

## PHOTOELECTROCHEMISTRY IN COLLOIDAL SYSTEMS: INTERFACIAL ELECTRON TRANSFER BETWEEN COLLOIDAL TiO<sub>2</sub> AND THIONINE IN ACETONITRILE

PRASHANT V. KAMAT

Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556 (U.S.A.)

(Received July 23, 1984)

### Summary

When adsorbed on a colloidal TiO<sub>2</sub> semiconductor suspension, the thiazine dye thionine exhibited a red shift in its absorption and emission spectra. The apparent association constant for the association of TiO<sub>2</sub> colloid and thionine in acetonitrile was determined to be  $2.75 \times 10^5 \text{ M}^{-1}$ . Reversible photoelectrochemical reduction of thionine was observed when the colloidal TiO<sub>2</sub> suspension in acetonitrile containing thionine was subjected to band gap illumination ( $\lambda < 380 \text{ nm}$ ). The interfacial electron transfer between colloidal TiO<sub>2</sub> and thionine in acetonitrile was investigated by means of steady state photolysis and nanosecond laser flash photolysis techniques. The quantum yield for the photoelectrochemical reduction of thionine to semithionine was determined to be 0.1. The dependence of the photoelectrochemical production of semithionine on thionine concentration, the acidity of the medium and the intensity of excitation was examined.

---

### 1. Introduction

Semiconductor particles dispersed in various organic and inorganic systems are known to carry out efficient microphotoelectrolysis [1 - 3]. The increasing importance of the synthetically useful transformation of organic substrates calls for a better understanding of the mechanism of heterogeneous electron transfer reactions in non-aqueous media. Recently picosecond and nanosecond laser flash photolysis techniques have been employed to examine the dynamics of interfacial processes at the semiconductor surface [4 - 6]. The transparency of colloidal dispersions facilitates direct detection and monitoring of short-lived transients by fast kinetic spectroscopy.

Yoneyama *et al.* [7] have reported the reduction of methylene blue at an illuminated rutile electrode in methanolic solutions. This was achieved by first generating the methoxy radical at the TiO<sub>2</sub> anode which then reduced the methylene blue. Although this is one of the pioneering works in the field of photoelectrochemical synthesis, no direct evidence was

presented to establish the mechanism of photoelectrochemical reduction. Although viologens are considered to be attractive relay systems for the photoelectrochemical generation of molecular hydrogen, their usage for longer irradiation time scales has recently been questioned because of their facile hydrogenation on the surface of a platinum catalyst [8]. It has recently been shown that methyl viologen can form charge transfer complexes with ethylenediaminetetraacetate,  $\text{Cl}^-$ ,  $\text{SCN}^-$  etc. which exhibit their own photochemistry [9, 10]. Such a phenomenon is expected to complicate the mechanism of reduction of methyl viologen in photoelectrochemical systems. There is a need to explore alternative systems which could act as a relay in photoelectrochemical synthesis.

In the past thionine has been the subject of many photochemical and photogalvanic investigations [11 - 14]. Photochemical reduction of the dye to leucothionine in a photogalvanic cell led to the direct conversion of light energy into electricity. The dye in its leucoform is stable in an inert atmosphere and also possesses strong reducing properties. These interesting redox properties make thionine a suitable mediator in the photoelectrochemical conversion of solar energy. As part of the continuing efforts to seek a promising system for the photoelectrochemical conversion of solar energy, the investigation of the mechanistic details of electron transfer between the semiconductor colloid and thionine as a result of band gap excitation has been undertaken.

## 2. Experimental details

Thionine chloride (MCB) was purified over a chromatography column of neutral alumina [15]. Titanium(IV) 2-propoxide was obtained from Alfa Products. Acetonitrile (Aldrich Gold Label) was used as supplied.

The colloidal  $\text{TiO}_2$  in acetonitrile was prepared by injecting titanium-(IV) 2-propoxide in 2-propanol (10% in 0.5 ml) into 40 ml of acetonitrile kept stirred under a nitrogen atmosphere. The details of the method of preparation can be found elsewhere [4]. Although the colloidal dispersion was stable for 10 - 15 days, freshly prepared colloidal  $\text{TiO}_2$  dispersion was used in the present set of experiments. The stock suspension was diluted with acetonitrile to obtain the desired concentration of  $\text{TiO}_2$ . No attempts were made to exclude the traces of 2-propanol present in the colloidal dispersion. It was confirmed separately that 2-propanol present in trace quantities did not affect the photophysical or photochemical properties of the dye in acetonitrile. Unless otherwise specified, all  $\text{TiO}_2$  suspensions in acetonitrile contained about 0.4% 2-propanol and were deaerated with nitrogen. The effective hydrodynamic diameter of the colloidal particle, as measured previously, was  $0.15 \mu\text{m}$  [4].

