The relationship between squaraine dye surface morphology and sensitization behavior on SnS₂ electrodes

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This paper is dedicated to the memory of Heinz and Renata Gerischer.

Abstract

Bis(4-dimethylamino-2-dihydroxyphenyl)squaraine (1-OHSQ) dyes were deposited on van der Waals surfaces of SnS₂ single crystals by two methods, dipping in a dye solution and evaporation of dye solution. Dye morphologies and photosensitization properties on the same samples were studied with atomic force microscopy (AFM) and photoelectrochemical measurements. AFM experiments in air revealed two distinct morphologies of dye aggregates and photocurrent measurements on the same samples in aqueous electrolytes showed correspondingly different photocurrent spectra. Three-dimensional needle-shaped 1-OHSQ aggregates aligned along crystal directions and showed a broad excitation spectrum that extended into the near-IR region with a peak around 800 nm. In contrast, flat aggregates presumably consisting of monolayers of 1-OHSQ molecules, had a sensitization maximum around 680 nm. Both peaks were red-shifted from absorption peak of 1-OHSQ in bulk dichloromethane solution. Spectral differences between these dye aggregates are discussed in terms of intermolecular interactions. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since the classic work of Gerischer [1,2], interest in dye sensitization of semiconductor electrodes has recently increased due to the high solar to electric conversion efficiencies achieved in nanocrystalline TiO₂ solar cells [3,4]. Despite the efficiency gains, very little is known about the dye/semiconductor interface in the nanocrystalline system or in sensitization systems involving single crystal substrates. For instance, the orientation of the individual dye molecules, the state of aggregation (i.e. dimers, oligomers, islands, three-dimensional crystallites etc.) of the dye molecules and the preferred dye molecule adsorption sites are for the most part unknown. In this paper, we take some initial steps to look at the dye structure on a semiconductor surface at a near molecular scale. We then attempt to correlate the observed structural features with the sensitization behavior of the various observed dye morphologies. The semiconductor substrate is SnS₂ since it has a two-dimensional structure and can be prepared in single crystals with atomically flat areas of many square microns. The van der Waals surface of this material provides a surface that does not react with ambient air or water and so should be a relatively simple surface on which to study the effects of dye morphology. Previous work has shown that SnS₂ can be sensitized with a large variety of organic dyes [5]. In this study we focus on a squaraine dye for a number of reasons. It is of commercial interest as a photoconductor [6], it has a variety of
known polymorphs and aggregate structures [7–9] and squaraines tend to have very high absorption coefficients. The very high absorption coefficients make photocurrents at small dye coverages easier to measure.

2. Experimental section

2.1. Materials

Bis(4-dimethylamino-2-dihydroxyphenyl)squaraine (1-1 OHSQ, structure shown below) was a generous gift from Lexmark Corp. and used as received. Tin disulfide single crystals were prepared from stoichiometric amounts of Sn metal (puratronic, Alfa Aesar) and sulfur (puratronic, Alfa Aesar) by a Bridgman method, and were n-doped with chlorine. The doping density determined by Hall measurements was $7 \times 10^{16} \text{ cm}^{-3}$. Details of crystal growth will be presented elsewhere [10]. Dichloromethane (spectralyzed grade) and lithium chloride were purchased from Fischer scientific. Hydroquinone was reagent grade and used as received. Water was purified with Milli-Q water purification system (Millipore, > 18 MΩ cm).

2.2. Preparation of 1-1 OHSQ/SnS$_2$ samples

1-1 OHSQ was found to be soluble in dichloromethane up to $\sim 15 \mu\text{mol l}^{-1}$ at room temperature. Typically, 10 μmol l$^{-1}$ stock solutions of 1-1 OHSQ in dichloromethane were prepared and stored in the dark. Electronic absorption spectra of squaraine solutions were measured with Hewlett-Packard 8452A diode array spectrometer. Dye solutions were filtered through Anodisc 13 (Whatman) with a pore diameter of 0.02 μm before use to remove any insoluble dye impurities and other small particles.

