

Improving Dye-Sensitized Solar Cell Efficiency by Modification of Electrode Surface Charge

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Abstract: Dye-sensitized solar cells (DSSCs) are considered a promising future source of low-cost solar power. At present, however, the most efficient DSSC designs utilize iodide-based electrolytes, which are highly corrosive and absorb strongly in some regions of the visible spectrum. We have been able to generate significant efficiency increases in DSSCs employing a novel sulfide/thiolate redox couple which was developed by Wang et al. via functionalization of their mesoporous substrates with positive charges. At the moment, unfortunately, our control cell efficiencies are approximately an order of magnitude lower than those reported by Wang et al.—something which needs to be fixed before we publish our results. Nevertheless, Wang’s paper currently holds the world record for the highest DSSC efficiency ever reported using a non-iodide-based electrolyte. Thus, if we are able to significantly improve on his efficiency, it will be a major step towards the development of a commercially viable DSSC.

Introduction

Dye-sensitized solar cells (DSSCs) are currently considered highly promising as a method for the efficient and economical conversion of solar energy to electric power. Advantages of DSSCs over conventional silicon photovoltaics include relative ease of fabrication, low production costs, and potential for sensitization over a wide range of bandgaps.^[1] However, since the research group of Prof. Michael Grätzel first reported a DSSC light-to-electricity conversion efficiency of 10% in 1993,^[2] top literature efficiencies have only been increased another 1-2% by nearly two decades of intense research.^[3] Furthermore, large-scale commercial deployment of so-called “Grätzel cells” has been hampered both by the extreme rarity of ruthenium, an essential component of the cells’ high-performance photosensitizing dye, and by the corrosiveness and the relative opacity of the iodide-based electrolyte which is employed in Grätzel cells.^[1,3]

A recent paper by Wang et al. (2010) reported the synthesis of a disulfide/thiolate (T^-/T_2) based redox couple which, when used in place of iodide/triiodide (I^-/I_3^-) in Grätzel cells, yielded a 6.4% overall efficiency. This is the highest efficiency yet reported for any DSSC not

employing an iodide-based electrolyte, and since T^-/T_2 is much less corrosive and much more transparent than I^-/I_3^- , Wang’s electrolyte has the potential to eliminate one of the major barriers to the commercial manufacture of DSSCs.^[1] We are, therefore, attempting to further raise the efficiency of T^-/T_2 -based DSSCs by taking advantage of another unique feature of Wang’s sulfur-based electrolyte—the difference in overall charge between T^- ions and T_2 molecules.

Experimental Rationale

Fundamentally, we seek to facilitate the diffusion of T^- towards the surfaces of our TiO_2 substrates by functionalizing the TiO_2 ’s surface with positive charges. In mesoporous films, a high surface-area-to-fluid-volume ratio means that effective penetration of electrolyte ions deep into the film depends to some extent on whether the ions are attracted to or repelled by the film’s surface charge. Therefore, if we functionalize the TiO_2 with positive charges, we expect more rapid and thorough circulation of electrolyte in the mesoporous film, which, in turn, should correspond to a higher current through the cell and so yield an increase in light-to-electricity conversion efficiency.

In order to firmly affix positive charges to the surfaces of our dye-sensitized mesoporous TiO₂ films (fabricated according to the procedure described in Appendix A), we coated the portion of films' surfaces not covered by dye with a monolayer of functionalized alkoxy silanes, as shown in Figures 1a and 1b below.

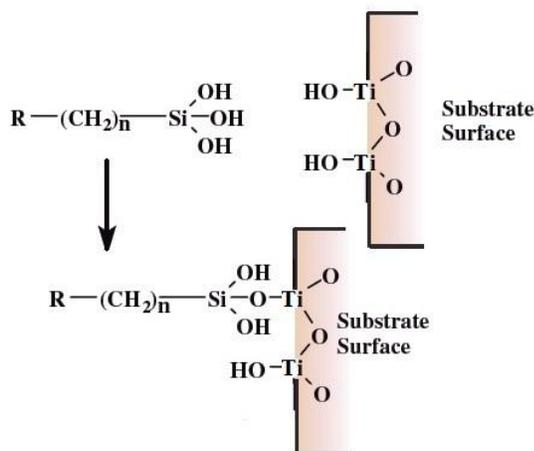


Figure 1a: Reaction of a Trialkoxysilane with a TiO₂ Substrate (Image Credit: Gelest, Inc.)