The absorption spectra were recorded with a Cary 219 spectrophotometer. The emission spectra were recorded at room temperature with an SLM single-photon-counting fluorescence spectrometer in a right-angle

viewing mode. The excitation and emission bandpass slits were 8 nm and 4 nm respectively.

The flash photolysis experiments were performed using a 337 nm laser pulse (2 - 3 mJ; pulse width, 8 ns) from a Molectron UV-400 nitrogen laser system for the band gap excitation of  $\text{TiO}_2$ . In the experiments where thionine alone was excited, the source of excitation was a 532 nm laser pulse (100 mJ; pulse width, 6 ns) from a Quanta-Ray neodymium-doped yttrium aluminum garnet laser system. The details of the flash photolysis set-up are described elsewhere [16]. The experiments were performed in a rectangular quartz cell with a 5 mm path length along the monitoring light. A typical experiment consisted of a series of five to ten replicate shots per sample, and the average signal was processed with an LSI-11 microprocessor interfaced with a PDP 11/55 computer.

Steady state photolysis experiments were carried out using a collimated beam from a 500 W xenon lamp filtered through a Pyrex glass filter.

### 3. Results and discussion

#### 3.1. Absorption and emission characteristics

The absorption spectrum of colloidal  $\text{TiO}_2$  suspension in acetonitrile (Fig. 1 (curve A)) showed strong absorbance at wavelengths less than 380 nm which closely matched the previously reported spectrum of colloidal  $\text{TiO}_2$  in aqueous solution [17]. The absorption and emission characteristics of thionine in neat acetonitrile and in colloidal suspension are given in Table 1 and Figs. 1 and 2. The absorption maximum shifted from 592 nm to 610 nm when the concentration of  $\text{TiO}_2$  in the thionine solution was increased to  $4.5 \times 10^{-4}$  M. As reported earlier [18] such a red shift in the absorption maximum indicates the strong adsorption of thionine on the  $\text{TiO}_2$  surface. The polar environment of the  $\text{TiO}_2$  colloid is expected to

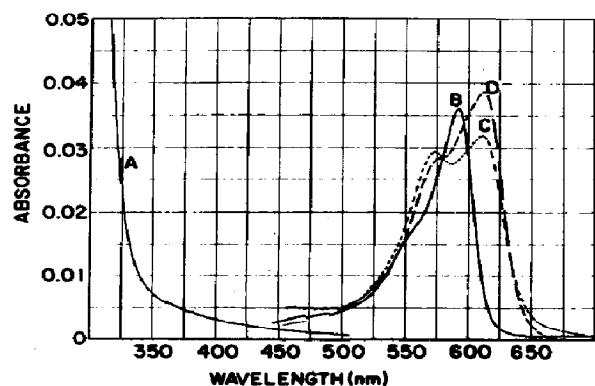


Fig. 1. Absorption spectra of  $10^{-4}$  M colloidal  $\text{TiO}_2$  in acetonitrile (curve A) and of  $5 \times 10^{-6}$  M thionine in acetonitrile containing 0 M (curve B),  $10^{-4}$  M (curve C) and  $4.5 \times 10^{-4}$  M (curve D) colloidal  $\text{TiO}_2$ .

TABLE 1

Absorption and emission characteristics of thionine<sup>a</sup>

	<i>No TiO<sub>2</sub></i>	<i>In 4.5 × 10<sup>-4</sup> M TiO<sub>2</sub> suspension</i>
Absorption maximum S <sub>0</sub> -S <sub>1</sub> (nm)	592	610
Emission maximum S <sub>1</sub> -S <sub>0</sub> (nm)	607	620
Relative fluorescence yield	1.0	0.4
Triplet lifetime (μs)	14.8	12.6

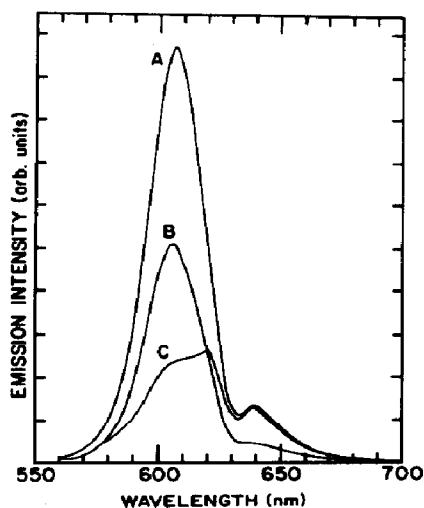
<sup>a</sup>5 × 10<sup>-6</sup> M thionine in acetonitrile.

