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ELECTRON INJECTION FROM ADSORBED OXAZINE INTO SnS_2

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Abstract The injection of photo-generated electrons from an adsorbed dye into a SnS_2 crystal has been studied using time-correlated single photon counting. The system studied was oxazine 1 on SnS_2. The oxazine S_1 level lies .35 eV above the conduction band edge; thus, electron injection should be essentially barrierless. The fluorescence lifetime of adsorbed oxazine was determined to be less than 40 psec, the instrument response time. The fluorescence quenching of the system was determined to be quenched by a factor of nearly 10^5 (relative to oxazine on an inert surface, 3M tape) using time-correlated techniques to take advantage of the improved background and signal to noise ratio. This places the fluorescence lifetime of oxazine on SnS_2 at 40 $\pm$ 20 fsec and the rate constant for electron injecton at approximately 3 X 10^{13} sec^{-1}. This ultrafast rate implies strong coupling between the molecular state and the electronic quasi-continuum of the conduction band, suggesting that this electron transfer takes place in a regime where the standard assumptions of Marcus theory may no longer be valid.

Keywords: Oxazine, electron injection, tin disulfide (SnS_2), dye adsorption, fluorescence lifetime

INTRODUCTION

Perhaps the most fundamental physical process in chemistry is electron transfer. Injection of electrons from photo-excited adsorbed species into semiconductors is a subject of primary interest in the field of photography, as well as being of elementary scientific interest. In recent years, much work has been done investigating electron injection in various systems[1–12]. Many of the systems studied exhibit complex behavior due to the presence of surface states, different adsorption sites, and competition from energy transfer among other complications. For this reason, SnS_2 was chosen for the studies presented here. SnS_2 is known to cleave with large, atomically smooth regions which have a very low surface state density[13]. Hence, it should serve as a near ideal substrate for studying electron injection.

The dye chosen as adsorbate was oxazine 1. Its S_1 state lies approximately 0.35 eV above the conduction band edge resulting in barrierless electron injection (see figure 1). The localized molecular state is coupled to the quasi-continuum of the conduction band. Therefore, the electron can scatter into the large momentum space available, away from

the resonant transfer level, and no large change in reaction coordinate is necessary for the injection to occur. Consequently, the electron injection might be expected to occur on a subpicosecond timescale.

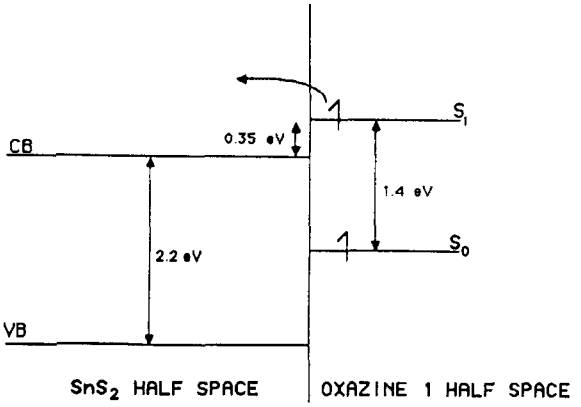

FIGURE 1 Diagram of the system energetics. Note that the S_1 state of the oxazine is well above the conduction band edge[13]. The SnS_2 samples are unintentionally doped, to limit the formation of a space charge electric field barrier to electron-parent cation recombination.

Previous investigations have centered on the study of the fluorescence decays of the adsorbed dye[1–12]. This study has extended that methodology by analyzing both the fluorescence decay curves and the fluorescence quenching of the oxazine on SnS_2 as compared with oxazine adsorbed on an inert substrate. Since the dye coverages on the inert substrate are similar to those on the SnS_2 samples, no new nonradiative decay channels are expected other than the electron injection route. Therefore any decrease in the fluorescence yield is construed to be due to a decrease in the fluorescent lifetime due to population depletion by electron injection into the SnS_2.

EXPERIMENTAL

The SnS_2 substrates were grown as described previously[13]. The inert substrate used was the adhesive side of 3M tape. The oxazine 1 dye was purchased from Exciton as a standard laser grade dye. A 2.25 X 10^{-3} M solution was prepared in methanol and then diluted with water to the appropriate concentrations. Dye was adsorbed by placing a drop of the oxazine solution on the substrate, waiting for 60 seconds and then blotting the surface with lens paper. The coverage was then estimated by taking the absorbance spectrum using a Perkin-Elmer Lambda 9 Spectrometer equipped with an integrating sphere to collect any scattered light.