SnS$_2$ crystals were cut with razor blades to make thin pieces of typical areas of 1.0 cm$^2$. Basal planes of SnS$_2$ were cleaved with Scotch adhesive tape (3 M) to expose fresh surfaces. Deposition of dyes onto SnS$_2$ was performed by two techniques, (A) SnS$_2$ crystals were dipped in dichloromethane solutions of 1-1 OHSQ (10 μmol l$^{-1}$) for various times. Then samples were withdrawn from the solution and the basal planes of SnS$_2$ were kept vertical to drain excess solution. (B) Aliquots of 10 μmol l$^{-1}$ 1-1 OHSQ solution (approximately one monolayer equivalent) were dropped on and spread over cleaved SnS$_2$ surfaces. One monolayer equivalent amounts were calculated based on the packing densities of 1-1 OHSQ on graphite substrate found in previous STM studies [9] corresponding to $\sim 1 \times 10^{-10} \text{ mol cm}^{-2}$. After applying the solution, solvents were allowed to evaporate in ambient air. Dye deposited SnS$_2$ crystals were mounted on a steel plate (Ted Pella Inc.) an electrically contacted by rubbing silver paste (SPI supplies) between them. These samples were transferable between the AFM studies and the photoelectrochemical measurements.

2.3. Atomic force microscopy and photoelectrochemical measurements

The morphologies of the squaraine dyes on SnS$_2$ surfaces were investigated by atomic force microscopy (AFM). A nanoscope IIIa scanning probe microscope (Digital Instruments) was operated in tapping mode with a J-scanner. Conical silicon AFM tips (Ultra-levers™ Park Scientific Instruments) with a spring constant of 0.26 N m$^{-1}$ were used. All measurements were conducted in ambient air.

After AFM observations, the same samples were used to make working electrodes for photoelectrochemical measurements. Samples were mounted on a copper plate in a plastic holder, through which electrical contacts were made. A flat rubber O-ring (opening 0.32 cm$^2$) was used to determine the area exposed to the electrolyte and to seal the back contact from exposure to the electrolyte. A very thin film of high vacuum grease (dow corning) was used to aid the sealing. Bare SnS$_2$ electrodes were prepared in the same way.

Photoelectrochemical measurements were conducted in a conventional three-compartment electrochemical cell with a flat Pyrex optical window. A Pt gauze was used as a counter electrode and a saturated calomel electrode (SCE) was used as a reference electrode. Electrolytes were aqueous solutions containing 1.0 mol l$^{-1}$ LiCl and 10 mmol l$^{-1}$ hydroquinone as a regenerator. Electrolytes were bubbled with N$_2$ for at least 15 min prior to measurements. Potentiostatic control of electrodes was provided by EG&G PAR 174A potentiostat. Electrodes were provided by EG&G PAR 174A potentiostat. A 50 W tungsten halogen lamp (Osram HLX 64610 with a Newport model 780 lamp source) was used as a light source. Illumination was made through a Jarrell-Ash MonoSpec 27 monochromator and a 500 nm cutoff filter, and the light beam was focused as $\sim 2 \times 3$ mm spots on the electrode surface by a rectangular slit and a collimating lens. The illumination source was modulated with a mechanical chopper (Stanford Research Systems, model SR540) and photocurrents were obtained using a lock-in amplifier (Stanford Research Systems, model SR830). Lamp spectra were obtained with a thermopile that was calibrated daily with a calibrated photodiode. A typical light irradiance was 13 μW at 680 nm.

3. Results and discussion

3.1. Morphologies of 1-1 OHSQ on SnS$_2$

AFM observations of bare SnS$_2$ usually revealed atomically flat surfaces over several microns with occa-
Fig. 1. (a) Tapping mode AFM image of 1-1 OHSQ aggregates on SnS₂ prepared by dipping for 12 min. Scan size was 10 × 10 μm. Z-range was 1 nm. (b) Cross-section analysis of AFM image along the line drew in part (a).

Fig. 2. (a) Tapping mode AFM image of 1-1 OHSQ aggregates on SnS₂ prepared by dropping 1 ml equivalent amount dye solution and dried in ambient air. Scan size was 10 × 10 μm. Z-range was 20 nm. (b) Cross-section analysis of AFM image along the line drew in part (a).