Fig. 2. Emission spectra of  $5 \times 10^{-6}$  M thionine in acetonitrile at various colloidal  $\text{TiO}_2$  concentrations: curve A, 0 M; curve B,  $5 \times 10^{-6}$  M; curve C,  $4.5 \times 10^{-4}$  M. (Excitation wavelength, 550 nm.)

facilitate the adsorption of the cationic dye. The apparent association constant  $K_a$  for the association of  $\text{TiO}_2$  and thionine, which was determined by the Benesi-Hildebrand method, was  $2.75 \times 10^5 \text{ M}^{-1}$ . The large value of  $K_a$  highlights the strong physical interaction between thionine and  $\text{TiO}_2$  colloid. Since  $\text{TiO}_2$  molecules exist in an aggregated form in a colloidal particle, we would expect many adsorbing sites on the colloidal surface.

The fluorescence yield of thionine decreased upon increasing the concentration of  $\text{TiO}_2$  in the thionine- $\text{TiO}_2$  system (Fig. 2). At high  $\text{TiO}_2$  concentrations ( $4.5 \times 10^{-4}$  M) a new emission maximum appeared at 620 nm. The shoulder observed at 607 nm was attributed to the free dye molecules present in the solution. Similar changes in the emission spectra have been observed recently for many polycyclic aromatic molecules adsorbed on  $\text{TiO}_2$  semiconductor [18]. The quantum yield of fluorescence of thionine decreased markedly when it was adsorbed on the  $\text{TiO}_2$  surface. The

consequences of such an equilibrium between adsorbed and unadsorbed molecules on the emission characteristics and singlet lifetimes of the Erythrosin B-TiO<sub>2</sub> system have been discussed earlier [4]. The fluorescence of Erythrosin B adsorbed on TiO<sub>2</sub> was found to decay an order of magnitude faster than that of the unadsorbed molecule. Quenching of the excited singlet state is attributed to the energy of the electron transfer from the sensitizer to the semiconductor colloid. Such a process of photoelectrochemical sensitization is of interest in extending the photoreponse of semiconductors with large band gaps. The adsorption on the TiO<sub>2</sub> surface had little influence on the triplet lifetime of thionine (Table 1).

### 3.2. Steady state photolysis of the TiO<sub>2</sub>-thionine system

The consequences of the band gap excitation of TiO<sub>2</sub> in the TiO<sub>2</sub>-thionine system was studied by both steady state photolysis and laser flash photolysis. The excitation of a deaerated solution of thionine in the presence of TiO<sub>2</sub> suspension by exposure to a xenon lamp for 2 - 3 min resulted in the bleaching of the dye solution (Fig. 3(a)). In a deaerated solution the bleached dye was found to be quite stable. For example less than 10% of the dye was found to recover in a deaerated solution on standing for 1 day. The bleached dye was found to recover if the system was exposed to air. The recovery was faster at higher oxygen concentrations.

The reversibility of this photochemical reaction in a partially deaerated solution can be seen in Fig. 3(b). Nearly 95% of the dye was recovered over a period of 60 min. This suggested that the destruction, if any, of the dye in each photochemical cycle was about 5%. However, oxygenated solutions