Background absorbance spectra of the samples were taken before adsorbing dye and were then subtracted from the absorbance spectra of the treated samples. Steady state fluorescence spectra were measured using a Spex Fluorolog II spectrofluorimeter, equipped with double monochromators in both excitation and emission channels.

Time-resolved fluorescence data was taken using a time-correlated single photon counting setup. The excitation laser was a Coherent 7200 series cavity-dumped dye laser with Pyridine 1 as the gain medium which was synchronously pumped by 750 mW of

doubled Nd:YAG. The samples were pumped at 668 nm for the inert substrate samples and 685 nm for the SnS_2 substrate samples using a 1 mm spot size. The pulse energies were 5 nJ/pulse at 668 nm and 10 nJ/pusle at 685 nm, the repetition rate was 1.9 MHz, the pulse duration 4 psec.Fluorescence detection was done 30 nm red of the pump using a 0.25 m monochrometer with 0.3 mm slits and a 6 micron microchannel plate, with a Hammamatsu R2809-11 photocathode. A Hoya Optics R-72 infrared passing filter was placed over the fluorescence collecting lens to filter out the 685 nm pump. The instrument response time was 40 psec with the single photon counting electronics in their standard configuration. The dye concentrations used for these measurements were 4.95×10^{-7} M, 1.8×10^{-6} M, and 3.6×10^{-6} M. Fluorescence decay curves were taken both before and after adsorbing dye. The background decay curves were subtracted and the curves were fit using a multivariable exponential fitting routine.

RESULTS AND DISCUSSION

The steady state fluorescence spectra of oxazine on SnS_2 show strong fluorescence quenching when compared to the oxazine on tape, as shown in Fig. 2. When excited at 640 nm, the sensitized SnS_2 showed a weak fluorescence with a spectrum similar to the oxazine on tape, indicating that this fluorescence originates from molecules not strongly coupled to the surface, since the red shift associated with surface adsorption is absent. When excited at 680 nm, a wavelength close to the peak for the adsorbed oxazine, no fluorescence above the scattered light background was observed. From these data, a fluorescence quenching of at least 10^3 could be calculated.

Fluorescence decay curves for the oxazine samples are given in Fig. 3. The decays of the oxazine on tape samples were fit to a single exponential decay with a $2.6 \pm .1$ nsec lifetime. The analysis of the oxazine on SnS_2 decays was not so straight forward. The decays of the SnS_2 samples were fit to two exponentials, an instrument response limited decay of 40 psec, and a longer decay of 900 ± 100 psec. The longer, nanosecond decay is concentration dependent in intensity and virtually disappears at very low dye coverages. This decay is attributed to fluorescence from dye molecules not adsorbed or strongly coupled electronically to the surface, as noted above in the steady state spectra. These molecules are isolated from the surface either by intervening dye molecules or noncoupling surface sites, or poorly coupled due to orientational effects. The instrument response limited decay is attributed to the fluorescence from the dye molecules adsorbed to the surface. From this analysis, we can conclude that the electron injection rate is faster than 40 psec. This conclusion is consistent with studies of cresyl violet on SnS_2, which put the electron injection rate at less than 10 psec[11,12].

Even though the decay times are faster than the instrument response, the electron transfer rate can be estimated from a determination of the fluorescence quantum yield for the dye on SnS_2 relative to the inert substrate. By taking advantage of the greatly reduced dark current of time-correlated single photon counting, a much more accurate determination of the fluorescence quenching on SnS_2 can be made relative to the steady state method discussed above (the time-correlated technique being at least two orders of magnitude more sensitive than the steady state measurements). After subtracting the background decay curve, the short component of the time-resolved decay component was integrated and the total number of counts compared to the integrations of the oxazine on tape curves. The integrations were normalized with respect to the fluorescence collection times. The number of counts was further corrected for the absorbance of the dye at the

excitation wavelength, the transmission of the filters used, multi-channel plate sensitivity, and the excitation energy. This analysis yielded a factor of 9 X 10^4 ± 5 X 10^4 fewer counts for the SnS_2 samples relative to the tape samples. These values are constant for the three concentrations studied. Assuming the decrease to be due only to electron injection places the timescale of the electron injection at 40 ± 20 fsec with the resulting electron injection rate of approximately 3 X 10^{13}.