After depositing 1-1 OHSQ, several distinct morphologies were observed. Fig. 1a shows a typical 10 × 10 μm AFM scan obtained for 1-1 OHSQ/ SnS₂ samples prepared by dipping in 10 μmol 1× 1-1 OHSQ dichloromethane solution for 12 min. Groups of island structures, of typical dimension of 500 nm to 2 μm, form fractal-like morphologies on the SnS₂ surface. The cross-section analysis, shown in Fig. 1b, reveals a vertical height of 0.2–0.3 nm for the flat islands. We assume these islands consist of monolayers of 1-1 OHSQ molecules lying flat on the surface since the height of the islands is consistent with the thickness of the 1-1 OHSQ molecule. This observation is consistent with a recent STM study from our group where this and similar molecules were shown to lie flat on basal planes of HOPG [9]. Image analysis of the AFM images from several areas of this particular sample resulted in a dye coverage of approximately 30%.

Needle-shaped aggregates of various vertical heights were also frequently observed. A 10 × 10 μm scan AFM image is shown in Fig. 2a that was obtained for the sample prepared by dropping approximately one monolayer equivalent amount of 1-1 OHSQ solution on SnS₂ (method B). Each needle-shaped aggregate seen in Fig. 2a has a length of about 2–4 μm and a width of about 100 nm. Fig. 2b shows the section analysis of the AFM image along the line shown in Fig. 2a. It appears that the cross-sections of these aggregates are not flat. The height of needles on this sample ranged from about 2 to 20 nm at their apexes. The needle-shaped aggregates are taller than the two-dimensional aggregates seen in Fig. 1a. These aggregates may be microscopic bulk crystallites. Presently we do not know how squaraine molecules are oriented within these aggregates, however, it is clear that multilayers of 1-1 OHSQ are present in these needles. Fig. 2a shows bundles of needles that are oriented along certain directions. The alignment is probably a result of interactions between 1-1 OHSQ aggregates and the underlying hexagonal sulfur layers of SnS₂. Angles of 30, 60, 90 and 120° between these groups of needles are quite common and are consistent with the hexagonal structure of the un-
in dichloromethane solution is shown for comparison. Absorption spectrum of 1-1 OHSQ AFM image shown in Fig. 2a. Quantum yields were calculated J-aggregates formed at the mica isotropic growth of dye aggregates of pseudoiocyanine derlying layer. Recent AFM studies have shown an- ever, since only van der Waals forces exist between the adsorption of positively charged dye molecules was favored on the negatively charged surface sites. How- 3, closed circles). This peak is somewhat broadened and (Fig. 1a) show a sensitization peak around 680 nm (Fig. 3, open circles) showed pronounced anodic photocurrents at wavelengths shorter than 570 nm, corresponding to its band gap (2.2 eV). Deposition of 1-1 OHSQ onto the surface results in peaks at longer wavelengths as a result of electron injection from ex- cited states of the dyes into the SnS2 conduction band. Electrodes with two-dimensional dye morphologies (Fig. 1a) show a sensitization peak around 680 nm (Fig. 3, closed circles). This peak is somewhat broadened and ~40 nm red-shifted from the absorption peak of 1-1 OHSQ in dichloromethane solution as shown in the same figure. A red-shift of the spectrum is related to the different environment of adsorbed dyes when compared with bulk solution due to interaction with the semicon- ducting surface and/or other dye molecules. In a previ- ous study on dye sensitization of SnS2 single crystals, a similar red-shift of the excitation spectra for monomeric dyes was observed [5]. It was attributed to changes in solvation of dye molecules upon adsorption on SnS2 surfaces. Similar effects can be also expected in the present study. Another possible contribution is the electronic interaction of adsorbed dye molecules with the SnS2 surface. Such a charge transfer interaction was used to explain a new absorption band of bis(2,4,6-tri- hydroxyphenyl)squaraine dye aggregates upon adsorp- tion onto TiO2 colloids [13]. However, we cannot preclude the effect of dye aggregation where inter- molecular interactions cause the shift in absorption spectrum. In addition to 680 nm peak, a shoulder around 600 nm appeared in the photoaction spectrum of the two-dimensional aggregates. This shoulder is blue-shifted from the peak in the dichloromethane solu- tion spectrum. This might be related either to the existence of different forms of dye aggregates within the flat aggregates or to dyes at the edge of the islands whose electronic environment is different from the dyes in the center of the islands. At this time we cannot

