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"Surface Binding and Organization of Sensitizing Dyes on Metal Oxide Single Crystal Surfaces"

Summaries of publications over the last three years of support.

Mark T. Spitler and B. A. Parkinson, "Dye Sensitization of Single Crystal Semiconductor Electrodes", Accounts of Chemical Research, 42, 2017-2029, (2009)

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 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 photo-induced 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.

Laura Sharp, David Soltz and B. A. Parkinson, "Growth and Characterization of Tin Disulfide Single Crystals", Crystal Growth & Design, 6(6), 1523-1527, (2006)

Tin disulfide is a layered semiconductor, crystallizing in the cadmium iodide structure, with a band gap of 2.2 eV. The layered structure makes it useful for many experiments where a semiconductor with a reproducible renewable surface is needed. The easy cleavage of the surface exposes a clean atomically flat surface for use as a substrate for the deposition of solid-state materials or molecules or scanning probe microscopy experiments. Its semiconducting properties are also useful for photoelectrochemical dye sensitization studies. We report the crystal growth of this material by a Bridgman method with control of the dopant identity and level to obtain useful n-type semiconducting properties. Doping levels measured with both Hall effect and Mott Schottky analysis were well correlated. The electron mobility and hole diffusion lengths were also measured for the various doped crystals using solid-state and photoelectrochemical techniques.

Yunfeng Lu, Dae-jin Choi, Jimmy Nelson, O-Bong Yang and B. A. Parkinson, "Adsorption, Desorption, and Sensitization of Low-Index Anatase and Rutile Surfaces by the Ruthenium Complex Dye N3", Journal of the Electrochemical Society, 153(8), E131-E137, (2006)

Single crystal anatase (101), (001) and rutile (100), (001) surfaces with atomically flat terraces were prepared and their structure verified with atomic force microscopy (AFM). A ruthenium complex dye, cis-di(thiocyanato)- bis(2,2'-bipyridyl -4,4'- dicarboxylate) ruthenium(II) (usually known as N3) was used to sensitize these surfaces. The N3 coverage dependence of the incident photon to current efficiencies (IPCE) was measured for all four surfaces. IPCE values were much higher on anatase (101) and rutile (100) than on the other two surfaces. The kinetics of N3 adsorption and was also studied on the four surfaces. The 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 are discussed based on the structure of the N3 and the geometry and reactivity of the binding sites on the four surfaces.

Yunfeng Lu, Bengt Jäckel and B. A. Parkinson, "Preparation and Characterization of Terraced Surfaces of Low-Index Faces of Anatase, Rutile, and Brookite". Langmuir, 22(10), 4472-4475, (2006)

Simple polishing and relatively low temperature annealing procedures for preparing atomically flat terraced surfaces of various single-crystal TiO_2 polymorphs are described. Anatase (101), anatase (001), rutile (100), rutile (110) and brookite (111) surfaces could all prepared with a terraced surface structure as revealed in AFM images. The rutile (100), (110) and anatase (101) surfaces were also shown to produce acceptable LEED patterns immediately upon insertion into a UHV system without the usual sputter and anneal cycles.

Yunfeng Lu, Mark T. Spitler and B. A. Parkinson, "Photochronocoulometric Measurement of the Coverage of Surface Bound Dyes on Titanium Dioxide Crystal Surfaces", J. Phys. Chem. B, 110, 25273-25278, (2006) Atomically flat terraced single crystal anatase and rutile surfaces can be prepared allowing for the reproducible adsorption of covalently attached sensitizing dyes. Once reproducible surfaces and dye coverages are achieved, a photochronocoulometric technique is developed to measure the surface coverage of the dyes, an important parameter in determining the efficiency of sensitization. The surface-bound dyes are irreversibly oxidized by exposure to a light pulse with the n-type oxide semiconductor electrode held in depletion. A double exponential decay of the subsequent photocurrent is then measured, where the integration of the faster decay is associated with the adsorbed dye coverage and the second much slower decay is attributed to trace regenerators, including water, in the non-aqueous electrolyte. The ruthenium based N3 dye shows the expected linear dependence of the rate constant on light intensity whereas a dicarboxylated thiacyanine dye shows a square root dependence of its photooxidation rate on light intensity. The sublinear response of the thiacyanine dye is discussed in terms of the more complex surface chemistry that is known for this family of sensitizing dyes.

