

Dye Sensitization of Single Crystal Semiconductor Electrodes

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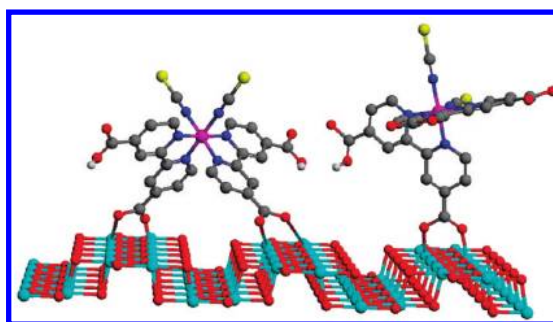
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CON SPECTUS

Even though investigations of dye-sensitized nanocrystalline semiconductors in solar cells has dominated research on dye-sensitized semiconductors over the past two decades, single crystal electrodes represent far simpler model systems for studying the sensitization process with a continuing train of studies dating back more than 40 years. Even today single crystal surfaces prove to be more controlled experimental models for the study of dye-sensitized semiconductors than the nanocrystalline substrates.

This Account analyzes the scientific advances in the model sensitized single crystal systems that preceded the introduction of nanocrystalline semiconductor electrodes. It then follows the single crystal research to the present, illustrating both their striking simplicity of use and clarity of interpretation relative to nanocrystalline electrodes. Researchers have employed many electrochemical, photochemical, and scanning probe techniques for studying monolayer quantities of sensitizing dyes at specific crystallographic faces of different semiconductors. These methods include photochronocoulometry, electronic spectroscopy, and flash photolysis of dyes at potential-controlled semiconductor electrodes and the use of total internal reflection methods. In addition, we describe the preparation of surfaces of single crystal SnS_2 and TiO_2 electrodes to serve as reproducible model systems for charge separation at dye-sensitized solar cells. This process involves cleaving the SnS_2 electrodes and a photoelectrochemical surface treatment for TiO_2 that produces clean surfaces for sensitization (as verified by AFM) resulting in near unity yields for electron transfer from the molecular excited dyes into the conduction band.

In recent experiments with ruthenium complexes at TiO_2 and with carboxylated cyanine dyes, we demonstrate the promise of this simple model for understanding dye-sensitized solar cells. In each of these systems, we can observe and analyze the complex photochemistry in a quantitative manner. Molecules of the well-known N3 ruthenium complex attach to four different crystallographic faces of anatase and rutile TiO_2 at different rates and to a different extent. With carboxylated cyanine dye sensitizers on these surfaces, molecular aggregation on the surface is a function of molecular structure and crystallographic face. In contrast with the N3 sensitizer these organic dyes undergo a photoinduced dimerization and desorption reaction when hydroquinone regenerators are present. With both classes of sensitizers, we demonstrate a new photochronocoulometric technique that quantifies the amount of attached dye on the electrode surface. We have completed initial experiments examining quantum dot sensitization of TiO_2 crystals, which could eventually lead to sensitizers with higher stability and absorption coefficients. Although these single crystal electrode models show promise for providing insights and predictive value in understanding the sensitization process, more sophisticated models will be needed to fully understand the charge transfer from the localized electronic states of the sensitizer to the extended states of the semiconductor.



Introduction and Background

The use of visible light absorbing dye molecules for spectral sensitization of large band gap semiconductors dates back to the early development

of photography when silver halide microcrystals in photographic emulsions were coated with dyes to capture images of the world around us. Decades of research and development of this technology

led to versatile, sensitive, and accurate color photographic films that were in widespread use. The development of digital imaging technologies has quickly replaced the majority of the photographic film and diminished research efforts in silver halide sensitization, but the renewed interest in solar energy conversion has increased interest in extending the spectral response of stable large band gap semiconductors to visible light to increase their efficiency for solar fuel and electricity generation. This Account will give a historical perspective of research on spectral sensitization of macroscopic crystal semiconductor electrodes with an emphasis on the coauthors own individual and collaborative research in this area.

The electrochemistry of dye-sensitized semiconductors first surfaced as a research area in the late 1960s through the work of Gerischer and Tributsch where the ability of organic dyes to produce photocurrents when adsorbed at ZnO single-crystal electrodes was investigated as an analog to spectral sensitization in photography.^{1,2} At that time, photographic scientists were uncertain as to the mechanism of spectral sensitization of silver halide crystals by organic dyes, whether it was through energy transfer from the dye to defect centers in the underlying crystal or through direct electron transfer from the excited states of the dye.³ This early electrochemical work, performed as a model of the photographic process, demonstrated that excited dyes on the surface of the ZnO were oxidized to produce photocurrents that could be amplified or sustained through the addition of reducing agents or sensitizers (sometimes called regenerators and akin to the developers used in photography) to the solution that would reduce the photooxidized dye. The work lent strong support to the electron transfer model. Soon thereafter, for the first time, Tributsch and Calvin stated the vision that spectral sensitization of metal oxide semiconductors could play a role in solar energy conversion using the example of the sensitization of ZnO single crystal electrodes with chlorophyll molecules as an inorganic analog of the primary photosystems in photosynthesis.^{4,5}

Gerischer and Willig formulated the early physical models to describe the oxidation of an excited dye at a semiconductor electrode.⁶ The aspects of this model are illustrated in Figure 1.⁷

In order to test this model, quantitative studies of the photochemical yield for the electron transfer soon followed.^{8,9} In a straightforward manner, the adsorption isotherms and electronic absorption spectra of xanthene and rhodamine dyes on large area single crystal surfaces of TiO₂ and ZnO were measured and compared with photocurrents and the spectral dependence of the photocurrents when the dyes were

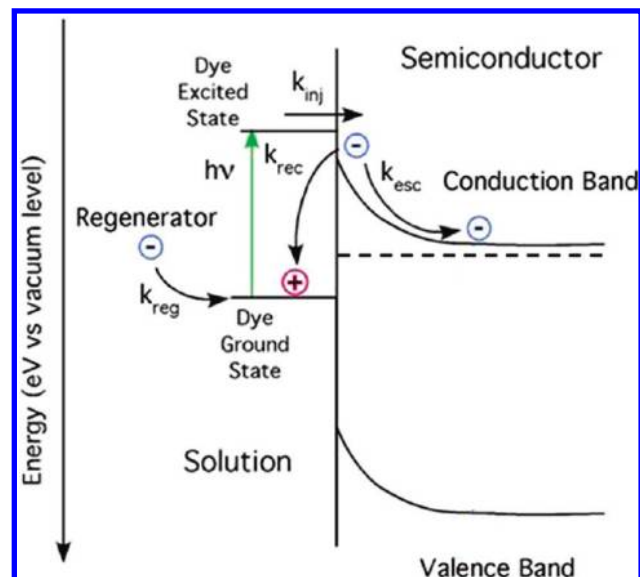


FIGURE 1. Rate processes at a dye-sensitized single crystal electrode are depicted for electron transfer into an n-type semiconductor biased to produce a depletion layer. Excitation of an electron from the ground state of a dye at a specific energy to an excited state level results in electron transfer to the semiconductor conduction band with a rate k_{inj} . This is accomplished at a photon energy less than that needed to excite the band gap of the semiconductor. This charge is drawn off as current as the electrons escape the surface at a rate depicted as k_{esc} . The electrons at the semiconductor surface can also recombine (k_{rec}) with the oxidized dye in competition with a reduction by the regenerating agent (k_{reg}).