3.2. Photosensitization behavior of 1-1 OHSQ aggregates

Photosensitization properties of the prepared samples were investigated in aqueous electrolyte solutions. The dye molecules used in this study do not dissolve in water, and so we expect that their morphologies were not changed by immersing in aqueous electrolytes. Fig. 3 shows photocurrent action spectra taken at +0.7 V versus SCE for bare SnS2 and 1-1 OHSQ/SnS2 with the dye morphologies shown in Figs. 1 and 2. Quantum yields in this figure were calculated per incident photon. Bare SnS2 (Fig. 3, open circles) showed pronounced anodic photocurrents at wavelengths shorter than 570 nm, corresponding to its band gap (2.2 eV). Deposition of 1-1 OHSQ onto the surface results in peaks at longer wavelengths as a result of electron injection from excited states of the dyes into the SnS2 conduction band. Electrodes with two-dimensional dye morphologies (Fig. 1a) show a sensitization peak around 680 nm (Fig. 3, closed circles). This peak is somewhat broadened and ~40 nm red-shifted from the absorption peak of 1-1 OHSQ in dichloromethane solution as shown in the same figure. A red-shift of the spectrum is related to the different environment of adsorbed dyes when compared with bulk solution due to interaction with the semiconducting surface and/or other dye molecules. In a previous study on dye sensitization of SnS2 single crystals, a similar red-shift of the excitation spectra for monomeric dyes was observed [5]. It was attributed to changes in solvation of dye molecules upon adsorption on SnS2 surfaces. Similar effects can be also expected in the present study. Another possible contribution is the electronic interaction of adsorbed dye molecules with the SnS2 surface. Such a charge transfer interaction was used to explain a new absorption band of bis(2,4,6-tri-hydroxyphenyl)squaraine dye aggregates upon adsorption onto TiO2 colloids [13]. However, we cannot preclude the effect of dye aggregation where intermolecular interactions cause the shift in absorption spectrum. In addition to 680 nm peak, a shoulder around 600 nm appeared in the photoaction spectrum of the two-dimensional aggregates. This shoulder is blue-shifted from the peak in the dichloromethane solution spectrum. This might be related either to the existence of different forms of dye aggregates within the flat aggregates or to dyes at the edge of the islands whose electronic environment is different from the dyes in the center of the islands. At this time we cannot

Fig. 3. Photocurrent quantum yield action spectra measured at +0.7 V vs. SCE bias in aqueous 1.0 mol l−1 LiCl electrolyte containing 10 mmol l−1 hydroquinone as a regenerator. Open circles, bare SnS2; closed circles, 1-1 OHSQ on SnS2 deposited by dipping for 12 min corresponds to AFM image shown in Fig. 1a; closed triangles, ca. 1 ml equivalent amount of 1-1 OHSQ on SnS2 deposited by dropping method corresponds to AFM image shown in Fig. 2a. Quantum yields were calculated per incident photon flux. Absorption spectrum of 1-1 OHSQ in dichloromethane solution is shown for comparison.
assign these peaks to specific aggregate structure or position of the dye within the aggregate of 1-1 OHSQ molecules. Recent STM studies in our lab have revealed the existence of several different ordered structures of 1-1 OHSQ dyes adsorbed on HOPG surfaces [9]. It is not unreasonable to consider that the different polymorphs gave different excitation spectra if we assume similar polymorphs of dyes were formed on SnS$_2$ surface studied herein.

On the other hand, needle-shaped aggregates of 1-1 OHSQ adsorbed on SnS$_2$ show further red-shifted spectrum comprising $\sim$ 800 nm broad peak and two additional shoulders around 700 and 620 nm (Fig. 3, closed triangles). The pronounced near-IR response, which is not seen in flat aggregate spectrum, appears to be related to the different aggregate structures found in the AFM images.

