The Essential Interface: Studies in High Surface Area Solar Cells

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The fundamental characteristics of organic-based, high surface area (HSA) solar cells are discussed. Most of the examples are taken from dye sensitized solar cells (DSSCs), but the relationships with other HSA cells, such as the conducting polymer/C_{60} cells, are emphasized.

One universal aspect of HSA cells is that there are multiple possible current pathways through the cell, and the relative resistance of the pathways changes with illumination, applied potential, etc.[1] In most cases, these cells cannot be modeled as if only a single voltage were applied to the whole cell. A simple distributed resistance model is proposed to qualitatively describe the spatial distribution of the potential applied to HSA cells without electrolyte (Figure 1). Addition of electrolyte reinforces the qualitatitive effects of the distributed resistance.

In conventional solar cells the built-in potential, ϕ_{bi}, determines the maximum possible V_{oc}, not because of any thermodynamic necessity, but because ϕ_{bi} drives charge separation. In DSSCs, charge separation is driven almost entirely by photoinduced interfacial chemical potential gradients, ∇n, while electrical potential gradients, $\nabla\phi$, are screened by the mobile electrolyte.[2] Therefore the maximum V_{oc} is almost entirely determined by ∇n, not by built-in potentials at electrical junctions. But there is still substantial disagreement about this point as some groups insist that there must be a p-n junction in DSSCs to account for the photovoltaic effect. As one means of disproving this notion, we have moved the TiO_2/doped SnO_2 "p-n" junction out into solution, where it is surrounded by electrolyte, by applying a thin layer of doped, nanoparticulate SnO_2 to the SnO_2 substrate electrode. Now the built-in field at the putative "p-n" junction is eliminated by electrolyte screening. Junction models predict there can be no photovoltaic effect in such cells, but, experimentally this change makes almost no difference (Figure 2), showing that electrical junctions play little or no role in DSSCs.

The efficiency of DSSCs sensitized with many dyes improves dramatically (up to ~40 fold) when illuminated with UV light for a short time.[3] We recently discovered that this UV treatment reversibly produces a high density of surface states in the TiO_2 that are ~exponentially distributed in energy (Figure 3). These states can be made to appear (by UV illumination) and disappear (by rinsing the cell), with correspondingly huge changes in photoconversion efficiency. This provides an excellent and unexpected opportunity to understand the effect of surface states in photosensitized HSA films. We present an overview of our experiments on the UV effect, show how it can be used to optimize the efficiency of dye sensitized cells, and attempt to explain how such a large increase in "defect" density can lead to a huge *improvement* in photoconversion efficiency.

(1) Gregg, B. A., in "Semiconductor Photochemistry and Photophysics", Schanze, K. S. and Ramamurthy, V., Eds., Marcel Dekker, New York, *in press*.
(2) Pichot, F., Gregg, B. A., *J. Phys. Chem. B.* **2000**, *104*, 6.
(3) Ferrere, S.; Gregg, B.A., *J. Phys. Chem. B* **2001**, *105*, 7602.

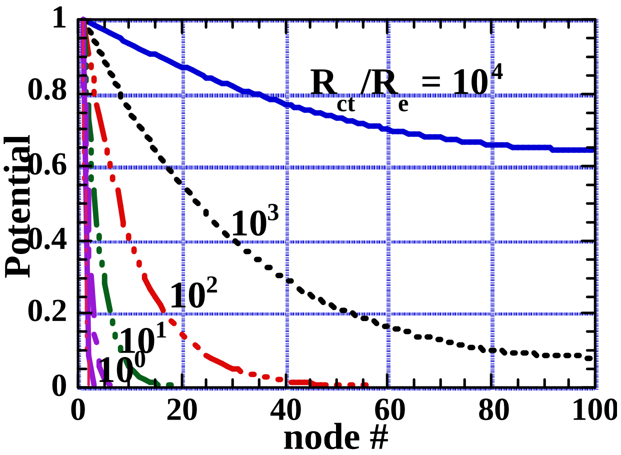

Figure 1. The calculated applied potential distribution across an HSA cell modeled by a distributed resistor network. The node number corresponds to distance through the cell. Here we are modeling a DSSC, but without electrolyte. R_{ct} is the TiO_2/solution interfacial charge transfer resistance, and R_e is the particle-particle resistance to charge transfer through the TiO_2 network.

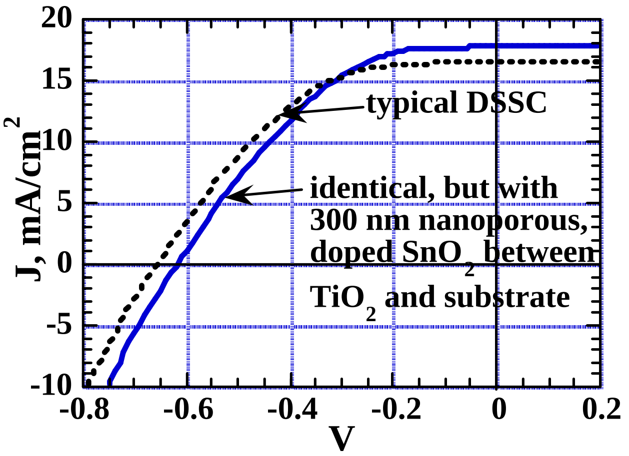

Figure 2. JV curves of DSSCs under ~1 sun. The solid line shows cells identical to the typical ones except for the inclusion of a doped nanoparticulate SnO_2 layer between the substrate and the TiO_2 film. This screens electrically the effect of any putative p-n junction and shows that such junctions play little or no role in DSSCs. Each curve is the average of two cells.

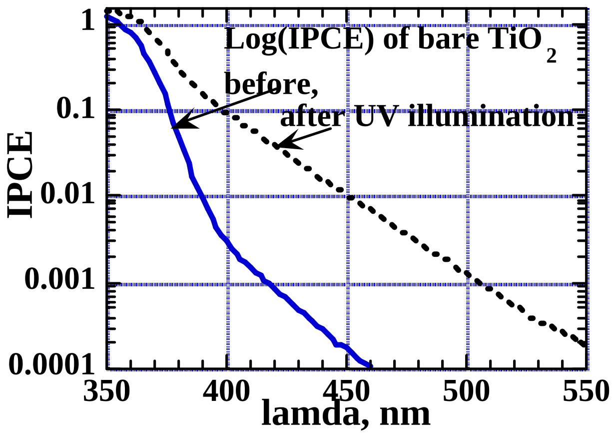

Figure 3. IPCE of a bare (non-sensitized) nanoporous TiO_2 electrode before and after exposure to UV light for 15 min. The huge increase in apparent surface state density is completely reversible.