adsorbed from aqueous solution onto these same surfaces. (There are two often-reported numbers for the efficiency of photocurrent generation, not to be confused with the power conversion efficiency. These are the incident photon current efficiency (IPCE), sometimes called the external quantum yield or quantum yield per incident photon, and the absorbed photon current efficiency (APCE) called the quantum yield per absorbed photon or the internal quantum efficiency). The photocurrent spectra were found to follow the absorption spectra of the adsorbed dye, but the APCE for these experiments in an aqueous electrolyte was found to be low, about 1–2%. This low efficiency was in contrast to the near unity injection yields found for the photooxidation of excited Ru(bpy)₃²⁺ in an acetonitrile electrolyte when the photoexcited molecule diffused to the surface of a rutile TiO₂ electrode.¹⁰

In further work in Gerischer's laboratories at the Fritz Haber Institute in Berlin, attenuated total internal reflection techniques were introduced to dye sensitization studies in order to obtain an instantaneous measure of the yield for electron transfer. The method enabled the measurement of photon absorption by a monolayer or submonolayer chromophore coverage of the electrodes with simultaneous photocurrent measurements, allowing for the direct determination of

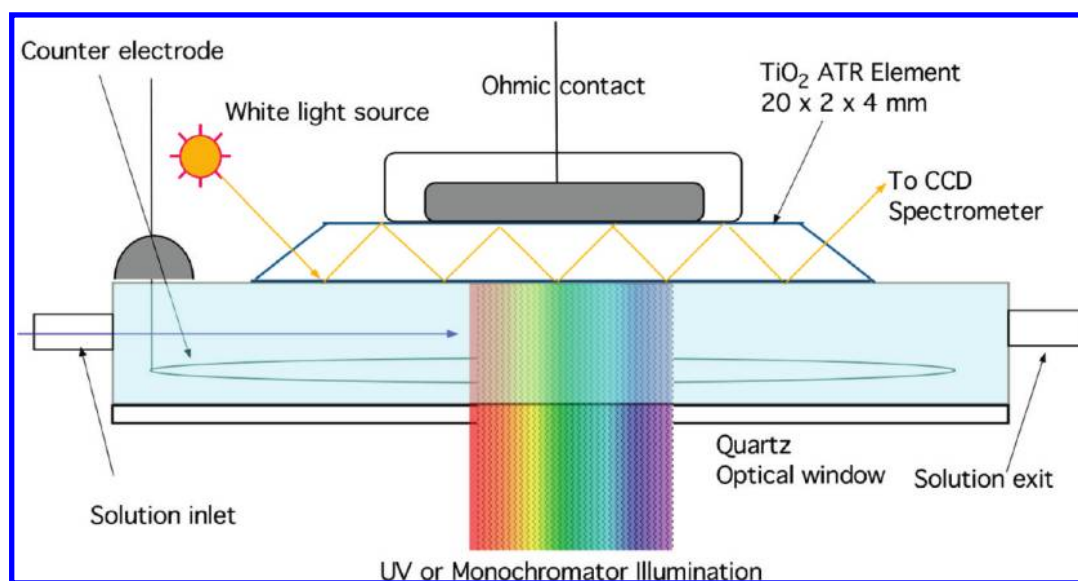


FIGURE 2. A schematic diagram for the use of attenuated total reflection spectroscopy to monitor the dye on the surface of a large band gap metal oxide electrode shaped and polished into a prismatic internal reflection element. A flow cell arrangement for the electrolyte allows a time-dependent spectral characterization of the adsorption of the dye on the surface as well as an *in situ* determination of IPCE as the actinic light produces current at the ohmic contact. The electrode surface can be illuminated at specific wavelengths in the visible through the use of a monochromator or can be exposed to UV radiation for the surface regeneration procedure.

APCE.¹¹ ZnO single crystal electrodes were shaped as internal reflection prisms reflecting the photometric light multiple times from the dye-covered surface and serving as the actinic light for photocurrent production producing the desired instantaneous measure of photocurrent yield. A diagram of a typical experimental set up is shown in Figure 2. This internal reflection technique was subsequently expanded to allow the recording of the entire absorption spectrum of the adsorbed dye layer. This proved very useful for the study of cyanine dyes aggregated to form H or J aggregates on ZnO, TiO₂, or indium tin oxide electrodes (H aggregates have a blue-shifted absorption maximum, whereas J aggregates have a very sharp red-shifted absorption maximum). In addition, internal reflection flash photolysis experiments were performed with eosin, where the photochemistry of the adsorbed dye could be correlated with current production at the electrode surface.^{12–14} Figure 3 shows the photocurrent spectrum for a thiocarbocyanine dye adsorbed onto a ZnO crystal formed into an internal reflection prism in order to measure the relative adsorption and photocurrent generation from the dye. Monomeric, J aggregated, and H aggregated dye could all be detected on the surface, and the J aggregate, with virtually no light absorption, yielded a relatively much higher photocurrent signal. In other experiments, the band edges of the oxide crystals were moved by the variation of the solution pH, whereas the dye excited state potential was not influenced by pH changes. In one case, the APCE of 2,2-diethyl-oxadiazocarbocyanine adsorbed onto a SrTiO₃ single crystal electrode as the electrolyte pH is

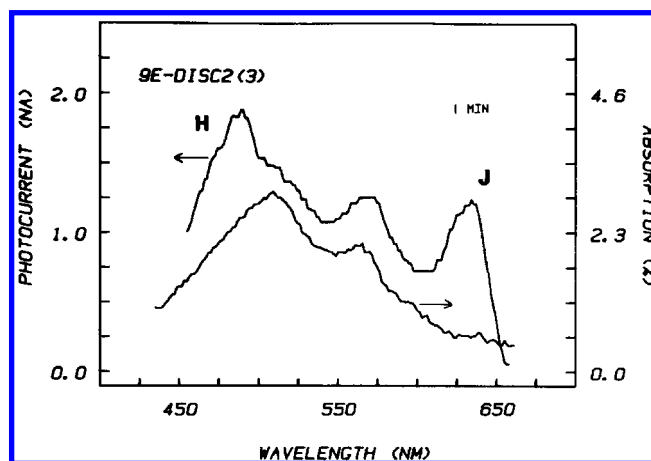


FIGURE 3. The photocurrent spectrum in nanoamps of the dye 9-ethylthiacarbocyanine on ZnO single crystal electrodes in aqueous 0.1 M NaCl is found to reflect current from the monomer absorption at 560 nm as well from the H-aggregate and J-aggregate forms at 480 and 630 nm. A comparison of the current with the absorption spectrum taken of the adsorbed dye on this electrode surface reveals the APCE of the J aggregate to be far higher than that of the H aggregate or monomer form of the dye.

changed from pH 4 to 11 showed a threshold as the energy of the excited donor state of the dye drops below that of the conduction band edge. The application of models for electron transfer resulted in a reorganization energy for the adsorbed excited dye of between 250 and 300 mV. All of this experimentation involved the study of organic dyes adsorbed from the electrolyte onto the surface of the semiconductor electrode with measurements being made under equilibrium between dye in solution and on the surface.

