Large Increases in Photocurrents and Solar Conversion Efficiencies by UV Illumination of Dye Sensitized Solar Cells

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Ultraviolet (UV) treatment of dye sensitized solar cells (DSSCs) containing tetra-*n*-butylammonium iodide electrolyte increases photocurrents dramatically. The effect remains after cessation of UV illumination. Depending upon the photosensitizing dye, the increase in photocurrent can be as much as 2 orders of magnitude. The photocurrent increase more than compensates for slight decreases in photovoltage and fill factor, resulting in overall solar conversion efficiency increases up to $45 \times$ for some dyes. The primary effect of the UV treatment appears to be a positive shift in the conduction band of the nanocrystalline titanium dioxide, which promotes electron injection from the dye. The dyes and the solar cells are both found to be stable to this treatment. This effect offers the ability to tune the properties of the semiconductor to match the requirements of a specific dye, thus providing a versatile analytical tool for characterizing DSSCs while also enabling the use of new classes of sensitizing dyes. This letter describes the UV effect and summarizes the results of its application to a number of perylene-based sensitizers and two ruthenium bipyridyl sensitizers.

Introduction

A recent analysis found both the solar conversion efficiency and production cost of the dye sensitized solar cell (DSSC) to be competitive with amorphous silicon.¹ In theory, there are many possibilities for dye sensitized configurations, that is, dyes, semiconductors, and electrolytes could be mixed and matched according to individual properties such as energetics, chemical structure or functionality, and kinetic behavior. In reality, only a very specific combination (titanium dioxide (TiO2) semiconductor, a ruthenium based photosensitizing dye (N3), and the I^-/I_3^- electrolyte) gives an efficiency that is competitive with traditional photovoltaics.^{2,3} The excellent performance of this system relies on a well-tuned interplay between components. The ruthenium based dyes are excellent energetic matches to the TiO₂ conduction band and bind to the semiconductor surface with strong orbital overlap, resulting in a nearly quantitative charge injection yield.⁴ Similarly, iodide (I⁻) has favorable energetics and kinetics for regeneration of the ruthenium dye, whereas triiodide (I_3^-) displays uniquely slow kinetics for recombination with conduction band electrons at the TiO₂ interface but fast kinetics for reduction at the platinum counter electrode.5,6 Thus, each component has a very specialized fit within the system.

Unfortunately, there are currently many more dyes than there are semiconductors to pair them with in a dye sensitized configuration. Nanocrystalline TiO₂ remains the most commonly employed semiconductor because its conduction band energetics are in a region accessible to many types of dyes, and it has useful surface chemistry and excellent materials properties. However, many of the dyes heretofore investigated on TiO₂ show much lower efficiencies than N3.^{4,7–9} The poorer performance of other dyes can often be related to insufficient energetic matching of their excited states with the TiO₂ conduction band.^{8,9} Thus, a strategy by which the semiconductor properties could be adjusted in order to improve the semiconductor's match to the sensitizing dye would be beneficial.

We present here a method by which the solar conversion efficiency of DSSC devices can be markedly improved by exposure to ultraviolet (UV) light. The effect is most dramatic for cells containing photosensitizers with very poor initial quantum yields. For the perylene sensitizers included here, the short circuit photocurrent improvements range from 3- to more than 100-fold. Accompanied by some loss in photovoltage and fill factor, the improvements in overall conversion efficiencies range from 2-fold to 45-fold. The UV exposure appears to shift the conduction band edge positively, which increases the yield of photoinjection. Although there are previous reports of band edge shift brought about by UV illumination,^{10,11} this is the first demonstration that it can markedly improve device performance. However, the band edge shift cannot explain all of our observations, which suggest that other effects, such as the formation of a surface dipole which opposes recombination and promotes injection, also contribute to the improved device performance.

