

Topology and Electron Transfer at Nanocrystalline Electrodes

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In the field of dye-sensitized solar cells, nanocrystalline materials have been used to great effect in the increase of the optical density of the absorbing dye on the semiconductor electrode. This use of nanocrystalline materials has introduced idiosyncratic physical characteristics into the solar cell that influence and/or determine its behavior. The use of sintered nanospheres of semiconductors creates contact points and interstices between nanoparticles. Thus, the dielectric environment within these spaces varies sharply with the changes in the geometry of the environment. Nonuniform diffusion flow within the mesoporous electrode occurs in such environments. Transport of charge within the electrode differs greatly from that of a solid material.

The studies of this presentation explore some of these idiosyncrasies of the nanocrystalline electrode. The spatial topology of the sintered spheres is probed with a series of planar, carboxylated organic dyes with a systematic substitutional variation. They are sufficiently flat to fit into interstices. The variation in substitution allows a comparative study of the effect of dye-dye interactions upon attachment to the surface. It is also evident that near the boundaries of the particles, and at their intersection, the variation of the dielectric constant will result in a variation of the activation energy for electron transfer through the environmental effect upon the outer sphere reorganization energy for any reactive molecule.

The dye molecules under study in this work are the carboxylated thiocarbocyanine dyes depicted in Figure 1. They are all derivatized with two methylcarboxy functions to enhance attachment to the TiO₂ surface. Variations in these dyes are found at the 9 position on the methine bridge and at the 5,5' positions on the benzothiazole nuclei, where ethyl, methyl and methoxy functions are attached.

Absorption spectra of these dyes on nanocrystalline TiO₂ electrode layers were measured for electrode material immersed in concentrated 3x10⁻⁴ M dye in dried ethanol and in more dilute 3x10⁻⁵ M dye. Whereas all dyes aggregated extensively on the surface of the TiO₂ when attached from the high concentration solution, the spectra of dyed electrodes formed from the lower concentration solutions showed distinct structural influence upon the extent of aggregation. Dyes were limited in their aggregation to dimers or aggregated to create broad regions of absorption. Action spectra of these electrode materials in the short circuit configuration of a dye-sensitized solar cell were also recorded and compared with their absorption spectra. A time evolution of the action spectrum was observed for the highly aggregated dyes. Solar conversion efficiencies were determined with 4 μm thick TiO₂ electrodes. In such cells, N3 control samples had efficiencies of 5% and single dye cells with the G series of Figure 1 had efficiencies of 4-5%.

Calculations of outer sphere rearrangement energies λ_0

for molecules in the environment of a nanocrystalline metallic array were made using considerations in electrostatics. These calculations were extended to semiconductor nanocrystal electrodes such as are found in dye sensitized solar cells. Various corrections are made in the course of this work to the classical dielectric approach to the problem.

λ_0 evaluations were made for molecules near metallic and semiconducting spheres as the radius of the sphere was changed. This configuration is shown in Figure 2a. It was found that λ_0 at the surface of nanometer-sized spheres could be twice as large as the λ_0 at planar metal electrodes because a nanometer-sized sphere cannot support an image charge to the same extent as a larger planar electrode.

Two other configurations were examined. They are shown in Figure 2b where the molecule approaches the intersection of two particles along the bisector of the two, and in Figure 2c where the molecule is slid along the surface of one sphere to the intersection point with another. λ_0 for a molecule near the intersection is found to be near zero. Rates of electron transfer are expected to vary by many orders of magnitude along these approach paths and this is a function solely of the position of the molecule on the electrode surface and its proximity to neighboring nanoparticles.

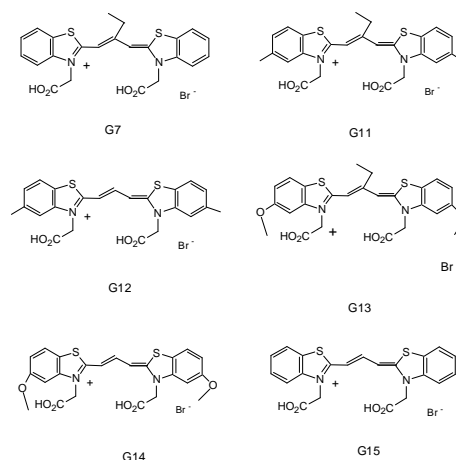


Figure 1: Structure of sensitizing dyes

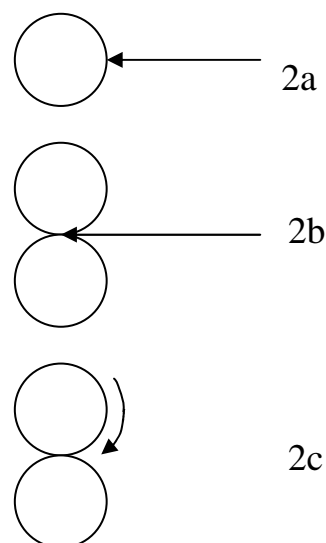


Figure 2 Configurations of nanosphere calculations.