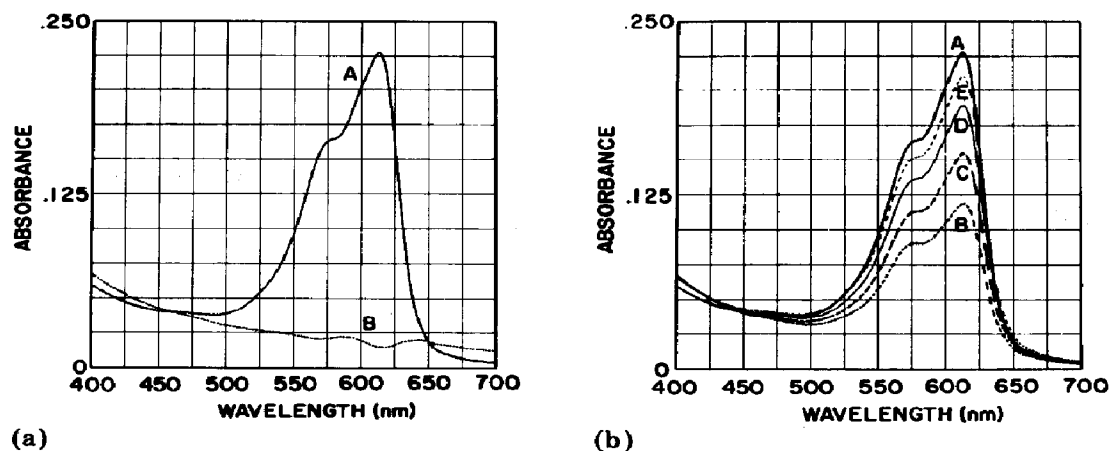


Fig. 3. (a) Absorption spectra of a solution of  $4.5 \times 10^{-4}$  M TiO<sub>2</sub> and  $2.5 \times 10^{-6}$  M thionine in acetonitrile (deaerated) before photolysis (curve A) and after photolysis (curve B); (b) absorption spectra of a solution of  $4.5 \times 10^{-4}$  M TiO<sub>2</sub> and  $2.5 \times 10^{-6}$  M thionine in acetonitrile (partially deaerated) before steady state photolysis (curve A) and showing recovery 5 min (curve B), 10 min (curve C), 30 min (curve D) and 60 min (curve E) after photolysis.

exhibited a higher degree of irreversibility, probably because of the irreversible photo-oxidation of the dye.

No bleaching was observed when the excitation of the  $\text{TiO}_2$ -thionine system was limited to the  $S_0$ - $S_1$  absorption of the dye ( $\lambda > 470$  nm). This clearly indicated that the photobleaching observed on irradiation with a xenon lamp was initiated by band gap excitation of  $\text{TiO}_2$ .

### 3.3. Flash photolysis experiments

The absorption spectrum of the transient formed on the excitation of the  $\text{TiO}_2$ -thionine system with a 337 nm laser pulse is shown in Fig. 4. The transient was long lived and decayed very little over a period of 70  $\mu\text{s}$ . The contribution of the excited dye to the generation of this long-lived transient was minimal because the absorbance of the dye at 337 nm was very small compared with the absorbance of the  $\text{TiO}_2$  colloid. The transient formed on band gap excitation of  $\text{TiO}_2$  exhibited absorption maxima around 420 and 750 nm which corresponded to the depletion of ground state absorption in the region of 600 nm. This absorption spectrum was found to match the previously reported absorption spectrum of semithionine [19].

The reaction between the conduction band electron and the adsorbed dye which led to the formation of semithionine confirmed that the interfacial electron transfer process was a one-electron reduction process. As can be seen from Fig. 5, the appearance of the transient absorption at 420 nm was prompt and the interfacial electron transfer was found to occur within the lifetime of the laser pulse (about 10 ns). The absence of growth in the semithionine absorbance after the laser pulse ruled out any diffusion-limited electron transfer to the free dye molecules in the solution. This contrasts with the previously observed diffusion-limited electron transfer between colloidal  $\text{TiO}_2$  and methyl viologen [6].

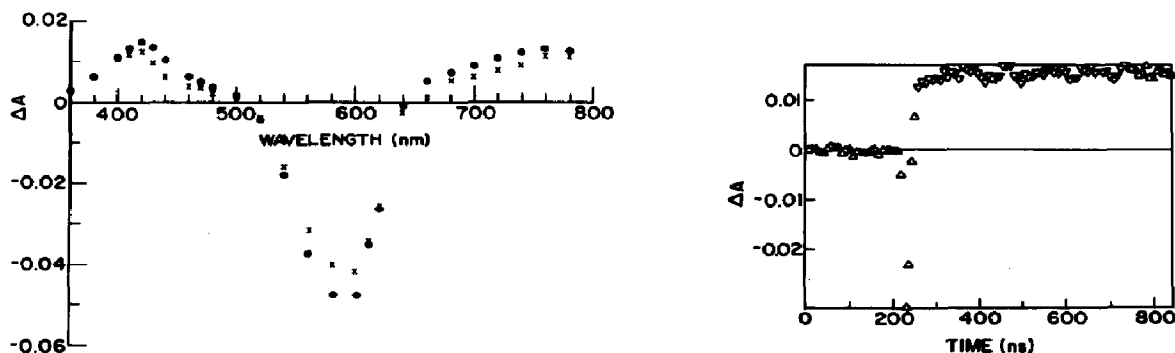


Fig. 4. Transient absorption on laser pulse excitation (337 nm) of a solution containing  $2 \times 10^{-4}$  M  $\text{TiO}_2$  and  $2 \times 10^{-5}$  M thionine in acetonitrile:  $\bullet$ , immediately after the flash;  $\times$ , 70  $\mu\text{s}$  after the flash.

