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ABSTRACT

The objective of this research is to determine the operational characteristics key to efficient, low-cost, stable solar cells based on dye-sensitized mesoporous films (in collaboration with DOE's Office of Science Program). Toward this end, we have investigated the mechanism by which the adsorbent chenodeoxycholate, cografed with a sensitizer onto TiO₂ nanocrystals, improves the open-circuit photovoltage (V_{OC}) and short-circuit photocurrent density (J_{SC}).¹ We find that adding chenodeoxycholate not only shifts the TiO₂ conduction-band edge to negative potentials but also accelerates the rate of recombination. The net effect of these opposing phenomena is to produce a higher photovoltage. It is also found that chenodeoxycholate reduces the dye loading significantly but has only a modest effect on J_{SC} . Implications of these results to developing more efficient cells are discussed.

1. Objectives

The dye-sensitized solar cell (DSC) is a promising future generation concept for achieving efficient solar-to-electric energy conversion with very inexpensive materials and manufacturing processes. These cells feature dye molecules chemisorbed on the surface of TiO₂ nanocrystals that have been sintered into a highly porous thin film. The pores of the film are filled with a hole-conducting electrolyte. Photoexcited dye molecules inject electrons into the conduction band of TiO₂, and species in the electrolyte transport the holes from the oxidized dye molecules to the counter electrode. While J_{SC} is mostly controlled by the light-harvesting and charge-injection efficiencies of the dye, V_{OC} is determined by the difference between the quasi-Fermi level of electrons in the TiO₂ film and the energy of the redox couple in the electrolyte.

Over the past decade, numerous studies have reported that chemically treating the TiO₂ surface with certain organic molecules influences the photovoltage and/or the photocurrent. Passivation or shielding of recombination centers by adsorbed molecules is generally given as the explanation for the observed effect. However, there is evidence that adsorbed molecules can improve the cell performance by inducing band-edge movement.² In most studies, the proposed mechanism for the improved cell performance is based on measurements that do not distinguish between shielding and band-edge

movement. To devise more effective surface treatment strategies, it is critical to understand the mechanism by which the surface treatment affects cell performance. In this paper, we examine the basic physical processes by which the adsorbent, chenodeoxycholate, affects V_{OC} and J_{SC} in dye-sensitized solar cells.¹ Chenodeoxycholate is a cholesterol-based molecule that has been shown to improve J_{SC} and V_{OC} .

Understanding the fundamental phenomena governing cell performance is critical for underpinning the development of this new solar cell technology. Of programmatic importance is that sensitized nanoparticle solar cells represent the distinct technological promise for achieving mass-produced, ultra-low-cost solar panels with good efficiency.

2. Technical Approach

J - V measurements combined with optical absorption studies of dye desorption were used to evaluate the influence of tetrabutylammonium chenodeoxycholate on dye coverage, binding strength of dye, extent of dye aggregation, and J_{SC} under a variety of conditions in which the TiO₂ films were exposed to the coadsorbent and sensitizing dye TBA₂[RuL₂(NCS)₂] (L = 4-carboxylic acid-4'-carboxylate-2,2'-bipyridine; TBA = tetrabutylammonium). These measurements and associated calculations were performed to quantify the relationship of dye coverage to the light-harvesting efficiency of the cells. Measurements of V_{OC} as a function of the photocharge density (determined by infrared transmittance) were conducted to determine whether the changes in J_{SC} and V_{OC} (resulting from surface treatment) were caused by altering the band edge position and/or the rate of recombination.

3. Results and Accomplishments

The influence of chenodeoxycholate on dye loading was investigated under a variety of conditions in which the TiO₂ film was exposed to the sensitizing dye and coadsorbent. J - V measurements and desorption studies revealed that adding chenodeoxycholate reduces the dye loading by as much as 60% while having a relatively small effect on J_{SC} . While twice exposing a TiO₂ film to dye solution had no effect on the amount of dye coverage relative to a single exposure, the resulting dye layer was more resistant to displacement by chenodeoxycholate. These observations suggest that single dyeing of a TiO₂ film

leads to strongly and weakly adsorbed forms of the dye resulting from either different binding conformations or aggregates. A comparison of adsorption conditions revealed that although chenodeoxycholate reduced the dye coverage by about 60%, J_{SC} decreased by only 14%, from 13.2 to 11.4 mA cm⁻². Calculations using the Beer-Lambert Law along with measurements suggest that even at low loading enough dye is present to account for the otherwise surprisingly small drop in J_{SC} .

Figure 1 shows that at the same photoinduced charge density (1.5×10^{17} cm⁻³) the photovoltage of the cell with the dye and chenodeoxycholate-covered film was about 80 mV higher than that of the cell with a film exposed to just the dye. This result indicates that the adsorbent causes the TiO₂ bands to move upward by about 80 mV.

