

Photoinduced Charge Separation in Dye-Sensitized Films of Smooth and Nanocrystalline TiO_2



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Photoinduced Charge Separation In Dyesensitized Films Of Smooth Nanocrystalline Tio

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Photoinduced Charge Separation In Dyesensitized Films Of Smooth Nanocrystalline TiO₂:

Photoinduced Charge Separation in Dye-sensitized Films of Smooth and Nanocrystalline TiO₂ J. E. Kroeze, 2004
This is a Ph D dissertation Life on earth is powered by the sun Green plants and many bacteria use sunlight to provide their energy needs Moreover while it is the earth's only inexhaustible energy source solar light forms the most important source of sustainable energy As the energy needs of the earth are likely to double in the next 50 years while the fossil fuel reserves will only last for another 200 years the stage is set for a major energy shortage unless renewable energy sources can cover this deficit The annual solar radiation received by the earth amounts to 31024 J 5% of which is UV 43% visible and 52% IR light This number exceeds the present world energy consumption by several thousand times Contents include Introduction Materials and methods Contactless determination of the efficiency of photo induced charge separation in a porphyrin TiO₂ bilayer Photo induced charge separation in TiO₂ Porphyrin bilayers studied by time resolved microwave conductivity Efficient charge separation in a smooth TiO₂ Palladium porphyrin bilayer via long distance triplet state diffusion Singlet and triplet exciton diffusion in a self organizing porphyrin antenna layer Electrodeless determination of the trap density decay kinetics and charge separation efficiency of dye sensitized nanocrystalline TiO₂ Contactless determination of the photoconductivity action spectrum exciton diffusion length and charge separation efficiency in polythiophene sensitized TiO₂ bilayers Triplet exciton diffusion and delayed interfacial charge separation in a TiO₂/PdTPPC bilayer Monte Carlo simulations The application of a low bandgap conjugated oligomer for the sensitization of SnO₂ and TiO₂ Photoinduced Charge Separation in Molecular Films Nigel A. Surridge, 1987 **Canvas of Optics behind Nanocrystalline TiO₂ Film Engaged in Dye-Sensitized Solar Cells**, 2015 *Dye Sensitized N-p Heterojunctions of Titanium Dioxide and Copper Thiocyanate, a New Interface for Photoinduced Charge Separation* Brian C. O'Regan, 1998 **Effect of Electron-Electron Interaction on Transport in Dye-Sensitized Nanocrystalline TiO₂** A. J. Frank, J. Van de Lagemaat, N. Kopidakis, N. R. Neale, 2005
Experimental measurements and continuous time random walk simulations on sensitized electrolyte infused porous nanocrystalline TiO₂ films show that the actual electronic charge in the films is significantly larger than that estimated from small perturbation methods by a constant light intensity independent factor This observation can be explained by small perturbation techniques measuring the chemical diffusion coefficient of electrons instead of the normally assumed tracer diffusion coefficient of electrons The difference between the two diffusion coefficients is attributed to the presence of an exponential density of states through which electrons interact At high light intensities an additional extra component owing to Coulomb interactions between the electrons is expected to arise **Surface Binding and Organization of Sensitizing Dyes on Metal Oxide Single Crystal Surfaces**, 2010 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 forty years Even today single crystal surfaces prove to be more controlled experimental models for the study of dye sensitized semiconductors than the nanocrystalline substrates We analyzed 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 SnS₂ and TiO₂ electrodes to serve as reproducible model systems for charge separation at dye sensitized solar cells This process involves cleaving the SnS₂ electrodes and a photoelectrochemical surface treatment for TiO₂ 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

Preparation of nanocrystalline TiO₂ films and their further modification with noble metal nanoparticles for Dye-Sensitized Solar Cell □□□,2009 *Novel Soft*

Chemistry Synthesis of Titanium Dioxide for Applications in Dye-Sensitized Solar Cells and Photocatalysis Aiat