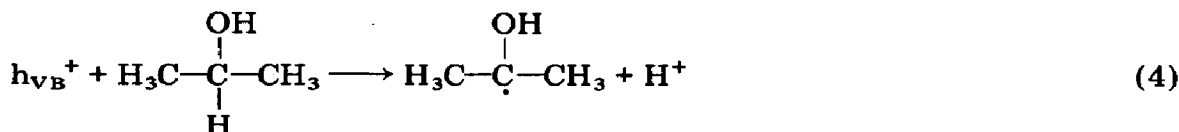
Fig. 5. Transient absorption at 420 nm on excitation of a solution of  $10^{-5}$  M thionine and  $2 \times 10^{-4}$  M  $\text{TiO}_2$  in acetonitrile with a 337 nm laser pulse.

### 3.4. Mechanism

The dynamics of the interfacial electron transfer between a semiconductor colloid and an electron acceptor like methyl viologen has previously been illustrated [6]. Band gap excitation of a  $\text{TiO}_2$  semiconductor ( $E_g \approx 3.2$  eV) colloid leads to the charge separation within its band structure:



Since the diffusion length for the charge carriers is expected to be larger than the diameter of the colloidal particle,  $h_{\text{VB}}^+$  and  $e_{\text{CB}}^-$  are expected to reach the surface rapidly [5]. If the energetics are favorable, these charge carriers can chemically react with the molecules adsorbed on the semiconductor surface. A competing reaction for such an interfacial electron transfer process would be the  $h^+e^-$  recombination. The reduction of thionine following the charge separation in the semiconductor colloid can be represented as follows:



where D,  $\text{D}^-$  and  $\text{D}^{2-}$  represent thionine, semithionine and leucothionine respectively.

The reduction potential of thionine ( $\text{D} + e \rightarrow \text{D}^-$ ) is reported to be about 0.2 V *versus* the saturated calomel electrode (SCE) [20]. The conduction band of  $\text{TiO}_2$  in neutral solution, which is reported to be about -0.8 V (SCE), can energetically favor the electron transfer to thionine (reaction (2)). Disproportionation of semithionine would result in the formation of leucothionine which is quite stable in an inert atmosphere (reaction (3)). The holes reaching the semiconductor surface are scavenged by 2-propanol (reaction (4)).

### 3.5. Quantum yield measurements

The concentration of semithionine was determined from the absorbance at 420 nm ( $\epsilon_{420} \approx 12\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) and the bleaching of the dye at 600 nm ( $\epsilon_{600} \approx 60\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) 100  $\mu\text{s}$  after the flash. The quantum yields  $\phi_{\text{obs}}$  at various thionine concentrations were determined from the flash photolysis experiments with the 337 nm laser pulse as the excitation source and the anthracene triplet as reference [21]. Since the absorbance of the colloidal  $\text{TiO}_2$  suspension at 337 nm did not change on increasing the concentration of thionine it can be assumed that the extinction coefficients of the  $\text{TiO}_2$  colloid and the associated complex of the  $\text{TiO}_2$  colloid and

thionine are the same at the excitation wavelength. Under these conditions the role of the associated complex of colloidal  $\text{TiO}_2$  and thionine in the production of semithionine can be elucidated using the expression [10]

$$\phi_{\text{obs}} = \phi \frac{K_a [D]}{1 + K_a [D]}$$

where  $\phi$  is the true quantum yield and  $K_a [D]/(1 + K_a [D])$  is the fraction of the dye present in the associated form. If the observed semithionine production is entirely due to the associated complex of colloidal  $\text{TiO}_2$  and thionine, this expression should give a linear plot of  $1/\phi_{\text{obs}}$  versus  $1/[D]$  with the intercept equal to  $1/\phi$  and the slope equal to  $1/\phi K_a$ . The linear plot shown in Fig. 6 suggests that this is indeed true. The plot in Fig. 6 gave values of  $\phi = 0.1$  and  $K_a = 2.9 \times 10^5 \text{ M}^{-1}$ . This value of  $K_a$  was in close agreement with the apparent association constant ( $2.75 \times 10^5 \text{ M}^{-1}$ ) obtained from the Benesi-Hildebrand plot.

The value of 0.1 obtained for the quantum yield by this method sets the upper limit for the photoelectrochemical production of semithionine from an associated complex of  $\text{TiO}_2$  colloid and thionine under the present set of experimental conditions. This analysis also shows the importance of the association of the  $\text{TiO}_2$  colloid and thionine in the interfacial electron transfer process. The quantum yield of 0.1 for the photoelectrochemical production of semithionine indicates that a large fraction of the photo-generated charge carriers in the  $\text{TiO}_2$  colloid is lost in the recombination process. By selectively scavenging the holes after the initial charge separation, it should be possible to increase the efficiency of photoelectrochemical production of semithionine. The validity of this argument was tested by increasing the concentration of 2-propanol which can scavenge the holes (reaction (4)). As can be seen from Table 2, the observed quantum yield for the photoelectrochemical production of semithionine increased upon

