

Cation Controlled Energetics of Nanocrystalline and Thin Film TiO₂ for Dye-Sensitized Solar Cells

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The energetics of dye-sensitized solar cells are being studied on TiO₂ in both the nanocrystalline and thin film form. Optimization of the semiconductor energetics may lead to significant improvement of open circuit photovoltage and photocurrent and hence power conversion efficiency in dye-sensitized nanocrystalline solar cells.

A fundamental problem in optimization is that there is no unambiguous method for determining Fermi levels and conduction band edge positions in nanocrystalline TiO₂ films. The objectives are thus to probe the energetics of the molecule-semiconductor interface using photoelectrochemical, optical and electrochemical techniques. Here we report photoaction spectra, absorbance, photoluminescence, cyclic voltammetry, spectroelectrochemistry, and impedance studies on nanocrystalline and thin film TiO₂ as a function of electrolyte composition and surface pretreatment.

Through the use of luminescent dyes on nanocrystalline semiconductors, the luminescence quenching can be observed. The quenching is attributed to electron injection into TiO₂. Shown in figure 1 are the spectral changes with increasing Ca²⁺ concentration. The luminescence intensity decreases with increasing presence of Ca(ClO₄)₂. The inset shows a plot of photoluminescence intensity measured at 654 nm relative to 684 nm as a function of Ca(ClO₄)₂ concentration in acetonitrile. Also, this luminescence quenching can be reversible. The result indicates that this combination of dye and colloid may be useful as a ratiometric sensor for alkali or alkaline earth metal cations. Moreover, the excited state reduction potential of the dye is known and can be used as a contactless probe to estimate the position of the conduction band.

Nanocrystalline TiO₂ solar cell efficiencies are dependent on the electrolyte composition. It has been observed that electrolytes comprised of small alkali iodides result in improved photocurrents and incident photon-to-current conversion efficiencies (IPCE) relative to iodide salts with large cations. Shown in figure 2 is a comparison between lithium and tetrabutyl ammonium iodide-based electrolyte solutions for the same kind of dye-sensitized TiO₂ electrode.

In addition, the flat-band potential shifts have been seen by capacitance measurements on thin film TiO₂ on titanium using electrochemical impedance spectroscopy. Shown in figure 3 are Mott-Schottky plots of the films in 1 M H₂SO₄. The frequency dependence is small in this regime. The observed flat band potential shifts correspond to the 59 mV/pH unit as reported in earlier work in this field.

In this presentation, subtle differences between alkali cations are demonstrated in their IPCE's, photoluminescence quenching, and capacitance measurements. The technique of probing flat-band potential shifts by electrochemical impedance spectroscopy paves the way for a coupled approach in nonaqueous solutions correlating flat-band potentials with photoelectrochemical behavior.

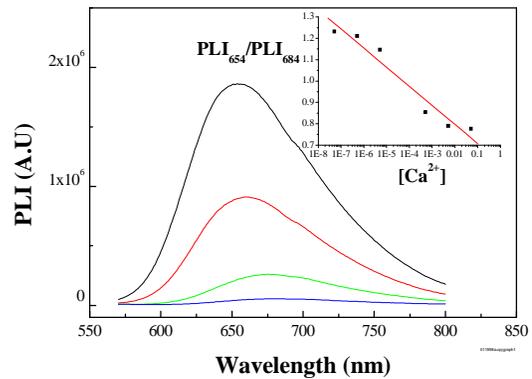


Fig. 1. Photoluminescence quenching on Ru(deeb)(bpy)₂²⁺/TiO₂ in 0, 5 x 10⁻⁶, 5 x 10⁻⁴, 5 x 10⁻² M Ca(ClO₄)₂ in neat acetonitrile. The inset shows the near linearity of ratios of intensities at two selected wavelengths with log-[Ca²⁺].

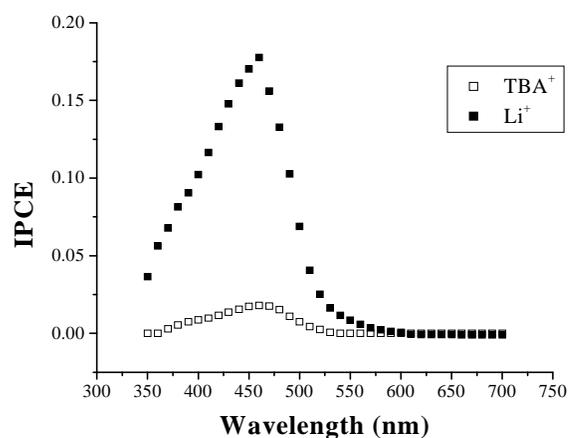


Fig.2. Incident photon-to-current conversion efficiency (IPCE) vs. wavelength for 0.2 M LiI, 0.02 M I₂ and for 0.2 M tetrabutyl ammonium iodide (TBAI), 0.02 M I₂ in propylene carbonate on a Ru(deeb)(bpy)₂²⁺/TiO₂ photoanode.

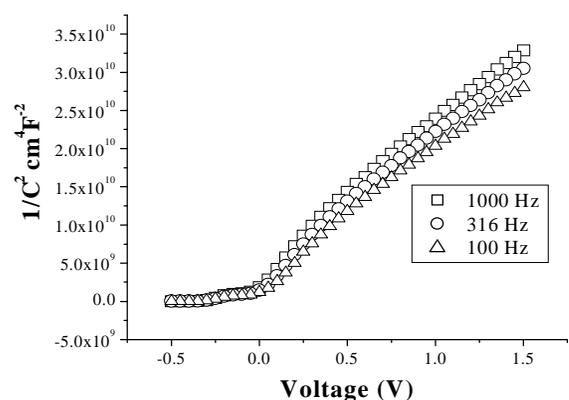


Fig. 3. Mott-Schottky plots of thin film TiO₂ on titanium in 1 M H₂SO₄ for 3 frequencies.