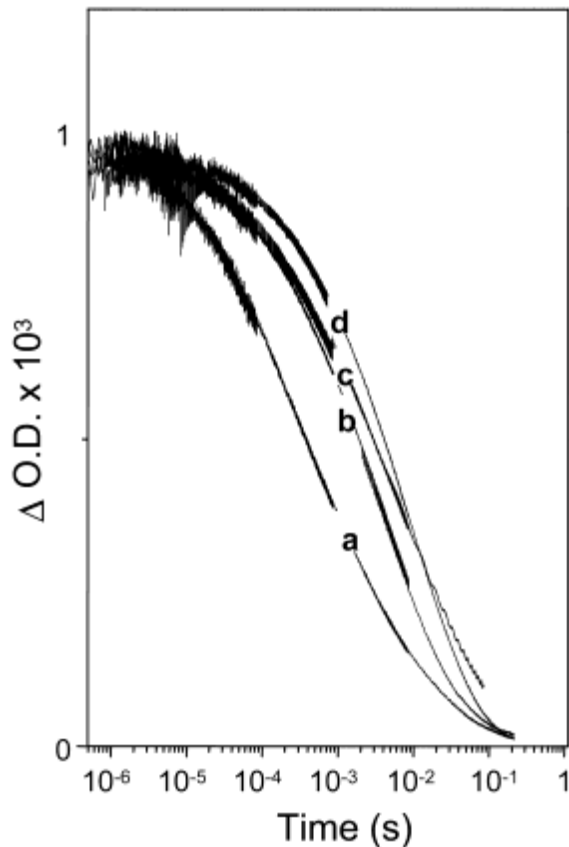


Figure 1.1: Transient absorption data of the absorption of the RuL₂(NCS)₂ cation following optical excitation of the dye adsorbed on (a) TiO₂, (b) Al₂O₃/TiO₂, (c) SiO₂/TiO₂, and (d) ZrO₂/TiO₂. The signal decay is attributed to charge recombination of the dye cation with the electrons in the band states of the semiconductor.

Figure 1.1 demonstrates a clear reduction in the degree of unfavorable recombination resulting in an overall improvement of cell efficiency^[4].

Chapter 3. Experimental Section

3.1 Preparing the Metal Oxide Suspension

A mortar and pestle was filled with 6 g of the metal oxide powder.. While grinding, 9 mL of acetic acid (pH 3.03) was added in 1-mL increments. Before each increment was added, the leftover suspension was scraped off of the sides and the pestle with a rubber spatula. This process takes approximately 30 minutes. After all the acetic acid was added, 1 mL of Triton X 100 solution as a surfactant was added. The suspension was then stored in a dram vial and sealed with Parafilm.

3.2 Preparing the TiO₂/ZrO₂ Suspension

A mortar and pestle was filled with 1.5 g of TiO₂ and ZrO₂ powder. While grinding, 5 mL of acetic acid (pH 3.03) was added in 1-mL increments. The process proceeded the same as above.

3.3 Coating the Suspension

Two SnO₂ coated glass slides were aligned side by side, one with the conductive side face-up and one with it face-down. Two pieces of Scotch tape were applied to the top faces of the glass slide along the longer edges followed by one additional piece along the conductive glass edge perpendicular to the rest. Several drops of the suspension were added to the top of the conductive side and the side of a Pasteur pipet was used to spread the suspension by sliding it

back and forth over the exposed glass. Once the layer appeared uniform, the slides were allowed to sit for several minutes before the tape was removed. Excess suspension along the edges and bottom of the slide was removed carefully with a cotton swab or Kimwipe. The conductive, coated slide was then placed on a hot plate at around 500°C for around 30 minutes. The slides were then allowed to cool to room temperature.

3.4 Extra Suspension Coating

For one trial, existing TiO₂ coated slides were reassembled in the same manner as described above only with two layers of tape instead of one. ZrO₂ was then applied in the same manner on top of the existing TiO₂ layer and then reheated at around 500°C for around 30 minutes.