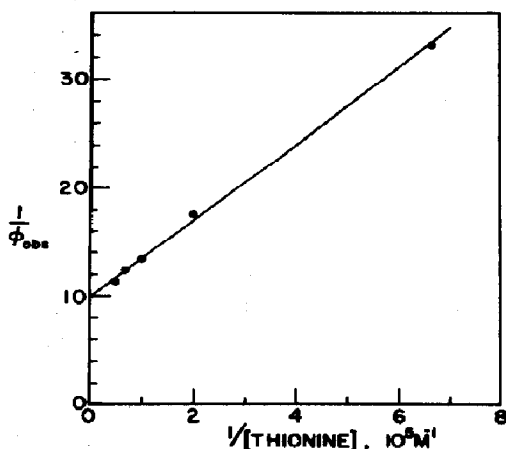


Fig. 6. Dependence of the inverse of the observed quantum yield of the photoelectrochemical production of semithionine on the inverse of the thionine concentration in acetonitrile containing  $2 \times 10^{-4} \text{ M TiO}_2$ .



TABLE 2

Influence of the composition of the TiO<sub>2</sub>-thionine system on the observed quantum yield  $\phi_{\text{obs}}$  of semithionine production in acetonitrile

[TiO <sub>2</sub> ] (10 <sup>-4</sup> M)	[Thionine] (10 <sup>-5</sup> M)	$\phi_{\text{obs}}$
2.0	0 (N <sub>2</sub> ) <sup>a</sup>	0
0	2.0 (N <sub>2</sub> ) <sup>a</sup>	0
0.5	2.0 (N <sub>2</sub> ) <sup>a</sup>	0.04
2.0	2.0 (N <sub>2</sub> ) <sup>a</sup>	0.08
2.0	2.0 (O <sub>2</sub> ) <sup>a</sup>	0.05
2.0	2.0 (N <sub>2</sub> ) <sup>b</sup>	0.09
2.0	2.0 (N <sub>2</sub> ) <sup>c</sup>	0.11

Laser pulse excitation at 337 nm.

<sup>a</sup>About 0.4% 2-propanol.

<sup>b</sup>1.5% 2-propanol.

<sup>c</sup>5% 2-propanol.

increasing the concentration of 2-propanol. Similar enhancement in  $\phi_{\text{obs}}$  was also observed when a hole scavenger like *t*-stilbene was employed.

The dependence of the photoelectrochemical yield of semithionine on other experimental conditions is summarized in Table 2. The dependence on the TiO<sub>2</sub> colloid concentration highlighted the role of the TiO<sub>2</sub> semiconductor in the production of semithionine. The presence of oxygen in the TiO<sub>2</sub>-thionine system was found to decrease the yield of semithionine. Oxygen is expected to compete with thionine in the interfacial electron transfer process as the photoelectrochemical reduction of molecular oxygen by the TiO<sub>2</sub> semiconductor colloid is energetically favorable ( $E^{\circ}_{\text{O}_2/\text{O}_2^-} = -0.78$  V (SCE)). The role of molecular oxygen in scavenging conduction band electrons has been reported earlier [1].

### 3.6. Effect of acidity and light intensity

A qualitative study of the influence of the acidity/basicity of the medium on the photoelectrochemical production of semithionine was carried out by the addition of H<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>OH to the TiO<sub>2</sub> suspension in acetonitrile. (A flocculation problem limited the use of buffered solutions. The acidity of the medium was varied according to the method employed earlier [22].) The p*K*<sub>a</sub> values reported for the protonated forms of thionine and semithionine are -0.7 and 8.2 respectively [12]. The ground state thionine is expected to be in the protonated form in the acidity range employed for the measurements in Fig. 6. The production of semithionine was monitored from the ground state depletion of thionine at 600 nm. As can be seen from Fig. 7, on increasing the acidity of the medium the observed photoelectrochemical yield of semithionine decreased sharply.  $\phi_{\text{obs}}$  was unaffected in basic solutions. A similar dependence of the generation of the methyl viologen radical cation on the pH of the TiO<sub>2</sub> suspension has

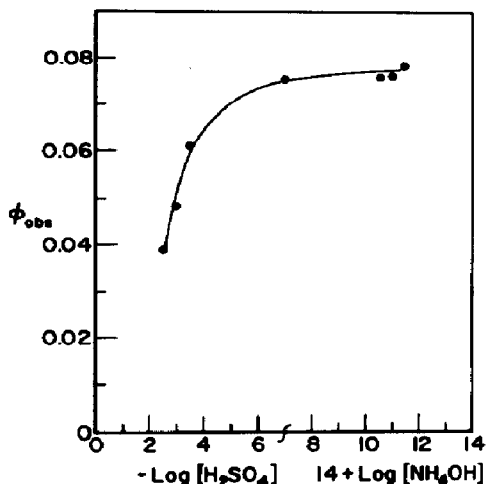


Fig. 7. Plot of the observed photoelectrochemical quantum yield of semithionine vs. the acidity of the medium ( $10^{-5}$  M thionine and  $2 \times 10^{-4}$  M  $\text{TiO}_2$  in acetonitrile).