Values of photocurrent quantum yields calculated per incident photon shown in Fig. 3 were comparable for the two samples with different morphologies. Since we do not know the absorptivity of two different aggregates, we cannot deduce any conclusion about effect of dye morphologies on photosensitization efficiencies. Further study is needed to clarify this issue.

3.3. Intermolecular interactions within 1-1 OHSQ dye aggregates and their photosensitization properties

As described in the previous section, two samples of 1-1 OHSQ/SnS$_2$ with different morphologies gave different spectral responses for sensitized photocurrent generation. Spectral changes associated with aggregate formation in the dye sensitization of semiconductors have been already reported [5,13–18]. One of the particularly interesting findings in this study is the appearance of near-IR responses in the photocurrent action spectrum. It is known that the absorption spectra of squaraine dyes are extended into the near-IR region in the solid state [6,19]. These absorption bands were attributed to intermolecular charge transfer processes. X-ray crystal structure studies, on structurally similar squaraine dyes, showed that the charge transfer is facilitated by stacking squaraine molecules in a staircase arrangement (J-aggregate-like packing) in which the donor part of the dyes on one layer is adjacent to the acceptor part of the dyes on another layer [7,8,20]. The shape of the photocurrent action spectrum, shown in Fig. 3, is somewhat different from the solid-state absorption spectrum of 1-1 OHSQ found in the literature. The literature spectrum showed two broadened absorption bands around 550–600 and 700–800 nm [6,19]. Broadening in the latter spectrum might be related to the increased number of molecules in the crystallites or the existence of different polymorphs in the sample. However, it is still likely that similar interactions are operating in the needle-shaped aggregates that we observe. Although we do not know the exact solid state structure of the needle-like aggregates, we assume that the structure facilitates $\pi$-stacking interactions between the squaraine molecules, as is the case in the X-ray crystal structures of known polymorphs.

On the other hand, 1-1 OHSQ molecules in flat aggregates shown in Fig. 1a are arranged in a two-dimensional structure where the overlap of $\pi$-orbitals is small. In that case, the intermolecular charge transfer discussed above would not occur efficiently. This agrees with the lack of near-IR response in the photocurrent action spectrum (Fig. 3). Therefore, the $\sim$ 680 nm band seen in the action spectrum can be attributed to the intramolecular transition, associated with the monomeric form of 1-1 OHSQ dyes. Aggregation effects are still possible for the flat aggregates. Dipole–dipole interactions can induce changes of transition energies of dye aggregates, such as cyanine dye J- and H-aggregates [21]. Law attributed the blue-shifted absorption spectrum of bis(4-methoxyphenyl)squaraine aggregates to C–O dipole interactions [22]. Such aggregation effects might be responsible for the blue-shifted shoulder ($\sim$ 600 nm) found in the action spectrum of 1-1 OHSQ flat aggregates. Optical transitions similar to those of the flat aggregates would be also allowed for needle-shaped aggregates, since shoulders in these wavelengths region are also seen in its photocurrent action spectrum.

Charge transport through the thickness of the needle-shaped aggregates is another issue that must be considered. Unlike the flat aggregates, where every photoexcited molecule is in direct contact with the semiconductor surface, photoexcited electrons or excitons produced by the outermost molecules in the needle-like aggregates must migrate through the crystallites to the semiconductor/dye interface in order to appear as photocurrent. Squaraine dyes are commercially used as photocconductors so we expect that this process will be efficient. Our data supports this since the maximum quantum yield for the needle like aggregates, that cover a relatively small fraction of the surface, is about 70% of that of the 30% coverage monolayer. Again an understanding of the absorption coefficients of the two aggregate types will be necessary to sort out transport and coverage effects in the both types of aggregates.

4. Conclusions

AFM provided a convenient and powerful method for studying the morphologies of dye aggregates formed on the basal plane of SnS$_2$ single crystals. Spectral changes associated with the distinct morphologies of squaraine dye aggregates produced in this study provide the opportunity for further investigation of
structure–property relationships in studies of dye sensitization of semiconductors. Further investigation is needed regarding photosensitization efficiencies (quantum yields) of the dye aggregates. Future study will also attempt to correlate photosensitization properties with molecular level ordering of dye aggregates and examining the photoresponse of individual dye molecules and aggregates.

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