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How Porosity Modifies the Photovoltaic Effect in Nanocrystalline Solar Cells

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ABSTRACT

The porosity of the nanocrystalline semiconductor affects many aspects of the photoconversion process in dye-sensitized solar cells, thus distinguishing them mechanistically from conventional photovoltaic and photoelectro-chemical cells. We discuss several examples from our recent work.

1. Electric Fields

The porosity influences the location and magnitude of equilibrium, photogenerated, and applied electric fields because ion motion throughout the film neutralizes electric fields over a short range (nanometers).¹ This results in having no macroscopic (only nanoscopic) electric fields in the device either at equilibrium or under illumination. Therefore, charge carrier motion occurs via diffusion rather than drift. Photoinduced charge separation induces a transient electric field that is rapidly neutralized by ion motion in the conventional cell. But solid state versions often lack supporting electrolyte and thus exhibit rapid charge recombination. Thus, a viable solid state cell will require excess mobile electrolyte.

2. Potential of Sensitizing Dye

Because the adsorbed sensitizing dye sits in the electrochemical double layer, its redox potential is not fixed relative to either the semiconductor or the solution. When the dye is mostly inside the double layer, its potential will tend to follow the semiconductor; when it is mostly outside,

its potential will be almost independent of the semiconductor.²

3. Photovoltage-Determining Mechanism

To distinguish experimentally between two competing models of the photovoltage-determining mechanism in nanoporous solar cells, we deposited dye-sensitized TiO₂ films on four different substrates having vacuum work functions spanning a 1.4 eV range. We then measured the photovoltage obtained from these films in three different redox electrolyte solutions. No significant differences in photovoltage were obtained on the different substrates, showing that the photovoltage is determined by photoinduced chemical potential gradients, not by equilibrium electric fields,³ (see Figure 1).

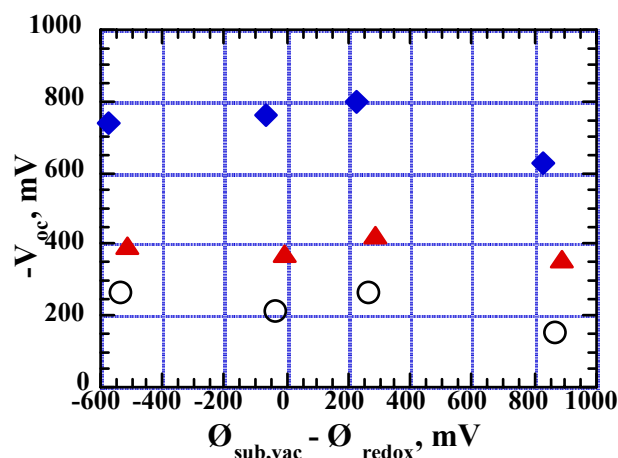


Figure 1. V_{oc} plotted vs the difference between the work function of the substrate (for 4 different substrates) and the

solution redox potential (3 different solutions). This shows that V_{oc} is not determined by the equilibrium electric field.

4. Passivating Recombination Sites

The high surface area of the nanocrystalline film puts severe constraints on the hole conductor, because the hole can only escape recombination with electrons in the TiO_2 if the recombination rate is unusually slow. The conventional hole conductor, I_2/I_3^- , has very slow kinetics for reduction and thus allows holes to escape recombination, but some of its other properties are less than ideal. Figure 2 shows J-V curves for a cell made with the conventional I_2/I_3^- electrolyte and also for a cell made with the much faster redox couple ferrocene/ferrocenium. A faster redox couple eliminates the photovoltaic effect because of the rapid recombination reaction. We discuss two strategies for passivating recombination sites in nanocrystalline solar cells in order to facilitate the use of other redox couples, such as those needed for solid state versions of the dye cells.

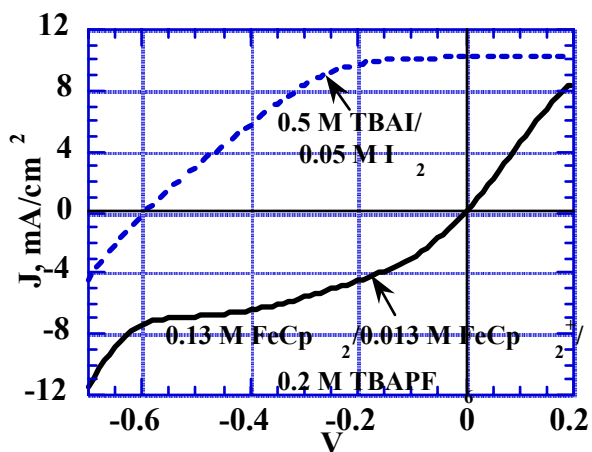


Figure 2. J-V curves under illumination of a standard dye cell using the I_2/I_3^- couple and one using a faster redox couple, ferrocene $^{+/0}$. The faster couple shows no PV effect but one can be induced with proper surface treatments.

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