



Tailoring the Interface to Improve Voc in Dye-Sensitized Solar Cells

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Tailoring the Interface to Improve V_{oc} in Dye-Sensitized Solar Cells

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ABSTRACT

Adding certain adsorbents in conjunction with the sensitizing dye employed in high-efficiency TiO_2 nanoparticle solar cells has been shown to increase the photovoltage. It is has been speculated that the increased photovoltage is due to these hydrophobic adsorbents passivating surface states that mitigate the recombination of photojected electrons with redox species in the electrolyte. In collaboration with the DOE Office of Science Program, we are conducting transient-photovoltage measurements to determine the mechanism for the improved photovoltage.

1. Objectives

Dye-sensitized solar cells (DSSC) are an attractive low-cost alterative to traditional solid-state solar photovoltaic devices. Efficiencies above 11% have been reported for these cells. Unlike solid-state photovoltaic devices, dye-sensitized photoelectrochemical cells are based on interpenetrating networks. These cells feature a dye molecule chemisorbed on a porous, nanocrystalline TiO_2 film. The pores of the film are filled with a liquid electrolyte. Photo-excited dye molecules inject electrons into the conduction band of TiO_2 , and redox species in the electrolyte reduce the oxidized dye molecules back to their original state.

Recombination with oxidized species in the redox electrolyte is one factor that limits the efficiency of these cells. A recent strategy employed for mitigating this type of recombination involves adding certain components to the electrolyte that are believed to adsorb to and passivate the surface of the TiO_2 [1,2]. However, to date, molecular species added to the electrolyte have been shown to increase the recombination rate instead of passivating the TiO_2 surface [3].

This work examines the basic physical processes by which an adsorbent affects the open circuit photovoltage (V_{oc}). Knowledge of this mechanism should allow optimization of the photovoltage and further the commercial potential of DSSCs.

2. Technical Approach

2.1 Sample preparation. Colloidal TiO_2 nanoparticles were prepared as described elsewhere [1]. The TiO_2 paste was spread on top of a conducting glass plate (F:SnO₂ glass) and sintered to 450 °C for 45 min. Typical film thickness and porosity was 10 μm and 60%, respectively. The films were sensitized for 20 h in a 5 × 10⁻⁴ M N3 1.3 H⁺/Ru dye solution in 'BuOH/MeCN (1:1, v/v). In several cases, a combined dye/adsorbent solution was used, which consisted

of the above dye solution with added adsorbent (5 × 10⁻⁴ M). Conducting glass covered with a Pt catalyst was used as the counter electrode. After sealing the cell, the electrolyte was introduced through predrilled holes in the counter electrode that were then quickly sealed. The electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium iodide, 0.03 M I₂, 0.5 M *tert*-butylpyridine, and 0.1 M guanidinium isothiocyanate in MeCN/'BuCN (85:15). For transient-photovoltage measurements, TPB and guanidinium isothiocyanate were excluded from the electrolyte.

2.2 Possible mechanisms. The interaction of molecular species with the surface of TiO_2 can affect the solar cell performance in two principal ways. First, they can alter the recombination kinetics of photoinduced electrons with the redox couple by passivating the TiO_2 . Second, they can charge the surface (either positively or negatively), which will lead to movement of the TiO_2 bands with respect to the electrochemical potential of the redox couple. Both effects will result in changing the V_{oc} of the cell, as has been shown for pyridine and ammonia [3].

2.3 Transient-photovoltage measurements. Recombination times were measured with the transient-photovoltage technique [4]. The sample was illuminated with steady-state bias light at 680 nm at open circuit. A short (duration ~3 ns) laser pulse at 540 nm created a small increase in the density of photocarriers. The characteristic time of the exponential decay of the photovoltage to the steady-state value after the end of the laser pulse is equal to the recombination lifetime of photocarriers at that bias-light intensity [4]. At a certain bias-light intensity, the photoinduced charge at open circuit is estimated as the product of the recombination time and the short-circuit current density.