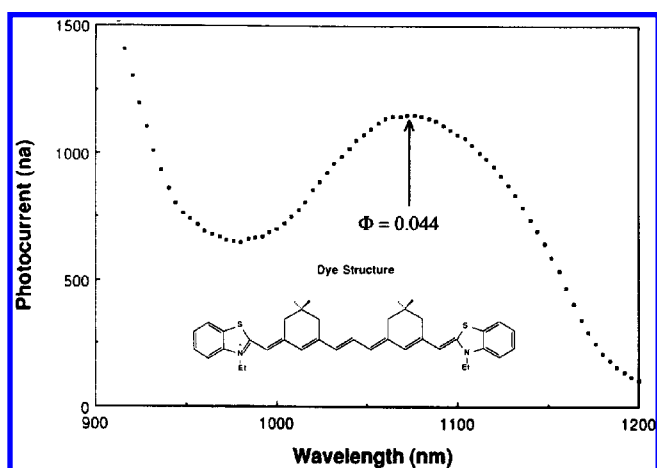


FIGURE 4. The photocurrent spectrum of an infrared absorbing thiapenta-carbocyanine dye (structure shown inset) is shown for a WSe_2 single crystal electrode where the use of a dry methanolic LiCl electrolyte both stabilized the dye and resulted in an IPCE of 4.4%. The atomically flat and clean surface of this semiconductor as a layer compound and the removal of water from the electrolyte resulted in an estimated APCE near 100%.

Overall the APCE values for electron transfer from the adsorbed excited dye to the semiconductor remained low at about 0.01 for low dye surface coverages up to monolayer coverage. Several factors may have contributed to this behavior. A hydrated or contaminated surface could interfere with the electronic coupling of the excited chromophore with the semiconductor conduction band or form a layer that traps electrons from the excited dye and leads to a very fast recombination. Given the low optical density of a single layer of dye and the instrumental techniques available at the time, it was not possible to distinguish these pathways for dye quenching.

About the time that one of the coauthors (M.T.S.) was measuring sensitization currents for dyes on metal oxide crystals, the other coauthor (B.A.P.) was investigating layered compound semiconductors such as MoS_2 , MoSe_2 , and WSe_2 for use in photoelectrochemical photovoltaic and photoelectrolysis cells.^{15–17} The two-dimensional layered structure of these materials allowed for easy cleavage of the crystals to expose a fresh, clean, and atomically flat surface devoid of surface states due to dangling bonds. The fortuitous arrival of M.T.S. for a sabbatical leave at the Solar Energy Research Institute (SERI now called the National Renewable Energy Laboratory) led to the first collaborative experiments on the sensitization of these crystals. The 1.1–1.2 eV band gaps of these compounds,²⁰ however, required an infrared cyanine dye to be used as a sensitizer and 3,3'-diethyl-9,11:15,17-dineopentylene-2,2'-thiapenta-carbocyanine (structure in Figure 4), was identified as a candidate dye. The experiment revealed that it efficiently sensitized n- WSe_2 at 1070 nm with IPCE values as

high as 4.4%, a remarkable value for a monolayer of a dye. An estimate of the absorption of a monolayer of this dye led to calculated APCE values for the dye-sensitized electron transfer of near 100%.¹⁸ Figure 4 shows a photocurrent spectrum for the sensitization of WSe_2 with this dye.

At this point, it was clear that the clean, renewable, and reproducible surfaces of layered semiconductors have advantages for studying dye sensitization. In order to extend the study of the sensitization of the layered semiconductors into the visible regime, where there are both more available dyes and more interest, semiconducting SnS_2 , a layered material with a larger band gap of 2.2 eV, was identified as a promising material. Large crystals of this material were grown using the Bridgman method and vapor transport, and after considerable trial and error, the doping level of the crystals could be controlled by chlorine substitution for sulfur.¹⁹ A typical crystal is shown in the top of Figure 5. This electrode material²⁰ allowed for the study of many dye sensitizers in the visible region.

The very high APCE values could be converted to high IPCE values when exfoliation of the SnS_2 layers allowed dye to penetrate between layers producing multiple dye/semiconductor interfaces, and IPCE values as high as 16% for methylene blue sensitization were observed on such areas. This approach was extended by developing an anisotropic oxidative etching procedure that formed porous structures within the SnS_2 electrode shown in Figure 5. The high surface area of these porous structures greatly increased the IPCE values for sensitization to as high as 35%.²¹

For semiconductors with a very low mobility perpendicular to the surface, to which class these layered compounds belong, a one-dimensional Onsager model was developed to describe the relation between current flow and applied potential.²² This model was derived in analogy to that used to describe the dye sensitization of organic molecular crystals²³ but represents a generalizable mathematical description of oxidation reactions at semiconductor electrodes. The work showed that with semiconductor doping densities as low as 10^{15} cm^{-3} , the reverse dark reduction reaction of electrons in the semiconductor with oxidized dyes on the surface was sufficiently fast that a bias of several hundred millivolts was required to obtain the complete separation of the injected electron from oxidized dye as indicated by a light-limited plateau of the sensitization current. The model also predicted that because of charge separation by the potential gradient near the semiconductor surface, the higher doped crystals should yield more ideal photocurrent voltage behavior and higher IPCE values than lower doped crystals. These predictions were

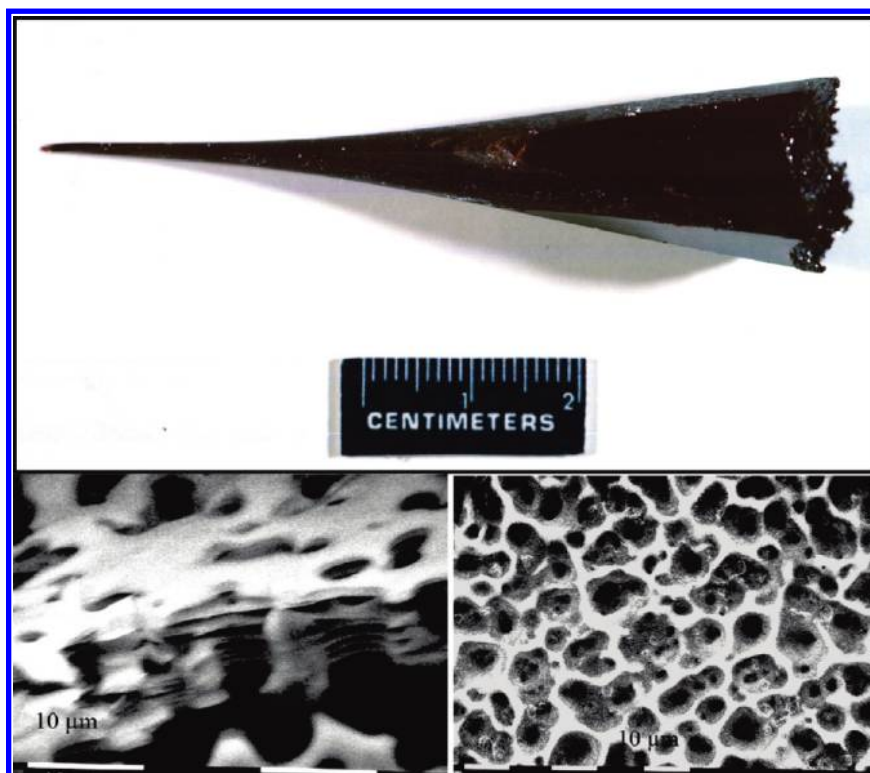


FIGURE 5. A photograph of a SnS_2 crystal that was grown using the Bridgman technique showing several cleavage planes from the twinned crystal (top). Bottom left shows a side view of the “parking garage” structure obtained from photetching a SnS_2 crystal to obtain a high surface area. Below right is a top view of the same photoetched crystal.