Experimental Section

The nanocrystalline titanium dioxide films were prepared as previously reported from TiO₂ colloids made with acetic acid.¹² Film thicknesses were measured on an Alpha Step Profiler (Tencor) and were in the range $6-7 \mu m$. Sandwich-like solar cells were assembled from a dyed TiO₂ film and a platinized conducting SnO₂ counter electrode as previously described.² A 3-methoxyproprionitrile solution containing 0.5 M tetra-nbutylammonium iodide (TBAI), 0.05 M iodine (I2), and 0.2 M 4-tert-butylpyridine was used as electrolyte. For UV treatments, assembled cells were illuminated with the entire spectrum of a Xenon arc lamp (PTI, model A 1010) which was passed through a water filter. The intensity was approximately 190 mW/cm², and current-time traces were recorded using a program written in LabView. Current-voltage (J-V) measurements were made at white light intensity approximating AM 1.5 (100 mW/cm²) solar emission for the wavelength region between 400 and 800 nm, obtained by filtering and adjusting the same Xenon arc

Photosensitizing Dye	Photocurrent, mA/cm ²		Photovoltage, V		Conversion Efficiency, %	
	before	after	before	after	before	after
	1.0	4	54	41	.26	.59
	3.1	8.9	63	54	.92	1.92
РЗ но,с ^N	.16	9.7	54	40	.052	1.2
Р4 Состарииска Сскарииска	.043	4.5	47	32	.01	.45
	2.7	9.8	50	41	.68	1.3
[Ru(bpy) ₂ (4,4'-dcb-bpy)]	1.4	6.1	63	57	.45	1.4
"N3" [Ru(4,4'-dcb-bpy)2(NCS)2]	17	21	61	59	3.9	4.4

 TABLE 1: Values of Cell Parameters Measured before and after UV Treatment^a

^{*a*} The results are averages of two dye-sensitized TiO₂ cells prepared from each sensitizer. Same conditions as for Figure 1.

source used for UV illumination. The data were collected and solar conversion efficiencies were calculated using a program written in LabView. The dye [Ru(4,4'-dicarboxy-2,2'-bipyridine)₂-(NCS)2] ("N3") was purchased from Solaronix and was adsorbed to the TiO₂ films out of ethanol. The dye [Ru(2,2'-bipyridine)₂-(4,4'-dicarboxy-2,2'-bipyridine)][PF₆]₂ was prepared analogously to previously reported RuL₂L complexes¹³ and was adsorbed out of acetonitrile. Perylene-3,4-dicarboxylic acid anhydride-N-(dodecyl)-9,10-carboximide (P4 in Table 1) was prepared by the reaction of monopotassium 3,4:9,10-perylene tetracarboxylate with dodecylamine.¹⁴ It was adsorbed to TiO₂ out of 1-methyl-2-pyrrolidinone. The dye 9-dioctylamino-perylene-3,4dicarboxylic acid anhydride (P2 in Table 1) was prepared by first reacting 9-bromo-N-(2,5-di-tert-butylphenyl)perylene-3,4dicarboximide15 with dioctylamine to yield 9-dioctylamino-N-(2,5-di-tert-butylphenyl)perylene-3,4-dicarboximide; the tertbutylphenyl group was then removed by treatment in base to yield the product.¹⁵ The dye 9-dioctylamino-N-(acetic acid)perylene-3,4-dicarboximide (P3 in Table 1) was prepared by the reaction of 9-dioctylamino-perylene-3,4-dicarboxylic acid anhydride with glycine. The dye 9-(dimethylamino)-perylene-3,4-dicarboxylic acid anhydride (P1 in Table 1) was obtained by hydrolyzing the tert-butylphenyl group from 9-(dimethylamino)-N-(2,5-di-tert-butylphenyl)perylene-3,4-dicarboximide,¹⁵ which had been obtained as a byproduct in the reaction of 9-bromo-N-(2,5-di-tert-butylphenyl)perylene-3,4-dicarboximide with diethyl iminodiacetate. Finally, 9-aminomethyl carboxylic acid-N-(2,5-di-tert-butylphenyl)perylene-3,4-dicarboximide (P5 in Table 1) was prepared by the reaction of 9-amino-N-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide¹⁵ with bromoacetic acid. The preceding four perylene derivatives were adsorbed to TiO₂ out of chloroform. All of the perylene dyes are novel sensitizers, and full synthetic details and sensitization behavior will be provided in a future publication.



Figure 1. Current versus time of UV illumination for nanocrystalline TiO₂ cells at short circuit in the presence of 0.5 M TBAI, 0.05 M I₂, and 0.2 M 4-*tert*-butylpyridine in 3-methoxyproprionitrile with a platinized SnO₂ counter electrode. Bare TiO₂ is shown in the lower curve and TiO₂ sensitized by [Ru(2,2'-bipyridine)(4,4'-dicarboxy-2,2'-bipyridine)] is shown in the upper curve.