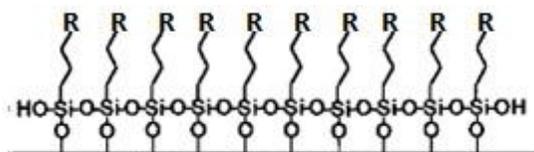


Figure 1b: An R-Functionalized Silane Monolayer (Image Credit: Liu et al. (1998))

In Fig. 1a, we see an R-functionalized alkoxy silane reacting with a dangling hydroxyl group on the surface of a TiO₂ substrate to eliminate water, forming a covalent link between the silicon atom in the alkoxy silane and the titanium atom in the TiO₂. Other alkoxy silanes react with adjacent surface hydroxyls to form similar covalent bonds with the titania, and then adjacent alkoxy silanes undergo dehydration reactions with each other to yield a strong, stable network of Si-O bonds that effectively anchors all of our R-groups to the TiO₂ surface.

An "R-group," of course, is chemical shorthand for "a functional group"; we knew we wanted to cover our TiO₂ surface with positive charges, so a primary

amine, -NH₃, was a natural choice as a functional group. However, we were concerned that the -NH₃ group might undergo some sort of reaction in our illuminated cell, so that an apparent increase in efficiency could result from the consumption of our functional groups. Furthermore, the physical presence of the alkoxy silane monolayer might increase cell efficiency by blocking exciton recombination (the leakage of excited electrons out of the TiO₂ and back into the electrolyte).

Thus, all experiments were conducted using four cells, each with a different surface configuration: (1) a control cell, which was not exposed to any alkoxy silanes; (2) a cell exposed to NH₃-functionalized propyl-triethoxysilanes (APTES); (3) a cell exposed to (N(CH₃)⁺)-functionalized propyl-trimethoxysilanes (MAPTMS), since (N(CH₃)⁺) has a positive charge just like primary amines do in solution, but cannot engage in any of the reactions which NH₃ would be prone to; and (4) a cell exposed to n-octyltrimethoxysilanes (nOcTMS), to control for the potential efficiency improvement which might be caused by a silane monolayer physically blocking recombination.

Results and Discussion

The synthesis of the (T⁺/T₂) redox couple is described by Wang et al.^[1] Details of DSSC fabrication and testing may be found in Appendix A. In brief, four DSSCs utilizing a ruthenium dye, a mesoporous TiO₂ substrate, and a (T⁺/T₂) redox couple were assembled and functionalized as described in the previous paragraph. They were then illuminated with an intensity and spectrum equivalent to that incident on a flat plate normal to the sun when it's directly overhead at sea level on a clear day (100 mW/cm², AM 1.5 spectrum). Cyclic voltammetry was then used to characterize each cell, and the maximum power point and overall cell efficiency were calculated for each cell based on the results of this characterization (see Figs. 3 & 4, Tables 1 & 2 (next page)).

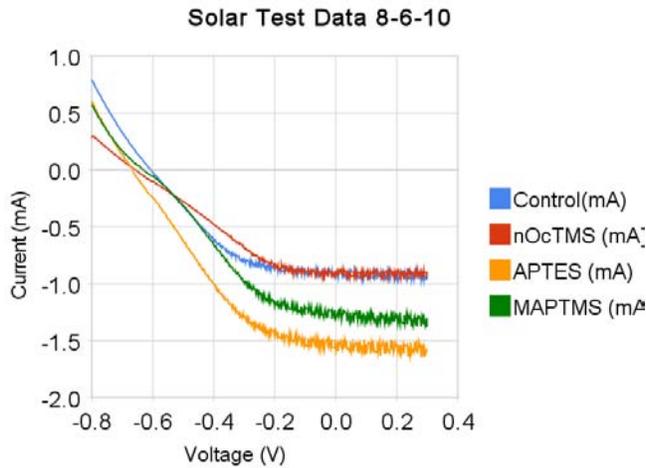


Figure 3: I-V Characteristics of Illuminated DSSCs Tested on 8-6-10

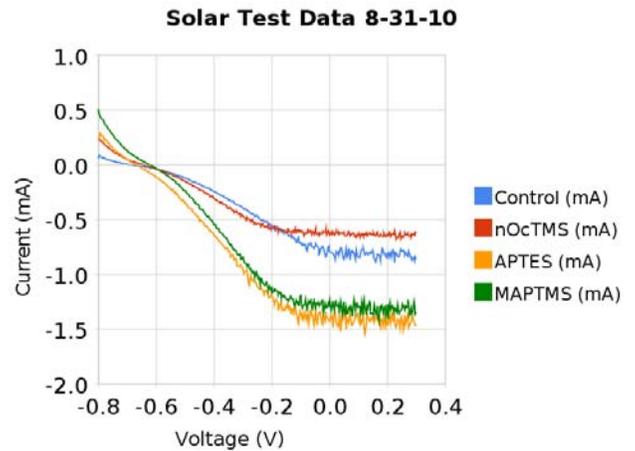


Figure 4: I-V Characteristics of Illuminated DSSCs Tested on 8-31-10

Func. Group	MPPT (mW)	Efficiency
Control	0.258	0.74%
nOcTMS	0.207	0.84%
MAPTMS	0.300	0.94%
APTES	0.415	1.38%

