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Comparison of Dye-Sensitized Rutile- and Anatase-Based TiO₂ Solar Cells

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ABSTRACT

The objective of this work is to develop and optimize the new dye-sensitized solar cell technology. For the first time, crack-free nanocrystalline rutile TiO₂ films with thicknesses of up to 12 μm were prepared and characterized. The photoelectrochemical properties of the rutile-based solar cell were compared with those of the *conventional* anatase-based cell. Intensity-modulated photocurrent spectroscopy and scanning electron microscopy studies indicate that electron transport is slower in the rutile layer than in the anatase layer due to differences in the extent of inter-particle connectivity associated with the particle packing density. In view of the infancy of rutile material development for solar cells, the PV response of the dye-sensitized rutile-based solar cell is remarkably close to that of the anatase-based cell.

1. Introduction

Dye-sensitized solar cells based on nanocrystalline porous films of TiO₂ are a promising new kind of PV cell. Technological interest in these cells stems from their demonstrated solar efficiencies of 10% – 11% (AM1.5), stability of the semiconductor material, potentially inexpensive manufacturing and materials cost, use of environmentally friendly components, and potential unique applications (transparent, various possible colored dyes). The most extensively studied cell consists of a monolayer of a Ru-bipyridyl-based charge-transfer dye adsorbed onto the surface of a thin nanocrystalline TiO₂ film supported on transparent SnO₂ conducting glass. The particles of the film are in contact with an electrolyte solution containing iodide

and triiodide ions as a redox relay and are sandwiched by a second plate of electrically conducting glass covered with platinum. The metal oxide is the recipient of injected electrons from optically excited dye molecules and provides the conductive pathway from the site of electron injection to the transparent back-contact. The redox species in solution transports the hole from the oxidized dye to the counter electrode, thus regenerating the original form of the dye and completing the oxidation-reduction cycle. The metal oxide can strongly influence the photovoltage, the fill factor, and the photon-to-current conversion efficiency (IPCE), which is determined by the light-harvesting efficiency of the dye, the quantum yield of electron injection, and the efficiency of collecting the injected electrons. Although most work on dye-sensitized nanocrystalline metal oxide solar cells has focused on the anatase form of TiO₂, rutile TiO₂ is potentially cheaper to produce and has superior light-scattering characteristics, which is a beneficial property from the perspective of effective light-harvesting. Recently, we showed that dye-sensitized solar cells based on rutile TiO₂ exhibit photovoltaic characteristics at one-sun light intensity comparable to those of conventional anatase TiO₂-based solar cells [1]. Nanocrystalline rutile films were directly deposited onto the transparent tin oxide back-contact from the ambient hydrolysis of TiCl₄ and subsequently annealed. High-quality films prepared by this method were limited to thicknesses of less than 5 microns, which is well below the requisite thickness for a commercially viable solar cell using the sensitizing dye Ru(LL')(NCS)₂ (where L = 2,2'-bipyridyl-4,4'-dicarboxylic acid, and L' = 2,2'-bipyridyl-4,4'-ditetrabutylammoniumcarboxylate).

We have refined our methodology to synthesize relatively thick (1- μm), crack-free, nanocrystalline rutile TiO_2 films. In this paper, we characterize these rutile-based solar cells and compare their photoelectrochemical properties with those of the anatase-based cell [2].

2. Results and Discussion

Scanning electron microscopy (SEM) shows that the rutile films consist of homogeneously distributed rod-shaped particles with an average dimension of 20×80 nm. Incident monochromatic photon-to-current conversion efficiency (IPCE) measurements imply that a significant fraction of light with wavelengths below 600 nm is absorbed in the first few microns of the dye-covered films due to strong absorption by the dye. In the longer-wavelength region, where the dye molecules absorb weakly, the short-circuit photocurrent increases in direct linear proportion to the film thickness, suggesting that the electron-injection rate throughout the cell is essentially homogeneous. Changing the thickness of the rutile films has only a small influence on the open-circuit photovoltage due to the offsetting effect associated with the dependence of the number of dye molecules and recombination centers on the surface area. The photocurrent–voltage responses of the dye-sensitized rutile and anatase films at one-sun light intensity are remarkably close in view of the early stage of rutile material development for solar cells. The photovoltage of the materials is essentially the same, whereas the short-circuit photocurrent of the rutile-based cell is about 30% lower than that of the anatase-based cell. The difference in photocurrent is found to be related to the smaller surface area of the rutile film compared with that of the anatase film per cell volume. Intensity-modulated photocurrent spectroscopy and SEM studies indicate that electron transport is slower in the rutile layer than in the anatase layer due to differences in the extent of inter-particle connectivity associated with the particle packing density. Possible ways to improve both the photocurrent and electron transport rate in the rutile films are discussed.

REFERENCES

- [1] N.-G. Park, G. Schlichthörl, J. van de Lagemaat, H. M. Cheong, A. Mascarenhas, and A. J. Frank: "Dye-Sensitized TiO_2 Solar Cells: Structural and Photoelectrochemical Characterization of Nanocrystalline Electrodes Formed from the Hydrolysis of TiCl_4 ," *J. Phys. Chem. B* 103 (1999) 3308.
- [2] N.-G. Park, J. van de Lagemaat, and A. J. Frank: "Comparison of Dye-Sensitized Rutile- and Anatase-Based TiO_2 Solar Cells," submitted.