Figure 2. Current density–voltage measurement under visible illumination for a TiO₂ cell sensitized by 9-dioctylamino-*N*-(acetic acid)-perylene-3,4-dicarboximide (P3), before (lower curve) and after (upper curve) UV treatment. Same conditions as for Figure 1. η is the solar conversion efficiency.

Results and Discussion

When a dye sensitized nanocrystalline TiO₂ solar cell containing TBAI and I₂ electrolyte is illuminated at short circuit with white light between 350 and 800 nm, the photocurrent increases steadily over a period of approximately 20 min (Figure 1). Figure 1 also indicates the effect for an unsensitized TiO₂ cell (lower trace). If the UV portion ($\lambda < 400$ nm) of the light is blocked during this illumination, the photocurrent is constant and stable. When current-voltage measurements (under visible illumination only) are made after UV treatment, there are significant improvements in short circuit photocurrent (Jsc), slight decreases in open circuit photovoltage (Voc), and decreases in the fill factor, as compared to initial values of these parameters. Figure 2 shows representative before and after current-voltage measurements for a film sensitized with 9-dioctylamino-N-(acetic acid)perylene-3,4-dicarboximide (P3 in Table 1). The solar conversion efficiency of the device increases by $25 \times$ with UV treatment. The accompanying incident photon-to-current efficiency (IPCE) curves are shown in Figure 3 for the same sensitizer. The change in quantum yield is remarkable: initially the IPCE is less than 1% and after



Figure 3. Incident photon-to-current efficiency versus wavelength, at short circuit, for the same device measured in Figure 2.

treatment it increases to more than 25%. Table 1 summarizes before and after J_{sc} , V_{oc} , and solar conversion efficiencies (η) for a variety of sensitizing dyes. In each case, the improvement in photocurrent significantly outweighs the decreases in other parameters, resulting in overall solar conversion efficiency improvements ranging from 13% (for N3) to 4400% (for P4). The trend among the dyes is that the lower the photocurrent and IPCE are to begin with, the greater the improvement under UV illumination. All of the dyes listed in Table 1 were stable to UV treatments in the cells. Many batches of TiO₂ films were investigated, and the effect was present in all samples.

When a UV treated cell remains assembled, but all illumination is discontinued, the cell can maintain most of the improved performance for hours (provided that it does not dry out). If a cell is disassembled, rinsed, and reassembled, most of its improved performance is lost; however, the increased efficiency can be fully regenerated by another UV treatment. The UV effect depends on electrolyte conditions. If the 4-tert-butylpyridine additive is eliminated, the J_{sc} increase is greater but the V_{oc} loss is also greater, resulting in a smaller increase in overall efficiency. Cells containing KI exhibit changes in photocurrent similar to TBAI-containing cells during UV illumination, whereas cells containing LiI exhibit only slight increases (5-10%) in current. As a measure of possible band edge motion during the evolution of the UV effect, J-V curves were recorded (with 400-800 nm illumination) under conditions where J_{sc} was kept constant by adjusting the incident light intensity. Voc decreased monotonically with UV illumination time, indicating a positive shift in the conduction band edge.¹⁶

The presence of the effect on bare TiO₂ and the stability of the dyes indicate that the UV light is acting upon the TiO₂ and not the adsorbed dye. Titanium dioxide's activity under band gap (UV) excitation, where electrons and highly oxidizing holes are generated, is an active area of photoelectrochemistry and photocatalysis.¹⁷ The presence of holes must be essential to the effect we observe, since it is the only difference between UV illumination and normal operation (visible illumination) of a DSSC, where only electrons are present in the TiO₂. Others have reported UV-induced changes in dye sensitized solar cells and presented hole-driven mechanisms to explain them.^{11,18} O'Regan and Schwartz found an efficiency enhancement after UV illumination of a solid-state DSSC which employed CuSCN as hole conductor. They reasoned that the TiO₂ valence band holes oxidized (SCN)⁻, leaving behind a polymeric thiocyanate species with better kinetics than CuSCN for regeneration of the oxidized dye.18 Both Hagfeldt et al. and Zaban et al. observed

that under UV illumination the flatband potential of a nanoporous TiO_2 film shifted positively.^{10,11} Hagfeldt and co-workers attributed the effect to an unpinning of the conduction band brought about by the accumulation of holes trapped in surface states. Furthermore, they confirmed a positive band shift by demonstrating that the photocurrent response for a dye with a very positive excited-state potential could be increased by background UV illumination of the cell.¹¹