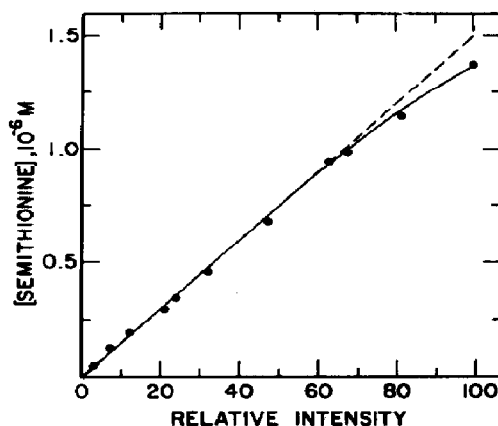


Fig. 8. Dependence of the photoelectrochemical production of semithionine on the intensity of the laser pulse (337 nm) excitation ( $2 \times 10^{-4}$  M  $\text{TiO}_2$  and  $2 \times 10^{-5}$  M thionine in acetonitrile).

also been reported [6]. The conduction band potential of the  $\text{TiO}_2$  semiconductor colloid was found to vary with the pH of the medium. Increased acidity of the medium is expected to decrease the energy gap between the conduction band of  $\text{TiO}_2$  and  $E^\circ_{\text{D}/\text{D}^-}$  which in turn would reduce the efficiency of the interfacial electron transfer process.

The dependence of the photoelectrochemical yield of semithionine on the intensity of excitation is shown in Fig. 8. The intensity of the 337 nm laser pulse (2 mJ) was varied with the aid of neutral density filters. At low excitation intensities a linear increase in the yield of semithionine was observed. However, a deviation from linearity was seen at higher excitation intensities. A similar dependence on the excitation intensity has been reported by Henglein [5] for the photoelectrochemical reduction of  $\text{I}^-$  with  $\text{TiO}_2$  colloid.

### 3.7. Disproportionation of semithionine

The observed photobleaching in the steady state photolysis experiments discussed earlier is attributed to the disproportionation of semithionine (reaction (3)). The kinetics of the photoelectrochemically generated semithionine was studied using a conventional flash photolysis set-up. The decay of semithionine produced on excitation of thionine solutions (300 - 350 nm) was monitored at its absorption maximum (420 nm). It followed a simple second-order kinetics in both neat acetonitrile and colloidal  $\text{TiO}_2$  suspension. In neat acetonitrile semithionine was generated via the ground state quenching process as reported earlier [15]. The second-order rate constant  $k_3$  for the disproportionation of semithionine in neat acetonitrile

was found to be  $1.63 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  which is in close agreement with the reported value of  $2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  in 92 vol.% acetonitrile [23]. However, in colloidal  $\text{TiO}_2$  suspension ( $10^{-4} \text{ M TiO}_2$ )  $k_3$  was  $1.58 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , which is nearly an order of magnitude larger than the rate constant observed in neat acetonitrile. It has been reported earlier that  $k_3$  is very sensitive to the polarity of the solvent [23]. Changes of up to two to three orders of magnitude in  $k_3$  can be observed on increasing the polarity of the solvent (e.g.  $k_3 = 2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in water). Although no evidence for association of semithionine and  $\text{TiO}_2$  has been sought, the polar environment of  $\text{TiO}_2$  colloid could well be responsible for facilitating the disproportionation of semithionine. Further studies to elucidate the mechanism of disproportionation in colloidal  $\text{TiO}_2$  suspension are currently being undertaken.

#### 4. Conclusions

Dyes are often used as sensitizers in extending the photoresponse of semiconductors with large band gaps. The consequences of an interfacial electron transfer process between the conduction band electron and the dye molecule, which could be important in elucidating the mechanistic details of photoelectrochemical sensitization are presented in this study. It has been shown that in an inert atmosphere a stable reduced form of thionine can be generated efficiently by band gap excitation of  $\text{TiO}_2$  in the absence of any catalyst. The photoelectrochemical generation of leucothionine opens the possibility of employing a colloidal semiconductor-thionine system in the photoelectrochemical storage or photogalvanic transduction of solar energy. Indeed, photogalvanic effects observed in the colloidal semiconductor systems will be discussed in future work.