not unambiguously verified by the experiments with SnS_2 crystals grown with various doping densities²¹ implying that the rate of the dark back reaction may be the controlling kinetic factor in this system. Competition from back electron transfer is consistent with the correlation of reduced IPCE values when the potential of the dye ground state approaches the energy of the conduction band edge as was observed on SnS_2 .²⁰

Spectral sensitization of semiconductor surfaces usually involves many dye molecules in close contact that interact to form various aggregates on the surface. These aggregates have been very well-known and exploited in silver halide spectral sensitization but only through the spectral shifts associated with H or J aggregation. The atomically flat van der Waals surface of the SnS_2 electrodes provided an ideal surface to examine the structure of dye aggregates on the surface. Some of the squaraine dyes that had their 2D surface ordering imaged with STM on HOPG^{24,25} were also capable of sensitizing SnS_2 . Figure 6 shows some AFM images and the corresponding photocurrent spectra for some SnS_2 electrodes. The high extinction coefficients of the squaraine dyes, which were adsorbed on both sides of the crystal, allowed for simultaneous photoelectrochemical and optical absorption measurements on the dye monolayer(s).^{26,27} The dye, which is

totally insoluble in the electrolyte where the photocurrent spectra were measured, was deposited on the SnS_2 surface either by dipping the crystal in a methylene chloride solution of the dye or dropping and evaporating the methylene chloride solution on the crystal. AFM images of the SnS_2 surface revealed that the dipping method produced flat layers of the dye covering the surface with both uncovered areas and areas showing a second dye layer as seen in Figure 6a,b, whereas the dropping method produced relatively very large and high 3D rod-like aggregates on the surface that tended to align along the 60° symmetry axes of the crystal with areas between these aggregates covered with feathery 2D structures as seen in Figure 6c,d. The photocurrent spectra of these two surfaces in Figure 7a,b show that the large structures prepared by the dropping method were associated with a J aggregate that was absent in the dipped samples. Furthermore the large aggregates also produced photocurrents of the opposite sign at negative biases (circles in Figure 7b) indicating that these aggregates were behaving as a bulk-like p-type semiconductor. In both samples, there was also some evidence for H-aggregation in the photocurrent spectra at around 615 nm that was not present in the absorption spectrum of the dry surface.

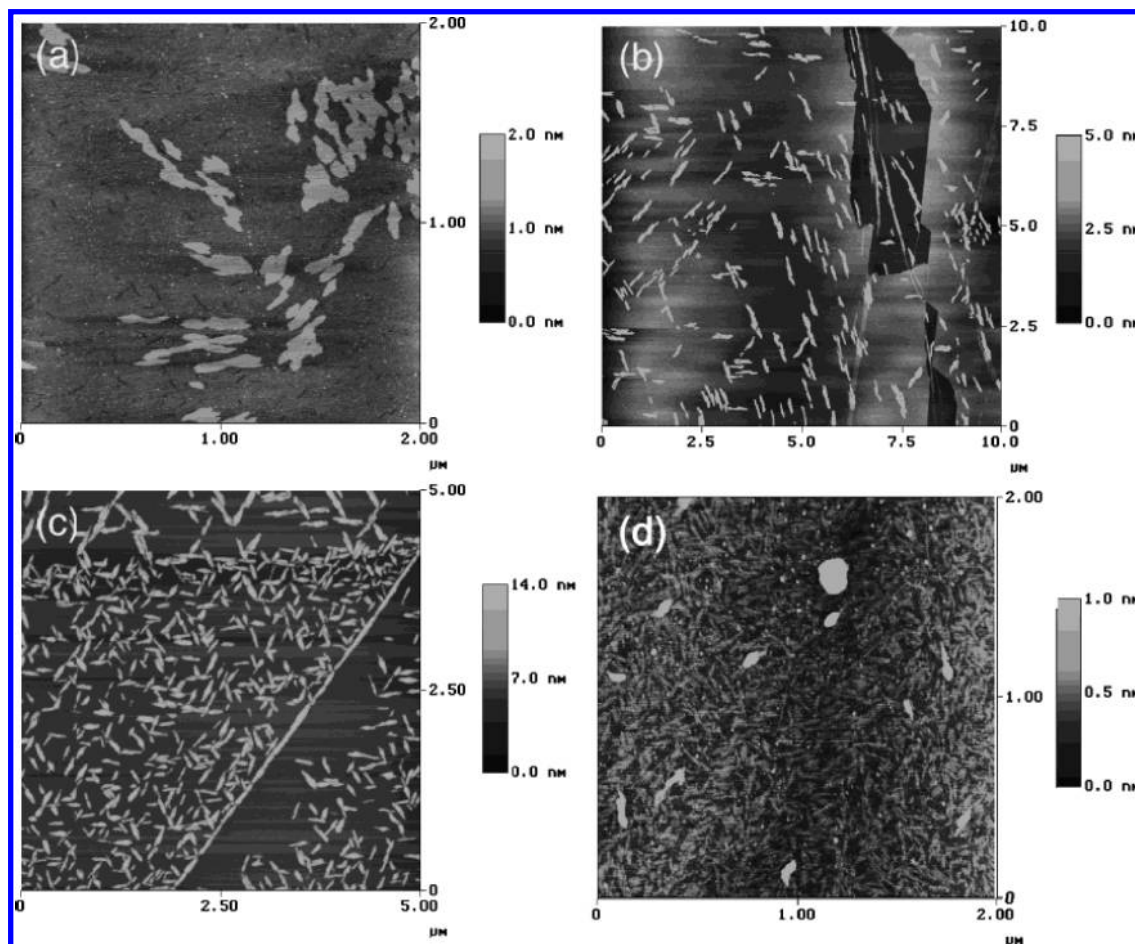


FIGURE 6. AFM images obtained for nanostructures of bis(4-dimethylamino-2-dihydroxyphenyl) squaraine (1-1OHSQ) adsorbed on SnS_2 . Deposition was performed by dipping a SnS_2 piece in $8 \mu\text{M}$ 1-1OHSQ solution (in dichloromethane) for 2 min (a, b) or by dropping dichloromethane solution containing ca. $1 \times 10^{-10} \text{ mol cm}^{-2}$ equivalent of 1-1OHSQ on SnS_2 followed by solvent evaporation (c, d). Notice the much greater z scale in panel c.