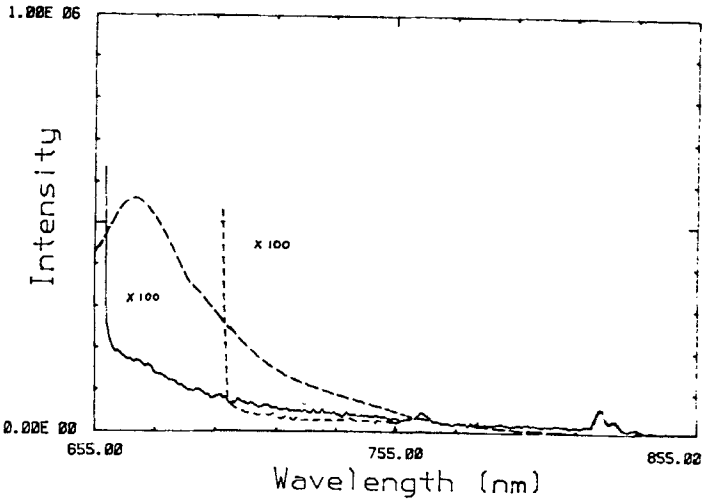

FIGURE 2 Steady state fluorescence of samples treated with 5 X 10^{-6} M oxazine solution. Long dashes: Treated tape excited at 640 nm. Solid line: Sensitized SnS_2 excited at 640 nm. Short dashes: Sensitized SnS_2 excited at 680 nm. Absorbance spectra of the samples have similar optical densities.

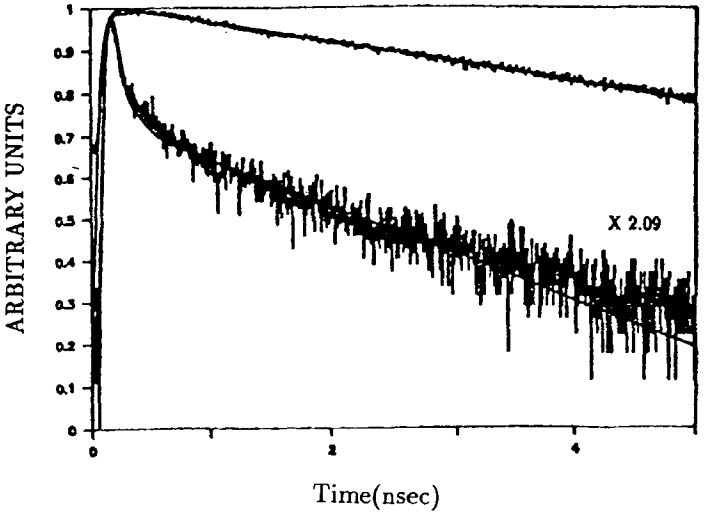

FIGURE 3 Log plot of time-resolved fluorescence of oxazine on SnS_2 superimposed on a log plot of oxazine on 3M tape. Integration of the tape sample shows a fluorescence yield 8.0X10^4 greater than the SnS_2 sample.

The SnS_2 samples used were unintentionally doped. The presence of a space charge field would drive the injected electrons into the bulk, and create a barrier to electron recombination with the parent cation. This is an important consideration as repopulation of the ground state of the oxazine would then be very slow and our samples subject to bleaching of the ground state under our excitation conditions. Hence, the quenching of the fluorescence would be due to slow ground state recovery in the presence of a barrier rather than the decreased fluorescence lifetime due to electron transfer. In the absence of a space charge field, the electrons are confined to the surface region of the semiconductor and the ground state recovery should be significantly faster. Varying the repetition rate by an order of magnitude showed no change in the quenching rate. If the samples were bleached, a decrease in repetition rate should have yielded a lower rate of quenching due to the longer time between shots for ground state recovery. Since there was no such dependence the possibility of ground state bleaching of the oxazine is considered remote.