3.5 Carbon Coating

The leftover suspension on the other slide was cleaned off. A pencil was then used to evenly coat the conductive side of the slide except for a small strip on one edge.

3.6 Dyeing the Semiconductor and Assembling the Cell

Raspberry juice (filtered from fresh, crushed raspberries) was poured into a Petri dish. The dish was covered and allowed to sit for several minutes to allow most of the bubbles to pop. The metal oxide coated slides were carefully placed (so as to avoid cracking and flaking of the metal oxide) face down in the juice and allowed to sit for at least 10 minutes. The slides were then carefully removed and rinsed with deionized water and then ethanol. The slides were either

patted dry with a Kim-wipe or allowed to air dry. Once dry, the carbon coated slide was placed on top and the two slides were oriented so the uncoated edges of each slide were exposed. The two slides were clipped together using binder clips on the sides perpendicular to the exposed parts. Finally, a drop of iodide electrolyte solution (0.5M KI mixed with 0.05M iodine) was placed in between the glass slides and the binder clips were repeatedly released and re-clamped so as to allow the electrolyte to spread on the inside surfaces of the slides by capillary action. The completed cell was allowed to sit for a time to stabilize and was then connected to a multimeter on the exposed edges.

Chapter 4. Results and Discussion

4.1 Single Material Semiconductors

The results for the average voltages of the single layer metal oxide suspension semiconductors are as follows:

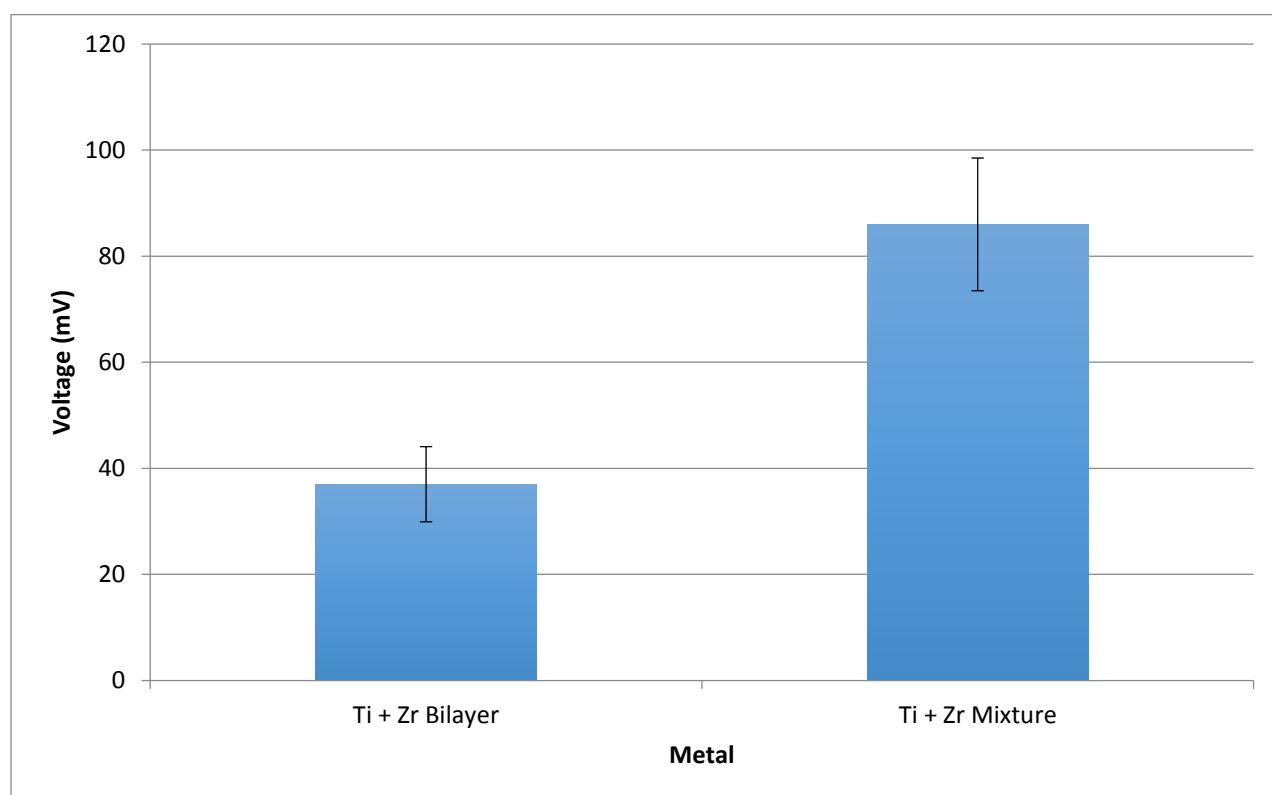


Figure 4.1: Average Voltages of Metal Oxide Suspension Semiconductors

The TiO_2 suspension coating seems to remain the most efficient coating for DSSCs. As expected, ZnO appears to be a strong alternative. While the efficiencies were clearly less, the

ZnO and even ZrO₂ suspension layers were noted to be easier to spread and significantly more likely to be stable during the annealing process. Furthermore, the ZnO layers also proved significantly less likely to flake off when dyeing with the raspberry juice.

Interestingly, the MgO suspension is just about as efficient as the ZnO. After the grinding and mixing of the MgO powder with the acetic acid, the suspension was significantly more viscous than the others. When creating the initial batch, the resulting solution solidified within a day, despite being in a sealed container with Parafilm. Because of this, it could be possible that some sort of reaction took place when combining the MgO powder with the acetic acid.

The ZrO₂ cells were far less stable than the rest. Although the ZrO₂ suspension appeared to form a very stable and uniform layer on the glass slide, it was very easily washed away by the raspberry juice dye, despite the annealing process. In addition, the electrolyte was very effective at displacing the ZrO₂ suspension particles, thus disrupting the otherwise uniform suspension layer. In addition to the unstable layer it makes, ZrO₂ has a much higher electron band edge than TiO₂ making it more difficult for its valence electrons to move to the conduction band.

4.2 Compound Material Semiconductors

The results for the average voltages of the compound metal oxide suspension semiconductors is as follows:

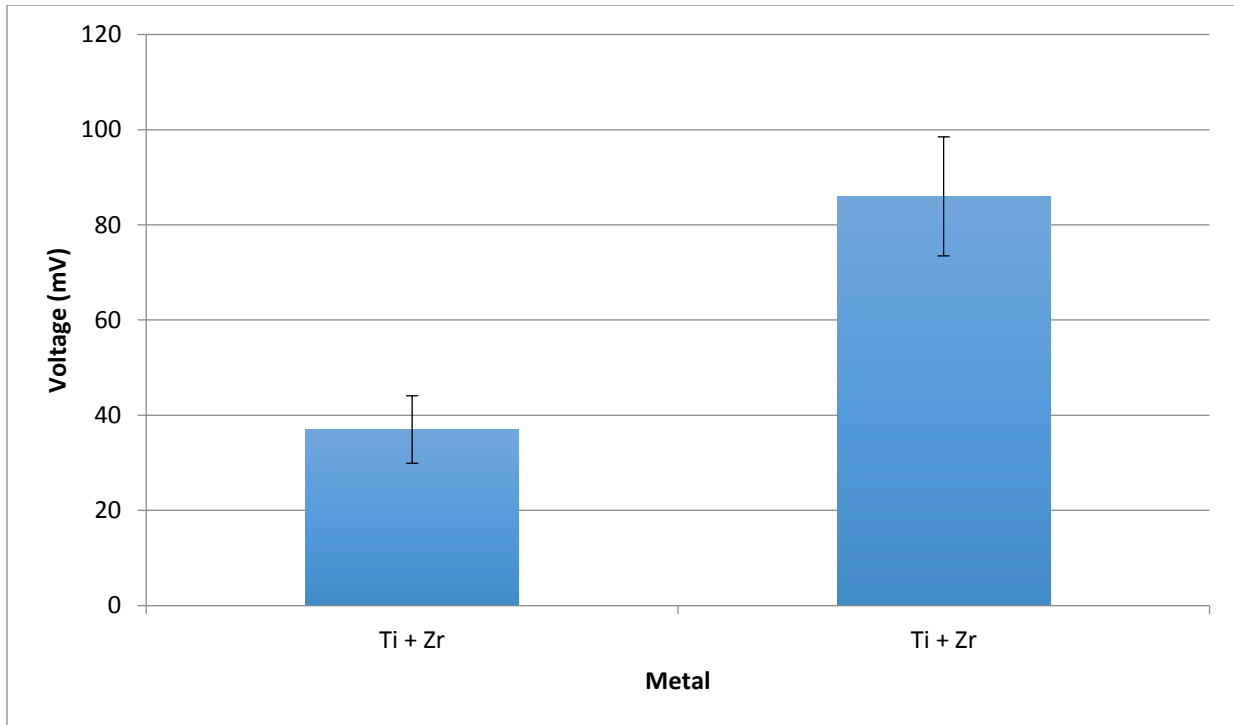


Figure 4.2: Average Voltages of Combined Metal Oxide Suspension Semiconductors

Just as before, ZrO_2 forms neither stable nor efficient semiconductors, even when paired with the efficient TiO_2 . Despite this, the ZrO_2 suspension layer was observed to be noticeably more resistant to being washed away or otherwise displaced by the dye and electrolyte solution.

It was expected that the addition of the ZrO_2 overlay would increase the separation between the injected electrons and the electrolyte redox pair, resulting in the retardation of the electron recombination that hinders efficiency. Ultimately, however, it seems that a similar

suspension of ZrO_2 does more harm than good to the efficiency due to its higher conduction band edge slowing the rate of electron injection.

Chapter 5. Conclusion

Unfortunately, the metal oxide suspensions tested did not prove to be more effective than the established standard, TiO_2 . As expected, ZnO and even surprisingly MgO , had high efficiencies that come somewhat close to rivaling TiO_2 . This suggests that they may have the potential to be viable replacements for TiO_2 . The reasons for the lesser efficiency may be rooted in the difference in particle size, as the ZnO and MgO had 44 μm sized particles in comparison to the 21 nm TiO_2 particles. Unfortunately, efforts to reduce the electron recombination rate with the electrolyte pair has been either unsuccessful or produced too strong of an efficiency tradeoff. Even if the addition of ZnO and ZrO_2 (even as overlays) did lessen electron loss to recombination, they hampered the ability of the TiO_2 to accept the injected electrons to facilitate the voltage, primarily due to their higher conduction band edge.

To rule out ZnO , ZrO_2 , and MgO as possible replacements or supplements to TiO_2 based solely on this incomplete study would be a mistake. The particle size difference in the tested compounds as well as the multitude of ways these compounds can be combined with TiO_2 allow for many additional possibilities to be investigated.

References

- [¹] National Renewable Energy Laboratory. Retrieved 5 October 201
- [²] [NRC \(2010\). *Advancing the Science of Climate Change*](#). National Research Council. The National Academies Press, Washington, DC, USA.
- [³] Zhang, Q.; Dandeneau, C. S.; Zhou, X.; Cao, G. ZnO Nanostructures for Dye-Sensitized Solar Cells. *Adv. Mater.* **2009**, 21, 4087–4108
- [⁴] Palomares, E.; Clifford, J. N.; Haque, S. A.; Lutz, T.; Durrant, J. R. Control of Charge Recombination Dynamics in Dye Sensitized Solar Cells by the Use of Conformally Deposited Metal Oxide Blocking Layers. *J. AM. CHEM. SOC.* **2003**, 125, 475-482
- [⁵] Smil (2006) p.12
- [⁶] Xu, F.; Sun, L. Solution-derived ZnO nanostructures for photoanodes of dye-sensitized solar cells. *Energy Environ. Sci.*, **2011**, 4, 818–841