Dye Sensitization of Oxides

A dye-sensitized solar cell made with a single crystal relies upon the space charge electric field within the semiconductor/liquid Schottky barrier to separate charge and is therefore photovoltaic in nature. This cell has low power conversion efficiencies owing to both the low optical density for light absorption leading to small photovoltages and a fast dark recombination reaction leading to low fill factors. Dye-sensitized solar cells were transformed into practical utility through the work of Grätzel with the introduction of porous nanocrystalline anatase TiO_2 electrodes derivatized with covalently attached carboxylated inorganic complex sensitizers.²⁸ This nanocrystalline dye-sensitized solar cell (DSSC) has no built-in electric fields to separate charge at the semiconductor–electrolyte interface but instead relies on photogenerated chemical potential gradients to produce current. The cell has a high surface area electrode and thereby solves the problem of the low optical density of a monolayer of dye on a sin-

gle crystal electrode by providing many interfaces for light absorption and electron injection. In addition, the direct attachment of carboxylated dyes to a dry recently prepared metal oxide surface avoids the deleterious effect of a hydrated or contaminated metal oxide surface layer upon the photocurrent production efficiency. The insulating nature of the anatase nanoparticles precludes the fast reduction of an oxidized sensitizer molecule and fortuitously has a very low exchange current density for the reduction of oxidized regenerator, which is usually triiodide.

Up to this point, all of the work on sensitizing TiO_2 single crystals had been done with commercially available rutile crystals and with dye molecules in solution with a dynamic equilibrium adsorption to the surface rather than covalently bound to the surface as in the DSSC. However, the lower temperature polytype of TiO_2 anatase is preferred over rutile in the DSSC, although both forms are found to work.²⁹ Large anatase crystals have not been artificially grown, but well-formed

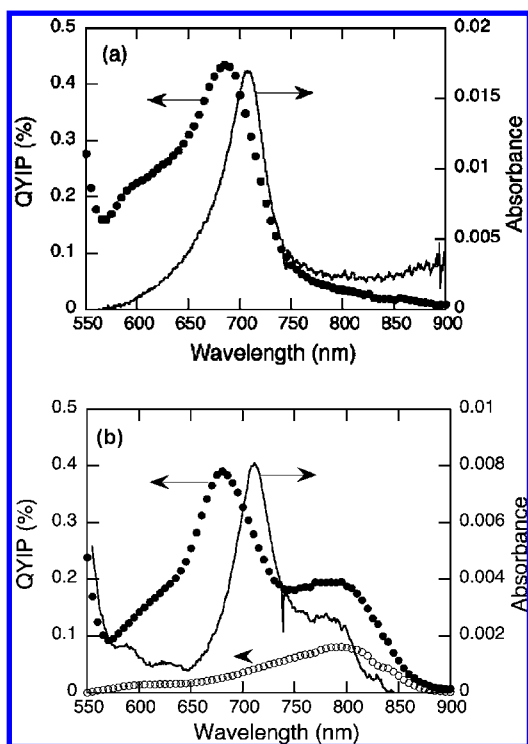


FIGURE 7. (a) Vis–NIR absorption spectrum (solid curve) and photocurrent (quantum yield per incident photon) spectrum obtained at +0.7 V vs SCE bias (open symbol) for 1-1OHSQ on SnS₂ prepared by the dipping method (8 μM for 2 min). Note that the absorption spectrum was taken in air and contains contributions from adsorbates on both sides of SnS₂ surface. (b) The same measurements are shown for the drop method of dye deposition. The open circles represent the action spectrum of a cathodic current observed at a negative bias.



FIGURE 8. A natural anatase crystal mined in Hargvidda, Tyssedal, in Norway shown on a matrix of small quartz crystals. The crystals are darkly colored indicating that they contained natural impurities or reduced Ti⁴⁺ sites. These bipyramidal crystals exhibit low-energy growth surfaces with the large wedge-shaped (101) faces and (001) end-caps (photograph by B.A.P.).

natural anatase crystals from Norway (Figure 8), Brazil, Pakistan, and some other locations are available. When the crystals were mounted as photoelectrodes, Mott–Schottky analysis revealed that their doping levels were in the low 10¹⁸ to low 10¹⁹ cm⁻³ range, producing good conductivity and allowing the formation of a space charge layer. AFM imaging and XPS measurements revealed that the surfaces of these crystals had large areas of atomically flat terraces and that the

surface concentration of impurities were minimal since only about one in less than a thousand surface atoms was an impurity atom. This gave us confidence that we could study the surface chemistry of these natural crystals and the results would be applicable to the nanocrystalline solar cell, since the 10–50 nm diameter nanocrystalline TiO₂ grains are not small enough to show quantum confinement effects and their faces are large compared with the size of the adsorbed dye molecules. The predominate faces of the natural anatase crystals were (101), also predominate in the nanocrystalline films, and (001). Our original publication reporting the sensitization of natural crystals of anatase TiO₂ with a ruthenium complex dye, *cis*-di(thiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(II) (commonly known as N3) showed very low IPCE values and required soaking of the electrode in dye solution overnight at each concentration to measure the dye adsorption isotherm.³⁰ Even then irreproducible dye-sensitized photocurrents were measured.

Given the importance of the sensitization of TiO₂ electrodes in a nanocrystalline dye-sensitized solar cell, a procedure was sought that would produce high APCE values for chromophores bound to TiO₂ single crystal electrodes providing an ideal simple model system for examining sensitization reactions at well-defined semiconductor surfaces. Aspects such as the actual dye binding sites, crystal face dependence of dye binding, competitive adsorption, dye adsorption and desorption kinetics, and ordering of dye molecules on the semiconductor surface could all be studied in a controlled fashion.

After extensive effort, a simple polishing and annealing procedure followed by a UV treatment of the electrodes was developed that not only provided reproducible dye coverages but also produced terraced surfaces with large regions of atomic flatness. Reproducible experiments resulted by simply repeating the UV treatment without having to repolish and reanneal the crystal, but eventually repeating the entire procedure is needed to rejuvenate the crystal surfaces. The UV treatment that produces highly oxidizing holes in the TiO₂ valence band and is well-known as a method to clean these surfaces should completely photooxidize any ubiquitous organic impurities that could competitively bind to or block the reactive sites on the metal oxide surface and prevent dye binding. This surface preparation procedure was used for single crystal anatase (101), (001); rutile (100), (001); and brookite surfaces and verified via AFM and low-energy electron diffraction (LEED) to produce atomically flat terraces as seen in Figure 9.³¹ AFM performed before and after many extended