Hegazy, University of Waterloo. Department of Chemical Engineering, 2012 Although the high cost of solar cells prevents them being a primary candidate for energy production great attention has been paid towards them because of the depletion of the conventional energy sources fossil fuels and the global warming effect and the need to provide power to remote communities disconnected from the power grid To reduce the cost thin film technologies for silicon solar cells have also been investigated and commercialized but dye sensitized solar cells DSSC have been considered as a promising alternative even for the silicon thin films with efficiency exceeding 10% Compared with silicon based photovoltaic devices DSSCs are quite complex systems that require an intimate interaction among components Within the last few years conclusive smart solutions have been provided to improve the efficiency of these cells with solar efficiency that makes them potential competitors against silicon devices The most successful systems use titanium oxide as a core material tuned to collect and transmit the electrons generated by the photo excitation of dye molecules However most of the solutions demonstrated so far require a thermal treatment of the TiO₂ photoelectrodes at temperatures that preclude using any flexible organic substrate This treatment prevents development of any roll to roll manufacturing process which would be the only way to achieve cost effective large scale production In order to overcome this major drawback a novel synthesis of TiO₂ at room temperature is described in the present document This synthesis leads to 4-6 nm nanocrystalline anatase the desired phase of titanium oxide for photoactive applications An intensive study was carried out to explore the properties of these nanoparticles via a mixture design study designed to analyze the influence of the starting composition on the final TiO₂ structure The influence of a post

synthesis thermal treatment was also explored This 4 nm nanocrystalline TiO₂ exhibits a high specific surface area and a good porosity that fulfills the requirements for an efficient photoanode a high surface area allows high dye loading and hence increases photocurrent and photo conversion efficiency Another important result of this study is the band gap as it confirmed that nanocrystalline anatase has an indirect band gap and a quantum confinement for a crystal size of less than 10 nm This result well known for bulk materials had been discussed in some previous publications that claimed the effectiveness of a direct band gap Following this synthesis and the structural and spectroscopic analyzes carried out in parallel photocatalytic study was an important tool to further explore the semiconducting properties of this material Additionally our material gave very promising results in photocatalytic dye degradation compared to the commercial products even if it was not initially synthesized for this application We assign these performances to the improved crystallinity resulting from thermal activation without changing the crystal size and to the ability to optimize the surface This photocatalytic study gave us insights into the methods that optimize the electronic structure of the titanium oxide Hence we decided to thermally activate the nanoparticles before the preparation of films to be inserted into DSSCs At this stage as the thermal activation applies to the powder the resulting material can still be used with flexible substrates We have successfully integrated these nanoparticles in dye sensitized solar cells Various organic additives were added to the TiO₂ paste used to prepare photoelectrode films to increase the porosity of the film and have a crack free film with good attachment to the substrate We demonstrated that the dye was chemically attached to the TiO₂ surface which led to better electron transport Different treatment methods UV and thermal were applied to the film to cure it from organic additives and improve the electronic connectivity between the particles When the UV treatment was applied as a single method i e without thermal treatment the cell performance was lower but a combination of thermal treatment and UV enhanced this performance We compared our nanoparticles to the reference material used in most of the studies on DSSC that is TiO₂ Degussa with cells prepared the same way Our nanoparticles revealed higher overall conversion efficiency As the dye attachment to the TiO₂ surface is an important parameter that enhances the cell efficiency so we checked via ATR FTIR how the dye attached to the TiO₂ surface In addition FTIR UV Vis and IV measurements revealed that the amount of dye adsorbed was increased through HCl treatment of the photoelectrode We also checked the internal resistance of the cell using impedance spectroscopy and the analysis proved a successful integration of the nanoparticles in dye sensitized solar cells as there was an increase in both the electron life time and the recombination resistance and a decrease in the charge transfer resistance compared to the commercial powder

Photo-induced Charge Transfer at Heterogeneous Interfaces Joseph M. Lanzafame, 1992 **Spectroscopic and Photoelectrochemical Studies of Metal-free Dyes for Applications in Dye-sensitized Solar Cells** Kacie Ryan Mulhern, 2013 In this dissertation we present a series of novel chalcogenorhodamine dyes bearing phosphonic acids and carboxylic acids for sensitizers of nanocrystalline TiO₂ in dye sensitized solar cells DSCs We studied the effect of surface