#### Acknowledgments

Helpful discussions with Dr. Thomas W. Ebbesen and the assistance of Dr. P. K. Das and Dr. G. Ferraudi with the flash photolysis experiments are greatly appreciated. The research described herein was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. This is Document NDRL-2545 from the Notre Dame Radiation Laboratory.

#### References

- 1 M. A. Fox, *Acc. Chem. Res.*, **16** (1983) 314, and references cited therein.
- 2 B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100** (1978) 2239, 5985.  
T. Inone, A. Fujishima, S. Konishi and K. Honda, *Nature (London)*, **277** (1979) 637.  
T. Kanno, T. Oguchi, H. Sakuragi and K. Tokumaru, *Tetrahedron Lett.*, **21** (1980) 467.
- 3 M. A. Fox, B. Lindig and C. C. Chen, *J. Am. Chem. Soc.*, **104** (1982) 5828.

- M. A. Fox and C. C. Chen, *J. Am. Chem. Soc.*, **103** (1981) 6757.  
M. J. Chen and M. A. Fox, *J. Am. Chem. Soc.*, **105** (1983) 4497.
- 4 P. V. Kamat and M. A. Fox, *Chem. Phys. Lett.*, **102** (1983) 379.
  - 5 A. Henglein, *Ber. Bunsenges Phys. Chem.*, **86** (1982) 241.
  - 6 D. Duonghong, J. Ramsden and J. Grätzel, *J. Am. Chem. Soc.*, **104** (1982) 2977.  
M. Grätzel and A. J. Frank, *J. Phys. Chem.*, **86** (1982) 2964.  
J. Moser and M. Grätzel, *J. Am. Chem. Soc.*, **105** (1983) 6547.
  - 7 H. Yoneyama, Y. Toyoguchi and H. Tamura, *J. Phys. Chem.*, **76** (1972) 3460.
  - 8 P. Keller, A. Moradpour, E. Amouyal and H. B. Kagen, *Nouv. J. Chim.*, **4** (1980) 377.  
P. Keller and A. Moradpour, *J. Am. Chem. Soc.*, **102** (1980) 7193.
  - 9 M. Z. Hoffman, D. R. Prasad, G. Jones and V. Malba, *J. Am. Chem. Soc.*, **105** (1983) 6360.
  - 10 T. W. Ebbesen and G. Ferraudi, *J. Phys. Chem.*, **87** (1983) 3717.  
T. W. Ebbesen, L. Manring and K. S. Peters, *J. Am. Chem. Soc.*, **106** (1984) 7400.
  - 11 P. V. Kamat, M. D. Karkhanavala and P. N. Moorthy, *J. Phys. Chem.*, **85** (1981) 810.  
T. L. Osif, N. N. Lichtin and M. Z. Hoffman, *J. Phys. Chem.*, **82** (1978) 1778.  
W. J. Albery, W. R. Bowen and M. D. Archer, *J. Photochem.*, **11** (1979) 15.
  - 12 M. Z. Hoffman and N. N. Lichtin, in R. R. Hautala, R. B. King and C. Kotal (eds.), *Solar Energy: Chemical Conversion and Storage*, Humana Press, Clifton, NJ, 1979, p. 153.
  - 13 M. D. Archer and M. I. C. Ferreria, in J. S. Connolly (ed.), *Photochemical Conversion and Storage of Solar Energy*, Academic Press, New York, 1981, p. 201.
  - 14 P. V. Kamat, M. D. Karkhanavala and P. N. Moorthy, *Indian J. Chem.*, **18A** (1979) 206, 210.
  - 15 P. V. Kamat and N. N. Lichtin, *J. Photochem.*, **18** (1982) 197.
  - 16 P. K. Das, M. V. Encinas, R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, **101** (1979) 6965.
  - 17 D. Duonghong, E. Borgarello and M. Grätzel, *J. Am. Chem. Soc.*, **103** (1981) 4685.
  - 18 K. Chandrasenkaran and J. K. Thomas, *J. Am. Chem. Soc.*, **105** (1983) 6383.
  - 19 U. Steiner, G. Winter and H. E. A. Kramer, *J. Phys. Chem.*, **81** (1977) 1104.
  - 20 P. D. Wildes and N. N. Lichtin, *J. Phys. Chem.*, **82** (1978) 981.
  - 21 B. Amand and R. Bensasson, *Chem. Phys. Lett.*, **34** (1975) 44.
  - 22 P. V. Kamat and N. N. Lichtin, *J. Phys. Chem.*, **85** (1981) 3864.
  - 23 P. D. Wildes, N. N. Lichtin and M. Z. Hoffman, *J. Am. Chem. Soc.*, **97** (1975) 2288.