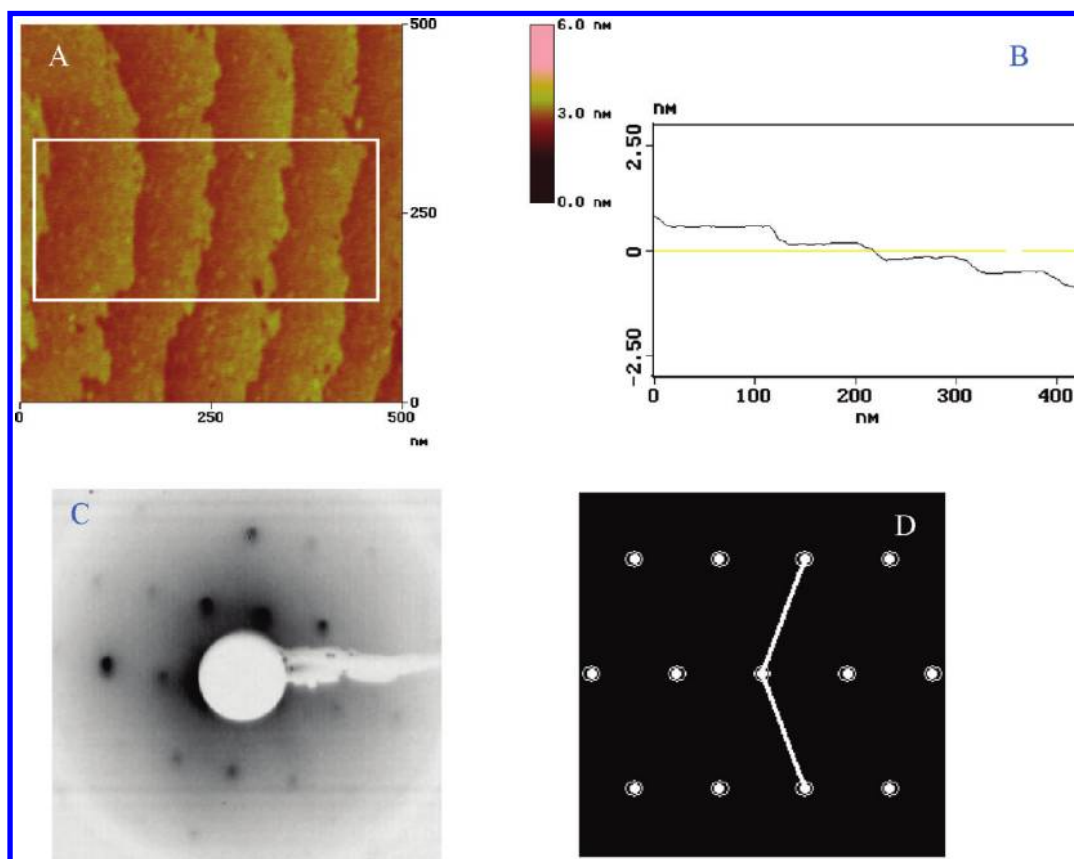


FIGURE 9. (A) Topographic AFM image and (B) section average of the anatase (101) surface. The average step height is 0.36 nm corresponding to a single unit cell step. (C) Observed LEED pattern (100 eV) of the as-prepared surface; a calculated LEED pattern is given in panel D.

UV treatments demonstrated that the photoelectrochemical process did not change the flat terraced structure of the surfaces.

In experimentation that utilized this pretreatment, N3 was used to sensitize four low-index anatase and rutile surfaces, and high IPCE values of nearly 0.01 were observed. The coverage dependence of the incident photon to current efficiencies (IPCE) was measured for all four surfaces to construct isotherms assuming that the IPCE was directly related to coverage. The IPCE was much higher on anatase (101) and rutile (100) than on the other two surfaces as can be seen in Figure 10. The APCE values on these two surfaces, estimated from a calculation of the absorbance of a monolayer of N3, were near unity for electron transfer from excited N3.³² The kinetics of N3 adsorption was also studied on the four surfaces by following the time dependence of current flow after N3 was added to the electrolyte. The initial adsorption step was very fast and not resolved by our slow measurement but adsorption kinetics for a slow adsorption step could be fit with a Langmuir kinetic model. The differences in the adsorption of N3 and the IPCE values were analyzed in terms of the structure of the N3 and the geometry and reactivity of the bind-

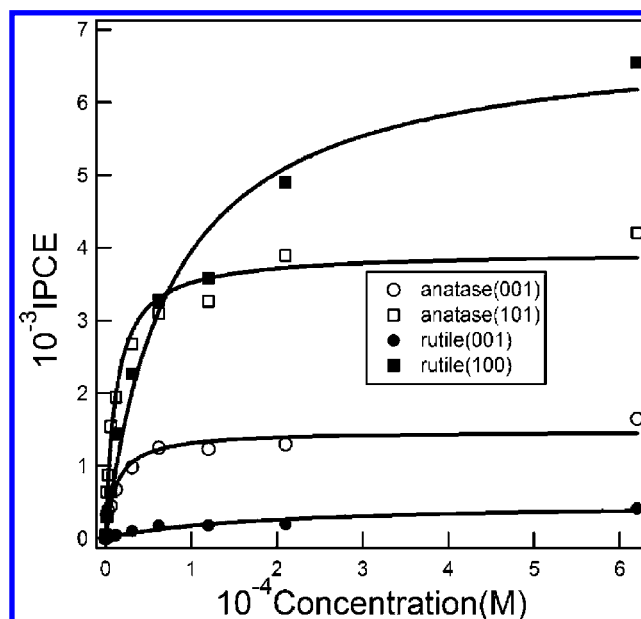


FIGURE 10. Isotherms for N3 adsorption onto the four TiO₂ crystal surfaces.

ing sites on the four surfaces. Desorption of N3 from the studied TiO₂ surfaces was very slow with very little loss of photocurrent over extended times. An immediate loss could

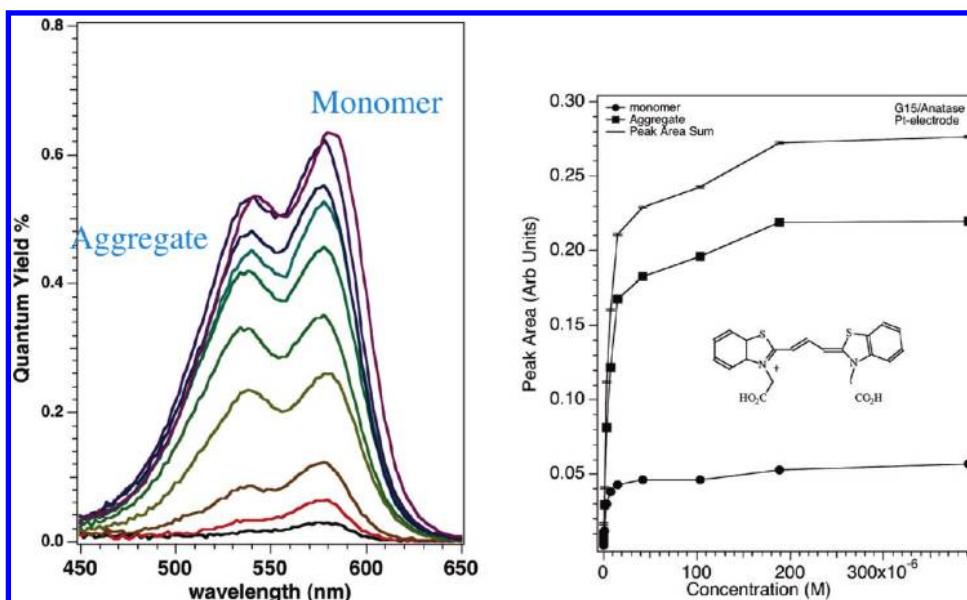


FIGURE 11. The IPCE spectra of a dicarboxylated thiacyanine dye reveals aggregation as the surface concentration of the dye increases. This is seen through the relative heights of the two peaks in the photocurrent spectrum. An analysis of these spectral features provides an effective adsorption isotherm for both the monomer and aggregate form of the dye on the surface.

be explained by loss of N3 molecules that were bound by only one carboxylate group, which were less tightly attached to TiO₂ than dyes with multiple attachments.