attachment functionality and aggregation on the persistence electron transfer reactivity and overall photoelectrochemical performance of the dyes on TiO₂ for DSCs. The dyes were constructed around a 3,6-bis(dimethylamino)chalcogenoxanthylum core and varied in the 9-substituent: 5-carboxythien-2-yl in dyes 1-E, 4-E, O-Se; 2-carboxythien-3-yl in dyes 2-E, 5-E, Se; 5-phosphonothien-2-yl in dyes 3-E, 4-E, O-Se; 4-carboxyphenyl in dyes 4-E, 5-E, O-S; and 4-phosphonophenyl in dyes 5-E, 4-E, O-Se. Monolayers of 1-E, 3-E, 4-E and 5-E on nanocrystalline TiO₂ films consisted of both H-aggregated and non-aggregated dyes, whereas 2-E underwent little or no aggregation upon adsorption. With the exception of 2-E, surface coverages of dyes and the extent of H-aggregation varied minimally with surface attachment functionality, structure of the 9-aryl group and identity of the chalcogen heteroatom. Carboxylic acid functionalized dyes 1-E and 4-E desorbed rapidly and completely from TiO₂ into acidified CH₃CN, but phosphonic acid functionalized dyes 3-E and 5-E persisted on TiO₂ for days. We used transient absorption spectroscopy to characterize excited state electron injection from a 1-Se, 2-Se and 3-Se to TiO₂. Injection of electrons from photoexcited dyes into TiO₂ yielded the dication radical 1-Se^{•+}, 2-Se^{•+} and 3-Se^{•+} and an associated transient absorption at wavelengths shorter than 540 nm, the amplitude of which was proportional to the quantum yield of electron injection, Φ_{inj} . Our data reveal that Φ_{inj} for H-aggregated 1-Se was approximately 2-fold greater than Φ_{inj} for non-aggregated 1-Se and approximately 3-fold greater than Φ_{inj} for non-aggregated 2-Se. Additionally, the Φ_{inj} from H-aggregated 3-Se was 2.0–1.3-fold greater than from monomeric 3-Se. Therefore, H-aggregation increased the efficiencies of both light harvesting and electron injection. Comparison of the analogous carboxylic acid functionalized dye 1-Se and phosphonic acid functionalized dye 3-Se revealed that Φ_{inj} via the carboxylate linkage was 2.3–1.1-fold greater than via the phosphonate linkage. Thus, electron injection reactivity is sensitive to both the aggregation state and the surface anchoring mode of these chalcogenorhodamine dyes. Short-circuit photocurrent action spectra of DSCs corresponded closely to absorbance spectra of dye functionalized films; thus, H-aggregation did not decrease the electron injection yield or charge collection efficiency. Maximum monochromatic incident photon to current efficiencies (IPCEs) of DSCs ranged from 53% to 95% and were slightly higher for carboxylic acid functionalized dyes 1-E and 4-E. The photoelectrochemical performance under monochromatic or white light illumination of 1-E and 4-E decayed significantly within 20–80 min of assembly of DSCs, due primarily to desorption of the dyes. In contrast, the performance of phosphonic acid functionalized dyes 3-E and 5-E remained stable or improved slightly on similar time scales. Power conversion efficiencies of DSCs under white light illumination were low (1%), suggesting that dye regeneration was inefficient at high light intensities. Preliminary transient photovoltage results support this proposition. Our findings suggest that controlled aggregation of organic dyes may represent an attractive strategy for improving the global energy conversion efficiencies of organic dye sensitized solar cells and photocatalysts. In addition, replacing carboxylic acids with phosphonic acids increased the inertness of chalcogenorhodamine/TiO₂ interfaces without greatly impacting aggregation of dyes or the interfacial electron transfer reactivity. The decrease of Φ_{subinj} for

phosphonic acid bearing dyes is offset by its enhanced stability and persistence on TiO₂ Crystals and Nanocrystalline Films with a Ruthenium Based Dye Akiko Fillinger, 2000

Dye Sensitization of TiO₂

Unveiling the Power of Verbal Art: An Psychological Sojourn through **Photoinduced Charge Separation In Dyesensitized Films Of Smooth Nanocrystalline Tio**

In a global inundated with displays and the cacophony of instantaneous conversation, the profound power and psychological resonance of verbal artistry frequently disappear in to obscurity, eclipsed by the continuous onslaught of noise and distractions. Yet, set within the musical pages of **Photoinduced Charge Separation In Dyesensitized Films Of Smooth Nanocrystalline Tio**, a charming function of fictional beauty that impulses with natural feelings, lies an remarkable trip waiting to be embarked upon. Penned by a virtuoso wordsmith, that enchanting opus courses visitors on an emotional odyssey, lightly exposing the latent possible and profound influence stuck within the complex web of language. Within the heart-wrenching expanse of this evocative analysis, we will embark upon an introspective exploration of the book is key subjects, dissect its interesting publishing design, and immerse ourselves in the indelible impression it leaves upon the depths of readers souls.

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