Table 1: Maximum Power Points and Overall Efficiencies for Functionalized DSSCs (8-6-10)

Clearly, the most striking result of our experiments is the markedly higher efficiencies observed in the cells which are functionalized with MAPTMS and APTES—the two positively charged functional groups in our test. Both Fig. 3 and Fig. 4 indicate that this efficiency increase is primarily due to an increase in the short-circuit current of the MAPTMS and APTES cells, as would be expected if our positive surface charges really were facilitating electrolyte diffusion through the cell’s mesopores. A smaller increase in efficiency is observed when cells are functionalized with nOcTMS—also expected, as physically separating the polar electrolyte and the polar TiO₂ surface with

Func. Group	MPPT (mW)	Efficiency
Control	0.121	0.38%
nOcTMS	0.143	0.51%
MAPTMS	0.270	0.84%
APTES	0.295	0.82%

Table 2: Maximum Power Points and Overall Efficiencies for Functionalized DSSCs (8-31-10)

a non-polar layer of n-octyl groups should reduce exciton recombination to some extent. This project is, as yet, far from finished. The most glaring problem, of course, is that our control cell efficiencies are approximately an order of magnitude lower than the 6.4% efficiency reported by Wang et al. This is, it seems to us, potentially both exciting and concerning. On the one hand, it means that if we are able to work out the issues which are causing our efficiencies to be so low, all of these cells might be expected to output as much as an order of magnitude more power than we observed in these tests. Were this best-case scenario to be realized, it would be difficult to overstate the importance of this finding—at the very least, we

would be setting a new world record for DSSC efficiency using a non-iodide based electrolyte.^[1]

On the other hand, such a significant discrepancy between our efficiencies and Wang's seems to imply some serious issues with our cells—and indeed, we have spent much of this past semester (Fall 2010) devising remedies for three significant problems which we identified with our DSSC fabrication after conducting these initial tests. Unfortunately, we did not have time to test out each of our remedies individually and then put them all together and re-test our functionalized DSSCs before the end of this past semester, but we plan to do this within a week or two of the resumption of classes in mid-January, and will be sure to keep the Energy Center posted as new data become available.

Additionally, we plan to run tests on functionalized cells which employ the traditional (I/I_3^-) redox couple, since the iodide and triiodide ions both have a negative charge, and so, if our functionalization really is facilitating penetration of negatively charged ions into our mesoporous film, we would expect to see the increase in cell efficiency caused by higher I^- concentrations near the TiO_2 's surface offset by increased exciton recombination due to increased I_3^- concentrations near the TiO_2 surface. Thus, functionalization with MAPTMS and APTES should result in less of an improvement in efficiency, or even no improvement at all, for cells using an (I/I_3^-) redox couple, in contrast with the significant efficiency improvement which we've observed in functionalized cells employing Wang's (T/T_2) redox couple.

Further characterization of both the physical and the electrochemical properties of our deposited layer of functional silanes is also warranted. We plan to measure the number of silanes deposited per unit of mesoporous surface area using BET analysis and TGA/DSC. This information will, in turn, be used to optimally design an electrochemical analysis of the cell using illuminated electrochemical impedance spectroscopy (EIS), from which we will be able to calculate such parameters as effective

electrolyte diffusion constants, average electron lifetimes (i.e., within the sintered TiO_2 nanoparticles), and Debye layer resistances and capacitances using the models for DSSCs' response to EIS developed by Kern et al.^[4] If, indeed, we are facilitating diffusion of negatively charged ions throughout the mesoporous TiO_2 electrode, we would expect this to be reflected in the results of our illuminated EIS, together with any other effects which aminofunctionalization is having on the electrochemistry of our DSSCs.

Conclusion

In conclusion, we have shown that functionalization of DSSCs' internal surfaces with positive charges can significantly improve their light-to-electricity conversion efficiencies when a (T/T_2) redox couple is being employed. A great deal of work remains to be done on this project before it is ready to be written up and submitted to a journal, including attaining control cell efficiencies which are closer to reported literature values, exploring the effect of positive-charge-functionalization on DSSCs which use an (I/I_3^-) redox couple, and further physical and electrochemical characterization of our functional silane monolayers and their effects on the operation of DSSCs. Nevertheless, initial testing has yielded very encouraging results, and if we are able to reproduce the increases in efficiency once our control cells have attained Wang's reported 6.4% light-to-electricity conversion, it will be a significant step towards the ultimate development of commercially viable DSSCs.