3. Results and Accomplishments

We have examined a cholic acid-based adsorbent to determine the fundamental effect of adsorbents in dye-sensitized solar cells. Various absorption studies revealed that the adsorbent competes with the dye for binding sites on the TiO_2 . Sensitization in the presence of the adsorbent significantly decreased the dye loading while only slightly reducing the photocurrent. The major effect of the adsorbent was to increase the photovoltage in a non-optimized cell by nearly 50 mV (Table 1). As was noted above (Sec. 2.2), this increase in V_{oc} may result from either shielding or band-edge movement [3].

The photoinduced electron density in the TiO_2 film was determined from the transient-photovoltage measurements described above. These data were used to calculate the open-circuit voltage and recombination rates in cells both with and without the adsorbent. As can be seen from Fig. 1,

the adsorbent increased the photovoltage by ca. 50 mV owing to a band-edge shift. Working against this enhancement is the fact that the adsorbent also increases recombination (Fig. 2), showing that this adsorbent does not passivate the surface of TiO₂. However, the band-edge shift is more significant than the increase in recombination rate, and an overall improvement in V_{oc} may be attributed to the adsorbent.

TiO ₂ Treatment	J _{SC} (mA/cm ²)	V _{oc} (V)	FF	(%)
Dye Only	12.6	0.761	0.760	7.65
Dye and Adsorbent	11.5	0.803	0.773	7.42

Table 1. JV characteristics of non-optimized DSSC's with and without adsorbent.

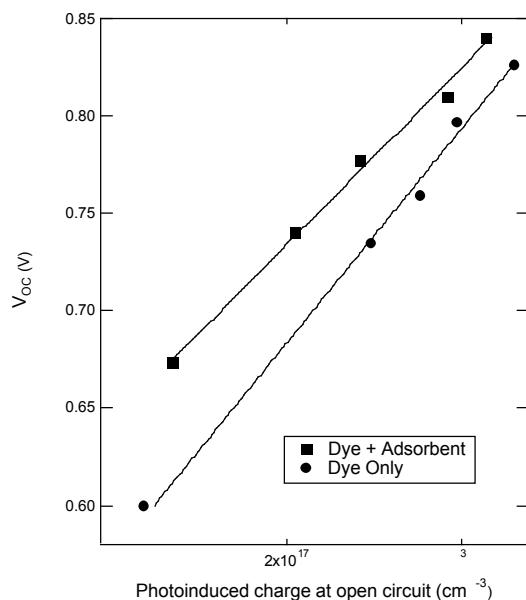


Fig. 1. Photovoltage increases with adsorbent.

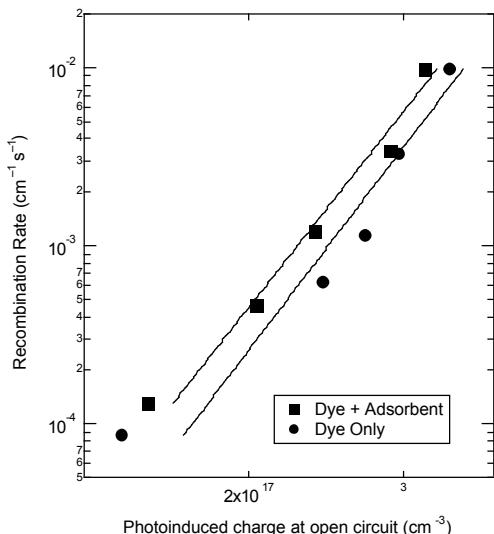


Fig. 2. Recombination rate increases with adsorbent.

4. Conclusions

A cholic acid-based adsorbent was shown to increase the photovoltage in dye-sensitized solar cells. The physical processes affected by this adsorbent were examined by transient photovoltage measurements. They suggest that a band-edge shift, not passivation, accounts for the increase in photovoltage by adsorbents.

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