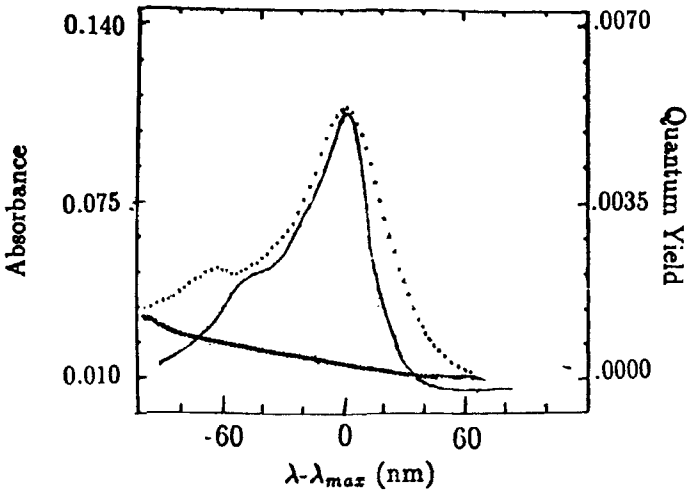

FIGURE 4 Comparison of oxazine absorption linewidths in solution and for sensitized photocurrent measurements on SnS_2. The absorption spectra are plotted relative to the absorption maxima. The photocurrent spectrum is red shifted by 27 nm relative to the methanol spectrum. The solid line represents the absorption spectrum of 1 X 10^{-6} M oxazine in methanol (left vertical scale). The dots represent the photocurrent spectrum of a low P-doped (10^{15} - 10^{16} cm^{-3}) SnS_2 crystal in 1 X 10^{-4} M oxazine (right scale), the diamonds represent the unsensitized background.

Further evidence in support of a 40 fsec electron transfer lifetime is provided by a line shape analysis. This extremely short lifetime should lead to observable lifetime line broadening even relative to room temperature solution spectra. In room temperature solutions, the absorption line shape is a composite of vibronic bands broadened by a 60-70 fsec electronic dephasing in solution[15]. Even with such broad line shapes, a 40 fsec lifetime broadened line should be observable. This comparison is made in figure 4. The normalized oxazine absorption spectra on SnS_2, determined by measuring the photocurrent for enhanced sensitivity, shows approximately 60 fsec of line broadening relative to the solution spectra. This comparison is subject to the standard reservation

regarding inhomogeneous versus homogeneous contributions to the line shape. However, it should be noted that SnS_2 can be atomically flat over extremely large areas (greater than 10,000 Angstroms^2) with few surface defects. It is the closest known approximation to an ideal, homogeneous surface. The observed line broadening is consistent with a 40 fsec lifetime, but this should be taken only as supporting evidence not conclusive proof.

CONCLUSIONS

The studies presented here show that electron injection from adsorbed oxazine 1 into SnS_2 is very fast. The fluorescence lifetime appears to be approximately 40 fsec which is much faster than any system previously studied. Electron transfer processes on this timescale raise interesting questions about the basic assumptions behind Marcus theory. Further investigation is necessary to directly measure the ground state recovery of the dye, an interesting process in itself, and to directly measure, in the time-domain, the appearance of the electron in the semiconductor. Surface restricted transient grating studies and space charge electo- optic sampling experiments are in progress in order to resolve these issues.

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REFERENCES

1. K. Hashimoto, M. Hiramoto, T. Kajiwara, and T. Sakata, J. Phys. Chem., 92, 4636(1988).
2. K. Kemnitz, N. Nakahima, K. Yoshihara, and H. Matsunami, J. Phys. Chem, 93, 6704(1989).
3. K. Hashimoto, M. Hiramoto, and T. Sakata, J. Phys. Chem, 92, 4272(1988).
4. K. Hahimoto, M. Hiramoto, A.B.P. Lever, and T. Sakata, J. Phys. Chem., 92, 1016(1988).
5. K. Itoh, Y. Chiyokawa, M. Nakao, and K. Honda, JACS, 106, 3553(1980).
6. Y. Liang, A.M. Ponte Goncalves, and D.K. Negus, J. Phys. Chem., 87, 1(1983).
7. Y. Liang, and A.M. Ponte Goncalves, J. Phys. Chem., 89, 3290(1985).
8. R.L. Crackel and W.S. Struve, Chem. Phys. Letters, 120, 473(1985).
9. P.V. Kamat, J.P. Chauvet and R.W. Fessenden, J. Phys. Chem., 90, 1389(1986).
10. M. Spitler, B. A. Parkinson, Langmuir, 2, 549(1986).
11. F. Willig, R. Eichberger, N.S. Sundrasen, and B.A. Parkinson, JACS, 112, 2702(1990).
12. R. Eichberger, and F. Willig, Chem. Phys., 141, 159(1990).
13. B.A. Parkinson, Langmuir, 4, 967(1988).
14. M. Spitler, J. Electroanal. Chem., 228, 69(1987).
15. P.C. Becker, H.L. Fragnito, J.Y. Bigot, C.H. Brito Cruz, R.L. Fork, and C.V. Shank, Phys. Rev. Lett., 63(5), 505(1989).