Appendix A: Experimental Procedure

Preparation of TiO_2 Spin-Coating Paste

Our procedure for preparation of the TiO_2 spin-coating paste was largely adapted from Ito et al.^[5] 1 g of titanium dioxide nanoparticles (anatase, <25 nm particle size) (Aldrich) were ground in a 2" ID agate mortar and then mixed with 1 mL glacial acetic acid, 1 mL nanopure water, and enough ethanol (2-4 mL) to form a smooth paste. The paste was ground for approximately 30 minutes in the

mortar before being transferred to a glass vial and left to be stirred vigorously with a magnetic stir bar overnight. The paste was then subjected to alternating 2 sec. intervals of ultrasonication and of rest for 2 minutes, followed by 15 more minutes of vigorous magnetic stirring. Finally, the paste was spin-coated onto FTO glass; however, initial spin-coats were typically quite thick and opaque, so 0.2 mL aliquots of EtOH were added progressively to the paste and stirred in for 15 minutes each until spun-on TiO₂ films were slightly translucent.

Preparation of dye-sensitized mesoporous TiO₂ film

Our procedure for preparation of dye-sensitized mesoporous TiO₂ films was largely adapted from Wei et al.^[6] Mesoporous TiO₂ films were prepared by spin-coating a TiO₂-ethanol paste, prepared as described above, onto FTO glass substrates. The films were then sintered at 400 °C for 3 hrs, followed by immersion in a 50 mM aqueous solution of TiCl₄ (Fluka) at 70 °C for 30 minutes. The TiCl₄ solution was then cooled to 20 °C, and the films were washed thoroughly with distilled water before being sintered again at 400 °C for 30 minutes. Finally, the films were immersed in 0.1 M aqueous HCl at 80 °C for 30 minutes, cooled to 20 °C, washed thoroughly with distilled water, and then dried at 130 °C on a hotplate.

A 0.3 mM solution of the ruthenium dye Z-907 ((*cis*-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II), Aldrich) was prepared under nitrogen, using an anhydrous 1:1 mixture of acetonitrile and 2-methyl-1-propanol (Sigma-Aldrich) as the solvent. The TiO₂ films were removed from the hotplate, allowed to cool to ~80 °C, then plunged into the dye solution and allowed to soak overnight under nitrogen.

Functionalization of dye-sensitized films

Our procedure for functionalization of dye-sensitized mesoporous TiO₂ films was largely adapted from Rohlfiing et al.^[7] Films were

immersed in a 40mM solution of either n-trimethoxysilylpropyl-n,n,n-tri-methylammonium chloride (50% in methanol) (MAPTMS), 3-aminopropyltriethoxysilane (APTES) or n-octyltriethoxysilane (nOcTMS) in anhydrous toluene (Sigma-Aldrich) under nitrogen for 3 hours. The cells were then removed from the solution and washed with anhydrous toluene and with ethanol, and were then cured at 75 °C for 30 minutes.

Assembly of DSSCs

An FTO-sputtered-glass counterelectrode was thermally platinized by drying a few drops of a 5 mM solution of hexachloroplatinic acid (Sigma-Aldrich) onto an FTO glass slide and then heating the slide to 400 °C for 30 minutes. A 2 mm diameter hole was drilled through the platinized end of the counterelectrode, and a piece of stretched-out Parafilm was placed over the hole and the surrounding platinized glass to act as a spacer between the dye-sensitized electrode and the counterelectrode. A rectangular hole approximately 7x5 mm was cut in the Parafilm with a razor blade such that the circular hole drilled through the counterelectrode was exposed. Correspondingly, dye-sensitized film was scraped off of its FTO electrode so that only a 6x4 mm rectangle of film was left. The two electrodes were then pressed together so that the rectangle of dye-sensitized TiO₂ fit into the hole in the counterelectrode's Parafilm, and the cell was then heated up to 65 °C to melt the film and seal its edges.

A solution of 0.4 M 5-mercapto-1-methyltetrazole N-tetramethylammonium salt (NMe₄⁺T⁻), 0.4 M di-5-(1-methyltetrazole) disulfide (T₂), 0.5 M 4-*tert*-butylpyridine (Aldrich) and 0.05 M LiClO₄ (Aldrich) in acetonitrile (Sigma-Aldrich) was employed as a electrolyte in our DSSC. Synthesis of the electrolyte components was described by Wei et al.^[1] The electrolyte was purged with nitrogen for 10 minutes in a glove bag, and then a few drops of electrolyte were placed over the hole drilled through the DSSC counterelectrode. The DSSC was then placed under vacuum, pulling all of

the air of its interior, so when the vacuum was released, the electrolyte was pulled into the DSSC. The hole was then sealed with Parafilm.

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