The N3 dye and related ruthenium-based dyes have extended spectral coverage making them good choices for dye-sensitized solar cells, but the metal-to-ligand charge transfer excitations do not have very high extinction coefficients, resulting in the need for thicker nanocrystalline oxide layer for a more complete harvest of solar photons. Organic dyes with π to π^* transitions have much higher extinction coefficients and can extend their spectral coverage by formation of H and J aggregates as mentioned above. Therefore a series of structurally similar dicarboxylated thiacyanine dyes that had previously been investigated for use in nanocrystalline solar cells^{33,34} were investigated on the single crystal TiO₂ surfaces.³⁵ Calculated APCE values from 5% to 100% were measured for the sensitization of anatase (101) surfaces, and photocurrent spectroscopy showed that the various dyes had differing amounts of H aggregates and dimers on the surface, the relative amounts of which could be determined by fitting the photocurrent spectra. An example showing a series of photocurrent spectra and the relative coverage of the various forms of dye on the surface is shown in Figure 11. In order to extend the spectral coverage of the thiacyanine dyes over the entire visible spectrum, a single crystal was exposed to a “cocktail” of various dyes chosen for their overlapping spectral range. Figure 12 shows the result of

the multidye sensitization. An interesting observation is that the H aggregates that are prominent in the photocurrent spectra of the individual dyes are mostly absent when the dyes are combined. Apparently the mixture of dyes interferes with the formation of the aggregates.

Owing to the small absorbance of submonolayer coverages of adsorbed dyes, direct optical measurements of the amount of dye bound to the surface require the use of multiple reflection optical techniques. Therefore a previously developed photochronocoulometric method was adapted to oxide semiconductors sensitized with covalently attached dyes to measure the amount of adsorbed dye.³⁶ This technique was developed in the early 1980s to measure adsorbed triiodide on layered semiconductor electrodes.³⁷ Directly measuring the surface coverage of the dyes helps to verify our assumption that the IPCE values measured were directly proportional to dye coverage. The surface-bound dyes with no regenerator in solution are irreversibly oxidized by exposure to a light pulse at the sensitization wavelength when the semiconductor electrode is in depletion rather than a potential step that is used for chronocoulometry on a metal electrode. The ruthenium-based N3 dye shows the expected linear dependence of the photooxidation rate constant on light intensity, whereas a dicarboxylated thiacyanine dye shows a square root dependence of its photooxidation rate on light intensity. A typical photocurrent transient for a thiacyanine dye is shown in Figure 13.

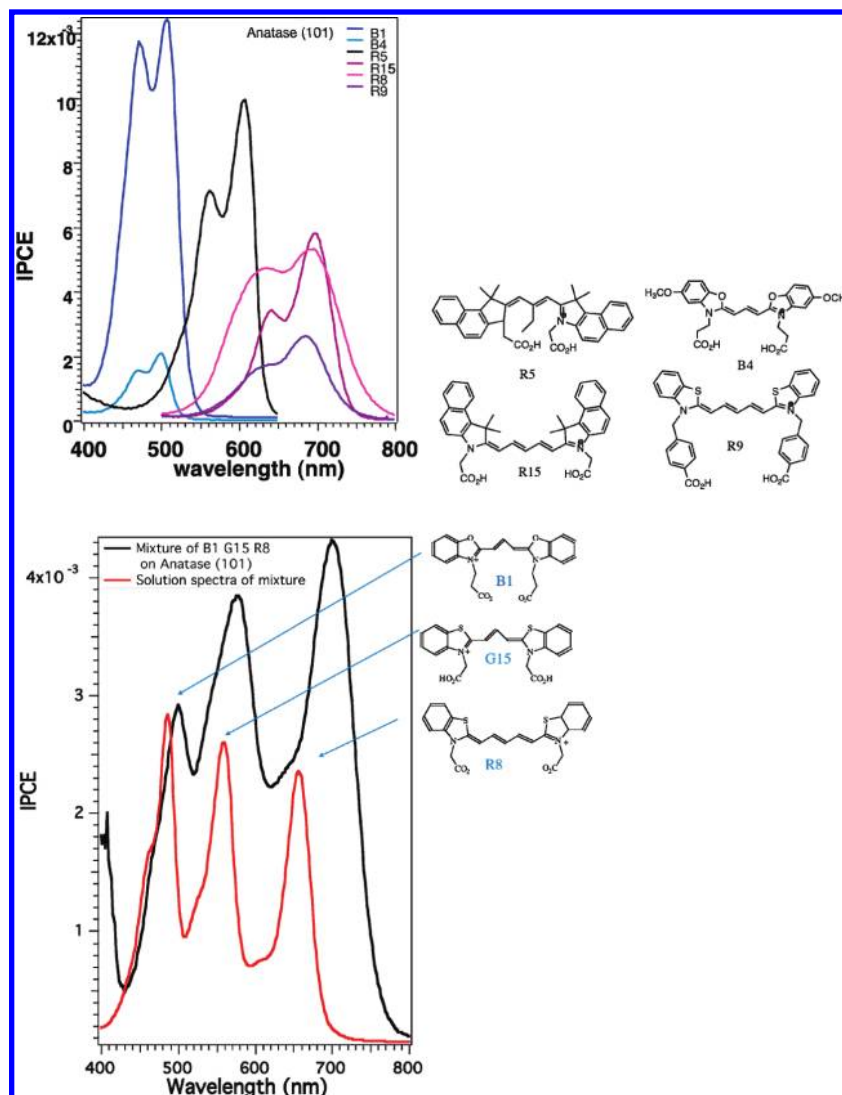


FIGURE 12. (top) The photocurrent response spectra of various individual dicarboxylated cyanine dyes on TiO_2 anatase (101) single crystal electrode surfaces reveals aggregated forms of the dyes with very high IPCE values. The dye structures not shown in the bottom panel are shown to the right. (bottom) When a mixed solution of dyes B1, G15, and R8 is presented to the anatase (101), the dyes attach in a molecular mixture that precludes the aggregation evident for the single dyes in the top panel.

