

Probing Energetics of Molecule-Semiconductor Interfaces for Nanocrystalline TiO₂ Solar Cells

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There is interest in maximizing photocurrents and photovoltages of dye-sensitized nanocrystalline solar cells by tuning the conduction band edge energy with respect to the excited state of the sensitizer. Electrolyte modification of dye-sensitized nanocrystalline solar cells provides quantitative control of molecular excited-state transfer to ground state products or to charge-separated states via interfacial electron transfer.

Here we present studies of energetics involving planar rutile and sensitized nanocrystalline anatase as a function of electrolyte composition. Regenerative solar cells based on nanostructured TiO₂ and the dye Ru(deeb)(bpy)₂(PF₆)₂ where deeb is 4,4'-(CO₂CH₂CH₃)₂-2,2'-bipyridine and bpy is 2,2'-bipyridine, have increased photocurrent efficiency when in the presence of cations with a high charge-to-radius ratio.

In situ photoluminescence of a regenerative solar cell is examined as a probe of relative electron injection efficiencies. It is known that cations in the electrolyte have a profound effect on the IPCE. The smaller the cation the higher the photocurrent and the more quenched the photoluminescence. Illustrated in Figure 1 is a plot of the *in situ* photoluminescence ratios of different cations to tetrabutyl ammonium cation, TBA⁺, at 460 nm excitation, plotted against ratios of simultaneously monitored short circuit currents, *i*_{sc}. The linearity of normalized photoluminescence with short circuit current measured *in situ* for the same sample of Ru(deeb)(bpy)₂(PF₆)₂/TiO₂ is conveniently demonstrated by simply varying the cations in the I/I_{3⁻} electrolyte.

Figure 2 exhibits the differences between Li⁺ and Na⁺ effects on relative electron injection quantum yield measured by transient absorbance experiments. By pumping with pulsed 532 nm laser light (Nd:YAG) and probing at the excited state-ground state isosbestic point, it was observed that the concentration of oxidized sensitizer, [Ru^{III}], increased with cation concentration. The presence of lithium cations led to a greater amount of injection when compared to similar concentrations of sodium cations.

Differences among cation adsorbing characteristics were also observed on planar TiO₂ surfaces in the absence of dye. The flat-band potentials of single crystal rutile TiO₂, which was cut along the (100) face, were quantified by Mott-Schottky analysis of capacitance data with cations in dry propylene carbonate and with protons in H₂O. Figure 3 shows that a significantly more positive flat-band potential shift was measured for Li⁺ and Na⁺ electrolytes relative to TBA⁺ in these nonaqueous electrolytes. Nearly Nernstian shifts in flat-band potential with pH were observed on a similar single crystal.

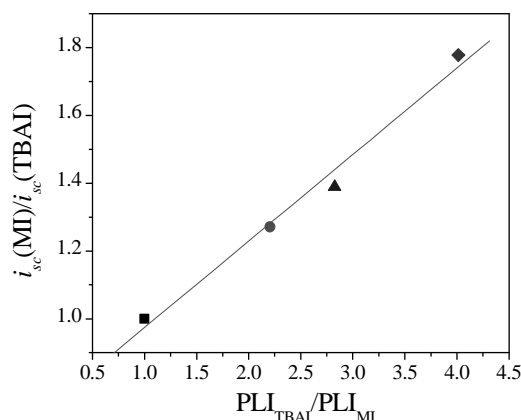


Figure 1. *In situ* photoluminescence ratios of different cations to a reference cation, TBA⁺ (square), at an excitation of 460 nm vs. ratios of simultaneously monitored short circuit current where M = K⁺ (circle), Na⁺ (triangle), or Li⁺ (diamond).

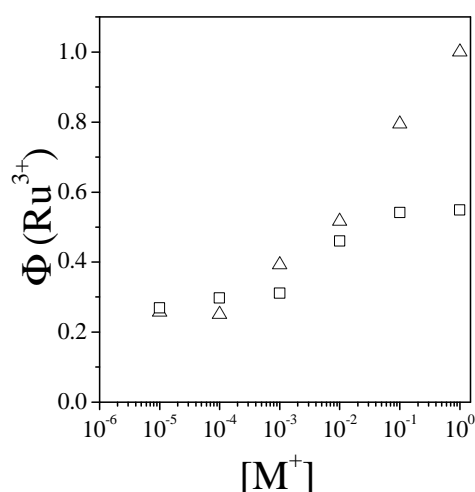


Figure 2. Relative injection quantum yields normalized to [Li⁺] = 1.0 M for Ru(deeb)(bpy)₂²⁺/TiO₂ films for lithium and sodium ions as a function of concentration, reported at 10 ns after excitation with 532 nm light monitored at 406 nm.

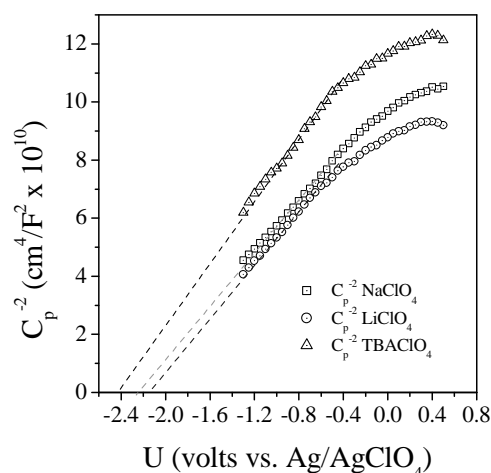


Figure 3. Mott-Schottky plots of rutile crystal in indicated propylene carbonate electrolytes. Parallel capacitance-voltage for 100 Hz using a 10 mV perturbation is displayed.