Light harvesting by the dye, excited-state electron injection, electron transport through the film, dye regeneration by I⁻, and recombination of injected electrons all contribute to the photocurrent in a DSSC; increases in Jsc must be related to changes in one or more of these processes. The dye spectra are stable and thus there are no changes in the light absorption capabilities of the dyes. If the photocurrent were initially limited by a collection or transport problem in the TiO₂, this would have been a common problem among all of the devices; yet some devices work quite well to start. Finally, none of the dyes should be energetically limited by regeneration from I⁻, and if they were, the initial trends among them would be different. If there were an inherent kinetic barrier to regeneration of the perylenes by I⁻, it too would be a common limitation. Thus, there is no evidence to suggest that the regeneration process is altered by the UV treatment. The recombination process with I3⁻ is already so slow that it is not current limiting in DSSCs,⁵ so any UVinduced change in this rate could not increase the current. The most likely explanation for our results is that excited-state electron injection is improved, although a decrease in recombination rate between the injected electron and the oxidized dye may also play a role. A positive shift in the conduction band of TiO₂ is expected to increase the injection rate of all dyes, because of an increased driving force for injection and a higher density of conduction band states accessible to the dye excited state. The effect should be most pronounced for dyes that originally have little or no driving force for injection.⁷ This explanation is supported by the trend that dyes with more positive excited states (P3 and P4) show the greatest relative increases in J_{sc}.

The positive conduction band shift is most likely due to a buildup of positive charge in the TiO₂ particles. It could arise from surface adsorption of positively charged specieselectrolyte components that have been oxidized by valence band holes, for example. If any species does adsorb to the surface, it is not strongly bound, as even cursory rinsing after the UV treatment returns the cell to its initial level of performance. The possibility that adsorbed oxygen or water is mediating such a surface reaction was discounted, since the UV effect also occurs when oxygen and water are excluded from the cells by using rigorously dried materials and making all measurements in a glovebox. Alternatively, the particles may accumulate positive charge from holes trapped in surface states, a mechanism suggested by Hagfeldt and co-workers.¹¹ A substantial amount of charge can be stored in surface states of these films because the nanocrystalline particles are dominated by their surface properties. Clearly, the mechanism warrants further study.

It is important to note the almost complete absence of the effect when Li^+ is present. Lithium ions are known to both adsorb to the surface and intercalate into TiO_2 films, whereas a large and bulky cation like TBA⁺ is not intercalated, nor can it closely approach the dye-covered surface.^{19–21} Thus, Li⁺ ions fix the band edges to more positive potentials than TBA⁺;¹⁰ this is manifest in the higher short circuit photocurrents and lower open circuit photovoltages typically observed for Li⁺-versus TBA⁺-containing cells. Here, the UV treatment effects

Letters

this positive shift to a controllable extent, allowing it to be optimized for each dye, and in many cases cells retain a higher photovoltage than for a Li⁺-containing cell. Thus, cells prepared with LiI using the sensitizers presented here always start out with higher efficiencies than the TBAI-containing cells but, after the UV treatment, the TBAI cells often have higher overall efficiencies. The fact that some cells have both higher V_{oc} and higher J_{sc} after UV illumination than cells with the same dye in LiI solution suggests that the positive band edge shift is not the only factor leading to the increased efficiency. Other possible factors include a decrease in recombination rate between injected electrons and the oxidized dye, and the formation of a dipole at the TiO₂ solution interface that enhances injection and slows recombination.

Conclusion

We have demonstrated that by illuminating a DSSC with UV light, large increases in photocurrent and solar cell efficiencies can occur. The primary mechanism appears to be a positive movement of the conduction band, which promotes electron injection. Thus, the UV treatment can be used to "adjust" the band edges for a photosensitizing dye with a poor injection yield. Further investigations are under way to understand this very interesting phenomenon.

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