

Oriented TiO₂ Nanotube Arrays for Dye-Sensitized Solar Cells: Effect of Nanostructure Order on Transport, Recombination, and Light Harvesting

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ABSTRACT

The objective of this research project is to determine the key operational characteristics for realizing efficient, low-cost, stable solar cells based on dye-sensitized mesoporous nanostructured films (in collaboration with DOE's Office of Science Program). Toward this end, we have investigated the structure and the dynamics of electron transport and recombination in dye-sensitized solar cells (DSSCs) incorporating oriented TiO₂ nanotube (NT) arrays. The anatase TiO₂ NTs are arranged in an approximately hexagonal close-packed array with wall thicknesses and inter-tube spacings of about 10 nm and pore diameters of about 30 nm. The transport and recombination properties of the aligned NT and traditional randomly packed nanoparticle (NP) films used in DSSCs are studied by frequency-resolved modulated photocurrent/photovoltage spectroscopies. Although both NT and NP morphologies display comparable transport times, recombination is 10 times slower in the NT films, indicating that the NT-based DSSCs have significantly higher charge-collection efficiencies than their NP-based counterparts. The NT-based DSSCs are found to display higher light-harvesting efficiencies than their NP-based DSSCs due to stronger internal light-scattering effects. Implications of these results for developing more efficient cells are discussed.

1. Objectives

The dye-sensitized solar cell (DSSC; Grätzel cell) is a promising future-generation concept for achieving efficient solar-to-electric energy conversion with very inexpensive materials and manufacturing processes. The traditional cells feature dye molecules chemisorbed on the surface of titanium dioxide 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 redox species in the electrolyte transport the holes from the oxidized dye molecules to the counter electrode. The injected electrons diffuse through the TiO₂ particle network to the collecting transparent conducting oxide substrate. From the light-intensity dependence of the electron diffusion coefficient in randomly packed TiO₂ nanoparticle (NP) films, it has been inferred that transport is limited by the residence time of electrons in traps and the morphology associated with both the particle network and the

interparticle contact area. Because the collection of photoinjected electrons competes with recombination, high charge-collection efficiency requires that transport is significantly faster than recombination.

Films constructed of oriented one-dimensional nanostructures, such as nanotube (NT) arrays, aligned perpendicular to the collecting substrate could potentially improve the charge-collection efficiency by promoting faster transport and slower recombination. The extent to which transport or recombination could be affected by an oriented architecture is expected to depend on mechanistic considerations, such as the density and location of structural defects, the crystallinity, and the composition of the redox electrolyte. Understanding the principal physical and chemical factors that govern or limit cell performance is critical for underpinning the development of this next-generation solar cell technology. Of programmatic importance is that sensitized nanostructured solar cells represent the distinct technological promise for achieving mass-produced, ultra-low-cost solar panels with good efficiency.

In this paper, we examine the morphology and electron dynamics in oriented TiO₂ NT arrays. The crystal structure of a single NT and the pore density, pore diameter, wall thickness, inter-tube spacing, and porosity of the NT films are characterized. The transport and recombination times of electrons in NT and NP films used in DSSCs are compared. The aligned NT arrays display markedly higher charge-collection efficiencies and light-harvesting efficiencies than the traditional NP films. The photovoltaic properties of NT- and NP-based DSSCs are also studied.

2. Technical Approach

Aligned TiO₂ NT arrays are prepared by electrochemically anodizing a Ti foil. Titania NT and NP films are stained with [tetrabutylammonium]₂[Ru(4-carboxylic acid-4'-carboxylate-2,2'-bipyridyl)₂(NCS)₂]. The morphology of the NT arrays is characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). The electrolyte is composed of 0.8 M 1-hexyl-2,3-dimethylimidazolium iodide and 50 mM iodine in methoxypropionitrile. Transport and recombination properties are measured by intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS). For these measurements, the DSSCs are probed with a modulated beam of 680-nm light superimposed on a

680-nm bias light. The probe and bias light enter the cell from the counter-electrode side.

3. Results and Accomplishments

Figure 1 shows typical SEM images of TiO₂ NT films. The arrays consist of approximately hexagonal close-packed NTs, several microns in length, with wall thicknesses of 8 nm and pore diameters of 30 nm. High-resolution TEM images of single NTs show that the material is fully crystalline anatase with lattice spacings of 3.52 Å, which correspond to the (101) plane. Although the average crystallite size is 28 nm as determined by XRD, the TEM shows that the NT walls comprise crystallites with lengths exceeding 50 nm. From a comparison of dye-desorption and gas-sorption measurements, we infer that both NT and NP morphologies have comparable dye loadings, surface areas, and roughness factors (ca. 90 μm⁻¹). Analyses of the data reveal that dye molecules cover both the interior and exterior walls of the NTs. From the experimentally determined roughness factor and wall thickness (8±1 nm), we estimate that the NT films have a porosity of 65±5% and that the inter-tube spacing is 10 nm. We also determine that the pore density is very high, about 3.7 × 10¹⁰ pores/cm².

IMPS and IMVS measurements of the NT- and NP-based DSSCs show that although both morphologies display comparable transport times, recombination is 10 times slower in the NT films, indicating that the NT-based DSSCs have significantly higher charge-collection efficiencies (ca. 25% higher) than their NP-based counterparts at the maximum power point. Photocurrent density (J_{sc}) measurements along with other measurements indicate that the light-harvesting efficiencies of NT-based DSSCs are >20% higher than those of NP-based DSSCs owing to stronger internal light scattering. The photocurrent densities of the NT-based DSSCs are higher than those of NP-based DSSCs, while their photovoltages are comparable. The fill factors (FFs) of the NT-based DSSCs are slightly lower than those of NP-based DSSCs owing to an insulating oxide layer that forms between the NTs and the substrate during the anodization process. The lower FF of the NT-based DSSCs offsets the gain in J_{sc} , resulting in both NT- and NP-based DSSCs having comparable AM1.5 solar conversion efficiencies at the same film thickness.

4. Conclusions

A comparison study of aligned NT and randomly packed NP films reveal that the charge-collection and light-harvesting efficiencies of the NT photoelectrodes are markedly enhanced. Future work will use the information from this study to develop more effective nanostructured architectures for improved cell efficiency.

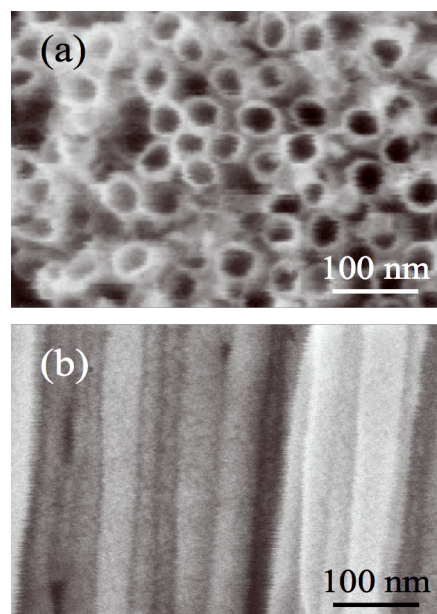


Figure 1. Surface (a) and cross-sectional (b) SEM images of as-deposited TiO₂ NT arrays. (Ref. 1)

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