Yunfeng Lu, Mark T. Spitler and B. A. Parkinson, "Regenerator Dependent Photo-Induced Desorption of a Dicarboxylated Cyanine Dye from the Surface of Single Crystal Rutile", Langmuir, 23, 11673-11642, (2007)

A photon-initiated desorption of a dicarboxylated thiacarbocyanine dye from a dye-sensitized semiconducting oxide crystal has been observed when hydroquinone is used as a regenerator. No desorption was found under the same conditions when KI was used as the regenerator. Intermittent illumination experiments suggest that the oxidation products of the hydroquinone regenerator compete 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.

Michael J. Scott, Michael Woodhouse, Bruce A. Parkinson and C. Michael Elliott "Spatially Resolved Current-Voltage Measurements--Evidence for Non-Uniform Photocurrents in Dye Sensitized Solar Cells", Journal of the Electrochem. Soc., 155(3), B290-B293, (2008) Spatial current distributions of dye-sensitized TiO2 solar cells _DSSCs_ mediated with a cobalt polypyridine complex are described. By rastering a laser over the surface of a DSSC while measuring the short-circuit current, a spatial current image is obtained. Experiments that highlight the potential uses of this technique are discussed. First, intentional damage inflicted on the photoanode and cathode of the DSSC are visualized with the scanning technique and second, the effects of increased pressure of the cell holder clamps are discussed and shown to warrant further investigation. Finally, other variations of the scanning technique are suggested.

Justin B. Sambur, Shannon C. Riha, Dae Jin Choi and B. A. Parkinson, " The Influence of Surface Chemistry on the Binding and Electronic Coupling of CdSe Quantum Dots to Single Crystal TiO_2 Surfaces", Langmuir, in press

Sensitization of mesoporous nanocrystalline TiO_2 solar cells with quantum confined semiconductor nanocrystals (QDs) has some advantages over organic dyes or inorganic complex sensitizers, yet the reported efficiencies of laboratory devices are not currently competitive with dye sensitized cells. Several methods previously utilized to bind CdSe QDs to the mesoporous TiO_2 films were investigated using low index faces of both anatase and rutile TiO_2 polytypes as model systems. The *in situ* ligand exchange method, where 3-mercaptopropionic acid (MPA) covered TiO_2 crystal surfaces are treated with trioctylphosphine (TOP)/trioctylphosphine oxide (TOPO) TOP/TOPO-capped CdSe QDs, resulted in very irreproducible and usually low sensitized photocurrents. The *ex situ* ligand exchange method, whereby MPA-capped QDs are synthesized and directly adsorbed onto bare TiO_2 single crystals, resulted in both reproducible sensitized photocurrents and surface coverages that are verified with atomic force microscopy (AFM). Purification of the nanocrystals and adjustment of the pH of the sensitization solution to >10.2 was found to prevent QD agglomeration and takes advantage of the dual chemical functionality of MPA to directly link the QDs to the TiO_2 surface. The spectral response of the incident photon to current efficiencies of CdSe QDs were directly compared to the commonly used sensitizer *cis*-di(thiocyanato)-bis(4,4;-di-carboxy-2,2'-bipyridine)ruthenium(II) (N3) on the same single crystals.

Justin B. Sambur and B. A. Parkinson, "CdSe/ZnS Core/Shell Quantum Dot Sensitization of Low Index TiO_2 Single Crystal Surfaces", J. Am. Chem. Soc., *J. Am. Chem. Soc.*, **2010**, *132* (7), pp 2130–2131

Quantum dots (QDs) are actively explored as alternative sensitizers to inorganic complexes in sensitized solar cells (SSC) due their interesting physical, optical and electronic properties. It is thought that the inorganic nature of QDs should provide enhanced stability over the entirely organic or inorganic complex dyes, yet the long-term stability of laboratory QD-SSC devices has not been investigated in detail. A general approach to synthesize high stability QDs involves coating the core material with a wide band gap inorganic shell material (type-I CS QD). However, the electronic structure of the resulting core/shell (CS) structure has potential barriers for both electron and hole transfer, suggesting inefficient charge carrier separation for type-I CS QDs. Herein we demonstrate that type-I CdSe/ZnS CS QDs can effectively sensitize single crystal TiO_2 electrodes and continue to operate in a regenerative mode in an aerated iodide electrolyte for more than 20 hours. Core CdSe QDs degrade rapidly in the same electrolyte presumably due to CdI_2 formation. The possibility of exploring new core/shell nanomaterials in a variety of electrolyte/mediator combinations may result in more efficient and stable QD-SSCs.