Figure 2 shows that at the same photocharge density, the recombination rate for the cell with chenodeoxycholate was five times higher than that for the cell without chenodeoxycholate. At constant photocharge density, an upward shift of the conduction band edge (Figure 1) would be expected to increase the rate of recombination (Figure 2) because the driving force for recombination is determined by the difference between the electron quasi-Fermi level and the electrochemical potential of the electrolyte. These measurements along with J - V data indicate that the net increase of V_{OC} as a result of both band-edge movement and recombination was more than 40 mV and that recombination diminished the effect of band-edge movement on V_{OC} by more than 40 mV.

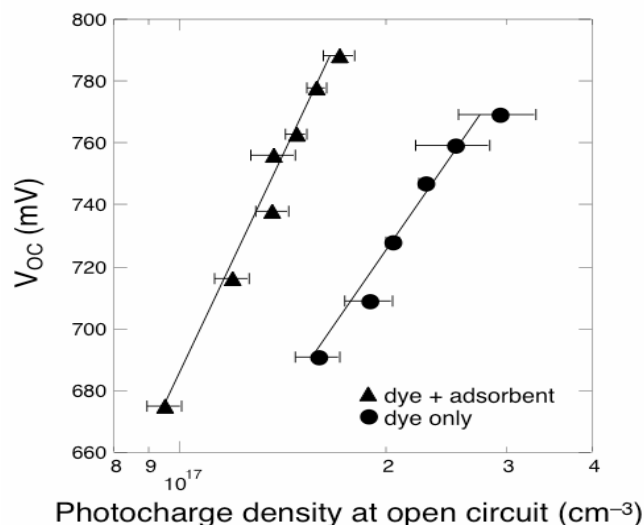


Fig. 1. Effect of chenodeoxycholate on the TiO₂ band-edge position.¹

4. Conclusions

The coadsorbent chenodeoxycholate is found to reduce the dye loading by about half but to have a disproportionately small effect on J_{SC} . Calculations reveal that even at such low dye loading enough dye

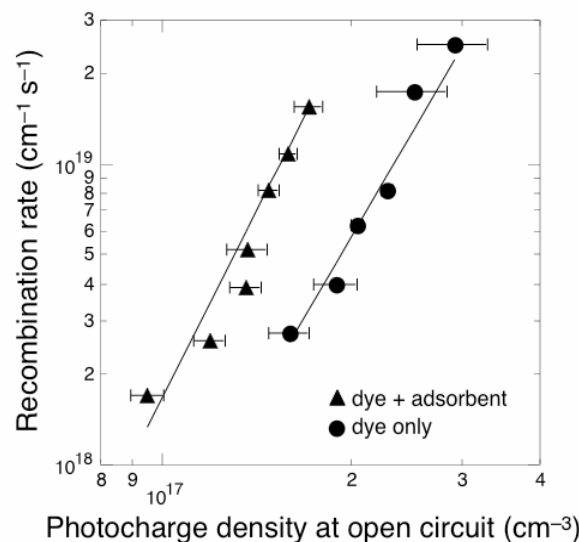


Fig. 2. Effect of chenodeoxycholate on the rate of recombination.¹

was present to absorb a significant fraction of incident light. Chenodeoxycholate is found to not only shift the band edges to negative potentials, but also to significantly increase the recombination rate. The net effect of adding chenodeoxycholate is, however, to improve the photovoltage. Future work will utilize the information from this study to devise a more effective surface treatment strategy for improved cell efficiency.

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REFERENCES

- ¹N. R. Neale, N. Kopidakis, J. van de Lagemaat, M. Grätzel, and A. J. Frank, *J. Phys. Chem. B.*, in press.
- ²G. Schlichthörl, S. Huang, J. Sprague, and A. J. Frank, *J. Phys. Chem. B* **101**, 8141 (1997).

MAJOR FY 2005 PUBLICATIONS

N. Kopidakis, N. R. Neale, K. Zhu, J. van de Lagemaat and A. J. Frank, "Spatial Location of Transport-Limiting Traps in TiO₂ Nanoparticle Films in Dye-Sensitized Solar Cells," *Appl. Phys. Lett.*, in press.

N. Kopidakis, K. D. Benkstein, J. van de Lagemaat, A. J. Frank, Q. Yuan and E. A. Schiff, "Temperature Dependence of the Electron Diffusion Coefficient in Electrolyte-Filled TiO₂ Nanoparticle Films: Evidence Against Multiple Trapping In Exponential Conduction Band Tails," *Phys. Rev. B.*, submitted.

J. van de Lagemaat, N. Kopidakis, N. R. Neale, and A. J. Frank, "Effect of Nonideal Statistics on Electron Diffusion in Sensitized Nanocrystalline TiO₂," *Phys. Rev. B.* **71**, 035304 (2005).

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