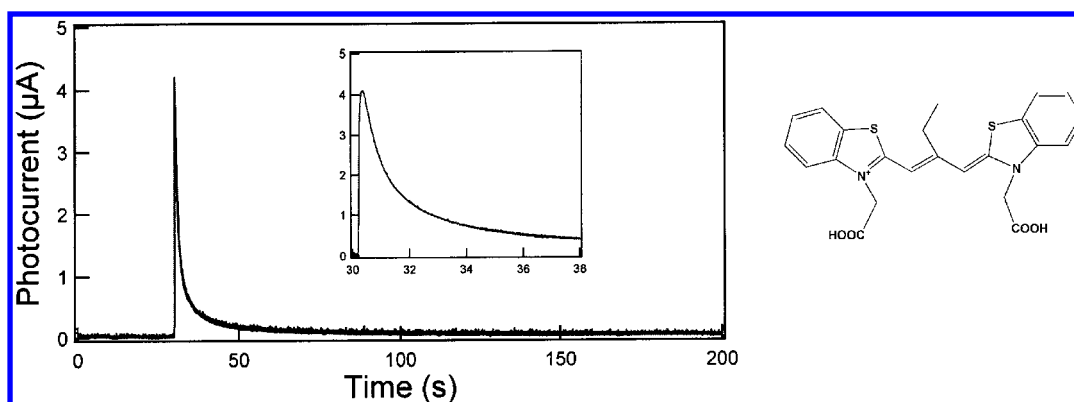


FIGURE 13. Transient photocurrent for photooxidation of G7 dye (structure shown to the right) adsorbed on a rutile(100) surface. The light pulse is initiated at about 30 s into the experiment. The inset shows a zoom-in of the early time transient. Integration of the current transient yields a charge proportional to the coverage of the G7 dye.

During our TiO₂ sensitization experiments with the dicarboxylated thiocarbocyanine dyes and hydroquinone as the regenerator, it was observed that extended illumination resulted in desorption of a dye from semiconducting oxide crystal. Almost no desorption was found under the same conditions when KI was used as the regenerator for the thiocyanine dyes or for N3 even when hydroquinone was the regenerator. Intermittent illumination experiments suggest that the oxidation products of the hydroquinone regenerator competed for dye adsorption sites. By comparing the photocurrent decay at both dye monomer sensitization maximum and the dimer sensitization maximum, a rearrangement of monomer into dimer was observed. A kinetic model for the photocurrent decay as a function of desorption time was derived, and the desorption rate constants were obtained by fitting the experimental data to the model.³⁸ This work revealed that the surface chemistry, photophysics, and photochemistry of these dye–semiconductor interfaces contain many subtleties and that there is still much to be understood and discovered about them.

Quantum Dot Sensitization

Quantum dots (QDs) or nanocrystalline semiconductor particles have recently been investigated as sensitizers in porous nanocrystalline solar cells.^{39,40} The promising aspects of the quantum dots include higher absorption coefficients than dye molecules, based on a particle/molecule comparison rather than the number of atoms, and potentially increased stability owing to their inorganic nature. The possible exploitation of quantum confinement effects such as increased photocurrent yields as a result of multiple exciton generation (MEG) from photons of more than twice the lowest transition energy in the quantum dot has further stimulated investigation into their use as sensitizers.⁴¹ Our feeling is that the detection of these important effects will be more straightforward on well-characterized crystal surfaces. Presently no quantum dot sensitized nanocrystalline solar cell has approached the efficiency or stability of the conventional dye-sensitized solar cell. We therefore initiated some studies on sensitizing single crystal oxide surfaces with QDs to better investigate the role of coverage and arrangement of the quantum dots on the semiconductor surface, as well as the role of the ligands linking the QD to the surface and surfactant QD capping agents on the charge transfer from the QDs to the semiconductor.⁴² Preliminary data indicates that many of the surfactants are competitive binders for the surface sites, inhibiting binding of QDs or dyes such as N3, resulting in very irreproducible photocurrents from the QDs and other dyes on the TiO₂ surfaces. Figure 14 illustrates typical IPCE spectra of 3-mercaptopropionic

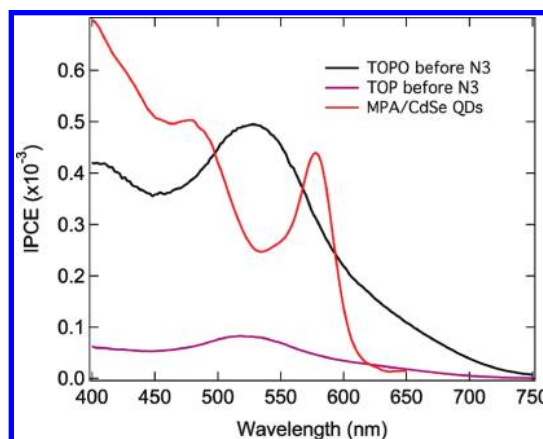


FIGURE 14. Sensitization of the (101) surface of an anatase crystal using CdSe QDs with a diameter of about 5 nm showing the sharp exciton feature at about 578 nm (red curve). The black curve was obtained for N3 dye after exposing the surface of the same crystal to trioctylphosphine oxide (TOPO), which shows nearly the same sensitization yield when compared with no exposure to TOPO. The lower (purple) sensitization spectrum is for the crystal sensitized with N3 after previously being exposed to trioctylphosphine (TOP).

acid (MPA)-capped CdSe QDs on an anatase (101) crystal surface where AFM images indicated a nearly complete monolayer of QDs on the surface and experiments indicate that excess MPA does not block QD binding. The deleterious effect of the presence of an excess of some organic surfactants, commonly used in the synthesis and stabilization of QDs, on the sensitization yield of N3 is also shown for comparison. The influence of various surface chemical treatments on QD binding leading to optimal surface coverages with high electron injection and collection yields is currently being investigated.

Summary, Conclusions, and Future Outlook

The study of the dye sensitization of semiconductor crystals using equilibrium adsorption from solution has evolved from having to detect very low IPCEs on oxide crystals to the measurement of much higher yields on freshly cleaved layered semiconductor materials. The development of the dye-sensitized solar cell has stimulated the extension of these studies to dyes covalently attached to single crystal oxide surfaces, where again high sensitization yields can be obtained. Simple models for the excited state dye injection process and the various recombination pathways have been developed and have qualitative agreement with the experimental values, showing promise for providing deep insight and predictive value in the sensitization process. However more sophisticated models for charge transfer from the localized electronic states of the sensitizer to the extended states of the semiconductor need to be developed. Scanning probe microscopies have only begun to provide the molecular level information about the orientation and organization of dyes and

QD structures on these surfaces, information that will be vital for developing the theoretical models that must include sensitizer–substrate and sensitizer–sensitizer interactions. Future studies will include simultaneous measurement of absorption spectra and photocurrent spectra to determine the absolute efficiencies of the adsorbed dyes, their various aggregates, and quantum dots. In addition, the application of single molecule spectroscopies combined with scanning probe techniques to the dye/QD semiconductor interface will supply information about the different nanoscopic environments on the semiconductor surface such as terraces, steps, kinks, defects and different chromophore arrangements in aggregate, cluster, and monomer form and their influence on light absorption and electron injection yields. Such studies will aid in the design of the next generation of efficient and stable sensitized solar cells for renewable energy that are cost-effective to scale up and manufacture.

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