

Studies Of Spectral Sensitization of Single Crystal Oxide Electrodes Using Carboxylated Cyanine Dyes

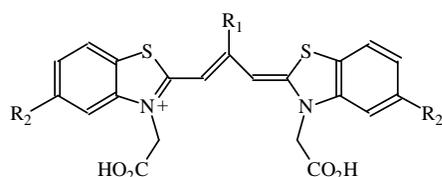
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The nanocrystals used in dye-sensitized solar cells are usually the anatase form of TiO₂. Although efficient and stable solar cells can be made from the dye sensitized nanocrystalline materials, there has been little fundamental information reported on the mode of dye binding or the organization of the dyes bound to the metal oxide surface. We report on the use of well-characterized terraced anatase single crystal surfaces as models for the nanocrystalline surface in order to elucidate aspects of the dye/semiconductor interface. A structurally similar series of thiacyanine dyes is used in combination with photocurrent spectroscopy, AFM and Monte Carlo simulations to help reveal details of the dye binding to the oxide surface. The presence of the ethyl group (R₁) on the bridge prevents aggregation of one set of dyes (G7, G11, G13) beyond dimers whereas extended aggregates are possible from the other dyes (G15, G12, G17).

Name	R ₁	R ₂
G15	H	H
G7	C ₂ H ₅	H
G12	H	CH ₃
G11	C ₂ H ₅	CH ₃
G17	H	OCH ₃
G13	C ₂ H ₅	OCH ₃



High incident photon current efficiency (IPCE) and absorbed photon current efficiency (APCE) values are obtained for these dyes bound to the anatase (101) surface. This is made possible through an ultraviolet (UV) light treatment of the anatase (101) surfaces immediately prior to dye adsorption, which improves both the reproducibility of dye coverage and the incident photon-to-current efficiencies (IPCE) for sensitization. The UV treatment does not pit or roughen the anatase surface (Figure 1) and results in IPCEs of up to 1% for sensitization of these single crystal substrates.

A well-defined surface structure allows the adsorption isotherms and adsorption and desorption kinetics of these dyes to be studied. The photocurrent spectra showed features associated with surface-bound dye monomers, dimers and aggregates that could be followed as a function of the dye surface coverage. Figure 2a shows photocurrent spectra as a function of dye coverage for dye G15. Peaks in the photocurrent spectrum can be identified with the monomer and H aggregate forms of the dye. Deconvolution of the

photocurrent peaks, as a function of dye concentration that the freshly phototreated surface was exposed to, reveals the contributions of the monomer and aggregate forms of the dye to the surface coverage (Figure 2b).

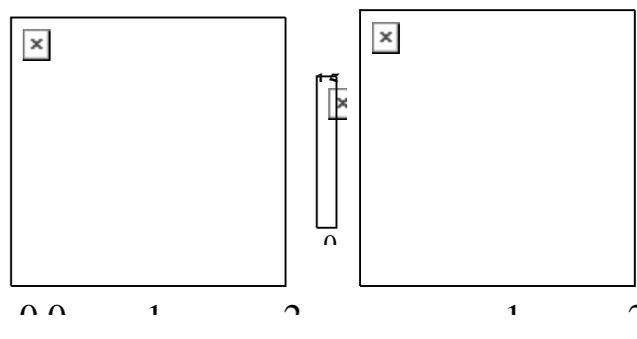


Figure 1. AFM images of anatase (101) surface after the polishing and annealing procedure (left) and after repeated UV treatments totaling almost two hours (right).

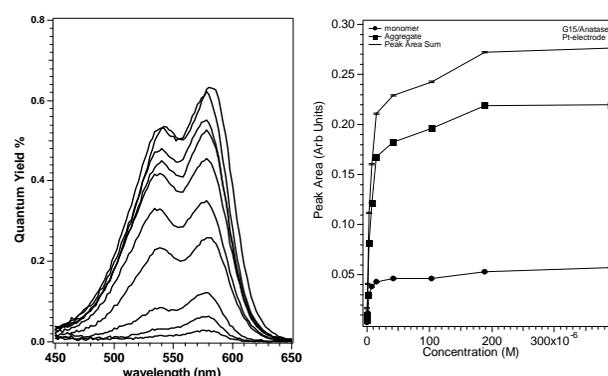


Figure 2 a) -Plot of the dye-sensitization of the anatase (101) surface by G15. b) - Isotherm generated from peak fitting the areas of the monomer and aggregate peaks of the G15 sensitization spectra shown in a).

The desorption kinetics of several of these dyes into pure acetonitrile solutions and solutions with added water (a competitive adsorber) were also studied. Strongly bound and more weakly bound populations of dye molecules were seen in all cases. Adsorption thermodynamics and surface dynamics of molecules adsorbed to a square lattice by two site attachments were simulated with Monte Carlo techniques. Diffusional “walking” of the molecules can result in the reorganization of molecules into ordered structures. Models for the surface structures of the adsorbed dye layers that are consistent with the simulations and photocurrent and desorption measurements are proposed and will be presented. Comparisons with data from nanocrystalline TiO₂ layers and other TiO₂ polytypes will also be made.